Metathesis ring-opening polymerization of some new aryl and fluoroaryl polycyclic alkenes, and related studies

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METATHESIS RING-OPENING POLYMERIZATION OF SOME NEW ARYL AND FLUOROARYL POLYCYCLIC ALKENES, AND RELATED STUDIES

By

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Thesis submitted for the Degree of Doctor of Philosophy
to the University of Durham, England.

1984

to

my father and my mother
my sisters: Salwa, Mysoon, Asma, Kalida and Yusra
my brothers: Ahmed, Kalid and Osama

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I would like to express my deepest thanks and gratitude to my supervisor, Dr. W.J. Feast, for his continuous guidance, invaluable assistance and kind encouragement during the supervision of this work. I also acknowledge my thanks to Dr. J.H. Edwards for his helpful discussions and practical advice and assistance. I also owe thanks to Dr. I. Sadler (University of Edinburgh) and to Professor K.J. Ivin and co-workers (Queen's University, Belfast) for recording the ^{13}C n.m.r. of the polymers; to Dr. R.S. Matthews for recording ^{13}C n.m.r. spectra of the monomers; and to Dr. M. Jones and Mr. V.J. McNeilly for recording mass spectra. Also I would like to express my thanks to Dr. G.M. Brooke for his help and advice.

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MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between January 1982 and June 1984. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

ABSTRACT

This thesis describes work on the metathesis ring-opening polymerization of a series of seven aryl and fluoroaryl derivatives of bicyclo[2.2.1]hepta-2,5-diene and a study of the potential of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene as a monomer for metathesis and anionic polymerizations. The thesis is divided into four chapters. In the first chapter the background of olefin metathesis, as it relates to this work, is discussed. The second chapter describes the synthesis, characterization and polymerization of the monomers used in this study. The attempted metathesis, and anionic polymerizations of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene are discussed in chapter three. The fourth chapter describes the characterization of the new polymers obtained in this study, the chief analytical method has been ^{13}C n.m.r. spectroscopy and it is shown that the polymer chain microstructure is a function of the catalyst (either $WCl_6/(CH_3)_4Sn$ or $MoCl_5/(CH_3)_4Sn$ in this work) and the monomer structure. Generally it appears that the molybdenum based catalyst leads to polymers with a higher proportion of cis vinylene units and a greater degree of stereoregulation than is found in polymers derived from the tungsten based catalyst.

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CHAPTER 1

Introduction and Background

1.1 Introduction

This thesis describes various studies of the polymerization and attempted polymerization of some novel polycyclic polyene monomers. Various techniques have been investigated including classical cationic and anionic initiation but the bulk of the work has used the relatively less well known method of ring-opening metathesis. The well established methods are not discussed in any detail here but at the appropriate points reference will be given to the relevant literature; however, it seems appropriate to discuss olefin metathesis and its application to polymerization in a little more detail and this topic forms the content of this chapter.

1.2 Definition of Olefin Metathesis

The word metathesis, is derived from the Greek meta (change) and tithemi (place). In chemistry it usually refers to the interchange of atoms between two molecules. In olefin chemistry the term metathesis is used to denote a bond reorganization reaction in which the total number and type of chemical bonds remains unchanged during the transformation of the initial olefins into products. Olefin metathesis reactions fall into three broad groups; exchange, or cross-metathesis; degradation; and ring-opening polymerization, Figure 1.1.

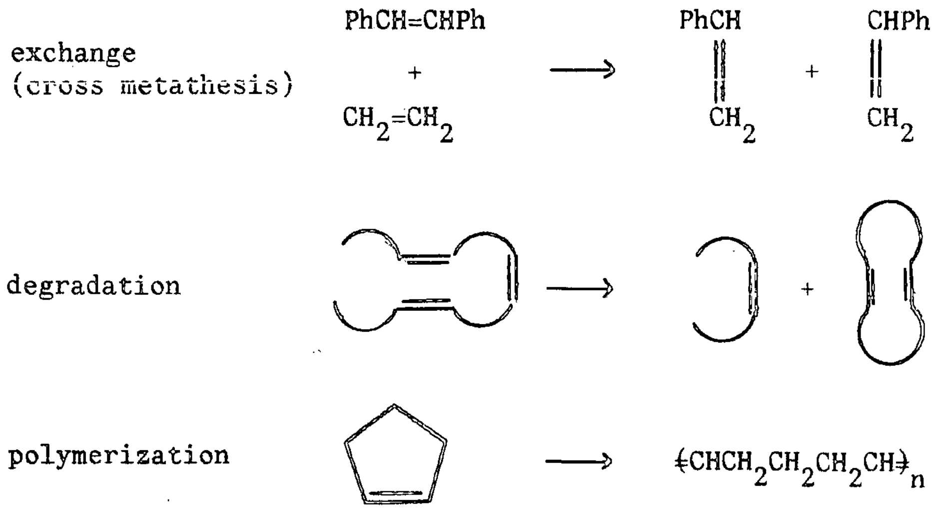


Figure 1.1

The reactions are generally reversible, and with the right catalyst system equilibrium can be attained in a matter of seconds. The earliest description of an olefin metathesis polymerization is probably that recorded in a 1955 patent to Anderson and Merckling,[1] but the expression "olefin metathesis" was introduced by Calderon (1967).[2] The first examples of the metathesis of linear alkenes or the exchange reaction were reported by Banks and Baily (1964),[3] who named the reaction "olefin disproportionation". The chemistry of the exchange reactions and polymerization reactions developed independently and it was Calderon who recognized that the two procedures were in fact examples of the same reaction type. Both types of reaction were remarkably late starters on the modern scene.

1.3 History of Olefin Metathesis

Probably the first citation of a metathesis reaction catalysed by a transition metal dates back to 1955,[1] when Anderson and Merckling successfully polymerized bicyclo[2.2.1]hept-2-ene to a high molecular weight polymer in which cyclopentane rings are inter-connected at the 1 and 3 positions by trans vinylene groups. They used a mixture of titanium tetrachloride activated by reducing agents as the catalyst, but it was not until 1960 that the polymer's structure was reported to be that of a polyalkenylene,[4] Figure 1.2.

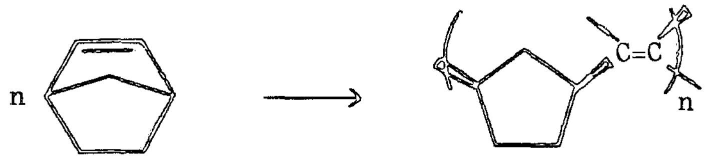


Figure 1.2

Expanding the work of Anderson and Merckling, Eleuterio[5] in 1957 disclosed an additional catalyst combination capable of inducing ring-opening polymerization of a variety of cycloolefins. He used a catalyst of molybdenum oxide on alumina activated by hydrogen reduction and further reacted with aluminium hydride, dicyclopentadiene, dihydrodicyclopentadiene, (5,6-trimethylene bicyclo[2.2.1]hept-2-ene), and bicyclo[2.2.1]-hept-2-ene were all readily polymerized by a ring-opening route. In the case of cyclopentene, trans-poly(1-pentenylene) was formed with a high degree of stereoregular structure but only in low yield.

Metathesis and Ziegler-Natta catalysts are similar, and in 1962, Natta and co-workers[6,7] reported the successful ring-opening polymerization of cyclobutene employing what would normally be regarded as Ziegler-type catalysts; for example, $TiCl_4/Et_3Al$, VCl_4/Hex_3Al, $MoCl_3/Et_3Al$. Later the same authors demonstrated the possibility of producing various stereoregular polymers from cyclobutene using different catalyst systems and reaction conditions, some of their results are listed in Table 1.1.

Table 1.1

Ring-opened cyclobutene polymers by transition metal catalyst

catalyst system	polymer structure
$TiCl_4/Et_3Al$/n-heptane	predominantly cis
$TiCl_4/R_3Al$/toluene	predominantly trans
$MoCl_5/Et_3Al$/toluene	predominantly cis
$RuCl_3/H_2O$	mixed cis and trans
$RuCl_3$/EtOH	trans

In 1964 Natta's[8] group reported the ring-opening polymerization of cyclopentene and showed that it was possible to prepare high cis or high trans-polypentenamer under very mild reaction conditions, employing catalysts derived from WCl_6 or $MoCl_5$ in combination with organoaluminium compounds. This disclosure triggered an avalanche of research activity on cycloolefin ring-opening polymerization. In 1967 Calderon[2,9,10] and co-workers reported their results related to the metathesis polymerization of cycloolefins with tungsten-based homogeneous catalysts and showed that metathesis exchange occurred when an acyclic olefin was treated with a catalyst derived tungsten hexachloride (or the product of the reaction of equimolar amounts of WCl_6 and an alcohol) and an organoaluminium compound. The contribution of this work to the evolution of the olefin metathesis concept was significant, in that it confirmed the notion that the seemingly unrelated olefin disproportionation and cycloolefin polymerization reactions were special cases of an entirely new transition metal catalysed reaction. These authors also suggested that a macrocyclization process accompanied cycloolefin metathesis, and this latter suggestion turned out to be somewhat misleading as far as the development of a mechanistic understanding of the reaction was concerned.

During the development of this remarkable reaction the number of substrate types has been enlarged to include substituted alkenes, non-conjugated dienes and polyenes, and also alkynes. It can be said that the quite extraordinary nature of the olefin metathesis reaction took chemists by surprise, and no one would have predicted in the 1950s or early 1960s that a reaction in which the double bond was apparently cleaved and the pieces put back together again was even remotely possible. Yet not only is it possible but in some cases it can proceed to equilibrium within seconds. Although olefin metathesis and ring-opening polymerization have been extensively reviewed many problems remain to be solved before a completely detailed understanding of the reaction will be established. The catalyst systems used, mechanistic rationalizations and synthetic applications are dealt with in the following sections of this chapter.

1.4 Olefin Metathesis Catalyst Systems

The metathesis of acyclic alkenes and the ring-opening polymerization of cycloalkenes are governed by a common mechanism but they differ in many chemical, kinetic and thermodynamic aspects and this results in different catalyst efficiencies. The number of catalyst systems that initiate olefin metathesis is very large indeed, and in this brief review only general trends are indicated. A single compound is sometimes effective but more commonly the catalyst system contains two, three, or more components. The systems may be heterogeneous or homogeneous, though it is often difficult to be sure whether a system is truly homogeneous and to know whether the catalyst activity resides in the homogeneous or the heterogeneous part.

1.4.a Heterogeneous catalysts

Heterogeneous catalysts generally consist of transition metal oxides or carbonyls (less frequently sulphides), preferably of tungsten, molybdenum or rhenium, supported on oxide or phosphate carriers, preferred supports are alumina, or silica-alumina mixtures. As pointed out by Banks[11] and Baily,[12] comparatively little has been reported on optimization of preparative procedures and operating conditions for various combinations of promoter and support materials. Generally either the support or the finished catalyst requires activation, usually achieved by heating under moisture free conditions as an inert gas. Heterogeneous catalysts are normally prepared by dry mixing the individual components, co-precipitation, or impregnation of substances which decompose at high temperatures to leave the promoter deposited on the support. The catalysts are sensitive to poisoning by polar compounds. Side reactions with lower selectivity, can be largely eliminated by treating the catalysts with various metal ions; thus, double bond shift isomerizations are common, but can be diminished by addition of metal ions chosen from alkali, alkaline earth,[13,14] copper, or silver.[15] Pennella reported dramatic increases in catalyst activity after pretreatment with hydrogen chloride, vinyl chloride or chlorinated hydrocarbons.[16,17] Heterogeneous catalysts acquire a considerable metathesis activity only at high temperatures (100 - 400°C). Hence, they are not very convenient for ring-opening polymerizations and are essentially only applied to olefin disproportionations. Recently heterogeneous catalysts based on rhenium oxide/alumina[18] have been gaining popularity because of their high activity at relatively low temperatures, high selectivity and resistance to catalyst poisons. More detailed examinations of the composition, preparation, activation and generation procedures, poisons and catalytic modifications have been given by Baily[12] and Banks.[11]

1.4.b Homogeneous catalysts

Homogeneous metathesis catalysts are comprised of (a) the transition metal compound, (b) a Lewis acid co-catalyst, and (c) modifiers. The former is usually a halide, oxyhalide, organosalt or olefin complex of tungsten, molybdenum, rhenium or tantalum. Tungsten is particularly effective, not only owing to its great versatility in promoting many different metathesis reactions, but also because it yields the most efficient catalyst for ring-opening polymerization of cycloolefins. Molybdenum, rhenium, and tantalum also yield quite efficient catalysts for ring opening polymerizations they are also effective in promoting metathetical disproportions of acyclic olefins. These four transition metals now seem to be the most important ones for industrial applications in metathesis reactions. All the other metals generally yield only poorly active systems with a relatively specialist application. However, it may be stressed that for these less frequently used metals (for example Ti, Cr, Ru, Rh) the formation of active species strongly depends on the mode of catalyst preparation and on the type of ligands or co-catalysts employed. The co-catalyst may be an organometallic compound of group I - IV metals (such catalysts are clearly similar to Ziegler-Natta type systems) or an electron deficient metal halide of the Friedel Crafts type. Notable co-catalyst types are aluminium alkyls, alkyl aluminium halides, Grignard reagents, lithium alkyls, tin alkyls, lithium aluminium hydride and sodium borohydride. Bridging between the tungsten compound and the co-catalyst may occur through chloride, hydride or alkyl ligands; or the Lewis acid properties of the organometallic or hydridic species may give rise to acid-base equilibria of the type shown in equation 1.1. Such reactions would allow the formation of a vacant co-ordination site for the incoming olefinic substrate molecule.[19]

$$WCl_x + AlCl_3 \rightleftharpoons [WCl_{x-1}]^+ + [AlCl_4]^- \qquad 1.1$$

The yield and stereoregularity of polyalkenamers obtained from the metathesis of cycloalkenes in the presence of the transition metals and co-catalyst mixtures (the two-component catalysts) depends on catalyst composition, type of co-catalyst,[20,21] type of cycloalkene,[22,23] variation of the transition metal to co-catalyst ratio,[20] polymerization temperature,[10-20,24,25] and monomer concentration.[26] Hence many variables must be considered when optimizing reaction conditions. More sophisticated catalyst systems of this class contain a promoter, a molecular weight regulator, and/or a modifier. The catalyst activator can be an oxygenated compound such as alcohol, ether, an organic acid, peroxide, water or molecular oxygen;[9,27-30] such catalyst activators are added to the catalyst system to enhance activity, increase reproducibility, improve the stability and solubility of the catalyst, increase the rate of polymerization, increase monomer conversion, and reduce side reactions. It has to be admitted that catalyst formulation remains a largely empirical process. Table 1.2 lists examples of the kinds of molecules commonly used in the preparation of homogeneous metathesis catalysts.

Table 1.2

Catalyst components for homogeneous metathesis

Transition metal derivative	Organometallics or Lewis acids	Modifiers
WCl_6, WCl_5, WCl_4	RLi, RMgCl, R_2Mg	O_2, H_2O, ROH
$WOCl_4$, WBr_5, WF_6	R_3Al, R_2AlCl, $R_3Al_2Cl_3$	RCOOH, RCOOR, RCOR
$W(CO)_6$, $W(\pi\text{-allyl})_4$	$RAlCl_2$, $AlCl_3$, R_2Zn	RCHO, RSH, RNH_2
$WCl_2(py)_2(NO)_2$, $MoCl_5$	R_4Sn, R_2Hg	
$MoCl_2(py)_2(NO_2)$, $ReCl_5$		

Three main factors govern the reactivity of a homogeneous catalyst towards the metathesis of any given olefinic substrate. First, a selection of a proper combination of catalyst compounds is necessary. Second, the molar ratio of the respective compounds ought to be optimized. Third, a suitable catalyst mixing procedure must be established in order to obtain optimum results. All catalyst components are frequently soluble in the monomer-solvent systems or become soluble after reaction with the monomer or with one of the other catalyst components. However, not all such catalyst systems maintain their solubility throughout their formation and subsequent polymerization. Thus, the term homogeneous catalyst does not strictly apply to all these systems. This class of catalyst, is of primary importance for ring-opening polymerization of cycloolefins, owing to their high activity and versatility. Also, their temperature of activity ranges from above room temperature down to $-50^{\circ}C$ and even below which makes them experimentally convenient for laboratory investigations.

1.5 The Mechanism of Olefin Metathesis

Ring-opening polymerizations of cycloolefins and olefin disproportionations are governed by a common mechanism called metathesis, therefore, it appears appropriate to describe both reactions jointly. The first mechanistic question that must be answered is which bonds are broken and formed in the reaction? This question has been answered for both homogeneous and heterogeneous catalyst systems.

There are two simple interchange processes which can be visualized as possible routes for the olefin metathesis reaction, as shown below.

(i) A transalkylation scheme, Figure 1.3, formally involves the interchange of alkyl groups via scission of a carbon-carbon single bond adjacent to the double bond.

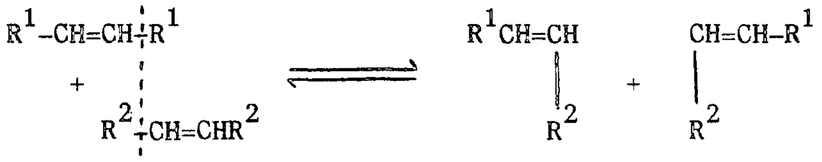


Figure 1.3

(ii) A transalkylidenation scheme, Figure 1.4, which involves cleavage of the double bond itself as a means of redistributing alkylidene species.

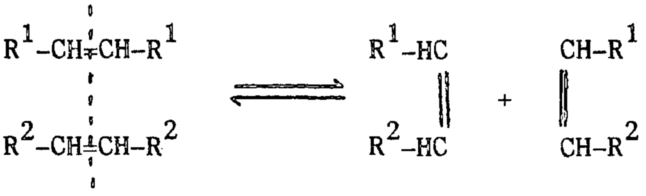
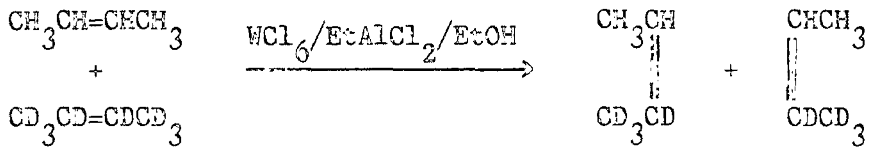


Figure 1.4

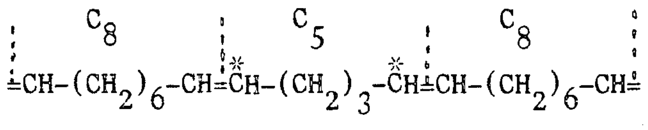
Isotopic labelling experiments with deuterated[9,10c] olefins and ^{14}C labelled compounds[31,32] were designed to distinguish between these alternative transalkylation and transalkylidenation mechanisms, and results have been reported by several workers. Calderon and co-workers examined the products of a cross metathesis between 2-butene and perdeutero-2-butene; the only product observed in equilibrium with the starting olefins was 2-butene-d_4, and this result is only consistent with double bond cleavage,[9,10a] Figure 1.5.



$$CH_3CH{=}CHCH_3 + CD_3CD{=}CDCD_3 \xrightarrow{WCl_6/EtAlCl_2/EtOH} \begin{matrix} CH_3CH \\ \| \\ CD_3CD \end{matrix} + \begin{matrix} CHCH_3 \\ \| \\ CDCD_3 \end{matrix}$$

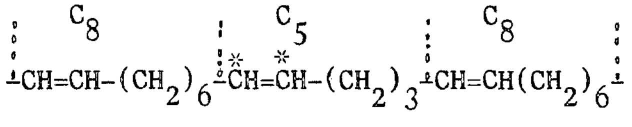
Figure 1.5

Calderon proposed the transalkylidenation scheme for ring-opening polymerization of cycloalkenes and metathesis of acyclic alkenes ruling out Natta's earlier proposal of transalkylation.[8] A further confirmation of the trans alkylidenation mechanism was provided by Dall'Asta and Motroni.[33,34] They copolymerized cyclooctene with cyclopentene in which the cyclopentene was ^{14}C-labelled at the double bond carbons. The resulting polymers may have the structures shown in Figure 1.6 depending on whether cleavage takes place at the double-bond or at the carbon-carbon single-bond adjacent to the double-bond. Ozonolysis of the two possible copolymers followed by reduction would produce the glycols shown in Figure 1.7.



$$\overset{C_8}{-CH-(CH_2)_6-CH}{=}\overset{C_5}{\overset{*}{C}H-(CH_2)_3-\overset{*}{C}H}{=}\overset{C_8}{CH-(CH_2)_6-CH}{=}$$

double bond cleavage



$$-\overset{C_8}{CH{=}CH-(CH_2)_6}-\overset{C_5}{\overset{*}{C}H{=}\overset{*}{C}H-(CH_2)_3}-\overset{C_8}{CH{=}CH(CH_2)_6}-$$

allylic-bond cleavage

(* denotes ^{14}C labelling)

Figure 1.6

$$HOH_2C-(CH_2)_6-CH_2OH + HOH_2\overset{*}{C}-(CH_2)_3-\overset{*}{C}H_2OH + HOH_2C-(CH_2)_6-CH_2OH$$

Glycol mixture derived from double-bond cleavage polymerization

$$HOH_2C-(CH_2)_6-\overset{*}{C}H_2OH + HOH_2\overset{*}{C}-(CH_2)_3-CH_2OH + HOH_2C-(CH_2)_6-CH_2OH$$

Glycol mixture derived from allylic-bond cleavage polymerization

Figure 1.7

The ozonolysis/reduction procedure was performed on the copolymer and labelled ^{14}C atoms were found to be present only in the pentanediol. Supporting evidence was obtained in a similar manner using cyclobutene/ 3-methyl cyclobutene copolymerization.[35]

Alkyne metathesis is perhaps even more surprising. Mortreux[36,37] has found that hex-2-yne undergoes metathesis on MoO_3/SiO_2 at 350°C. Isotopic labelling shows that in this reaction the triple bond is completely broken, Figure 1.8.

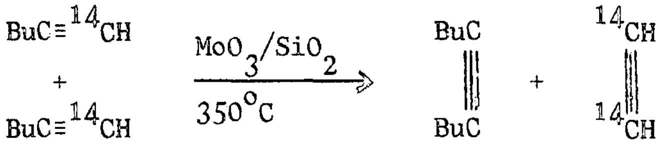


Figure 1.8

There are two distinct ways to accomplish this transformation, the first general pathway is a direct exchange of alkylidene units between a pair of olefins (pairwise); the second route involves a sequential breaking of double bonds one at a time with transfer of individual alkylidene units (non-pairwise).

1.5.a Pairwise mechanisms

Three different pairwise mechanistic rationalizations have been proposed, the intermediates postulated for these different mechanisms are either quasi-cyclobutanes, or tetramethylene transition state complexes, or metallocyclopentanes.

The quasi-cyclobutane proposal was put forward by Bradshaw in 1967,[13] it became popular and was widely supported.[10,38] The proposal was that two alkene double bonds were coordinated to the transition metal atom of the catalyst and then underwent pairwise alkylidene exchange via a quasi-cyclobutane intermediate as illustrated in Figure 1.9. The following year Calderon et al[10] suggested that this proposal could be

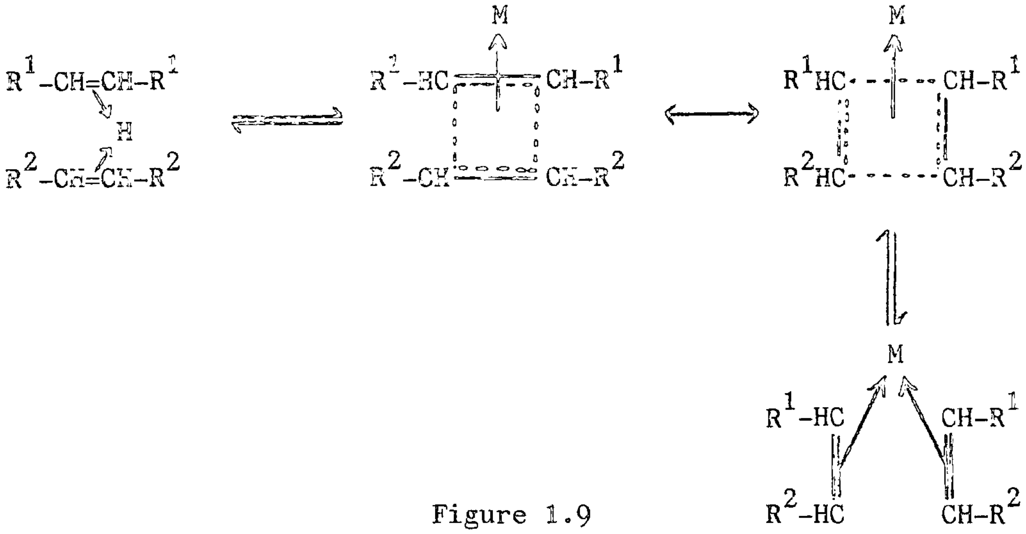


Figure 1.9

used to account for the polymerization of cyclic olefins and put forward the scheme shown in Figure 1.10, this scheme clearly implies a macrocyclization polymerization process.

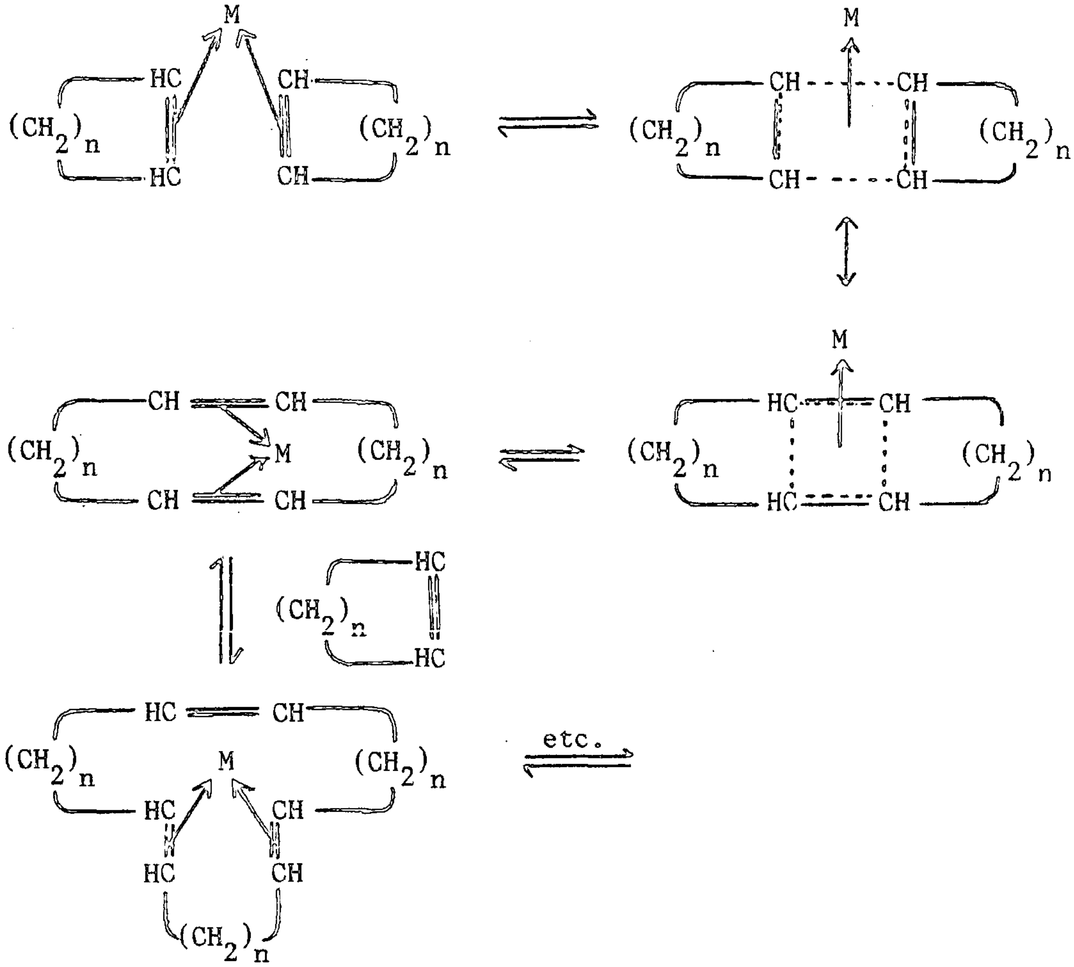
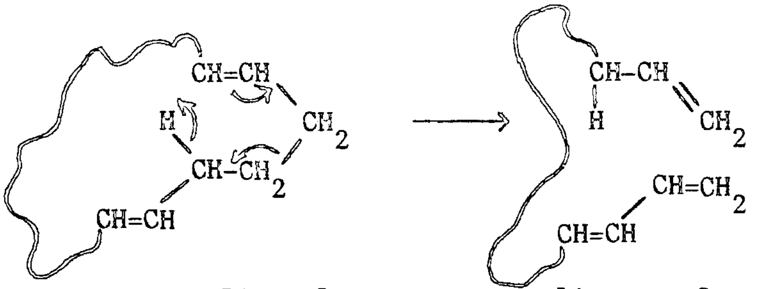


Figure 1.10

The observed formation of linear and macrocyclic species was explained on the basis of an interaction of the growing macrocycles with an acyclic alkene (fortuitously present as an impurity) which resulted in cleavage of the macrocycle. Alternative explanations of the formation of linear polymers have also been proposed, for example in the case of polypentenamer the scheme shown in Figure 1.11 has been advanced.[39]



macrocyclic polymer linear polymer

Figure 1.11

Mango and others[40] suggested on the basis of calculations and orbital symmetry considerations that the reaction could proceed by this pairwise mechanism in a concerted fashion with a low activation energy. Normally the conversion of two olefins to a cyclobutane is a high-energy process, and a concerted $\pi_s^2 + \pi_s^2$ cycloaddition is symmetry forbidden for simple olefins;[41] Mango suggested that the interaction of the olefin π-orbitals and the metal d orbitals removed the symmetry restriction for such reactions when they occurred in the coordination sphere of the metal. Since this mechanism implies a simple concerted pathway with no build-up of intermediates it is difficult to design an experimental test of the proposed scheme. However, the little circumstantial evidence available argued against this proposed mechanism. Thus if the intermediate has considerable cyclobutane character, it would be expected that cyclobutanes would be cleaved to olefins under the usual metathesis reaction conditions. Although there are numerous side products produced in many of the catalyst systems, there have been virtually no reports of the production of cyclobutanes. There was only one claim which purported to demonstrate a metathesis catalyst causing a two olefin → cyclobutane conversion and its reverse,[42] the two reactions are shown in Figure 1.12. Early work by Wilson in these laboratories showed that these observations were not relevant to the metathesis argument since the 2,3-bis-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene, which is described by Gassman and Johnson[42] as the product of interaction of the bis-trifluoromethyl quadricyclane with "a typical metathesis catalyst", is itself a monomer which is easily and rapidly converted to polymer by metathesis ring-opening at the unsubstituted double bond by any of a range of simple metathesis catalysts based on tungsten and molybdenum.[43] Thus, although the observations of Gassman and Johnson may well be correct they have no relevance to the mechanism of metathesis. It is worth noting that the "catalyst" described as $PhWCl_3$ which made several appearances in the early literature appears to have lost favour; indeed it is difficult to find convincing evidence that it was ever satisfactorily characterized.[44]

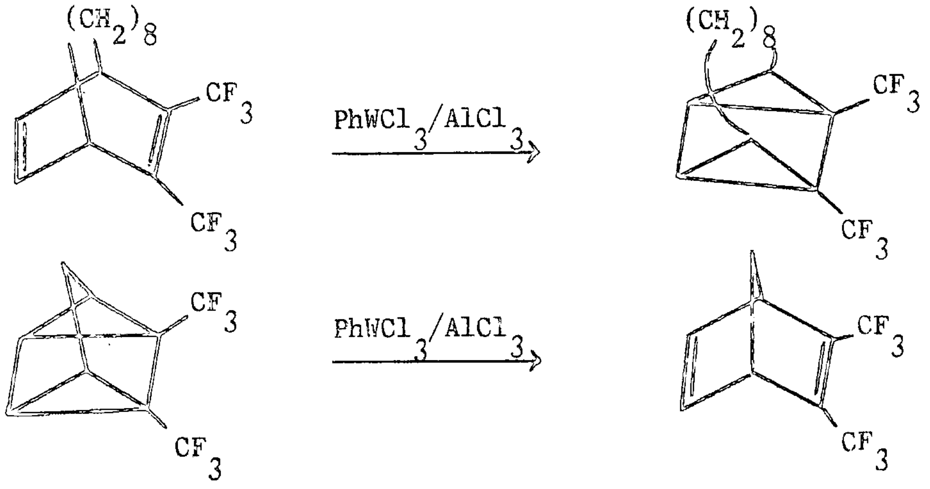


Figure 1.12

Pettit[45] demonstrated that cyclobutanes were unreactive under usual metathesis conditions. Although these results did not conclusively rule out this concerted quasi-cyclobutane mechanism, they suggested that other schemes might be more reasonable. Pettit visualized the process as involving a transition state in which the bonding is most conveniently described as resulting from the interaction of a basic set of metal atomic orbitals and four methylenic units, Figure 1.13 illustrates the transformation via the tetramethylene metal transition state.

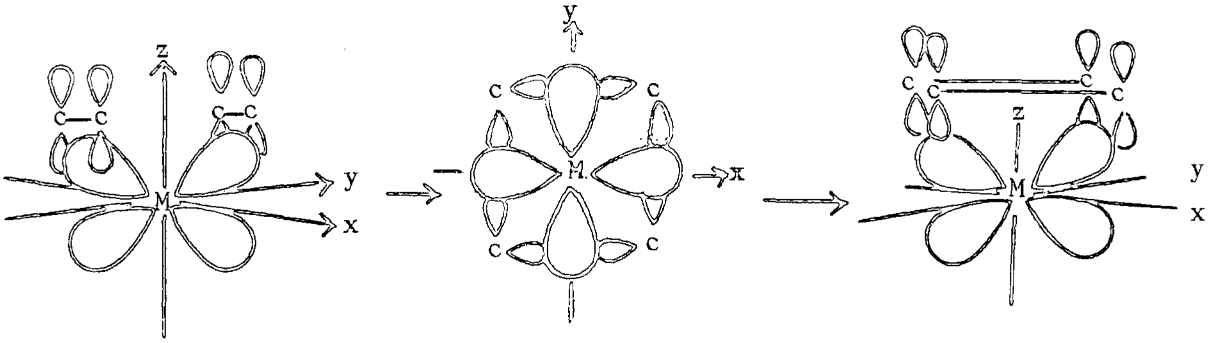


Figure 1.13

Suffice it to mention that the important feature of the proposed mechanism is that the transformation of the bis-olefin complex into the tetramethylene-metal transition state is accomplished by donation of four electrons from filled ligand orbitals to empty metal orbitals and back donation of four electrons from filled metal orbitals to empty ligand orbitals. Consequently, the carbon-carbon σ-bonds of the initial olefins are ruptured concurrently with the π-bonds, so that no genuine cyclobutane molecule is ever formed along the reaction coordinate. This mechanism was shown to be symmetry allowed by molecular orbital considerations. Owing to the difficulty of finding evidence to support the concerted diolefin, pairwise scheme, other mechanisms were considered, one of these was a pairwise non-concerted scheme. Grubbs and Brunck[46] suggested a mechanistic scheme based on the rearrangement of the complexed alkenes to a metallocyclopentane intermediate followed by a reorganization of the metallocycle and subsequent fragmentation of this new intermediate to give the new complexed alkenes, Figure 1.14.

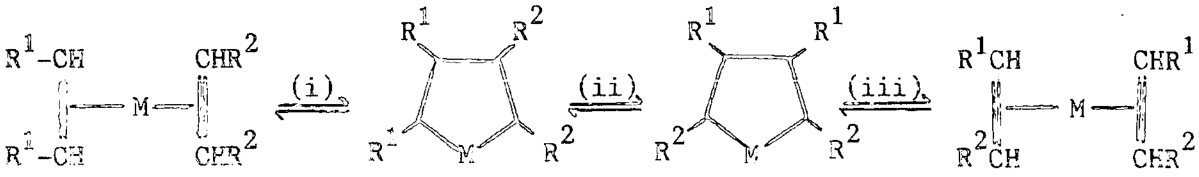


Figure 1.14

Evidence to support this hypothesis came from the investigation of 1,4-dilithiobutanes with tungsten hexachloride the intermediate produced in this reaction should be similar in structure to the proposed metallocyclopentane intermediate. When the reaction was carried out with labelled dilithiobutane, rearranged products were obtained (Figure 1.15) which was taken as evidence supporting the scheme shown in Figure 1.14.

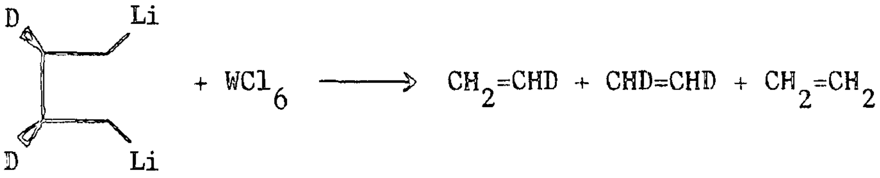


Figure 1.15

1.5.b Non-pairwise mechanisms

Substantial evidence points to a non-pairwise chain growth mechanism, which involves a carbene-bearing metal interacting with an incoming olefin to form a metallocyclobutane intermediate which then rearranges to give a new carbene-metal complex and a new olefin, Figure 1.16.

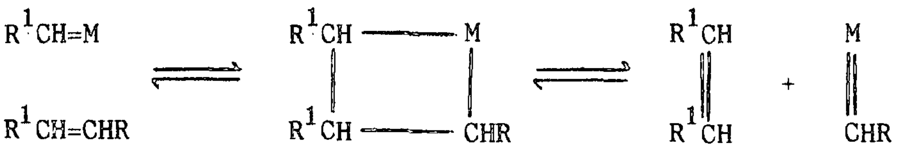


Figure 1.16

This mechanism was initially proposed by Hérisson and Chauvin in 1970,[47] they suggested that this scheme would account for the products and general characteristics of metathesis reactions just as well as the pairwise schemes. However, since the little that was known concerning the chemistry of metal-carbene complexes at that time was thought to be inconsistent with such species being intermediates in such reactions, this mechanism was considered unlikely until fairly recently. This mechanism is readily adapted to rationalise the formation of high molecular weight polyalkenamers from cycloalkenes by chain growth, Figure 1.17.

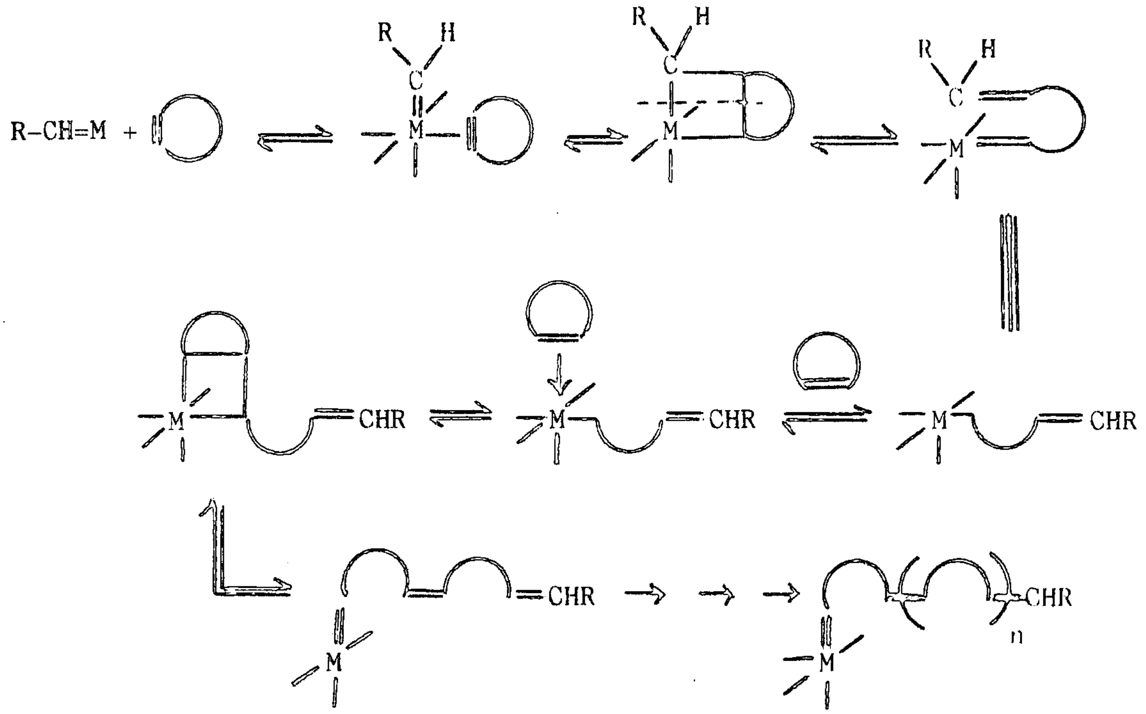
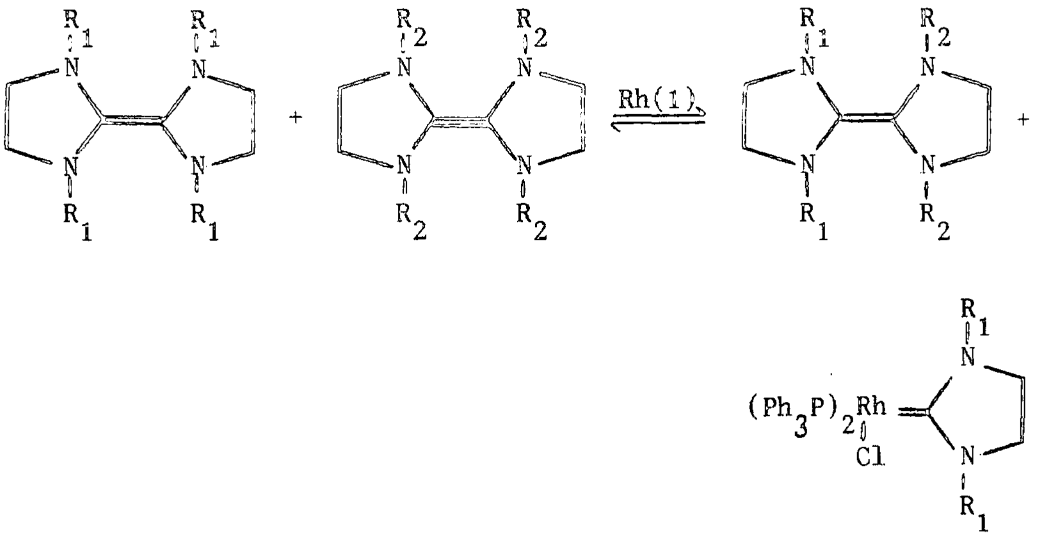


Figure 1.17

This mechanism overcomes the difficulty in the macrocyclization mechanism proposed, which would need acyclic alkene impurities to open the macrocycle and produce linear polyalkenamers; it also allows for the formation of macrocyclics via a "back-biting" mechanism.

A number of reactions have been discovered that provide models for each of the steps of this mechanism. Cardin et al[48] exposed a mixture of unsaturated amines to a rhodium phosphine catalyst and observed some disproportionation, as a side product they isolated a complex having one electron-rich alkylidene moiety complexed to Rh. They suggested a monocarbene complex (1) as illustrated, Figure 1.18.



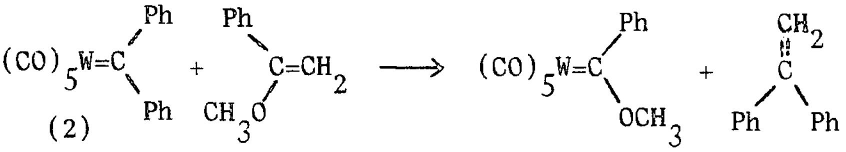
(1)

Figure 1.18

In 1976 Dolgoplosk[49] reported that the reaction of small quantities of $PhCHN_2$ with WCl_6 or $MoCl_5$ gave active catalysts for ring-opening polymerization, this was rationalized in terms of the formation metal-carbene complexes as shown in the equation below:

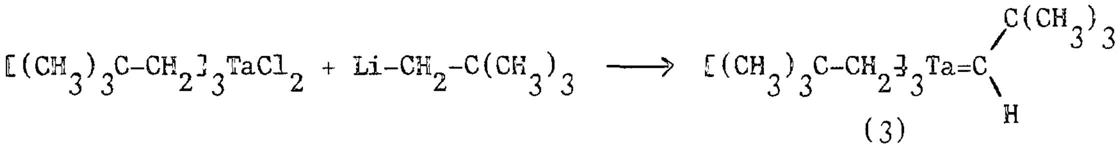
$$C_6H_5CHN_2 + MX_n \longrightarrow C_6H_5CH{=}MX_n + N_2\uparrow$$

Casey[50] provided an excellent model for one of the critical steps of the reaction, he demonstrated that a tungsten carbene (2) would undergo alkylidene exchange with an olefin as shown below.



$$\underset{(2)}{(CO)_5W{=}CPh_2} + Ph(CH_3O)C{=}CH_2 \longrightarrow (CO)_5W{=}C(Ph)(OCH_3) + CH_2{=}CPh_2$$

Later, these tungsten carbenes were used to initiated ring-opening polymerization of several cycloalkenes without the requirement of a co-catalyst.[22,51-54] Schrock[55] subsequently provided an example of the preparation of a metal-carbene complex (3) that was produced under conditions similar to those used to prepare metathesis catalysts.



$$[(CH_3)_3C\text{-}CH_2]_3TaCl_2 + Li\text{-}CH_2\text{-}C(CH_3)_3 \longrightarrow [(CH_3)_3C\text{-}CH_2]_3Ta{=}C\begin{matrix}\diagup C(CH_3)_3\\ \diagdown H\end{matrix}$$

(3)

These early observations lead to the new general acceptance of a chain growth mechanism involving metallo-carbenes and this is discussed in more detail below. The primary processes for all chain reactions are initiation, propagation and termination and these are discussed in the following three sections.

1.6.a Metal carbene initiation

If the non-pairwise carbene to metallocyclobutane mechanism is to be accepted, it becomes of interest to examine potential routes to the formation of the initial carbene-metal entity, for this purpose it is convenient to classify metathesis catalysts into three major categories:

(a) Catalyst combinations that do not involve an organometallic component; this is particularly relevant to almost all the heterogeneous catalysts.

(b) Combinations that involve organometallic co-catalysts e.g. $RAlCl_2/WCl_6$, R_4Sn/WCl_6, $MoCl_5/R_3Al$.

(c) Catalysts possessing stable carbene-metal ligands such as the Casey and Fischer carbenes.

Firstly, where organometallic co-catalysts are not present, three schemes have been proposed. Ephritikhine and Green[56] proposed the mechanism of initiation of metathesis shown in scheme 1.19, in which an olefin coordinates to a metal centre and then an allylic hydride to metal transfer occurs followed by a hydride to C_2 of the coordinated

η^3-allyl fragment to generate the metallocyclobutane. However, this mechanism could not be extended to highly reactive substrates such as norbornene where η^3-allyl formation is not possible because the allylic hydrogen which would have to be transferred is at a bridgehead.

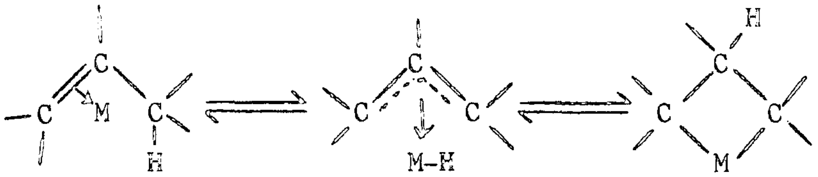


Figure 1.19

A second scheme has been proposed which involves the direct and reversible conversion of a coordinated olefin to a metallo-carbene in one step via a 1,2-hydride shift,[57] Figure 1.20.

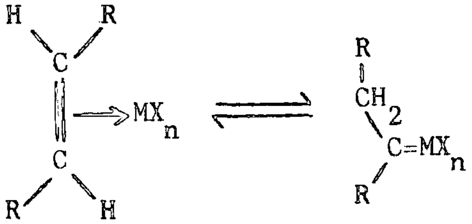


Figure 1.20

This proposal provides a rationalization for the generation of chain initiating metallo-carbenes and, since the isomerization is reversible, it also provides a possible chain termination mechanism. A recent report[58] provides supporting evidence for this proposal in that the carbene ligand in $RCH_2(Ph)C{=}W(CO)_5$ is readily isomerized to the corresponding olefinic ligand PhCH=CHR. However, this route to metallo carbenes may not apply to norbornene and other similarly sterically constrained but highly reactive cycloalkenes, since the transition state in equation 1.20 requires some distortion from the planarity of the olefinic group. A possible variation avoiding this difficulty requires a 1,2-hydride transfer to give a metal hydride followed by a 1,3-hydride shift to give the metallo carbene, Figure 1.21.

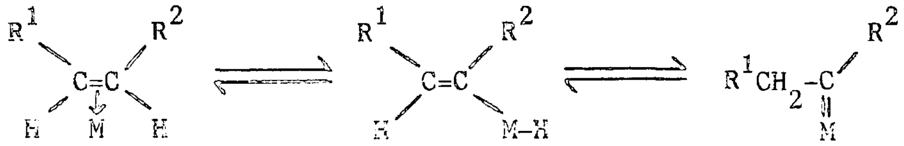


Figure 1.21

The third scheme which has been proposed involves a transition metal hydride, either present in the catalyst or formed during its preparation, Figure 1.22.

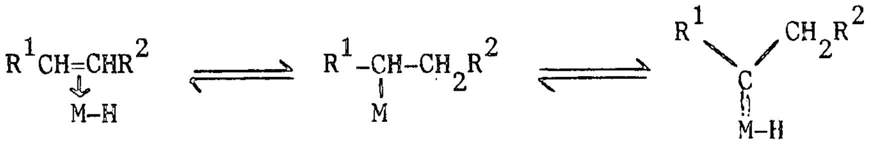


Figure 1.22

The transition metal-hydride may be formed by initial reaction between the transition metal and an oxygen containing activator such as an alcohol or water.[59]

The oxygen containing activator may act in two ways, either via a hydride shift, Figure 1.23, or less likely by a concerted-type reaction, Figure 1.24.

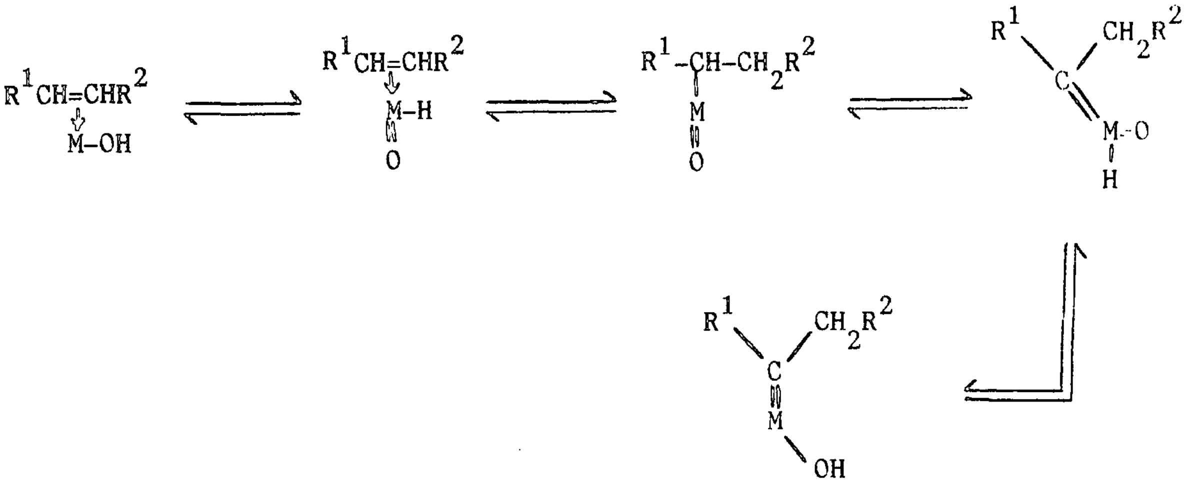


Figure 1.23

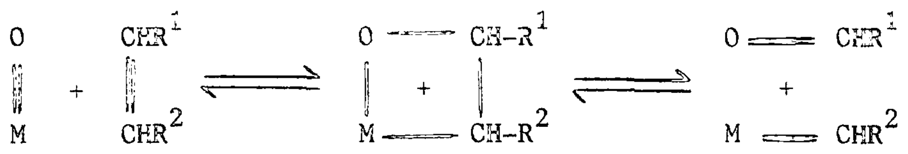


Figure 1.24

Recently, Amass[27,28] reported the formation of a W=O site for reactions which do not contain metal alkyl co-catalysts, Figure 1.25.

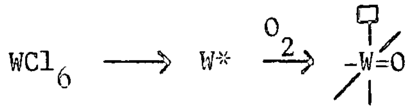
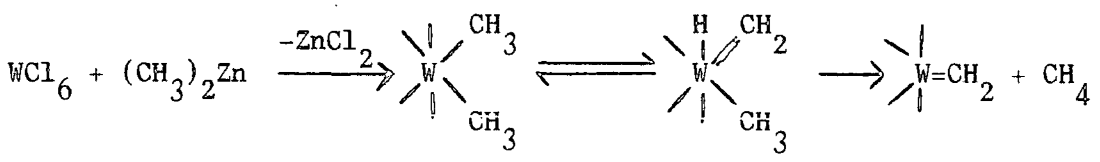
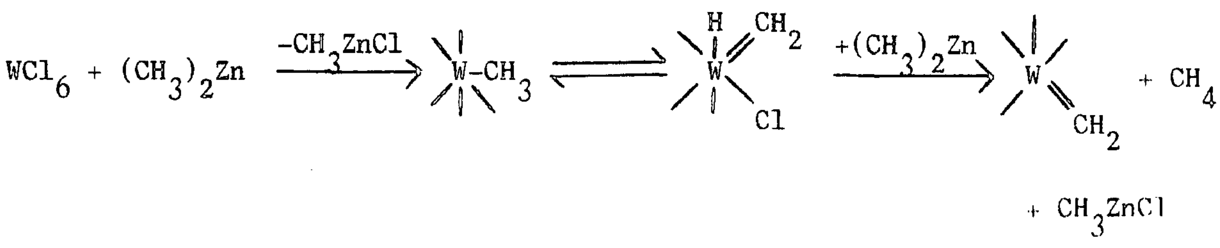


Figure 1.25

* = activated tungsten species
□ = vacant site

For systems containing a transition metal catalyst together with an organometallic co-catalyst, it has been well documented that organometallic co-catalysts do provide σ-bonded alkyl groups when reacted with transition metal derivatives. Muetterties[60,61] observed that methane was produced during the activation of WCl_6 with dimethyl zinc. When the reaction was repeated in deuterated solvent the methane produced contained no deuterium. The author proposed that the hydrocarbon resulted from the formation of a metal to carbon double-bonded species by one of the paths given below.





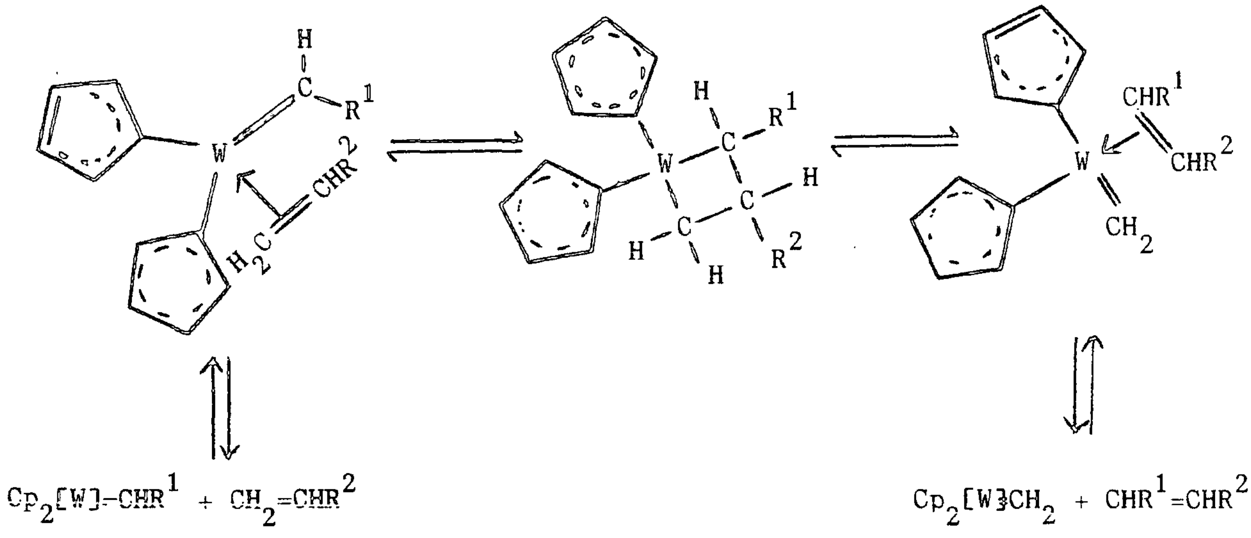
Reaction of selected transition metal compounds with the appropriate organometallic co-catalysts afforded methane and ethylene. Perdeuterated methane and ethylene were produced when the co-catalyst was $(CD_3)_4Sn$ as shown below.[62]

$$WCl_6 + (CD_3)_4Sn \longrightarrow CD_4 + CD_2{=}CD_2 + W\text{-catalyst}$$

Finally, Fischer and Casey carbenes are stable metathesis catalysts without the addition of co-catalysts.

1.6.b The propagation step

The propagation step in the olefin metathesis reaction involves metal-carbene to metallocyclobutane interconversion. There is evidence to support the formation of a metallocyclobutane as an intermediate. Green et al[63] showed that a stable metallocyclobutane of tungsten could be isolated, and that thermolysis or photolysis gave a metal-carbene and an alkene which was rationalized as shown in Figure 1.26.



(Cp = cyclopentadiene ligand)

Figure 1.26

The sequence shown in Figure 1.17 for the polymerization of cycloalkenes received convincing confirmation in recent work reported by Grubbs and co-workers.[64] They showed that the titanacyclobutane derivative shown in

Figure 1.27 reacted with one molecular proportion of norbornene at room temperature to give the exo-titanacyclobutane shown. When this 1:1 adduct was heated with an excess of norbornene ring-opening

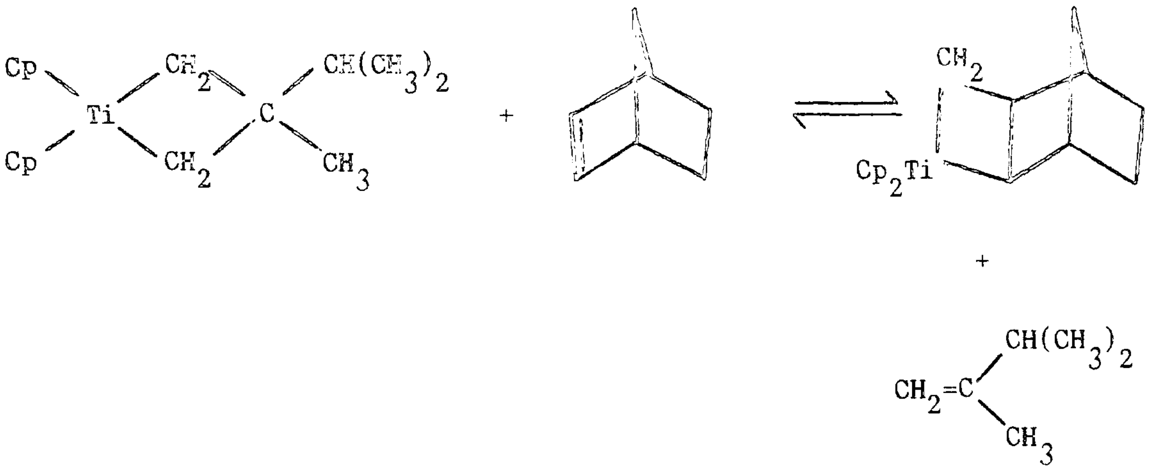


Figure 1.27

polymerization occurred to give polynorbornene. The propagation step is important in controlling the stereoselectivity of the polymer and much work has been carried out by Ivin and co-workers. This will be discussed in Chapter 4.

1.6.c Chain growth termination

Most chain reactions display one or more termination steps. In polymerizations there are those reactions which limit the molecular weight of the polymer by formation of a low molecular weight carbene species and dead polymer (usually described as chain transfer); and those reactions which terminate chain growth by destruction of the catalytic species. Reactions that destroy the catalytic intermediates are clearly more critical.

It is well established that the termination of the chain can be brought about through proton transfer by introduction of water or an alcohol, through nucleophilic substitution with alkyl halides or by addition of CO_2; these termination modes can be controlled by olefin purification and apparatus design. Very little work has been reported concerning the exact termination modes; however, sufficient model reactions are available to suggest some reasonable possibilities. For example a common reaction of carbenes is the formation of cyclopropanes as shown in Figure 1.28, and this is a plausible chain termination step.

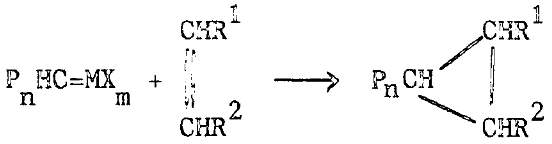


Figure 1.28

Recently, it was suggested that ring-opening polymerization and Ziegler-Natta polymerization are mechanistically related[65] and the metallo-carbene chain carrier of metathesis is easily related to the metal alkyl of Ziegler-Natta polymerization via 1,2-hydrogen shifts as shown in Figure 1.29. This analogy can be extended, termination via bimolecular hydrogen transfer can be postulated, this process is illustrated in Figure 1.30.

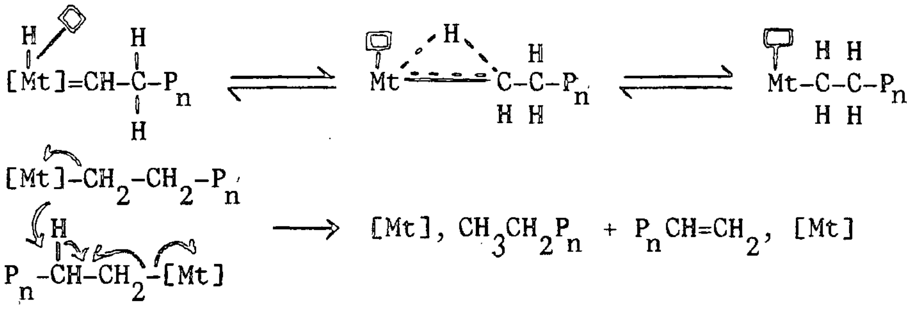
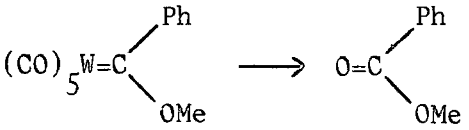
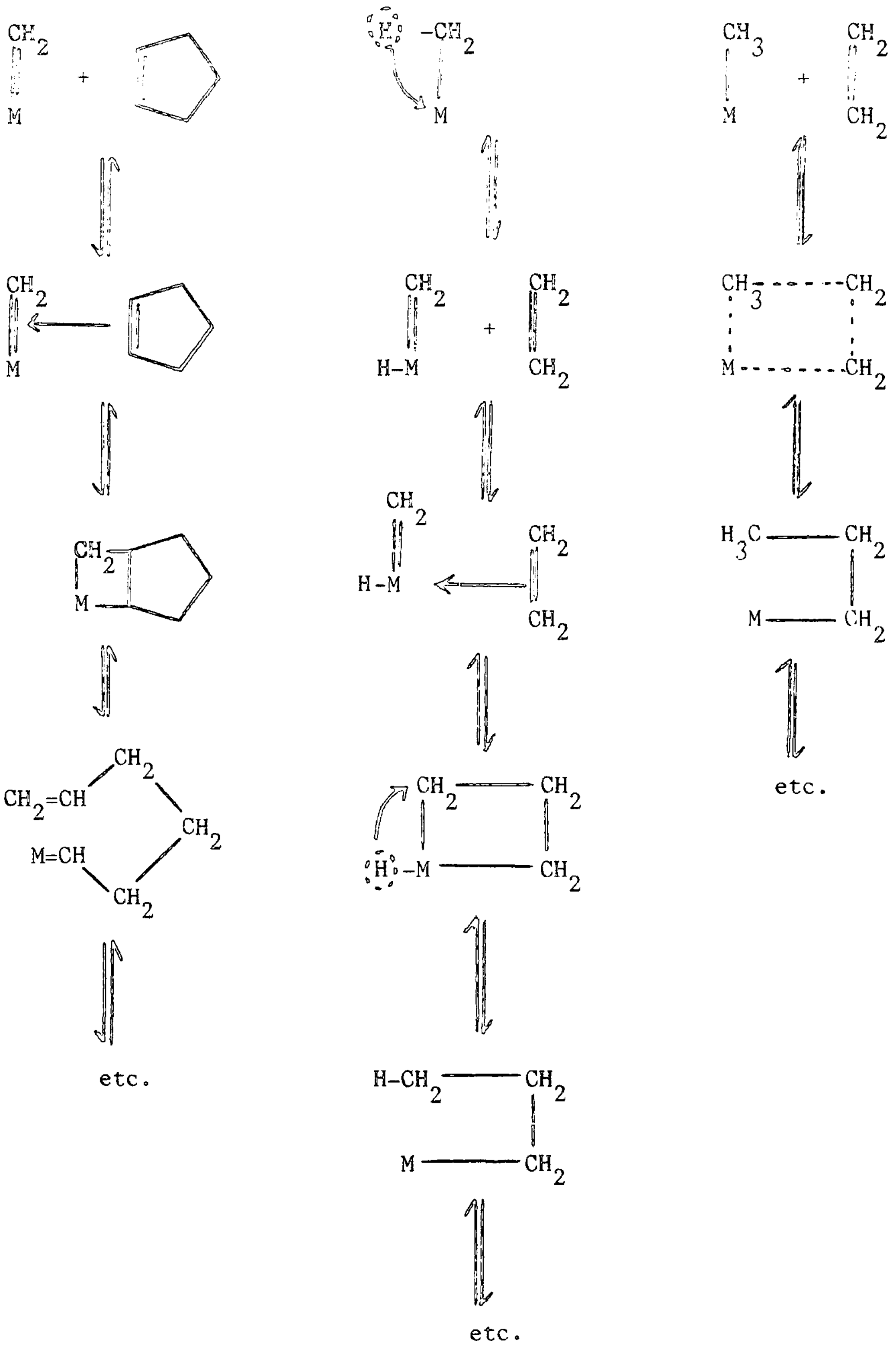


Figure 1.30

Another model reaction available is that of carbene complexes with oxygen which destroys the complex rapidly:[66]





olefin metathesis mechanism for the ring-opening polymerization of cycloalkenes

unconventional Ziegler-Natta polymerization mechanism

conventional Ziegler-Natta polymerization mechanism

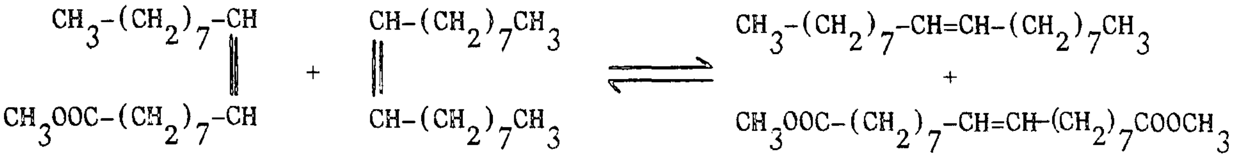
Figure 1.29

1.7 Metathesis of Substrates Bearing Polar Groups

At one time it was thought it would be difficult to extend the olefin metathesis reaction to compounds containing functional groups. The classical catalyst system $WCl_6/EtAlCl_2/EtOH$ rapidly loses its activity in the presence of an excess of such compounds. A major step forward was made in 1972[67] when it was shown that the metathesis of unsaturated esters could be brought about by WCl_6/Me_4Sn at 70°C. Heterogeneous catalysts effective for metathesis reactions involving alkenes carrying heteroatom polar groups are also known, polyunsaturated esters, unsaturated lactones, cycloalkenes carrying ester groups, nitriles, ketones, ethers, amides and amines have been shown to be susceptible to metathesis reactions. This aspect of metathesis is now in a state of rapid development, and its technological significance extends broadly into applications related to such areas as insect control, perfume chemistry, flame and oil-resistant elastomers, and speciality plastics.

1.7.a Functionalized acyclic olefins

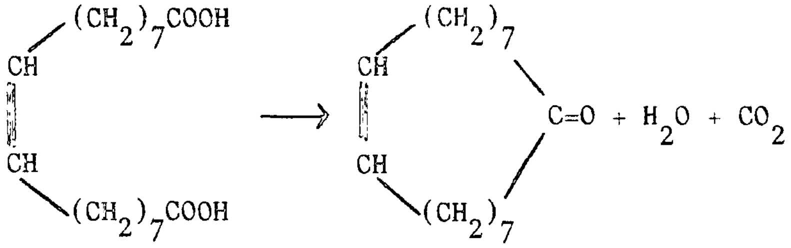
In 1972, Boelhouwer[67] reported the metathesis of the ester methyl oleate and its trans isomer, methyl elaidate with a homogeneous catalyst based on a 1/1.4 molar combination of $WCl_6/(CH_3)_4Sn$. At 70°C and an ester/W molar ratio of 33/1; 49% and 52% of the respective esters were converted to equal amounts of 9-octadecene and the dimethyl ester of 9-octadecene-1,18 dioic acid, Figure 1.31.



$$\begin{array}{c} CH_3\text{-}(CH_2)_7\text{-}CH \\ \| \\ CH_3OOC\text{-}(CH_2)_7\text{-}CH \end{array} + \begin{array}{c} CH\text{-}(CH_2)_7CH_3 \\ \| \\ CH\text{-}(CH_2)_7CH_3 \end{array} \rightleftharpoons \begin{array}{c} CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7CH_3 \\ + \\ CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7COOCH_3 \end{array}$$

Figure 1.31

Boelhouwer subsequently reported the successful metathesis of methyl esters of polyunsaturated linoleic and linolenic acids using the WCl_6/$(CH_3)_4Sn$ catalyst.[68] Unsaturated esters such as those found in sunflower seed oil, olive oil, linseed oil, and soya bean oil, may be converted into intermediates for the production of useful perfumes, polymers, etc. For example, the metathesis of olive oil, which consists chiefly of triglycerides of oleic acid, produces the glyceride of 9-octadecene-1,18-dioic acid from which can be obtained after saponification, acidification, and low temperature crystallization the free acid, which can be transformed by intermolecular condensation to Civetone,[69,70,71] Figure 1.32.



free acid Civetone

Figure 1.32

Boelhouwer found the $WCl_6/(CH_3)_4Sn$ combination to be unique for metathesis of fatty acid esters.[72] Seemingly related combinations, such as $WCl_6/(C_2H_5)_4Sn$, $WCl_6/(C_4H_9)_4Sn$, $WCl_6/(Ph)_4Sn$ and $MoCl_5/(Ph)_4Sn$ were surprisingly inactive in the homometathesis of fatty acid esters or in cross metathesis reactions with common olefins. Recently, additional catalyst systems which are effective for the methathesis of olefins bearing polar functional groups have been revealed. Nakamura and co-workers[73] found that either WCl_6 or $(C_2H_5O)_2MoCl_3$ in combination with triethyl borane gave catalysts capable of converting cis-9-octadecenyl acetate to 1,18-diacotoxy-9-octadecene and 9-octadecene at the rather high temperature of 178°C, Figure 1.33.

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc \rightleftharpoons \begin{array}{c} ACOCH_2(CH_2)_7CH{=}CH(CH_2)_7CH_2OAc \\ + \\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \end{array}$$

Figure 1.33

Nakamura[74] subsequently reported that catalyst systems derived from WCl_6, $MoCl_5$, $Mo(OC_2H_5)_2Cl_3$ and $W(CO)_6$ in combination with $(CH_3)_3Al_2Cl_3$ effected the metathesis of a variety of fatty acid esters, as well as alkenyl nitriles, ketones, ethers, amides and oxysilanes. Catalysts such as $WCl_6/C_2H_5OH/C_2H_5AlCl_2$, Re_2O_7/Al_2O_3, $WCl_6/(C_2H_5)_3Al_2Cl_3$ and $WCl_6/(C_2H_5)_3Al$ were found to be inactive towards these substrates. With $WCl_6/Me_3Al_2Cl_3$ as catalyst the substituted ketone $CH_3(CH_2)_7CH{=}CH(CH_2)_7{-}COC_2H_5$ gave a 5% yield of metathesis products; $CH_2{=}CH(CH_2)_2COCH_3$ gives a 10% yield, and $CH_3(CH_2)_7CH{=}CH(CH_2)_7CON(C_2H_5)_2$ a 3% yield. No reaction is observed when the functional group is COOH or $CONH_2$.[75] Ast and co-workers[76] reported the olefin metathesis of unsaturated ethers in the presence of the homogeneous catalyst $WCl_6/(CH_3)_4Sn$ for example the metathesis of 4-pentenyl-butyl ether (4) according to the following reaction scheme 1.34, under the following conditions:

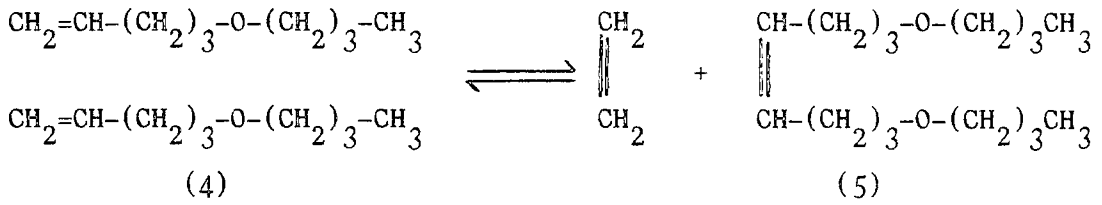


Figure 1.34

Molar ratio W/Sn/olefin is 1:3:10, reaction temperature 90°C, reaction time 24 hours, gave the maximum yield about 90%. The yield slightly decreased when using a 1:3:30 ratio but only traces of (5) could be detected when using a ratio lower than 1:3:100. Ast and co-workers also measured the influence of the distance between ether oxygen and the reactivity of the double bond. They found that with a homogeneous catalyst it is essential to have more than one methylene between the double bond and the ether function, and the reaction only proceeds in good yield when there are at least three intervening methylene groups.

With this system the catalyst/substrate ratio must be much higher than is required for olefins, otherwise the reaction becomes inefficient or will not proceed. Basset and co-workers[77] found that amino olefins such as allyl amine and the N,N dimethyl derivative failed to undergo metathesis but when the catalyst's molar ratios of olefin/(mesitylene) $W(CO)_3/C_2H_5AlCl_2/O_2$ and olefin/$Mo(NO)_2Cl_2[PPh_3]/C_2H_5AlCl_2$ 20/1/24/80 and 20/1/24 respectively were used, yields were in the 8 - 23% range, Figure 1.35.

$$CH_2{=}CHCH_2N(CH_3)_3Br \rightleftharpoons CH_2{=}CH_2 + Br(CH_3)_3NCH_2CH{=}CHCH_2N(CH_3)_3Br$$

Figure 1.35

The result is similar for other low-molecular-weight halogen substituted alkenes. In the nitrile case, the reaction of acrylonitrile with propene over a heterogeneous catalyst derived from ammonium tungstate to give ethylene and 1-cyano-propylene, has been claimed as shown in this Figure 1.36.[78] Nakamura[74] has reported that the heterogeneous

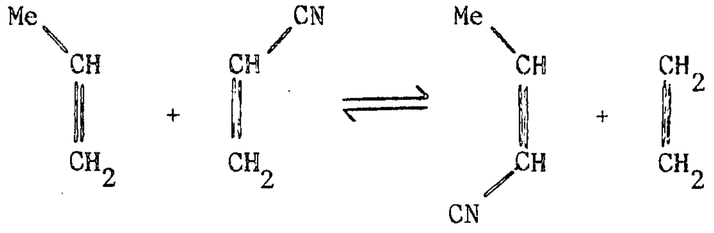
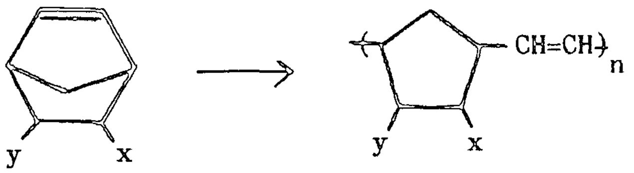


Figure 1.36

catalyst system $Re_2O_7/(CH_3)_4Sn$ is active towards the metathesis of methyl 4-pentenoate at 50°C, producing 4-octene-1,8-dioic acid dimethyl ester and ethylene in 51% yield. A ratio of olefin/Re/Sn of 219/6/1 was used, the degree of selectivity was > 99%, and the system was found to be inactive without $Sn(CH_3)_4$.

1.7.b Functionalized cycloolefins

The inhibitory effects of polar functional groups are not nearly as pronounced when the substituent is attached to a strained cycloalkene, where the release of ring strain acts as a significant driving force for metathesis. The norbornene ring system polymerizes easily by ring-opening thus numerous functionalized polymers have been prepared by the reaction shown below.



The earliest reported ring-opening polymerizations of functional norbornenes were carried out in protic solvents (alcohol, water) using iridium, ruthenium or osmium salts. Thus, norbornenes substituted with ester,[79,80] hydroxy,[80] chlorine,[81] alkoxy,[82] and imide[83] groups have been polymerized via metathesis using noble metal catalysts. Homogeneous catalysts based primarily on WCl_6 and organoaluminums have also been reported for norbornenes bearing ester,[83-91] nitrile,[92-97] amide,[89,90,94] imide,[85,90,96] chlorine,[95] anhydride,[89,90] pyridyl,[89,90] and alkoxy[98,99] functional groups. Monomer/W molar ratios generally in the range of 100 - 2000/1 were employed, catalyst modifiers were employed to increase metathesis activity.

Other functionally mono, bi and tetra substituted bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hepta-2,5-dienes which have been ring-open polymerized include fluorinated derivatives,[43,100,101] examples of which are shown in Figure 1.37 and aryl-substituted derivatives,[102] Figure 1.38; catalysts in this work consisted of WCl_6 or $MoCl_5$ together with organotin co-catalysts.

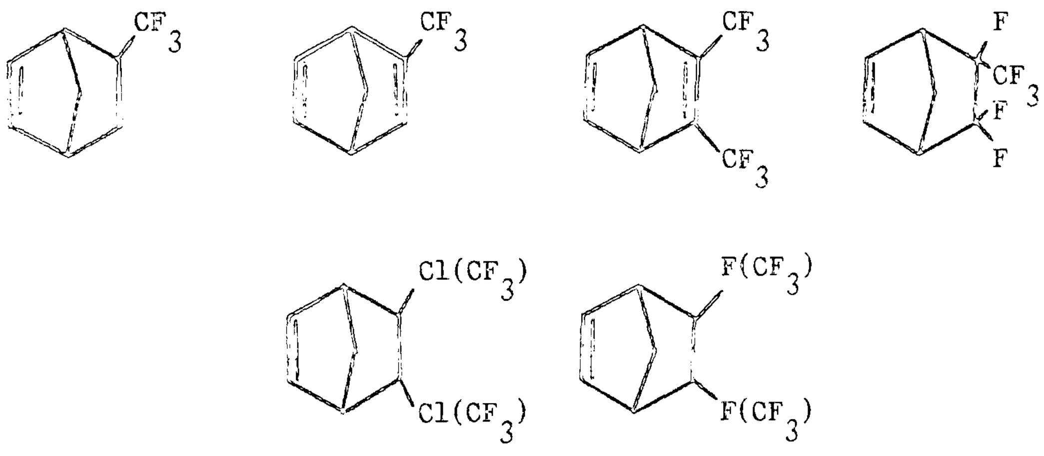


Figure 1.37

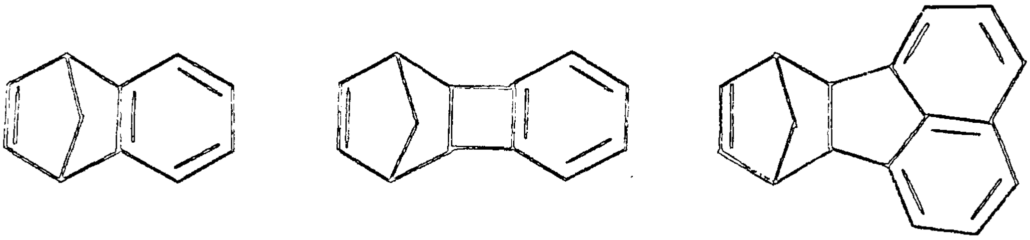
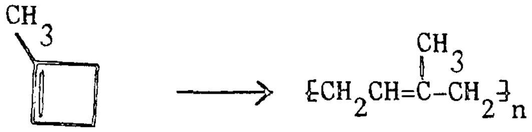


Figure 1.38

The polymerization of monomers substituted on the double bond has been reported, 1-methyl cyclobutene undergoes ring-opening polymerization in the presence both of $Ph_2C{=}W(CO)_5$ at 50°C and of WCl_6-based catalysts to give polyisoprene, Figure 1.39.[22,52,54,103]



$$\xrightarrow{} \;[CH_2CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2]_n$$

Figure 1.39

Subsequently, Katz (1980) reported the successful ring-opening polymerization of 1-trimethylsilylcyclobutene and 2-methyl bicyclo[2,2,1]-hept-2-ene, and Lee (1976) reported the ring-opening polymerization of 1-methylcyclooctene as shown in Figure 1.40.[53,104]

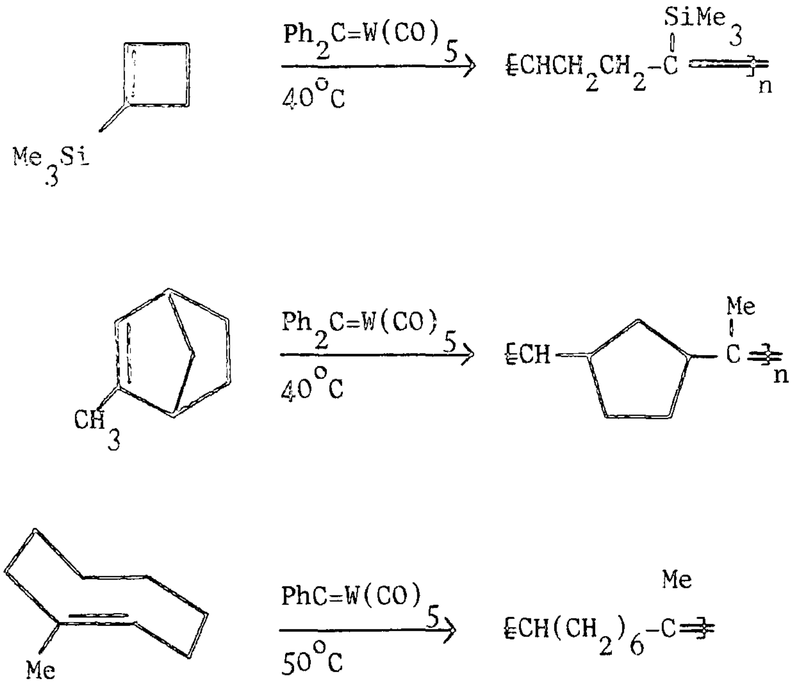
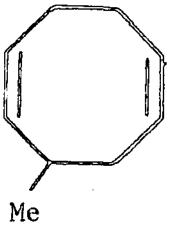


Figure 1.40

All the compounds 6 - 12 in Figure 1.41, except 12, are polymerizable by ring-opening[105-109] and it seems to be essential to leave at least one double bond free of substituents unless the double bond is strained by being in a small ring or having a trans structure.



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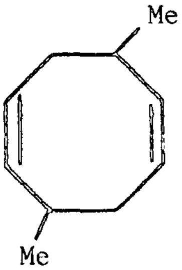

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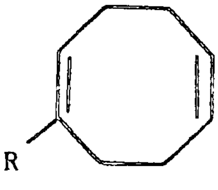
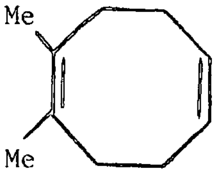


8 R = Me
9 R = Et



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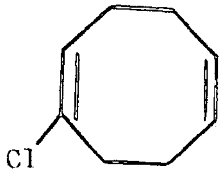

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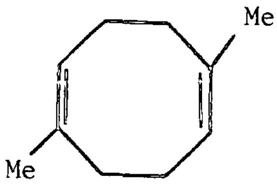


12

Figure 1.41

It seems reasonable to assume that reaction occurs mainly by ring-opening at the unsubstituted double bond.

Ring-opening polymerization and copolymerization of the Diels-Alder adduct of 1,5-cyclooctadiene and hexachlorocyclopentadiene occurred via reaction at the unsubstituted double bond,[110] Figure 1.42, the resulting polymers were found to be thermally stable flame and oil resistant materials.

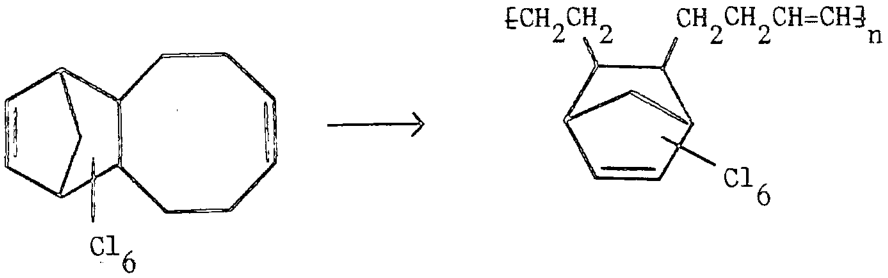


Figure 1.42

It has also been shown that the presence of an alkyl substituent at the allylic position of a strained cycloalkene does not affect the polymerizability, for example 1-methyl and 1-ethyl bicyclo[2.2.1]hept-2-enes readily polymerize by ring-opening, Figure 1.43;[111] however, in less

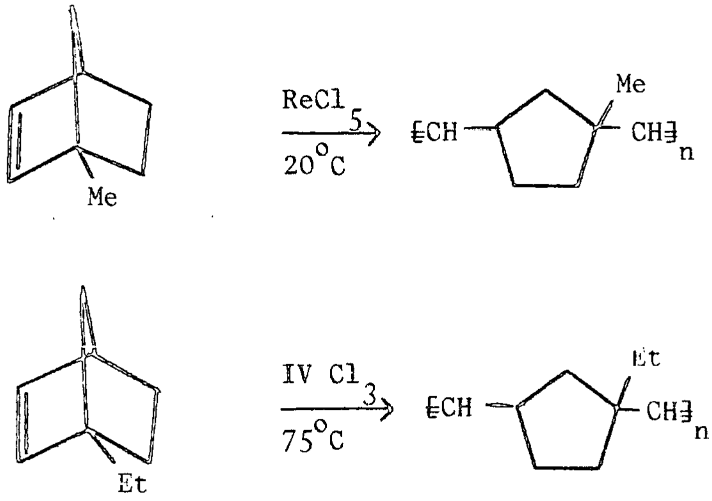


Figure 1.43

strained systems polymerizability decreases with the size of an allylic substituent.

Other substituted monomers containing pendant ester groups may be prepared by the reactions of ethyl diazoacetate with 1,5-cyclooctadiene, 1,5,9-cis, trans, trans-cyclododecatriene, and norbornadiene, respectively and undergo ring-opening polymerization, Figure 1.44.[111]

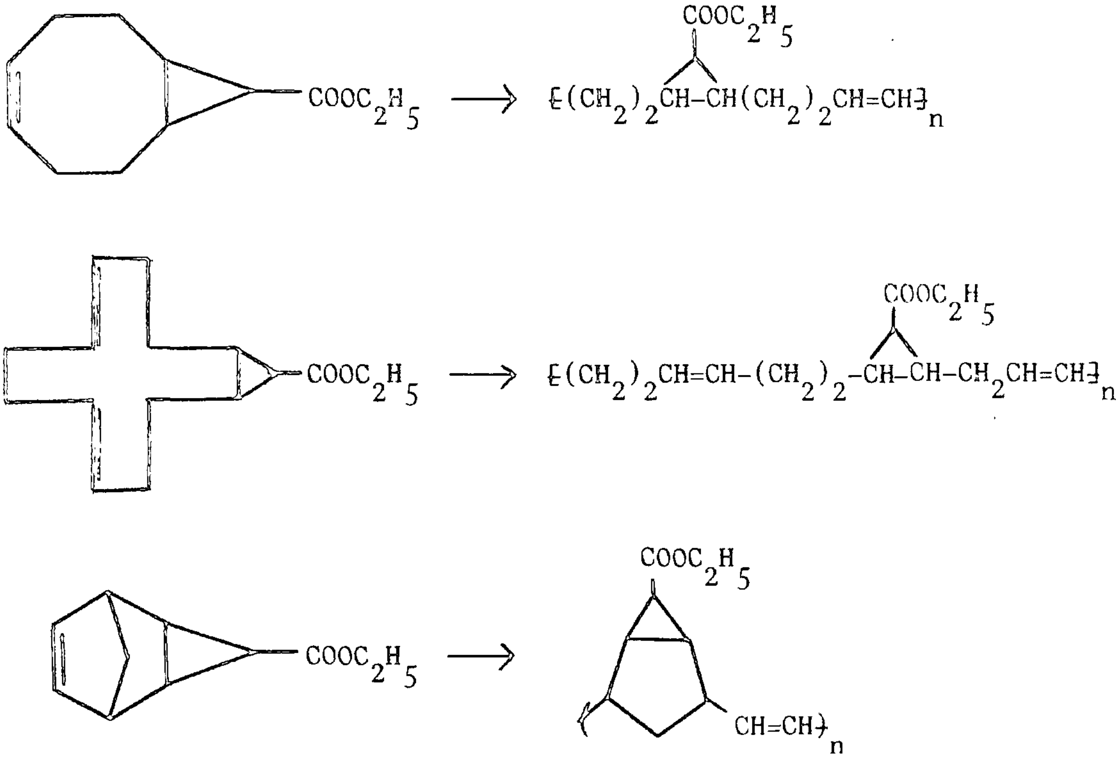


Figure 1.44

Recently, Streck[112] reported new silicon and tin containing polymers prepared from the monomers shown in Figure 1.45, the products derived having useful properties as adhesion promoters and biocides respectively.

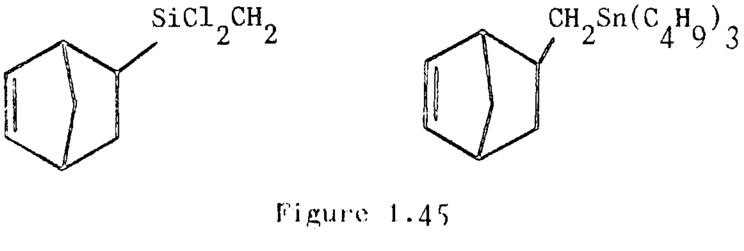
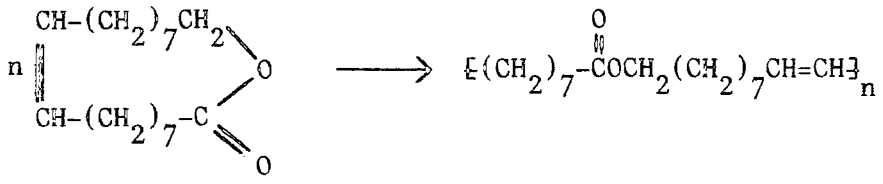


Figure 1.45

1.8 Ring-opening Polymerization of a Lactone by Metathesis

A naturally occurring lactone, ambrettolide was polymerized employing the $WCl_6/(CH_3)_4Sn$ catalyst in a molar ratio of monomer/W/Sn of 50/1/5, affording a high molecular weight unsaturated polyester,[113]



conversions of about 80% were obtained. The polymer could also be cleaved by cross-metathesis with an excess of 4-octene which gave, as the main product, 9-tridecenyl-7-undecenoate. The unsaturated lactone was also copolymerized with cyclooctene, 1,5-cyclooctadiene, and cyclopentene to afford linear copolymers which were high molecular weight, unsaturated rubbery[113] polyesters.

1.9 Applications of Metathesis

1.9.a Synthesis of macrocycles

The synthetic potential of the olefin metathesis reaction to polymer chemistry is enormous. Monocyclic alkenes from C_4 to C_{12} with the exception of cyclohexene[114] undergo ring-opening polymerization to produce polyalkenylenes and depending upon the structure of the repeat unit and the double bond configuration these polymers may possess properties ranging from amorphous elastomers to crystalline materials. By conducting the metathesis reaction of cycloolefins at high dilutions a relatively high yield of macrocyclic compounds can be obtained.[115-117] Of special interest is 1,9-cyclohexadecadiene, the cyclic dimer of cyclooctene, which can be converted to the macrocyclic musk-like ketone as shown in Figure 1.46.[118]

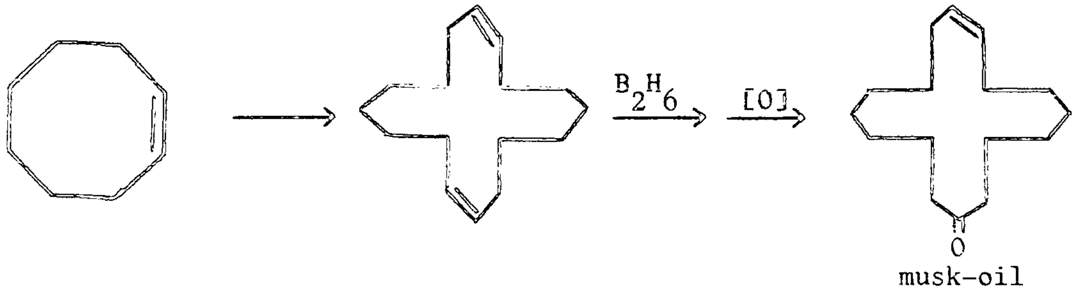


Figure 1.46

Studies by Wolovsky et al.[119] lead to the conclusion that interlocked ring systems are present in the mixture of macrocyclics obtained from metathesis of cyclododecene; the formation of catenanes[120] was accounted for by assuming a concerted intramolecular transalkylidenation of a twisted "strip" as illustrated in Figure 1.47.

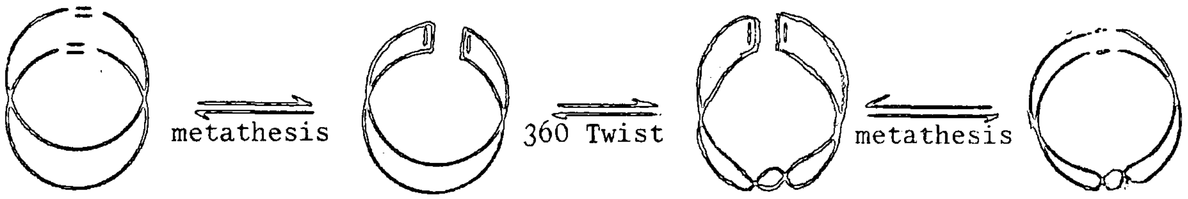


Figure 1.47

1.9.b Cross-metathesis

Cross-metathesis reactions of acyclic with cyclic olefins can be directed towards the formation of liquid polymers, diene, triene and other polyenes, depending on the ratio of acyclic/cyclic olefin employed.[121-127] Some examples of this type of process which have been achieved are the interaction of ethylene with cyclopentene, cyclooctene or cyclododecene to give hepta-1,6-diene, deca-1,9-diene and 1,13-tetradecadiene as shown in Figure 1.48.[121,128-132]

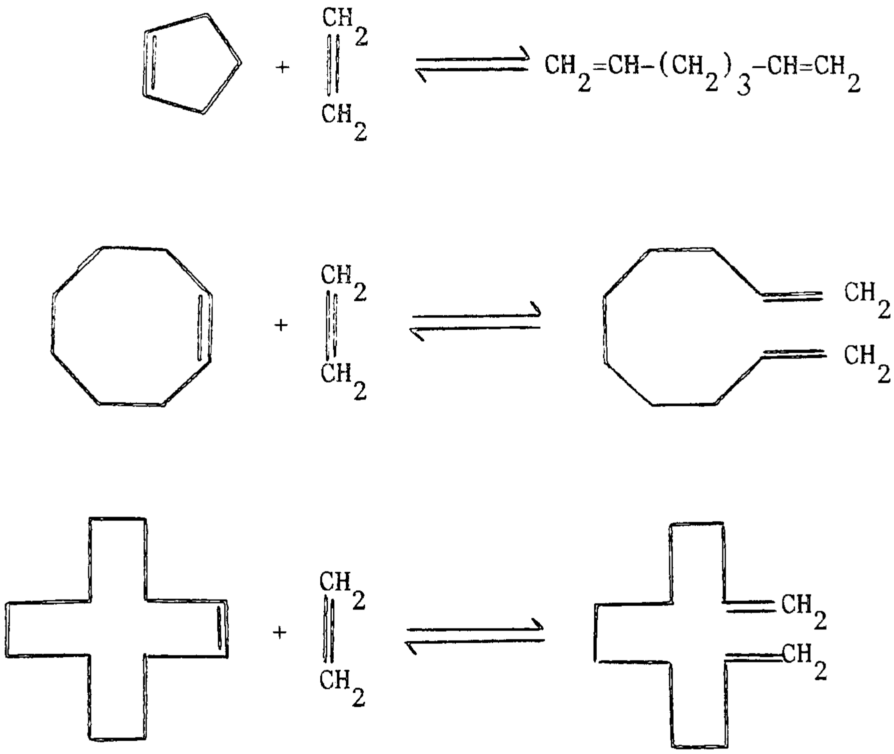
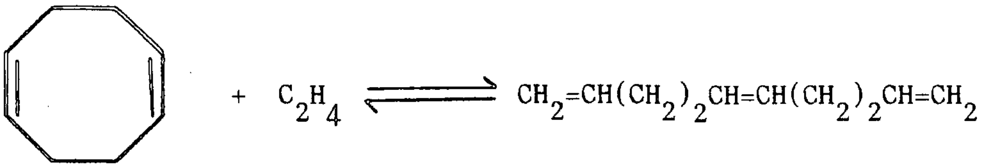
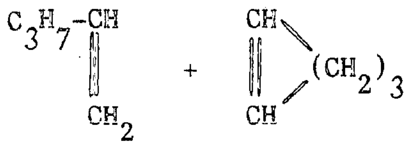


Figure 1.48

In all these kind of reactions, high ethylene pressures help to shift the equilibrium toward the diene. The symmetric triene 1,5,9-decatriene was obtained by the metathesis of ethylene with 1,5-cyclooctadiene as shown in the following equation.[121,131]



The product triene can react with an additional mole of ethylene to yield 1,5-hexadiene. The reaction products will be complex when the acyclic olefin is an unsymmetric olefin. Three series of polyenes can be produced by the cross-metathesis of 1-pentene and cyclopentene,[133] two symmetric and one unsymmetric, see Figure 1.49. The symmetric polyenes constitute less than 5% of the total products shown in Figure 1.49.



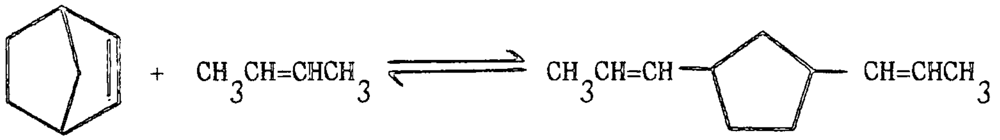
$CH_2{=}\{CH(CH_2)_3CH{=}\}_xCH_2$ - symmetric

$CH_2{=}CH(CH_2)_3CH{=}CHC_3H_7$ - unsymmetric

$C_3H_7CH{=}CH(CH_2)_3CH{=}CHC_3H_7$ - symmetric

Figure 1.49

Norbornene reacted with 2-butene to yield 11% of 1,3-bis(1-propenyl) cyclopentane as shown below.[129,134]



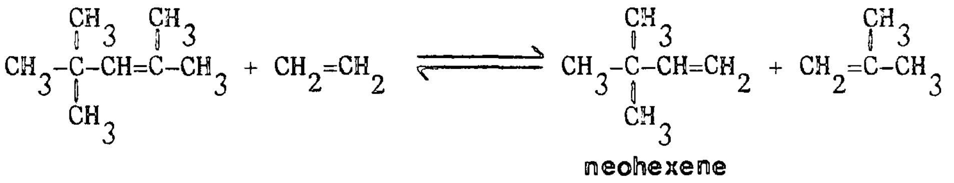
Cross-metathesis between cycloalkenes and functionalized alkenes gives new routes to long-chain linear mono- or di-functionalized compounds which are industrially attractive.

Cross-metathesis reactions have also been used in the characterization of unsaturated polymers.[135-142] The polymers are degraded to yield oligomers which are characterized giving information about the position of the unsaturated linkages in the polymer.

The extent to which a potential application can be translated into commercial production depends on the usual market forces; the supply and cost of the raw materials, costs of erection and maintenance of processing plant, and properties and price of product in relation to its competitors. Banks has reported a recent industrial use of metathesis in the large scale production of acyclic alkenes, historically the Phillips triolefin process was the first industrial application of the olefin metathesis reaction and involves the production of high purity ethene and but-2-ene from propene; reaction 1.2. The process was based on technology developed by the Phillips Petroleum Co.

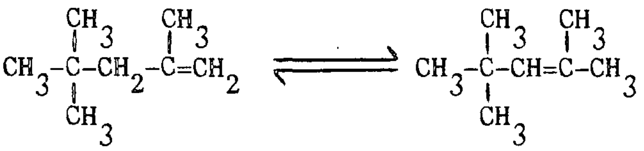
$$2CH_3CH{=}CH_2 \rightleftharpoons CH_2{=}CH_2 + CH_3CH{=}CHCH_3 \qquad 1.2$$

3,3-Dimethyl-but-1-ene (neohexene) is an important intermediate in the synthesis of an artificial musk perfume. The process is based on the dimer of isobutene which consists of a mixture of 2,4,4-trimethylpent-2-ene and 2,4,4-trimethylpent-1-ene. Cross-metathesis of the former with ethene yields the desired product (reaction 1.3),[143] the



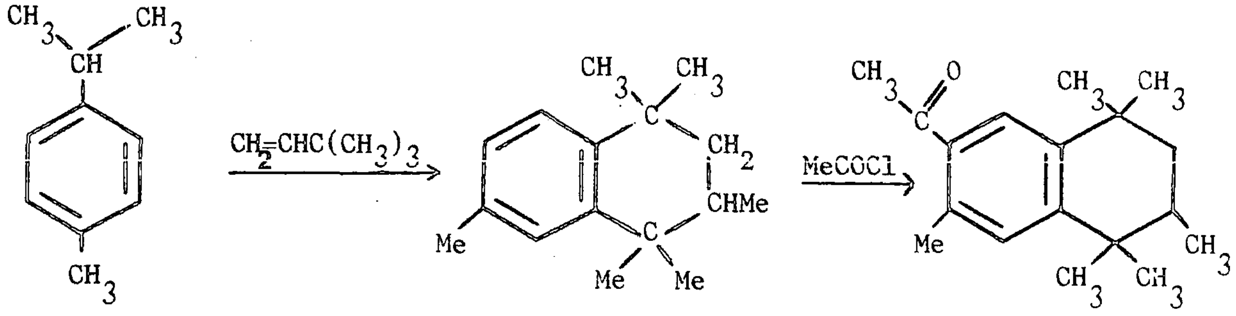
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 + CH_2=CH_2 \rightleftharpoons CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 + CH_2=\overset{CH_3}{C}-CH_3 \qquad 1.3$$

latter is not wasted since a dual catalyst $WO_3/SiO_2/MgO$, can be used to ensure that it is converted into 2,4,4-trimethylpent-2-ene as this gets used up by metathesis, reaction 1.4.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{C}=CH_2 \rightleftharpoons CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3 \qquad 1.4$$

Neohexene is employed to make the class of synthetic musks designated as bicyclic musks. The reaction with p-cymene, followed by acetylation, gives one such compound, 7-acetyl-1,1,3,4,4,6-hexamethyltetralin (13), Figure 1.50.



13

Figure 1.50

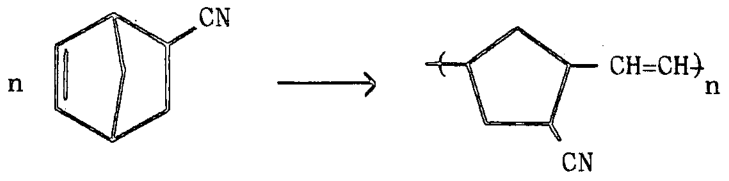
In the commercial manipulation of hydrocarbon feed stocks the metathesis reaction clearly provides a valuable new unit process which may be combined with other processes either in the same reactor using successive layers of the requisite catalysts, or in consecutive reactors,[132,144,145] two examples of these are shown in this scheme

$$CH_3CH{=}CH_2 \xrightarrow{\text{metathesis}} CH_3CH{=}CHCH_3 \xrightarrow[\text{alkylation}]{(CH_3)_3CH} CH_3CH_2CHCH_3(CH_3)_3$$

$$\text{Alkane} \xrightarrow{-H_2} \text{Alkene} \xrightarrow{\text{metathesis}} \text{Alkenes} \xrightarrow{H_2} \text{Alkanes.}$$

In recent years it has been shown that many insect sex attractants are either higher olefins or their simple derivatives. Some of them may be synthesized by olefin metathesis, such synthetic pheromones may provide valuable means of control of agricultural pests.[143,144,146,147] The ring-opened polymer of cyclooctene was first marketed in 1980, under the trade name Vestenamer 8012, this polymer also goes under the name trans-polyoctanemer (TOR).[112] The monomer is readily obtained by partial hydrogenation of cyclooctadiene which in turn is prepared from butadiene by catalytic dimerization. Vestenamer 8012 is especially suitable for use in blends with other rubbers.

The 90% trans polymer of norbornene was put on the market in 1976 by CdF Chimie under the trade name Norsorex, the monomer is made from cyclopentadiene and ethene.[148,149] Polymers made from norbornene derivatives have been the subject of numerous patents, but as yet there is no sign that they are likely to become commercially viable materials. The polymer from 5-cyano-bicyclo[2.2.1]hept-2-ene, poly(4-cyano-1,3-cyclopentylene vinylene), is under market research as a thermoplastic resin.[150]

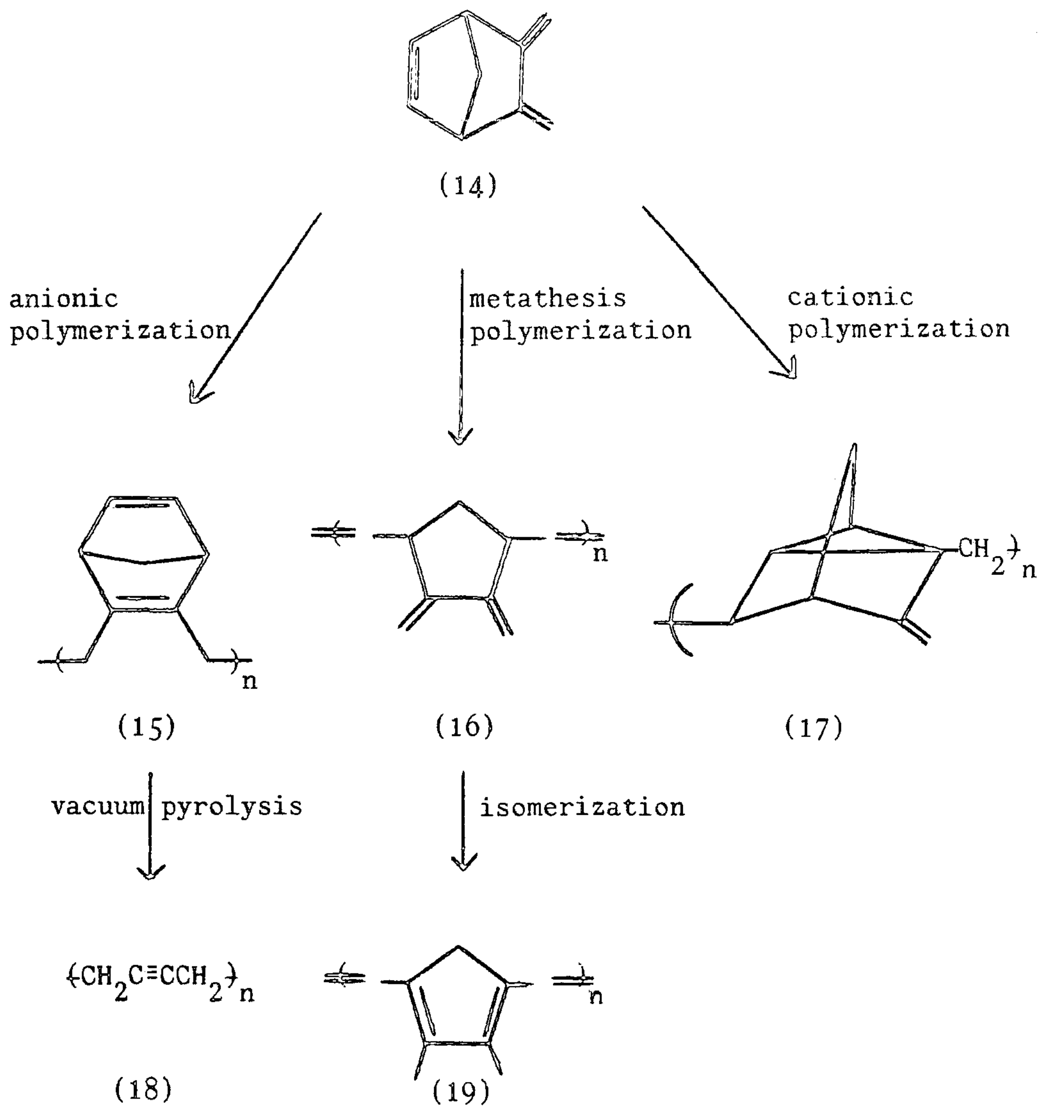


While in 1974 it seemed likely that trans-poly(1-pentenylene), sometimes termed trans-polypentenamer T.P.R., was about to make its debut as the new all-purpose synthetic elastomer which could be blended with, or take the place of, natural rubber.[151] Much time and money was spent on developing a method for the economic extraction of cyclopentadiene from the C_5 cut obtained by steam cracking of naphtha and for its selective hydrogenation to cyclopentene.[152] However, the economic recession of the last few years has resulted in changed circumstances and plans for the large-scale production of TPR made by at least one large company have therefore been shelved. However, since World demand for rubber is increasing by at least 4% per annum, there is a continuing incentive to produce a synthetic material comparable in properties to natural rubber and polypentenamers may yet find commercial exploitation.

1.10 Objectives of the Work Reported in this Thesis

The initial objectives of the work reported in this thesis were to investigate the polymerization of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (14) as indicated in Figure 1.51. The monomer (14) has been described previously[153-168] and its free radical initiated polymerization studied.[155] In the present work the anionic, metathesis ring-opening, and cationic polymerizations were thought to be worth investigation.

There is a lot of research on highly conjugated organic polymers at the present time,[169-171] this activity is based on the observation that several polymers of this type have interesting electrical properties. For example, polyacetylene, which may be regarded as the parent of this family of polymers, can be an insulator (cis-polymer) an intrinsic semiconductor (trans-polymer) and can also be modified by electron donors or acceptors to give first n- or p-type semiconductors

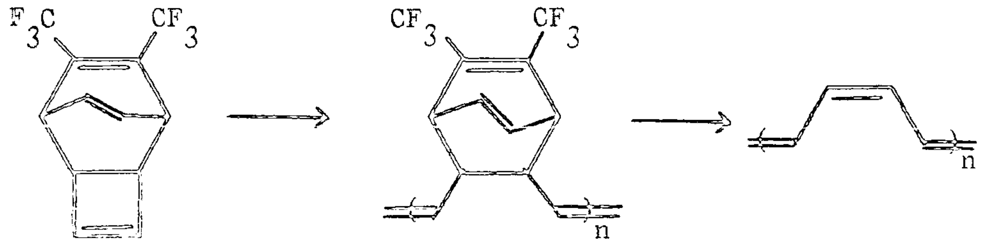


Hypothetical routes to polymers from monomer (14)

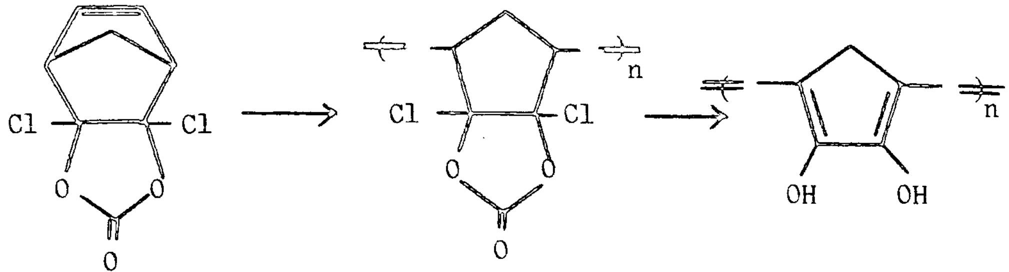
Figure 1.51

and eventually metal-like electrical conductivity.[172-175]

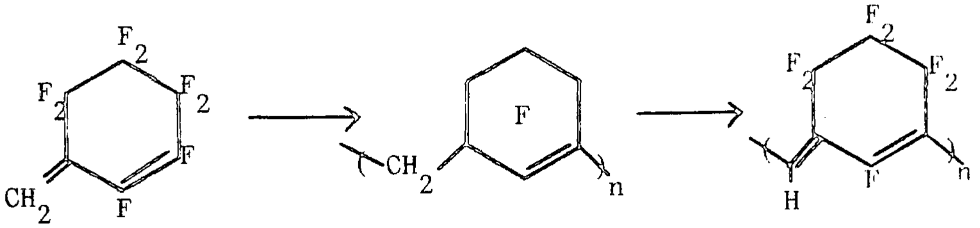
It was envisaged that if the monomer (14) could be ring-open polymerized the product polymer (16) would be subject to isomerization by 1,3-hydrogen shifts to generate a conjugated system (19) which might have interesting electrical properties. This approach to the synthesis of conjugated polymers is analogous to other two-step syntheses achieved by workers in this group as illustrated below.[169-171] An advantage of this approach is that the prepolymers (20), (21) and (22) are soluble and can be purified and processed whereas the product conjugated polymers



(20)



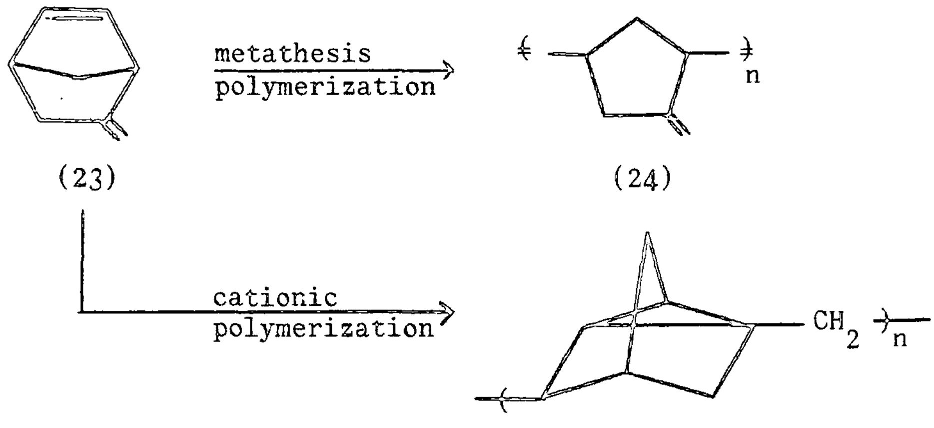
(21)



(22)

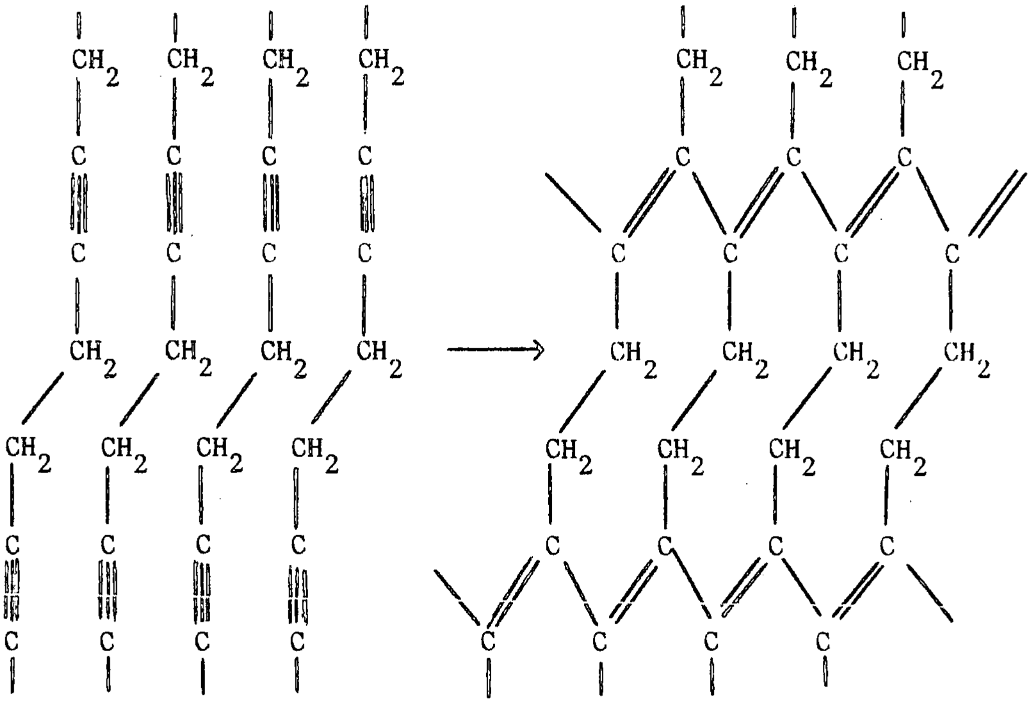
are generally intractable insoluble materials; it was hoped that (16) might be another example of this type of approach to conjugated polymers. It was already known that careful regulation of conditions allowed the polymerization of 5-methylene norbornene (23) by ring-opening to yield (24) but that any trace of cationic initiator gave polymer (25).[176] Examination of the cationic polymerization of (14) was therefore seen to be relevant to this study. A reservation concerning this planned work was the fact that there are apparently no successful examples of metathesis polymerization of conjugated diene monomers.

Another intended project using monomer (14) involved its anionic polymerization via the diene unit to give polymer (15) which it was hoped would generate polymer (18) on vacuum pyrolysis. Polymer (18) has a very

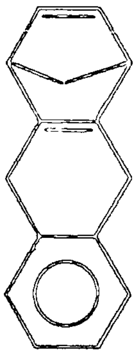


(23) (24) (25)

simple structure and it was anticipated that it ought to give a polymer in which the acetylene units could be cross-polymerized to yield an ordered conjugated polymer of the type shown below; diacetylene systems which are somewhat analogous to this have recently been examined by Lando and co-workers.[177]



Another part of the programme of work undertaken was a study of the extension of metathesis polymerizable monomers to include systems containing polycyclic aromatic ring systems and fluorinated aromatic rings, to this end the synthesis and polymerization of the seven monomers shown below was undertaken.



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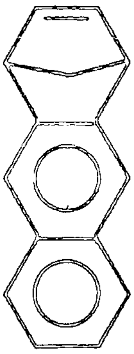

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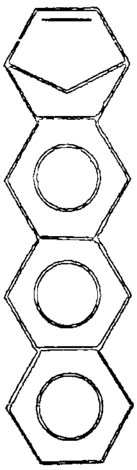

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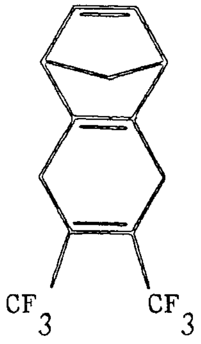

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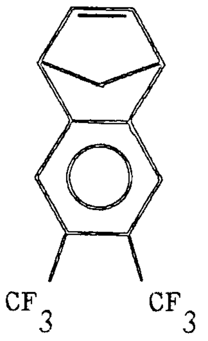

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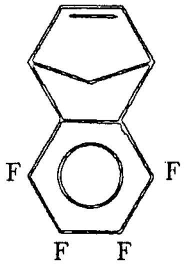

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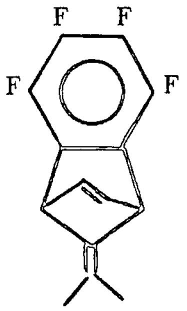

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Chapter two describes the synthesis of all the monomers used in these investigations, and the successful metathesis polymerizations of monomers 26 to 32. Chapter three describes the largely unsuccessful work carried out on monomer 14. Chapter four describes the characterization of the various polymers obtained in this study.

CHAPTER 2

Monomer Synthesis and Metathesis Ring-Opening Polymerizations

2.1 Synthesis of 5,6-dimethylene bicyclo[2.2.1]hept-2-ene

The synthesis of 5,6-dimethylene bicyclo[2.2.1]hept-2-ene (14) has been carried out using two literature routes.[153,155] In 1957 Hartung and Netz described the synthesis of triene (14) by the route shown in Figure 2.1. The Diels-Alder adduct (33) of cyclopentadiene and fumaryl chloride was reacted with dimethyl amine to give the 5,6-bis(carboxy dimethyl amide) of bicyclo[2.2.1]hept-2-ene (34); reduction of the amide with lithium aluminium hydride gave 5,6-bis(dimethyl amino methyl) bicyclo[2.2.1]hept-2-ene (35); this amine was treated with methyl iodide to form the quaternary ammonium iodide (36) which, after conversion to the hydroxide and pyrolysis gave 5,6-dimethylene bicyclo[2.2.1]hept-2-ene (14).

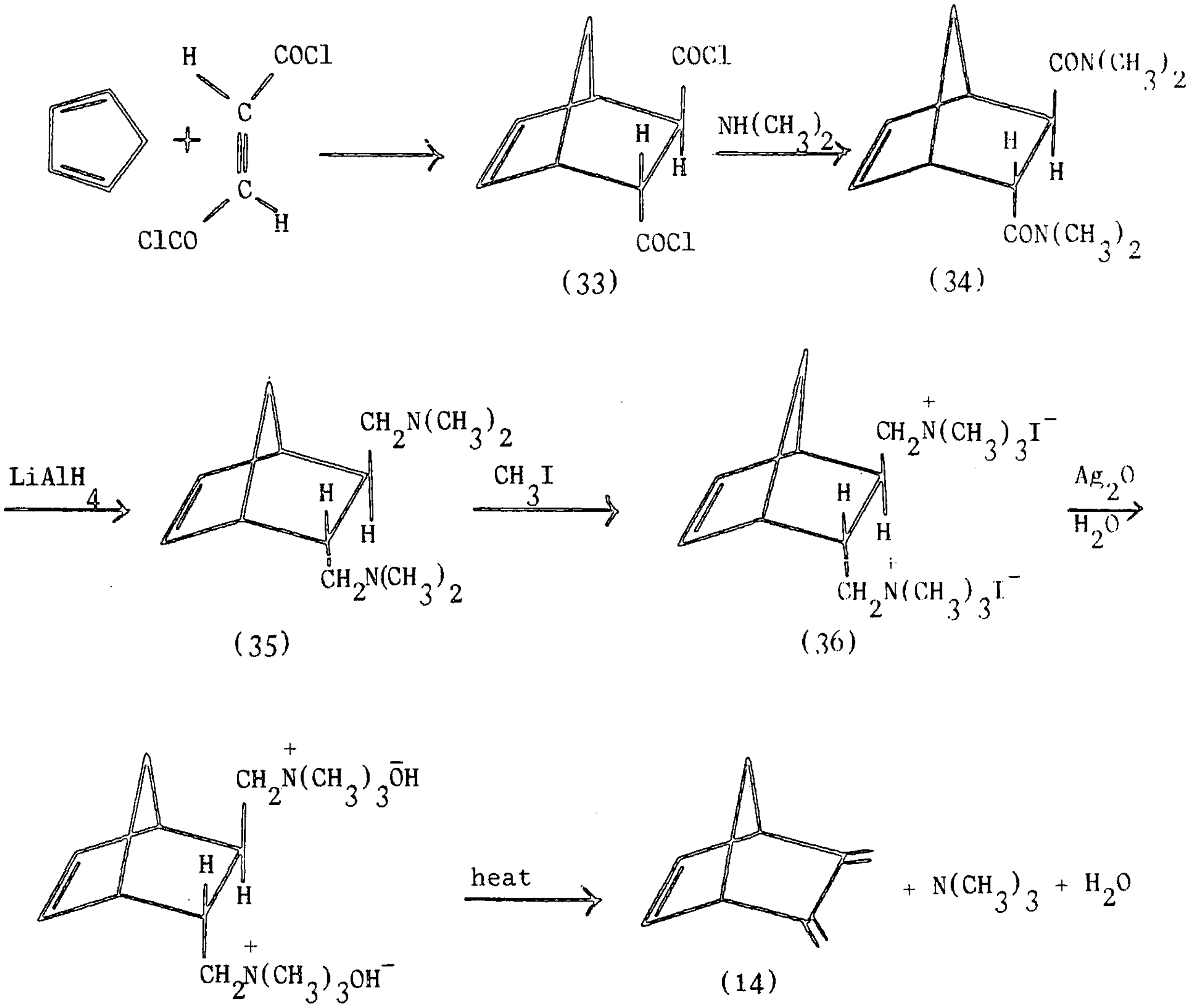
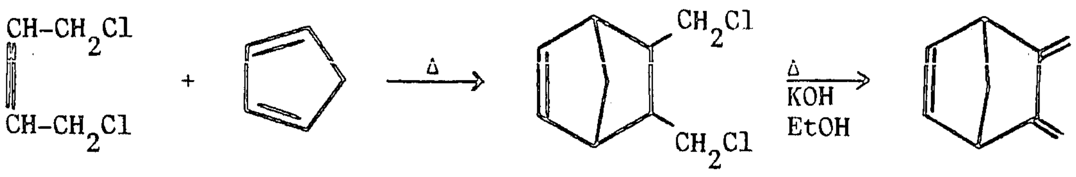


Figure 2.1

This synthesis has been the subject of two detailed studies, the present author has repeated the synthesis and full details of the preparation and purification of compounds (33 - 36, 14) shown in scheme (2.1) are given in the experimental section. The characterization of the intermediates (33 - 36) is also recorded in the experimental section and the appropriate appendices, although all the intermediates have been prepared previously, in some cases the details of their characterization have not been recorded. The sequence shown in scheme 2.1 gave 5,6-dimethylene[2.2.1]hept-2-ene in low overall yield (7.7%).

In 1960, Rose[155] and co-workers reported the synthesis of the triene by a more convenient route. Their preparation involved the reaction between 1,4-dichlorobut-2-ene and dicyclopentadiene (used directly without prior conversion to cyclopentadiene) at 200°C for 24 hours. To prevent side reactions a large excess of 1,4-dichloro-but-2-ene must be used, but unreacted dienophile is easily recovered. The product of this reaction, 5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (37) was recovered by distillation, and then heated under reflux for 40 hours with ethanoic potassium hydroxide, the resulting solution was diluted with water and the mixture extracted with petroleum ether to give 5,6-dimethylene bicyclo[2.2.1]hept-2-ene (14) after fractional distillation. The synthesis is summarized in Figure 2.2 below:



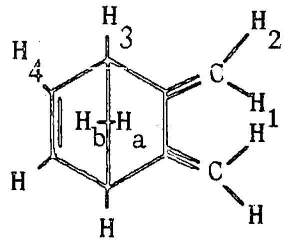
(37) (14)

Figure 2.2

As for the previous synthesis this route has been studied by many organic chemists.[156,157,159,162] The route has the advantages of using simple experimental procedures and relatively cheap starting materials, therefore it was decided to use it for the routine synthesis of triene (14). A further modification introduced to Rose's original procedure was claimed to improve the yield and to simplify the procedure even further by avoiding isolation of (37).[156] Full details of this modified procedure are given in the experimental section, but in practice the author found that Rose's original procedure was at least as good as the reported improvement. This synthesis gave triene (14) with overall yields routinely in excess of 40%. Analytical gas chromatography showed that compound (14) was a single component, the elemental analysis (see experimental part), i.r. spectrum (Appendix B, No. 5), mass spectroscopy (Appendix A, No. 2), ^1H n.m.r. (Table 2.1) and ^{13}C n.m.r. (Table 2.2) confirmed the assigned structure and were in reasonably good agreement with the literature data; the ^{13}C spectrum had not been previously reported and the assignments made in Table 2.2 are based on analogy with a series of related structures.[170,102]

Table 2.1

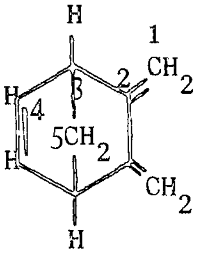
^1H N.m.r. shifts for compound 14, measured at 60 MHz relative to internal T.M.S. in $CDCl_3$ solution

		This Work	Ref. 156[a]	Ref. 160[b]
	H_1	5.28	4.97 d	5.06
	H_2	4.81		4.86
	H_3	3.19	3.24	3.22
	H_4	6.04	5.92	6.10
	H_a	$\delta_a = 1.86$ J_{ab} = 8.0 Hz	1.67	1.78
	H_b	$\delta_b = 1.50$		1.47

[a] Measured at 60 MHz in CS_2 solution; [b] at 100 MHz in CCl_4 internal T.M.S.

Table 2.2

^{13}C N.m.r. shifts for compound 14, measured at 75.47 MHz in $CDCl_3$ relative to internal T.M.S.

	Shifts	Assignment
	148.85	C_2
	136.56	C_4
	101.40	C_1
	51.51	C_3 and C_5
	50.79	

King and Stone[156] showed that when compound 14 was heated with a group VI metal carbonyl, such as molybdenum, chromium or tungsten hexacarbonyl, all three double bonds of the triene, because of their favourable steric disposition, would displace carbonyl groups from the hexacarbonyl to form a tricarbonyl complex $C_9H_{10}Mo(CO)_3$. Many other chemical and physical studies have been made of 5,6-dimethylenebicyclo-[2.2.1]hept-2-ene including photoelectron spectroscopy[161,164,168] and comparison between this triene and other dimethylene hydrocarbon compounds.[162]

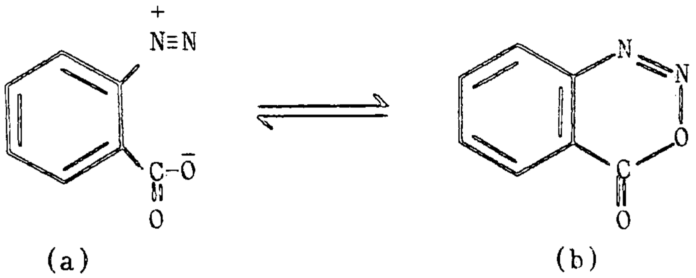
5,6-Dimethylenebicyclo[2.2.1]hept-2-ene has been used as a starting material for a variety of syntheses which involve a cycloaddition step.

2.2 Syntheses Involving Aryne and Alkyne Cycloaddition Reactions

2.2.a Introduction

Diazotization of anthranilic acid, 3-amino-2-naphthoic acid or a substituted anthranilic acid, yields an arene diazonium-2-carboxylate which can be pyrolyzed[178] or photolyzed[179] to produce benzyne, naphthalyne, or a substituted benzyne; such species are reactive as dienophiles in cycloaddition reactions.[180]

It has been found that anthranilic acids are readily diazotized by alkyl nitrites in aprotic media to give (38) (a and b) which undergoes fragmentation to benzyne, nitrogen and carbon dioxide.[181] Reaction can be effected by slow addition of a solution of the anthranilic acid to a refluxing stirred solution of alkyl nitrite and benzyne acceptor. If the reactants are mixed at room temperature and then heated a vigorous exothermic reaction ensues and the yield of desired product is greatly diminished. This is probably a result of the reaction of benzyne with unreacted anthranilic acid. When higher boiling solvents are used it is advantageous to add alkyl nitrite concurrently with the solution of anthranilic acid to minimize the thermally induced decomposition of nitrite. Witting and Krauss[182] have reported the generation of benzyne from o-bromofluorobenzene and magnesium. However, the formation of benzyne by the diazotization of anthranilic acid is more economical. Earlier reports have described the reaction of benzyne generated in this way, with dienes,[178] carboxylic acids,[178] t-butyl alcohol,[180] aryl azides,[183] compounds containing the acetylenic linkage and simple aromatic hydrocarbons such as benzene and naphthalene as well as the dimerization and trimerization reactions.[179]



(38)

Mich and co-workers[184] reported the synthesis of benzonorbornadiene from benzyne (generated from diazotization of anthranilic acid with amyl nitrite) and cyclopentadiene, they reported a violent explosion. They did their reaction at ambient temperature which was insufficient to promote the complete decomposition of diazonium salt (38) as it was generated in the reaction mixture, such materials are well known to be unstable particularly if allowed to dry, and it seems likely that the reported explosion can be related to an accumulation of (38). Feast and El-Saafin[102] adopted this method of preparing benzonorbornadiene using the approach outlined above to avoid any accumulation of (38) and consequent risk of isolating the explosive diazonium salt. In this study 2,3-naphtho bicyclo[2.2.1]hepta-2,5-diene (27) has been prepared via two routes using either naphthalyne addition to cyclopentadiene or benzyne addition to triene (14), see Figure 2.3. A further extension of this procedure allowed the synthesis of 2,3-anthracenobicyclo[2.2.1]-hepta-2,5-diene (28) via naphthalyne addition to triene (14). Bis-(trifluoromethyl)benzonorbornadiene (30) was prepared by dehydrogenation of the Diels-Alder adduct of (14) with hexafluorobut-2-yne. These syntheses together with those of compounds (31) and (32), generously provided by Dr. G.M. Brooke, are discussed in the following sections.

2.2.b Synthesis of 2,3-naphthobicyclo[2.2.1]hept-2,5-diene (27)

This monomer was prepared in two ways. The naphthalyne cycloaddition to cyclopentadiene was achieved by adding monoglyme (ethylene glycol dimethyl ether) solutions of freshly distilled cyclopentadiene, 3-amino-2-naphthoic acid, and amyl nitrite at the same rate to the refluxing solvent. Under these conditions, the diazonium salts decomposed immediately and the resulting naphthalyne was trapped with cyclopentadiene to give 2,3-naphthobicyclo[2.2.1]hepta-2,5-diene (27).

The other synthesis used the cycloaddition reaction between 5,6-dimethylene bicyclo[2.2.1]hept-2-ene (14) and benzyne, generated via the diazotization of anthranilic acid with amyl nitrite in monoglyme, to give 4,5-benzotricyclo[6,2,1,$0^{2,7}$]undeca-2 (7), 4,9-triene (26) in

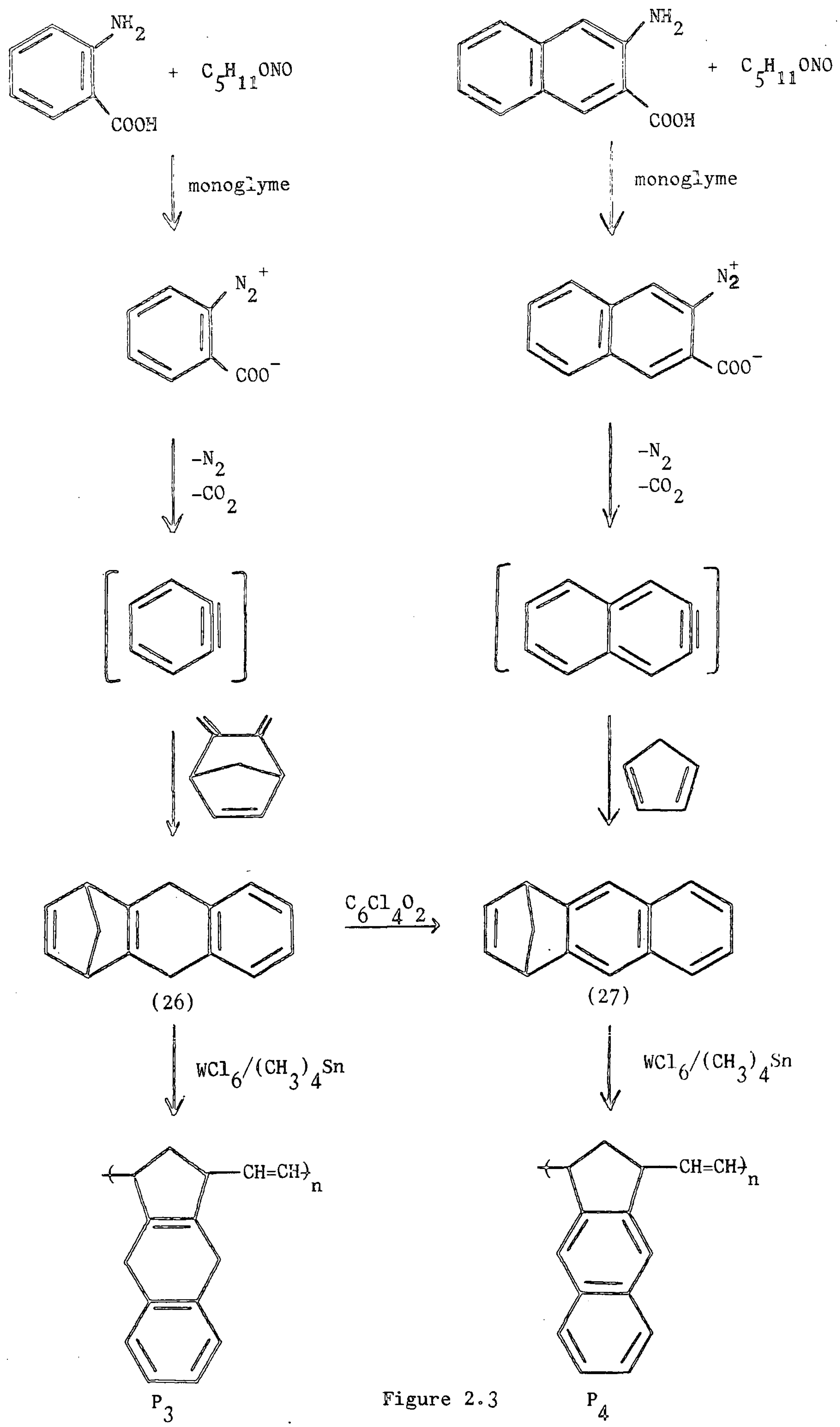
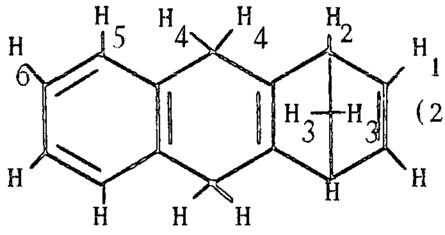
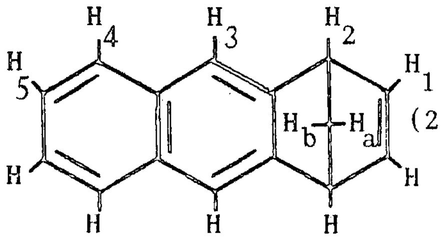

NH$_2$
COOH
+ $C_5H_{11}ONO$
monoglyme
N_2^+
COO^-
$-N_2$
$-CO_2$
(26)
$C_6Cl_4O_2$
(27)
$WCl_6/(CH_3)_4Sn$
$-CH{=}CH-)_n$
P_3
P_4

Figure 2.3

55% yield, this compound was dehydrogenated using chloranil in xylene to give compound (27). The two routes used are summarized in Figure 2.3, and the details of reaction conditions and yields are recorded in the experimental section. The structures of compounds (26) and (27) were confirmed by elemental analysis (see experimental section), i.r. (Appendix B, No. 6 and 8), Mass (Appendix A, No. 3 and 4), ^{1}H n.m.r. (Table 2.3 below) and ^{13}C n.m.r. (Table 2.4 below) spectroscopy; these compounds had not been previously reported. The structures follow in a straightforward manner from the mode of preparation and the spectroscopic data, the assignments recorded in Tables 2.3 and 2.4 are based on analogy with the spectra of a series of compounds with related structures and will be discussed in more detail later when monomer and derived polymer ^{13}C n.m.r. spectra are analysed in Chapter 4.

Table 2.3

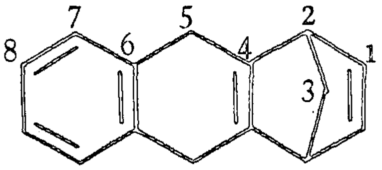
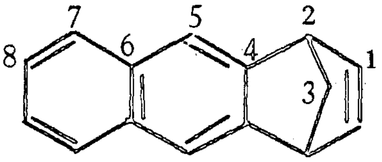
^{1}H N.m.r. shifts for compounds (26) and (27) measured at 60 MHz relative to internal T.M.S. in d_6 acetone

	Shift[a] (integrated intensity)	Assignment
 (26)	7·15 (4) m 6.80 (2) m 3·55 (2) bb 3.40 (4) bb 2.02 (2) bb	H_5/H_6 H_1 H_2 H_4 H_3
 (27)	7.6 - 7.4 (6) m 6.7 (2) s 3·95 (2) s $\left.\begin{matrix}\delta_A\ 2.21\\ \delta_B\ 2.37\end{matrix}\right\} J_{AB} = 8$ Hz	H_3, H_4, H_5 H_1 H_2 H_a H_b

[a] Chemical shifts are for centres of broad bands (bb) or partially resolved multiplets (m) unless otherwise described.

Table 2.4

^{13}C N.m.r. shifts for compounds 26 and 27 measured at 22.64 MHz in $CDCl_3$ relative to internal T.M.S.

Compound	Shifts	Assignments
	144.21	C_4
	142.39	C_1
	134.47	C_6
	129.01	C_8
	125.77	C_7
	71.33	C_3
	52.23	C_2
	31.05	C_5
	148.88	C_4
	141.86	C_1
	131.99	C_6
	127.96	C_8
	125.10	C_7
	119.26	C_5
	66.51	C_3
	49.49	C_2

2.2.c Synthesis of 2,3-anthracenobicyclo[2.2.1]hepta-2,5-diene (28)

Compound 28 was prepared by the route outlined in Figure 2.4. Naphthalyne, generated as described previously, readily added to triene

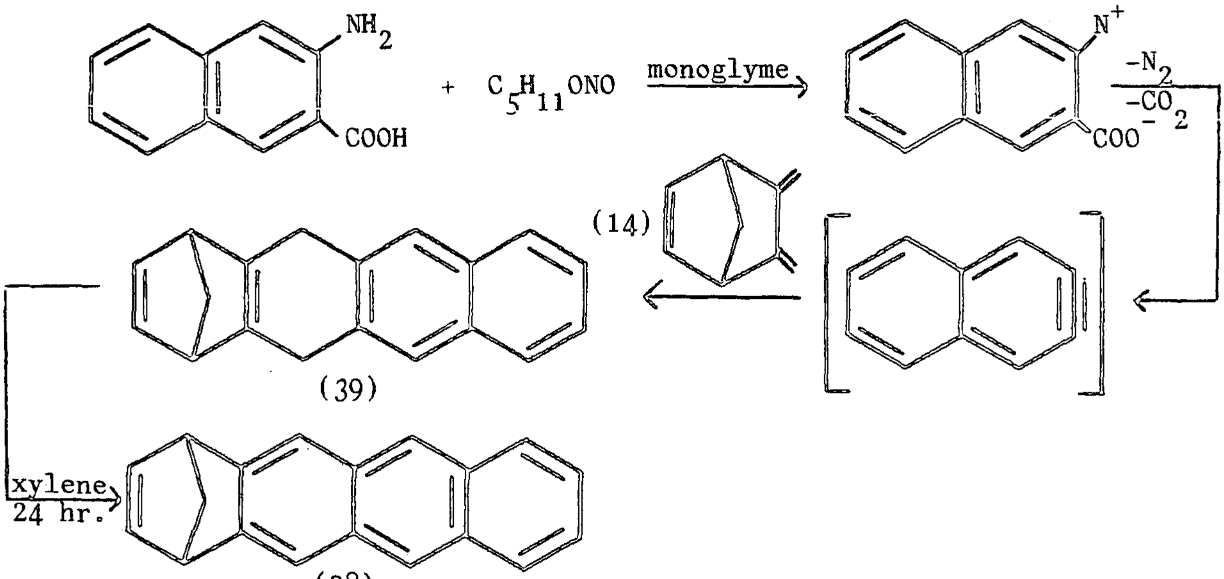


Figure 2.4

(14) to give the 1:1 Diels-Alder adduct (39). In practice it proved impossible to isolate a pure sample of compound (39) because it was so easily oxidized to yield the fully aromatized monomer (28). The easy oxidation of compound (39) is not too surprising because the hydrogens removed during oxidation are both allylic and benzylic and the product is aromatic. The initial product from the addition of naphthalyne to triene (14) was a pale yellow solid which was shown to be a mixture of compounds 39 and 28 by a combination of spectroscopic analyses. Thus, mass spectroscopy indicated a relatively strong parent peak at m/e 244 with P+1 and P+2 peaks of appropriate intensity for the formula $C_{19}H_{16}$ (39), this parent loses 2 amu easily to give a base peak at m/e 242, $C_{19}H_{14}$ (28). The ultraviolet spectrum of the crude reaction product is shown in Figure 2.5. It is clear from the spectra reproduced in Figure 2.5 that the band multiplicities and shapes in the spectrum of the reaction product are consistent with both naphthyl and anthracyl residues being present; however, it appears that the naphthyl bands are bathochromically shifted (i.e. to longer wavelength) whereas the anthracyl bands are hypsochromically shifted (i.e. to shorter wavelength). These observations are consistent with the expected effects of the structural features of compounds 39 and 28 on these chromophores. Thus, in compound 39 the naphthyl residue has two saturated ortho alkyl groups which would be expected to produce a bathochromic shift; for example, the bathochromic shift of toluene's λ_{max} with respect to that of benzene is about 5 nm,[185] similar bathochromic shifts are observed for alkyl substituted naphthalenes.[186] In the case of compound 28 the hypsochromic shift of the anthracyl bands is again consistent with structural effects, in this case the bridged bicyclic unit is expected to cause strain and increasing strain is often associated with a shift to shorter wavelength; for example λ_{max} for cyclopentadiene is

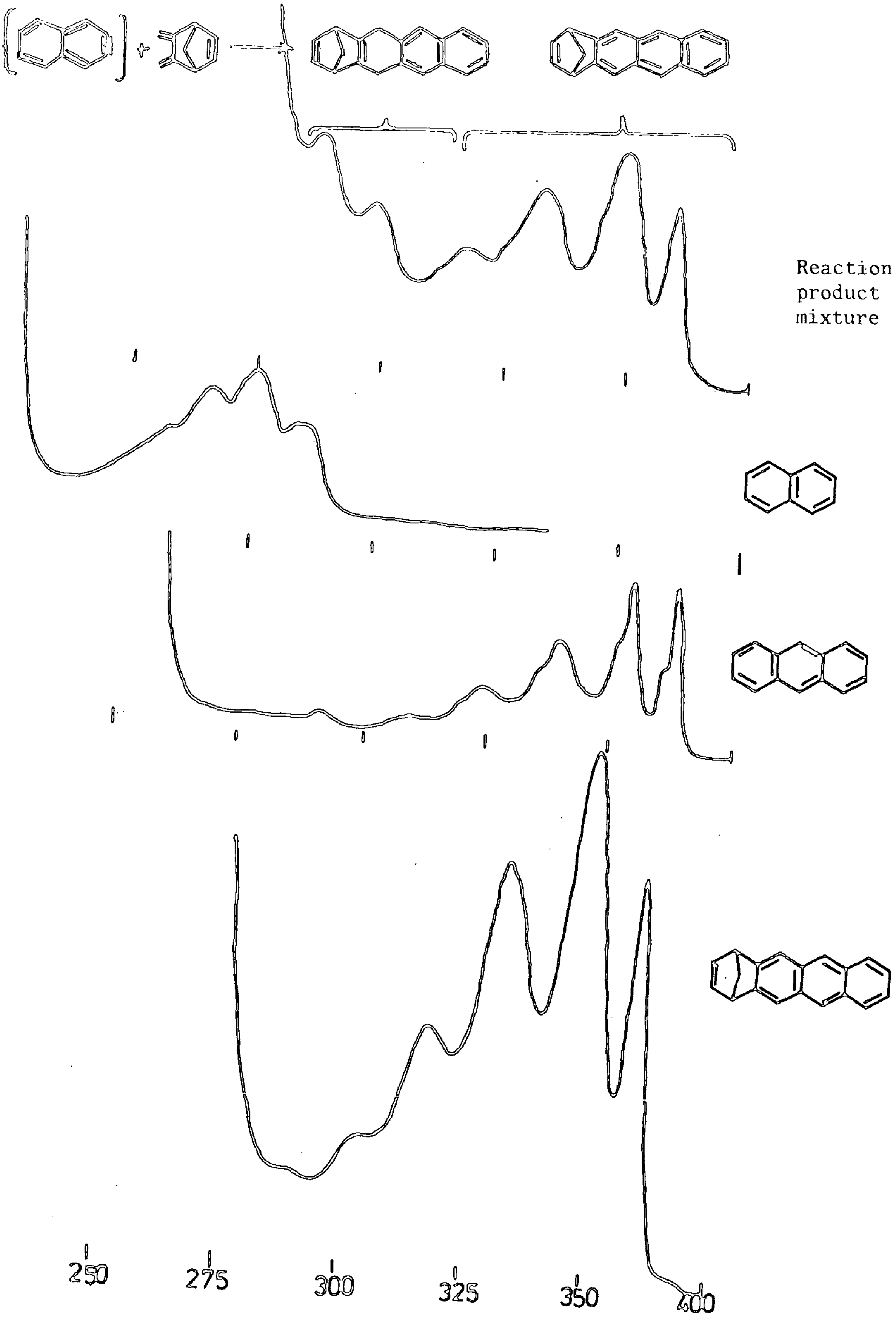


Figure 2.5

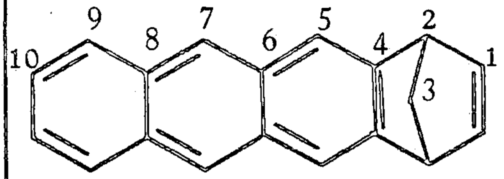
239 nm whereas for cyclohexadiene it is 256 nm.

In view of the oxidative sensitivity compound (39) it seemed of little interest as a monomer and so no serious attempt to obtain a pure sample was made but the whole reaction product was refluxed with chloranil in xylene for 24 hours in order to complete the dehydrogenation.

2,3-Anthracenobicyclo[2.2.1]hept-2,5-diene (28) was obtained as a crystalline white solid of low solubility which was characterized by elemental analysis (see experimental part), i.r. (Appendix B, No. 10), Mass (Appendix A, No. 5), ^{13}C n.m.r. (Table 2.5) and u.v. spectroscopy (Figure 2.5). Compound 28 has not previously been reported, the assignment of structures follows straightforwardly from the spectroscopic data, the ^{13}C shifts were analysed by analogy with the spectra of related compounds showing the same structural features.[102]

Table 2.5

^{13}C N.m.r. shifts for compound 28 measured at 75.47 MHz in $CDCl_3$ relative to internal T.M.S.

	Shifts	Assignments
 (28)	147.53	C_8
	141.44	C_1
	131.70	C_6
	131.18	C_4
	128.03	C_{10}
	125.68	C_9
	124.87	C_7
	118.91	C_5
	64.40	C_3
	49.38	C_2

2.2.d Synthesis of 4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraene (30)

Monomer (30) was synthesized by dehydrogenation of 4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene (29) using chloranil in xylene. Compound (29) was prepared from the Diels-Alder reaction between hexafluorobut-2-yne and 5,6-dimethylenebicyclo[2.2.1]hept-2-ene at room temperature as shown in Figure 2.6. Both monomers (29) and (30) were identified by their elemental analysis (see experimental section), i.r. spectra (Appendix B, No. 12 and 15), mass spectra (Appendix A, No. 6 and 7), ^{1}H n.m.r. and ^{13}C n.m.r. spectra (see Table 2.6 and 2.7 respectively). Compounds (29) and (30) are both new

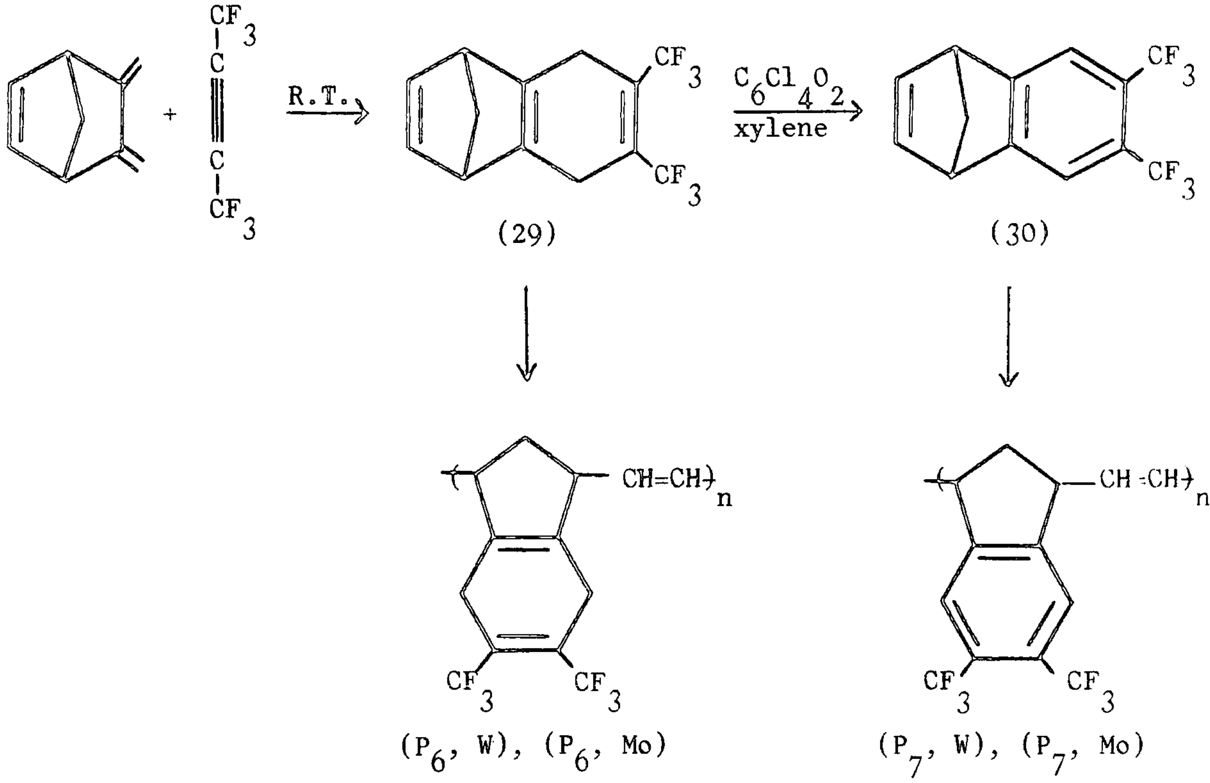


Figure 2.6

compounds but there is nothing unusual about their structures or spectra and their identification follows in a routine manner from the data recorded.

2.2.e Synthesis of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (31)

Cyclopentadiene reacts with tetrafluorobenzyne to give compound (31), tetrafluorobenzyne was prepared from pentafluorophenyl lithium

Table 2.6

^{1}H N.m.r. shifts for compound (29) and (30) measured at 60 MHz relative to internal T.M.S. in d_6 acetone

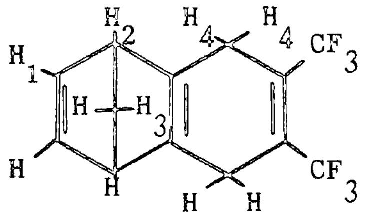
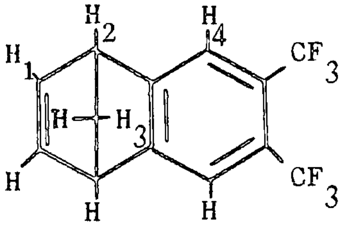
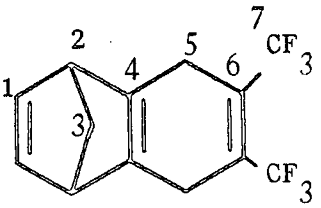
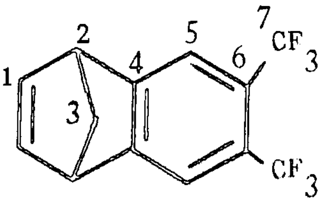
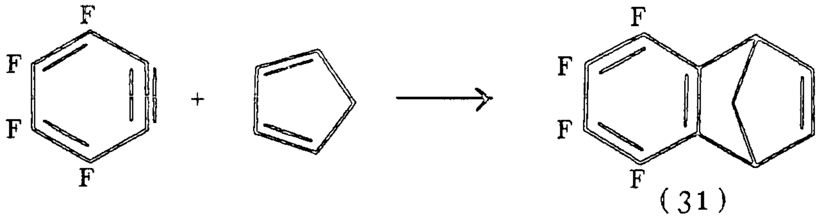
	Shift (integrated intensity)	Assignment
(29) 	6.8 (2) 3.4 (2) 3.2, 3.1 (4) 2 (2)	H_1 H_2 H_4 H_3
(30) 	7.54 (2) 6.7 (2) 3.92 (2) 2.31 (2)	H_4 H_1 H_2 H_3

Table 2.7

^{13}C N.m.r. shifts for compounds (29) and (30) measured at 22.64 (29) and 75.47 (30) MHz in $CDCl_3$ relative to internal T.M.S.

Compound	Shifts	Assignment
(29) 	142.53 ca. 131 qu J_{CCF} $\sim$ 20 Hz 129.7 qu J_{CF} = 310 Hz 71.9 52.1 28.5 unrecorded	C_1 C_6 C_7 C_3 C_2 C_5 C_4
(30) 	157.4 143.0 125.3 J_{CCF} $\sim$ 30 Hz 123.6 J_{CF} = 270 Hz 120.6 71.0 50.8	C_4 C_1 C_6 C_7 C_5 C_3 C_2

(made from bromopentafluorobenzene and n-butyl lithium, Figure 2.7. This compound was prepared by Dr. Brooke[187] (this department) who generously provided the sample of (31) used in this work. He found that the procedure outlined above was more convenient than that described in 1969 by Callander et al, who did the reaction at elevated temperature.[188] This sample had been characterized previously, only



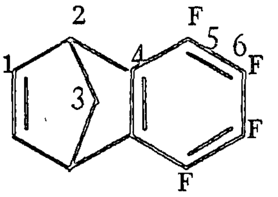
(31)

Figure 2.7

the ^{13}C n.m.r. spectrum (Table 2.8) was recorded as reference data for polymer ^{13}C n.m.r. spectral interpretation purposes.

Table 2.8

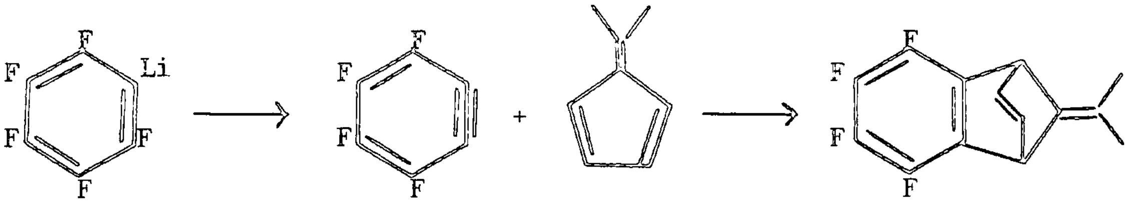
^{13}C N.m.r. shifts for compound (31) measured at 75.47 MHz in $CDCl_3$ relative to internal T.M.S.

Compound	Shifts	Assignments
	142.6 142.0* d J_{CF} = 255 Hz 137.9* d J_{CF} = 255 Hz 132.8* 69.2 47.1	C_1 C_6 C_5 C_4 C_3 C_2

* very weak signals

2.2.f Synthesis of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methano naphthalene (32)

This compound was also provided by Dr. Brooke,[189] he prepared the sample used in this work by the established literature method described in 1973 by Hankinson and co-workers,[190] which involves the cycloaddition of tetrafluorobenzyne generated from pentafluorophenyl lithium to 6,6-dimethyl fulvene as shown in Figure 2.8. This compound had been



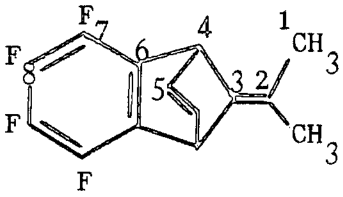
(32)

Figure 2.8

thoroughly characterized previously, only the ^{13}C n.m.r. spectrum has been recorded for reference in relation to polymer characterization.

Table 2.9

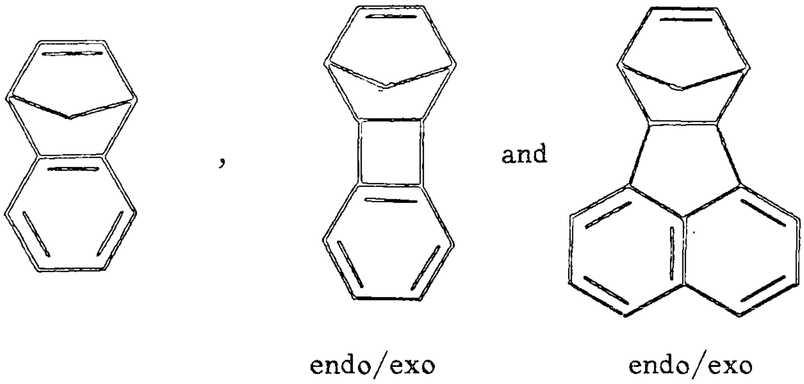
^{13}C N.m.r. shifts for compound (32) measured at 75.47 MHz in $CDCl_3$ relative to internal T.M.S.

Compound	Shifts	Assignments
	158.6	C_3
	142.5	C_5
	141.6 d J_{CF} = 255 Hz	C_8
	138.1 d J_{CF} = 255 Hz	C_7
	131.2	C_6
	104.8	C_2
	46.9	C_4
	18.71	C_1

2.3 The Polymerization of some Aryl Substituted Polycyclic Alkenes

2.3.a Introduction

This work expands earlier investigations of El-Saafin in which he showed that monomers carrying aryl substituents could be polymerized by catalysts based on tungsten hexachloride activated with tetraaryl or tetraalkyl tin.[102] Thus, at the beginning of this work it was known that the monomers shown below could be polymerized. The catalyst used in this earlier work (WCl_6/R_4Sn) is generally found to be very active and fairly non-selective with regard to stereoregulation. In this work

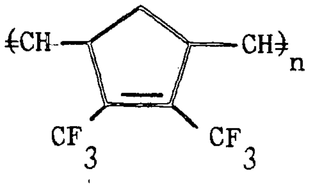


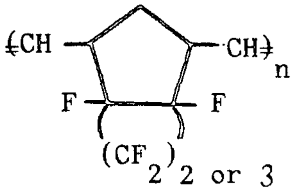
<u>Aryl substituted bicyclic olefins polymerized by El-Saafin</u>

Figure 2.9

the author's objectives were to extend the range of aryl substituted monomers which could be polymerized by this technique and to investigate the possibility of obtaining stereoregular polymers by use of the catalyst derived from molybdenum pentachloride, which generally regulates ring-open polymerization of cycloalkenes to give polymers with a high cis-vinylene content.

A further factor which emerged from earlier work in this department was that simple hydrocarbon polymers of the type derived from the monomers shown in Figure 2.9 were very readily oxidized; by contrast, the fluorinated systems[101] shown below are qualitatively much less

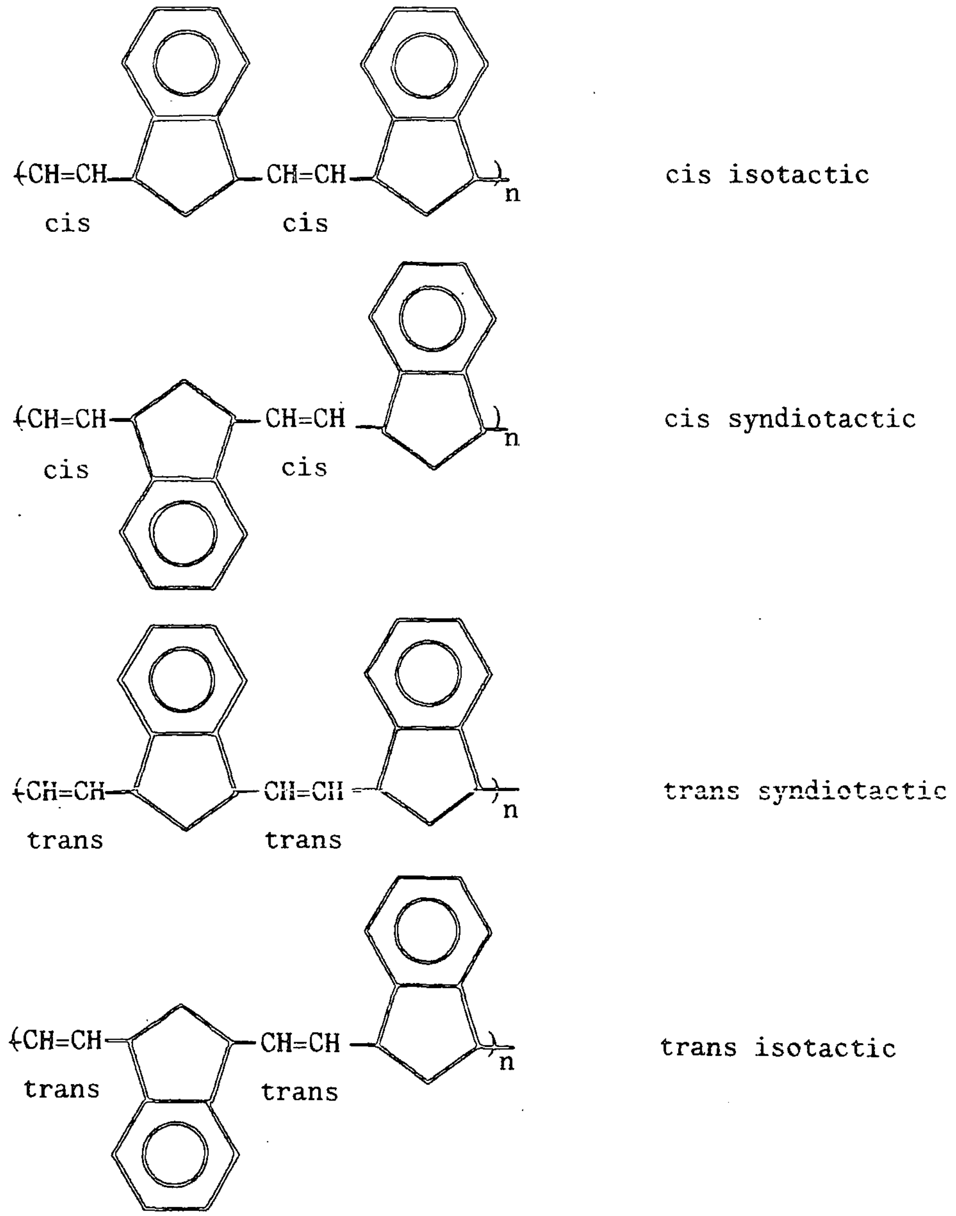




susceptible to oxidation although they also contain the tertiary allylic C-H bond which might be expected to be the site of initial oxidation reactions. In the light of this observation it was decided to examine the polymerization of some fluorinated aromatic monomers.

2.3.b Stereoregulation in ring-opening polymerization

This question will be discussed at greater length in the sections on polymer characterization in Chapter 4, but at this point it is worth noting that a simple bicyclic monomer such as benzonorbornadiene can, in principle, be polymerized by ring-opening via four assembly modes, as illustrated in Figure 2.10 (nomenclature is discussed in detail in Chapter 4). This kind of stereoregulation is different to that observed in the Ziegler-Natta polymerization of styrene[191] in that the aryl unit is much more rigidly oriented with respect to the polymer backbone because it is bound via two bonds and its rotation is



Assembly modes for polybenzonorbornadiene

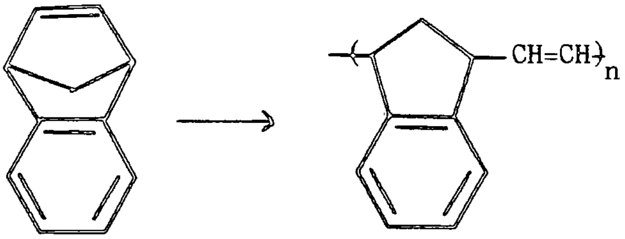
Figure 2.10

consequentially restricted. Qualitatively, therefore, such materials may be expected to be stiffer at a molecular level than the more familiar aryl substituted polymers (for example, polystyrene), and it may be that interactions between successive aryl units on the chain will be more rigidly defined. Such effects, if they exist, would be expected to be most marked in stereoregular rather than atactic polymers and one of the likely practical effects would be on solubility. In this work only WCl_6/Me_4Sn and $MoCl_5/Me_4Sn$ catalysts have been used and it soon emerged that the polymers derived from the molybdenum catalyst were less soluble than the polymers obtained from the same monomer using WCl_6/Me_4Sn catalyst, a result which created considerable practical problems in this investigation.

2.3.c Polymerizations

2.3.c.I Benzonorbornadiene

At the time of El-Saafin's work with this monomer it was established that WCl_6/Me_4Sn readily polymerized benzonorbornadiene (40) to give the expected polymer (P-1), Figure 2.11.[102] However, the product was found



(40) (P1)

Polymerization of benzonorbornadiene

Figure 2.11

to be very sensitive to air oxidation leading to rapid degradation and insolubility resulting from crosslinking. As a consequence it was difficult to record high resolution ^{13}C n.m.r. spectra and hence to deduce the microstructure of the product, although the overall features of the structure were clearly those shown in Figure 2.11 (P1), that is the ring-opened product rather than the vinyl addition product. In the period since this work was reported improved techniques for handling air sensitive polymers have been developed in these laboratories and so as a first exercise El-Saafin's work was repeated with the intention of comparing the polybenzonorbornadienes derived from WCl_6/Me_4Sn and $MoCl_5/Me_4Sn$ catalysts.

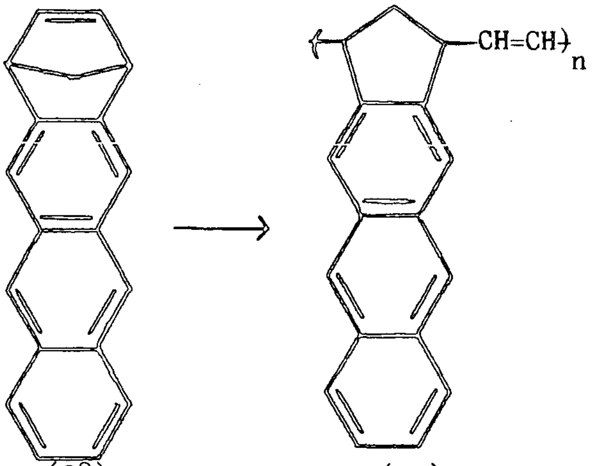
Following the standard technique (see experimental section) and rigorously excluding air at all stages, and particularly during the polymer purification stage, it proved possible to obtain polybenzonorbornadiene as a soluble white film forming material using the WCl_6/Me_4Sn catalyst, an excellent ^{13}C spectrum was obtained on this material (see Chapter 4). However in several attempts using $MoCl_5/Me_4Sn$ as catalyst the polybenzonorbornadiene obtained (P2) was insoluble in a wide range of solvents even after prolonged refluxing. In an attempt to overcome this difficulty the polymerization was carried out in the presence of oct-4-ene which can act as a molecular weight regulator either by chain transfer during polymerization or by cross-metathesis of polymer after formation; even with a Mo:Sn:monomer:oct-4-ene ratio of 1:2:200:10, which should give a fairly low d.p. product, it was found that the polybenzonorbornadiene produced was not very soluble, although it was readily swollen by $CDCl_3$ to allow ^{13}C spectra to be recorded. Experience gained in handling the WCl_6/Me_4Sn derived polymer makes it unlikely that this insolubility can be associated with crosslinking caused by air oxidation and it also seems unlikely that $MoCl_5$ would cause chemical reactions leading to crosslinking (other $MoCl_5$ derived polymers are not crosslinked) so this apparently inherent insolubility is probably a consequence of stereoregulation by the molybdenum based catalyst.

2.3.c.II 4,5-Benzotricyclo[6,2,1,$0^{2,7}$]undeca-2(7),4,9-triene (26) and 2,3-naphthotricyclo[2.2.1]hept-2,5-diene (27)

Compounds (26) and (27) were found to polymerize easily in chlorobenzene with $WCl_6/(CH_3)_4Sn$ catalyst to give, respectively, P3 and P4; the overall result is shown in Figure 2.3 (p.53). The products from these two monomers dissolved in chloroform, the former was readily dissolved while the latter was difficult to dissolve. A soluble fraction of P4 was obtained by refluxing with an excess of chloroform for about two days, the solution was filtered and the solvent was evaporated producing a viscous solution which was added dropwise to a vigorously stirred excess of methanol, and recovered by filtration and dried under vacuum. These polymeric materials were fully characterized (see experimental and Chapter 4). In view of the difficulties experienced with polybenzonorbornadiene and the relative insolubility of the WCl_6/Me_4Sn derived polymer P4, $MoCl_5/Me_4Sn$ initiated polymerization of these monomers was not investigated.

2.3.c.III 2,3-Anthracenobicyclo[2.2.1]hepta-2,5-diene (28)

Attempts to polymerize compound (28) in chlorobenzene solvent using both $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ catalysts were frustrated by the insolubility of the product polymer (P5), Figure 2.12 below. Thus, in



Polymerization of 2,3-anthracenobicyclo[2.2.1]hepta-2,5-diene

Figure 2.12

all of many attempts at different dilutions the polymer (P5) precipitated from solution almost immediately on addition to the active catalyst solution. This precipitated material was always obtained as a white powdery product which was resistant to all attempts to dissolve it, even on prolonged refluxing with aromatic solvents. It was clear from a comparison of the monomer (28) and polymer P5 infrared spectra (Appendix B, No. 10 and 11) that polymerization had occurred and the results described above are attributed to an inherent insolubility which results in precipitation at a relatively low d.p.

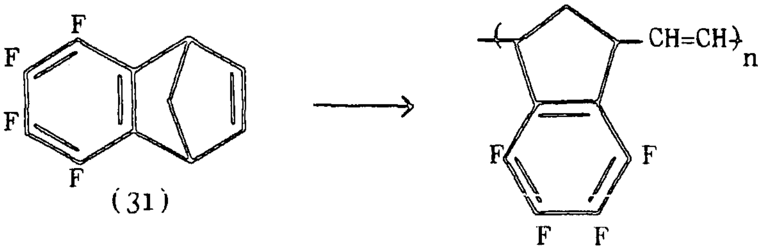
2.3.c.IV 4,5-Bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene (29) and 4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraene (30)

These two monomers were polymerized by conventional metathesis catalyst systems $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$. Using the polymerization technique in which an active catalyst mixture is injected into the monomer solutions, the products were purified by two reprecipitations from butanone or acetone into methanol, they were dried under vacuum, producing white solid materials; the overall result is shown in Figure 2.6 (p. 59). Identification of polymers (P6, W) and (P6, Mo) derived from monomer (29) using i.r. (Appendix B, No. 13 and 14) and ^{13}C n.m.r. spectroscopy (see Chapter 4) indicated, rather surprisingly, that these two polymers had the same structure and microtacticity. There are many important factors which affect the behaviour of the catalyst, including: the catalyst/co-catalyst ratio; the ageing time; the monomer concentration; and the temperature.[192-194] It is generally found that the cis content tends to fall as the reaction temperature is raised, because of this, attempts to polymerize monomer (29) at low temperature (-20°C) were undertaken. In the first experiment the monomer solution was added to the cooled catalyst solution ($-20^{\circ}C$) and in the second experiment the catalyst solution was added to the cooled monomer solution ($-25^{\circ}C$); the products from these two reactions still gave the same i.r. and ^{13}C spectra as the room temperature experiments (see Chapter 4).

Figure 2.6 shows the overall result of polymerizing monomer (30). The products from the two catalysts (P7, W) and (P7, Mo) showed, in contrast to the monomer 29 case, differences in their ^{13}C n.m.r. spectra attributable to expected tacticity differences. The details of tacticity for these two polymers will be discussed in Chapter 4.

2.3.c.V 5,6,7,8-Tetrafluoro-1,4-dihydro-1,4-methano naphthalene (31)

The ring-opening polymerization of monomer (31) was achieved at room temperature using the catalyst systems $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ (see experimental part, Table 2.10), the overall result is shown in Figure 2.13. Both polymers were produced as white solid materials, which were readily soluble in chloroform, T.H.F., toluene and chlorobenzene. The analysis of spectroscopic data for these materials is discussed in Chapter 4, in this case the tungsten and molybdenum derived polymers were different.



(31)

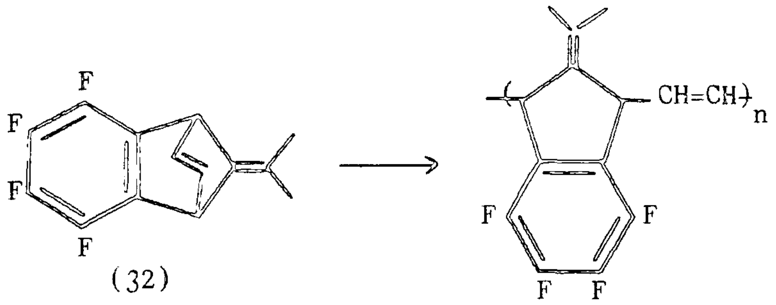
(P8, W), (P8, Mo)

Figure 2.13

2.3.c.VI 5,6,7,8-Tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methano naphthalene (32)

Monomer (32) was polymerized using $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$

catalyst systems, details of conditions are summarized in the experimental section, Table 2.10; Figure 2.14 shows the overall result for these polymerizations. Polymer (P9, W) was dissolved in toluene, precipitated in methanol, and dried under reduced pressure; while polymer (P9, Mo) was dissolved in chlorobenzene and precipitated in methanol. Polymer (P9, Mo) was found to be insoluble in T.H.F., while polymer (P9, W) was readily soluble. The practical result of this difference in solubility was that only for polymer (P9, W) was it possible to record GPC data. (P9, W) and (P9, Mo) were clearly different from their ^{13}C n.m.r. spectra (see Chapter 4) and the differences in solubility in T.H.F. also may be taken as an illustration of the effect of differences in stereoregularity.



(32)

(P9, W), (P9, Mo)

Figure 2.14

Experimental

2.4 Preparation of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene

2.4.a Reagents

Dicyclopentadiene, methyl iodide, lithium aluminium hydride, and silver nitrate were purchased from Koch-Light Laboratories Ltd. Fumaryl chloride from Lancaster Synthesis Ltd., anhydrous dimethyl amine and potassium hydroxide from B.D.H. Chemicals Ltd.

2.4.b Cyclopentadiene

Cyclopentadiene was prepared by thermal cracking[195] of dicyclopentadiene. The dimer was distilled at atmospheric pressure through a Vigreux column (40 cm) and the diene collected slowly in the range 40 - 45°C. Rapid distillation results in a temperature rise above 45°C, product collected under these conditions is contaminated with dimer. Cyclopentadiene was used without further purification, when necessary it was stored in the deep freeze (-20°C) and under these conditions it could be kept for several days.

2.4.c The Diels-Alder adduct of cyclopentadiene with fumaryl chloride (33)

Analar carbon tetrachloride was distilled from phosphorus pentaoxide, fumaryl chloride (10 g, 7.143 ml, 65.35 mmole) was dissolved in CCl_4 (200 ml) in a 3-necked round bottomed flask (500 ml), the middle neck was fitted with a mechanical stirrer, the second neck was fitted with a dropping funnel containing a diluted solution of cyclopentadiene (4.31 g, 5.39 ml, 65.30 mmoles) in CCl_4 (100 ml) and the third neck was attached to a water cooled condenser. The apparatus was purged with dry nitrogen during the course of the reaction. The reagent solution in the dropping funnel was added dropwise to the stirred mixture in the reaction flask, the addition took half an hour, the mixture was then heated from an oil bath until it refluxed gently; it was stirred continuously throughout the experiment. After stirring at reflux for 2 hours the solvent was removed by distillation and the product was then distilled under reduced pressure to give an oil (11.56 g, 52.8 mmoles, 81%) identified as endo, exo-5,6-dicarboxychloridebicyclo[2.2.1] hept-2-ene by infrared spectroscopy (Appendix B, No. 1) which showed vinylic CH (3080) and aliphatic CH (3000 - 2880), acid chloride (1800) and -HC=CH- (1460 cm^{-1}) stretching vibrations as expected.

2.4.d Preparation of bicyclo[2.2.1]hept-2-ene-5,6-dicarboxy-dimethyl amide (34)

Dimethylamine was dissolved in (150 ml) petroleum ether. This solution was added dropwise using a dropping funnel to a 2-necked round bottomed flask (1 l.) which had been charged with a solution of the cyclopentadiene/fumaryl chloride adduct (85.4 g, 0.389 mole) in petroleum ether (300 ml). The mixture in the flask was stirred continuously using a mechanical stirrer. The reaction flask was cooled with crushed ice throughout the experiment, there was considerable evolution of gases and the addition of dimethylamine was continued until the evolution of these gases stopped. The product mixture was filtered and the solvent was evaporated, the raw product (120 g) was extracted with ether by soxhlet extraction, and after concentrating of the ether solution the bis-dimethylamide crystallized as large prisms which were dried under vacuum (60.7 g, 0.27 mole, 66%). The product was characterized by elemental analysis (found: C, 66.3; H, 8.6; N, 11.5%, $C_{13}H_{20}N_2O_2$ requires C, 66.0; H, 8.47; N, 11.8%) and i.r. spectroscopy (Appendix B, No. 2) which showed the expected CH stretching (3060 - 2880 cm^{-1}) and diamide carbonyl (1635 cm^{-1}) bands.

2.4.e Preparation of 5,6-bis(dimethylaminomethyl)bicyclo[2.2.1]hept-2-ene (35)

A solution of the bis-dimethylamide (34) (20 g, 0.0847 mole) in dry ether (150 ml) was added gently with stirring to a suspension of lithium aluminium hydride (6.52 g, 0.1718 mole) in 300 ml of dry ether, contained in a one litre, 3-necked round bottomed flask, equipped with a stirrer, a condenser and a dropping funnel. After the mixture had been stirred for 5 hours it was treated carefully with distilled water, followed by excess of sodium hydroxide solution (15%), a strongly exothermic reaction occurred, the oily product was separated by steam distillation, the water layer from the steam distillation was extracted with ether using a separating funnel. The combined oil and ether extract was dried over sodium sulphate, the solvent was evaporated and the product was vacuum distilled, 52°C/0.1 mm Hg to yield the diamine (35) as a colourless oil (12.25 g, 0.0589 mole, 69.5%) which was characterized by infrared spectroscopy (Appendix B, No. 3), which showed the expected CH stretching absorptions and an absence of carbonyl functionality.

2.4.f Preparation of quaternary ammonium iodide (36)

A solution of methyl iodide (40.96 g, 17.96 ml, 0.29 mole) in petroleum ether was added dropwise using a dropping funnel to a 2-necked round bottomed flask, 1 l., which had been charged with diamine (25.27 g, 0.124903 mole) in petroleum ether (200 ml), the mixture in flask was stirred continuously using a mechanical stirrer. The reaction flask was cooled in ice throughout the experiment, the precipitated quaternary ammonium iodide was recovered by filtration and dried in the air to give (64.8 g, 0.0955 mole, 76%).

2.4.g Silver oxide reagent

A solution of silver nitrate (50 g, 0.29 mole) in 150 ml of distilled water was placed in a 500 ml, 2-necked, round bottomed flask. It was stirred vigorously while a solution of potassium hydroxide (20 g, 0.356 mole) in 106 ml of distilled water was added dropwise, the brown Ag_2O thus precipitated, was washed with water by decantation until the washing water was free of Ag^+, the Ag_2O was then used for the following reaction.

2.4.h Preparation of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (14)

The quaternary ammonium iodide (36) prepared in 2.4.f (46.8 g, 0.0955 mole) was dissolved in distilled water (1 l.) in a round bottomed flask. The solution was treated with an excess of freshly precipitated silver oxide, the precipitate was filtered, washed with water at about 70°C several times, and the collected filtrate was evaporated under vacuum at 30°C to dryness. The residue was heated under a nitrogen atmosphere in the presence of a trace of hydroquinone using an oil bath at 120 - 140°C, to give triene (14) as a brown liquid (3.1 g, 0.0263 mole, 28%). This product was dissolved in ether, then ether solution was washed with water (2 x 50 mls) and dried over anhydrous sodium sulphate. The solvent was evaporated and the product was distilled at 140°C at atmospheric pressure to give a colourless liquid which was identified by i.r. and mass spectroscopy (see below).

2.5 The Preparation of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene using 1,4-dichlorobut-2-ene with dicyclopentadiene

2.5.a Materials

1,4-Dichlorobut-2-ene was obtained from stock (Aldrich Chemical Co. Ltd.) it was purified by distillation, dicyclopentadiene was purchased from Koch-Light Laboratories Ltd. and used without further purification.

2.5.b The reaction of 1,4-dichlorobut-2-ene with dicyclopentadiene

A mixture of 1,4-dichlorobut-2-ene (244 g, 195.2 moles, 206 ml) and hydroquinone (0.2 g) was placed in a 2-necked round bottomed flask (1 l.) fitted with water cooled condenser, the other neck was fitted with a dropping funnel. The flask was heated using a silicone oil bath until the contents refluxed gently (*ca.* 160°C), the mixture was stirred using a magnetic stirrer throughout the experiment. Dicyclopentadiene (64.77 g, 69.66 ml, 48.99 moles) was added dropwise over a period of ca. 2 hours. After complete addition the mixture was refluxed for 18 hours. After cooling to room temperature, the product was separated into two main fractions; the excess of 1,4-dichlorobutene was recovered by rotary evaporation as the first fraction (138 g, 110 moles, 116.6 ml), the second fraction was recovered by vacuum distillation to give 5,6-dichloromethylbicyclo[2.2.1]hept-2-ene (37), 70 - 80°C/0.1 mm Hg lit. [118 - 122/15 mm).[155] Elemental analysis figures (Found C, 58.79; H, 6.6%, $C_9H_{12}Cl_2$ requires C, 56.6; H, 6.3%) indicate that this product was slightly contaminated with hydrocarbon (probably cyclopentadiene dimer). The infrared spectrum of this product (Appendix B, No. 4) was consistent with the assigned structure and the mass spectrum Appendix A, No. 1) showed a parent ion at m/e 190 with P+2 and P+4 isotope peaks indicative of 2 chlorines (calculated for $C_9H_{12}{}^{35}Cl_2$ M, 190). The yield of (37) calculated with respect to unrecovered dichlorobutene was 73%.

2.5.c The reaction of dichloromethylbicyclo[2.2.1]hept-2-ene with potassium hydroxide in ethanol

Dichloromethylbicycol[2.2.1]hept-2-ene (37) (185.33 g, 97.54 moles) was placed in a 2-necked round bottomed flask fitted with water cooled reflux condenser, the other neck was fitted with a dropping funnel containing potassium hydroxide (181.44 g, 323 moles) in absolute ethanol (468.60 ml), the dichloro compound was heated using an oil bath, and stirred using a magnetic follower, the potassium hydroxide solution was added, the mixture was heated under reflux for 42 hours, after cooling to room temperature, the mixture was diluted with (1 l.) of distilled water. The resulting solution was extracted with pentane (1l.) the extract was dried over anhydrous magnesium sulphate. After filtration and evaporation of the solvent the product was distilled under reduced pressure, Vigreux column 30 cm, 35°C/15 mm Hg (water pump) to give 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (68.17 g, 57.8 moles, 59%). This is a known compound[153-168] and it was identified by i.r., n.m.r. ^1H and ^{13}C and mass spectroscopy. The product obtained in this manner was a single component by g.l.c. (di-n-decylphalate and silicone oil stationary phases), elemental analysis gave(C, 91.50; H, 9.3%, C_9H_{10} requires C, 91.52; H, 8.47%) this material was found to be satisfactory for synthesis of monomers (26, 27, 28, 29, 30) but in view of difficulties in relation to attempts to polymerize it some product was refractionated on a high quality fractionating system (see Chapter 3).

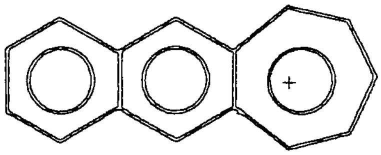
2.6 Synthesis of aromatic compounds (27, 28, 30)

2.6.a General procedure

Dry monoglyme was placed in a 3-necked round bottomed flask, the middle neck was fitted with a mechanical stirrer the second neck was fitted with a dropping funnel containing a solution of a required amounts of anthranilic acid or 3 amino-2-naphthoic acid and 5,6-dimethylenebicyclo[2.2.1]hept-2-ene or cyclopentadiene in dry monoglyme. The third neck was attached to a water condenser which was also fitted with a dropping funnel containing a solution of the required amount of amyl nitrite in monoglyme, the apparatus was purged with dry nitrogen, the solvent in the flask was heated from an oil bath until it refluxed gently, it was stirred continuously throughout the experiment; the compounds in the two dropping funnels were added to the refluxing solvent in the reaction flask at the same rate, there was considerable evolution of gases and the colour of the reaction mixture progressively darkened, the mixture was kept at reflux throughout the addition which took one or two hours. After complete addition of reagents the mixture was refluxed gently for one hour, the reaction was left to cool to room temperature, the mixture was dark red to black in colour, the solvent was evaporated and the product was dried under vacuum, it was examined by t.l.c.(silica, cyclohexane) which usually indicated the presence of two components. Generally, an attempt was made to separate the components of this mixture by "dry column" chromatography. The mixture was packed as a thin band on the top of a dry silica column, the column was then developed in the normal way using cyclohexane as eluent. The separated product was further purified by recrystallization and/or sublimation.

2.6.b Synthesis of 4,5-benzotricyclo[6,2,1,$0^{2,7}$]undeca - 2 (7), 4,9-triene (26)

Anthranilic acid (23.92 g, 17.44 moles), 5,6-dimethylenebicyclo-[2.2.1]hept-2-ene (20.577 g, 17.44 moles, 19.05 ml) and dry monoglyme (158 ml), were added to the refluxing monoglyme (200 ml) at the same rate as a solution of amyl nitrite (20.43 g, 17.44 moles, 23.32 ml) in monoglyme 150 ml, in the manner described above. The solvent was evaporated and the product purified using Column chromatography (Kieselgel 60/cyclohexane), recrystallization from acetone, and finally sublimation at 70°C/0.1 mm Hg to give 4,5-benzenotricyclo[6,2,1,$0^{2,7}$]undeca-2(7), 4,9-triene (26) (18.692 g, 96.353 moles, 55%), m.p. 78 - 79°C [Found C, 92.99; H, 7.28, calculated for $C_{15}H_{14}$, C, 92.78; H, 7.21%], the i.r. spectrum (Appendix B, No. 6) showed a multiplicity of CH stretching bands in the 2800 to 3100 cm^{-1} region and was consistent with the assigned structure; the mass spectrum (Appendix A, No. 3) showed a parent peak at m/e 194 (M) and base peak at 128, a fragment ion at m/e 191 represents an unusual P-3 pathway possibly due to the ion



2.6.c Synthesis of 2,3-naphthotricyclo[2.2.1]hept-2,5-diene (27)

Chloranil (2.16 g, 8.74 mmoles), xylene (100 ml) and 4,5-benzotricyclo-[6,2,1,$0^{2,7}$]undeca-2(7),4,9-triene (26) (0.85 g, 4.3814 mmoles), were placed in a (1 l.), one-neck flask fitted with a condenser, the solution was refluxed for 24 hours, after cooling, the xylene was removed using a rotary evaporator the remaining solid was purified by Column chromatography, a white powdery product was collected, 2,3-naphthotricyclo[2.2.1]hept-2,5-diene (0.75 g, 3.9 moles, 89.5%), and sublimed at 100 - 110°C and 0.001 mm Hg, m.p. 80°C, [Found, C, 93.76; H, 6.18, calculated for $C_{15}H_{12}$, C, 93.75; H, 6.25%], i.r. spectrum (Appendix B, No. 8) showed the CH stretching bands in the region between 2840 - 3050 cm^{-1}, the out of plane CH bending vibrations between 900 - 700 cm^{-1} and in plane bending band appear at 1300 cm^{-1}; the mass spectrum (Appendix A, No. 4) showed a parent peak at m/e 192 (M) as the base peak, and intense fragment ions at m/e 190 (P-2) and 165 (P-C_2H_3); the ^{13}C n.m.r. spectrum was consistent with the proposed structure (see discussion).

2.6.d Synthesis of 2,3-naphthotricyclo[2.2.1]hept-2,5-diene using 3-amino-2-naphthoic acid and cyclopentadiene with amyl nitrite

Freshly distilled cyclopentadiene (7.9 g, 10 ml, 11.97 moles) and 3-amino-2-naphthoic acid (15 g, 8.01 moles) were dissolved in monoglyme (350 ml) this mixture was added to refluxing monoglyme (100 ml) in the reaction flask at the same rate as a solution of amyl nitrite (10.7 g, 9.13 moles, 12.2 ml) in monoglyme (200 ml), the mixture was refluxed for 1 hour. On completion of reaction the solvent was evaporated and the product was purified by Column chromatography, (Kieselgel 60/cyclohexane), crystallization and sublimation at 100°C/0.001 mm Hg to give a white solid material, 2,3-naphthotricyclo[2.2.1]hept-2,5-diene (6.05 g, 31.51 mmole, 39%), [Found, C, 92.24 ; H, 7.62 calculated for

$C_{15}H_{12}$, C, 93.75; H, 6.25%], this material was examined by i.r., Mass and ^{13}C n.m.r. spectroscopy and shown to be identical with an authentic sample (see above).

2.6.e Synthesis of 2,3-anthracenotricyclo[2.2.1]hept-2,5-diene

Using the same procedure described in 2.6.a, 3-amino-2-naphthoic acid (20 g, 10.68 moles) and 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (15.1 g, 13.98 ml, 12.79 moles) were dissolved in dry monoglyme (500 ml). A solution of amyl nitrite (14.26 g, 16.27 ml, 12.18 moles) in dry monoglyme (200 ml), the two solutions were added to refluxing monoglyme in the reaction flask at the same rate, after cooling, the solvent was removed by evaporation and the residue purified using Column chromatography (Kieselgel 60) with cyclohexane/ethyl acetate 1:4 as eluent; a pale yellow compound was collected (5.4 g), [Found: C, 94.12; H, 6.20%, calculated for $C_{19}H_{16}$, C, 93.48; H, 6.55%], characterization by u.v. and Mass spectroscopy (see discussion section) showed that this product was a mixture of compounds (28) and (39). The objective was to prepare 2,3-anthracenotricyclo[2.2.1]hept-2,5-diene so this mixture (4 g) and chloranil (8.094 g, 32.78 mmoles) were refluxed in xylene (250 ml) with stirring under N_2 for 24 hours, and after evaporation of the solvent, the residue purified by Column chromatography (Kieselgel 60/cyclohexane) to give 2,3-anthracenotricyclo-[2.2.1]hept-2,5-diene as a white crystalline material (1.5 g, 6.2 mmoles 0.06%), m.p. 230°C, it was sublimed at 150°C/0.03 mm Hg, [Found C, 94.61; H, 5.7; $C_{19}H_{14}$ requires C, 94.21; H, 5.78%], i.r. spectrum (Appendix B, No. 10) showed the CH stretching bands between 2840 - 3040 cm^{-1}, the mass spectrum, (Appendix A, No. 5) showed a parent peak at m/e 242 (M) as base peak with an intense peak at 240 (P-2); the ^{13}C n.m.r. spectrum was consistent with the assigned structure (see discussion).

2.7.a Reaction of 5,6-dimethylenebicyclo[2.2.1]hept-2-ene with hexafluoro-2-butyne

A thick walled Pyrex ampoule (Carius tube) was charged with hydroquinone (0.03 g), it was attached to the vacuum line and evacuated, gaseous hexafluorobut-2-yne (6.60, 40.75 mmoles) and 5,6-dimethylenebicyclo[2.2.1]hept-2-ene (4.7 g, 4.4 ml, 39.83 mmoles) were then added by vacuum transfer. The tube was sealed under vacuum. It was left overnight (17 hours) at room temperature, it was cooled in liquid air, the seal was broken by "hot spotting", the product was recovered as white crystals using pentane as solvent, these crystals were dried under vacuum to give 4,5-bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene (29) (5.7 g, 20.36 mmoles, 51%), m.p. 40 - 44°C (Found: C, 55.54; H, 3.31; F, 40.11%, requires C, 55.72; H, 3.6; F, 40.70%). The i.r. spectrum,(Appendix B, No. 12) showed the expected vinylic (3050 cm^{-1}) and aliphatic (2800 - 2950 cm^{-1}) CH stretching vibrations and the strong absorptions characteristic of CF bands in the 1400 - 1100 cm^{-1} region; the mass spectrum (Appendix A, No. 6) showed a parent peak at m/e 280 which was also the base peak and a fragmentation parent consistent with the assigned structure.

2.7.b The dehydrogenation reaction of 4,5-bis(trifluoromethyltricyclo-[6,2,1,$0^{2,7}$]undeca-2,4,9-triene

4,5-Bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene (29) (8.27 g, 29.542 mmoles), chloranil (10.65 g, 43.137 mmoles) and xylene (400 ml) were placed in a one-neck round bottomed flask and refluxed for 24 hours. The solvent was removed under reduced pressure and the product obtained using Column chromatography (Kieselgel 60/cyclohexane eluent), the product fraction was collected, recrystallized from acetone and dried under reduced pressure to give 4,5-bis(trifluoromethyl)-tricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraene (30) (6.1 g, 21.95 mmoles, 74%) m.p. 53°C [Found: C, 56.28; H, 3.08; F, 41.20%, $C_{13}H_8F_6$ requires C, 56.13; H, 2.88; F, 40.99%] the i.r. spectrum (Appendix B, No. 15) displayed the expected range of C-H stretching vibrations and the strong bands in 1400 - 1100 cm^{-1} range typical of CF_3 groups; the mass spectrum(Appendix A, No. 7) showed a parent ion at m/e 278 (M) with a base peak at 209 ($M-CF_3$).

2.8 Polymerizations

2.8.a Reagents and methods

Analar chlorobenzene was purchased from B.D.H. Chemicals Ltd. distilled under dry N_2 from P_2O_5 and used directly as solvent for catalyst and monomers, tetramethyltin was purchased from Aldrich Chemical Company Inc. and it was used without any further purification. WCl_6 was prepared and purified by Dr. J.H. Edwards of this department, it was stored in Pyrex ampoules and manipulated in a N_2 glove box. A solution of WCl_6 in dry chlorobenzene was used in polymerizations, this solution was stored under dry nitrogen and had a maximum active catalytic life of 3 - 4 weeks. $MoCl_5$ was purchased from Alfa Products Ltd. and was used without further purification as a solution in dry chlorobenzene. $MeAlCl_3$ and Et_3Al was kindly supplied from stock by Mr. B. Hall of this department. Monomers were purified as described in previous sections and stored in the dark under dry nitrogen in a refrigerator. Precautions were taken to dry solvents, equipment and monomers; the nitrogen gas was dried by passing it through a bubbler of concentrated sulphuric acid, the nitrogen system connections were predominantly glass or nylon tubes, where flexible links were necessary short lengths of thick walled rubber or PVC tube was used. Three way taps were used to introduce the nitrogen into the reaction flask, one arm was connected to the nitrogen system and the other to a bubbler to avoid any chance of introducing air, the bore of the tube was flushed with nitrogen prior to connecting it to the reaction vessel. All the manipulations of solvents, catalyst mixtures and monomers were carried out under an atmosphere of dry nitrogen or using air-tight syringes. All the reaction flasks were dried overnight in the oven, evacuated, flamed and purged with dry nitrogen for at least ten minutes before use.

2.8.b General polymerization procedure

A 2-necked round bottomed flask (50 or 100 ml) containing a magnetic follower was used as reaction vessel, one of the necks was fitted with a three way teflon tap which was connected to the nitrogen system and a bubbler containing heavy white oil, the other neck was closed with a stopper, the reaction flask was flamed under vacuum, it was purged with dry nitrogen while cooling to room temperature. The required amount of monomer was dissolved in dry chlorobenzene. A separate flask (50 ml) was charged with the required amount of the catalyst $MoCl_5$ or WCl_6 solution in C_6H_5Cl, tetramethyltin co-catalyst was then introduced under the liquid surface of the solution using a micro syringe. A rapid colour change to a dark red-brown for the tungsten-based catalyst and dark chocolate brown for the molybdenum-based catalysts was observed. After an ageing time of 1 - 15 minutes the monomer solution was normally syringed into the polymerization flask, occasionally the reverse process (i.e. catalyst added to monomer solution) was followed. An increase in the viscosity of the solution was generally noticed for successful reactions, the time of onset and magnitude of this viscosity increase was dependent on the details of the particular reaction. The polymerization was stopped by addition of a small quantity of methanol. Any precipitate was collected, dried, dissolved in solvent and reprecipitated by dropwise addition to a viscous solution of polymer to a vigorously stirred excess of non-solvent. Polymer products were isolated by filtration and dried under reduced pressure.

Most experiments were repeated several times, the results presented in Table 2.10 represent a selection of many specific polymerization conditions used for the monomers investigated.

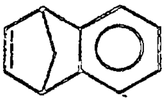
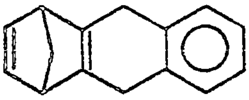
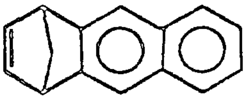
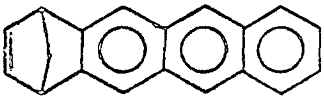
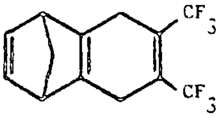
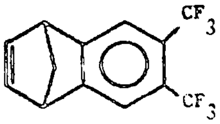
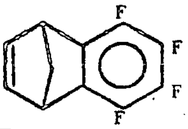
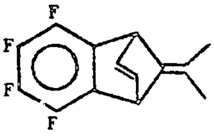
2.8.c The ring-opening polymerization of benzonorbornadiene 40 using octene as a transfer agent

In view of the insolubility of polybenzonorbornadiene prepared using $MoCl_5/(CH_3)_4Sn$ catalyst it was decided to try to obtain lower molecular weight material by polymerization in the presence of a chain transfer reagent.

The procedure described above was used. A catalyst solution $MoCl_5$ (0.005 g, 0.018 mmole, 0.5 ml), $(CH_3)_4Sn$ (0.0065 g, $5\mu l$) in C_6H_5Cl (0.5 ml) was added to a mixture of benzonorbornadiene (0.52 g, 0.0037 mmole, 0.47 ml) and octene (0.021 g, 20.5μ) in chlorobenzene (85 ml). The solution became viscous immediately and the yield was virtually 100%. The polymer was dissolved in chlorobenzene and chloroform and a viscous solution reprecipitated into methanol. The reprecipitated material was dried for 24 hours under vacuum to give white granules of polybenzonorbornadiene (0.4 g, 85%) which was examined by i.r. (Appendix B, No. 28) and ^{13}C n.m.r. spectroscopy (see Chapter 4).

Table 2.10

Ring-opening polymerization of some aromatic compounds using $MoCl_5$ or WCl_6/Me_4Sn in chlorobenzene

Expt. no.	monomer	monomer* m.mole	WCl_6 ($MoCl_5$) m.mole	Me_4Sn µl	chlorobenzene (mls)	time of reaction (minutes)	yield %
1	 (40)	12.6	0.025	22.5	70	1	60
		5.5	(0.042)	11.0	100	Insoluble swollen gel formed immediately	
2	 (26)	1.546	0.0079	2	2	1	33
3		7.32	0.0367	9.99	6	1	53
4	 (27)	4.167	0.02085	5.0	80	2	90
5	 (28)	1.458	0.0149	4	15	precipitated powdery material (insoluble product)	
6		1.736	(0.0174)	4.7	35		
7	 (29)	6.43	0.031	8.6	10	3	82
8		2.597	0.0129	3.5	2	1	65
9	 (30)	2.806	0.0142	3.86	8	20	64
10		2.555	(0.0125)	3.5	5	10	85
11	 (31)	1.355	0.0075	2	1.5	3	57
12		2.056	(0.01045)	2.8	3	4	61
13	 (32)	5.630	0.0286	7.8	2	3	91
15		3.949	(0.0977)	5.4	3	5	84

CHAPTER 3

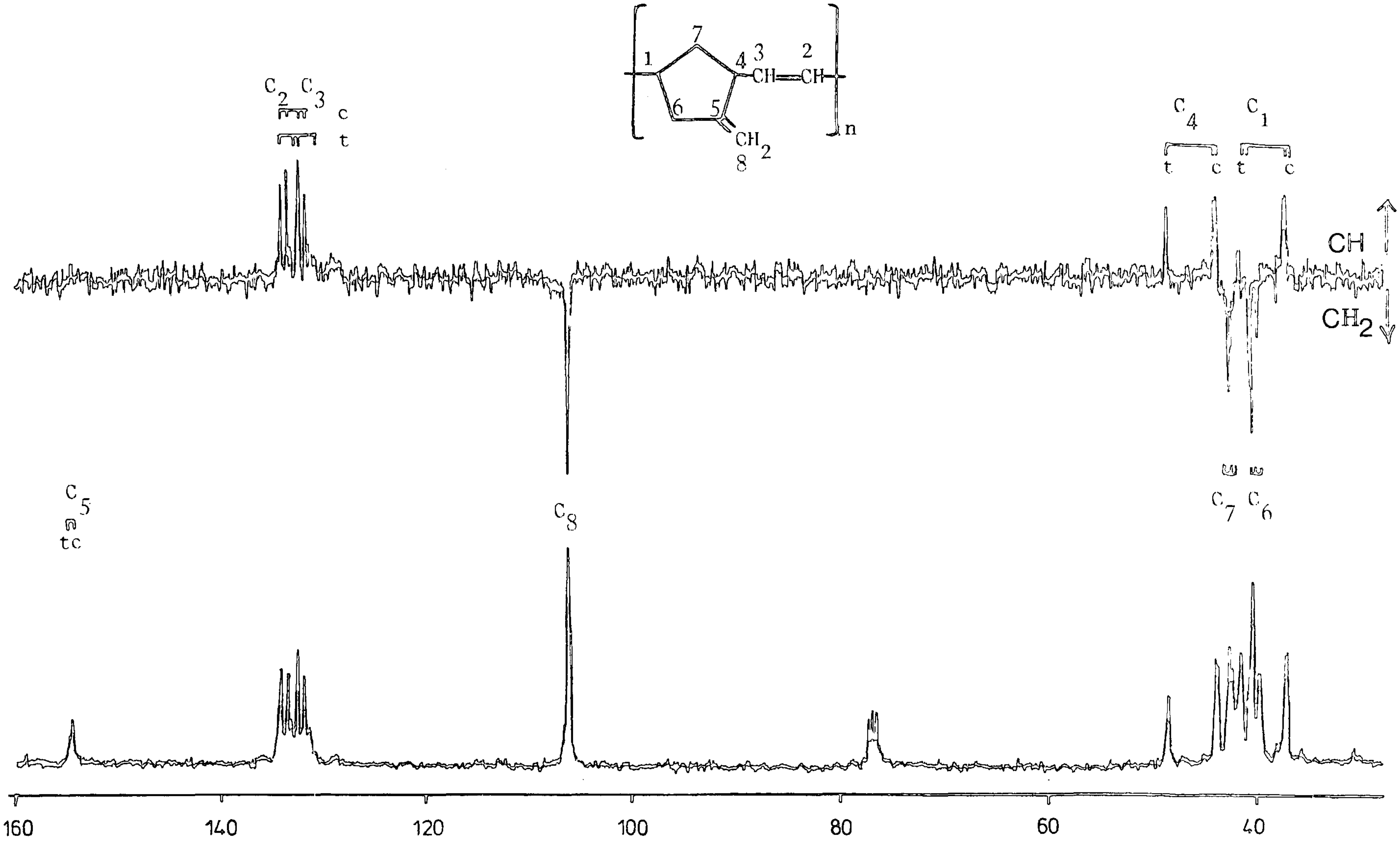
Attempted Metathesis, Cationic and Anionic Polymerizations of 5,6-Dimethylenebicyclo[2.2.1]hept-2-ene

3.1 Introduction

The reasons for investigating the behaviour of 5,6-dimethylenebicyclo-[2.2.1]hept-2-ene (14) as a monomer in metathesis ring-opening, anionic and cationic polymerization reactions were outlined in section 10 of Chapter 1. This monomer can be regarded as a substituted 1,3-diene or a substituted bicyclo[2.2.1]hept-2-ene. It was studied several years ago by Rose and co-workers who described its free radical polymerization and co-polymerization.[155] They thought that the 1,3-diene unit might be so much more reactive than the cycloalkene unit that it might prove possible to obtain linear cis-1,4-addition polymers with this monomer; however they invariably obtained insoluble polymers which were not characterized in any detail. The author has found no evidence that other polymerization techniques have been investigated with respect to this potentially interesting monomer. As was indicated in Chapter 1, the attempts to polymerize (14) to be reported here were essentially unsuccessful. The story of this work is briefly recorded here since the objectives of such syntheses remain attractive, the monomer is relatively easily obtained in a pure state (see Chapter 2), and a future investigation may find an alternative approach worth attempting in which case a record of the present work may be useful.

3.2 Attempted Metathesis Ring-Opening Polymerization of 5,6-Dimethylenebicyclo[2.2.1]hept-2-ene

The ring-opening polymerization of compound (14) was attempted using WCl_6/Et_3Al catalyst system at ambient temperature and molar ratio WCl_6:Et_3Al:(14) of 1:3:200, this reaction was repeated many times, no polymer was produced in any of several attempts. This result led to an examination of a similar type of monomer, 5-methylenenorbornene, in order to establish the reliability of the author's experimental technique and to find the best conditions for such a polymerization. The ring-opening polymerization of 5-methylenebicyclo[2.2.1]hept-2-ene has been reported previously.[176] There is a problem in relation to this polymerization in that (23) is particularly susceptible to cationic polymerization; thus, metathesis catalyst activators, for example $EtAlCl_2$[196] at -130°C and $AlBr_3$[197] at -78°C, and even conventional metathesis catalysts such as WCl_6/R_4Sn (R = Bu, Ph)[26] will all result in rapid cationic polymerization of this monomer. The structure (25) of the soluble polymer obtained by cationic polymerization was readily assigned on the basis of ^1H n.m.r. and i.r. spectroscopy since it contains no unsaturation (see the Figure at the top of page 45, Chapter 1), the reaction involves a transanular cyclopolymerization. In the case of the WCl_6/R_4Sn initiated polymerization there was a small fraction of the product which appeared to be similar (i.r. spectroscopy) to ring-opened polynorbornene,[198] this result led Ivin and co-workers to examine the reaction of a wide range of potential metathesis catalysts with monomer (23). They found that most catalyst systems of the metathesis type gave structure (25) rather than (24). In summary, they showed that using either chlorobenzene, or 1,2-dichloroethane (DCE) as solvent the catalysts WCl_6/R_4Sn (1:1 or 2 R = Ph, Bu or Me; not in DCE); $WCl_6/EtAlCl_2$, WCl_6, $MoCl_5$, $TiCl_4$; $TiCl_4/Et_3Al$ (1:3.8 to 6.6), $EtAlCl_2$ and, $ReCl_5$ all gave essentially pure cationic polymerization with monomer (23). Three catalyst systems gave pure ring-opening polymerization, these were WCl_6/Et_3Al (1:1 to 1:5) in C_6H_5Cl or DCE, $MoCl_5/Et_3Al$ (1:2) in DCE and WCl_6/Me_4Sn in the presence of the base spartein (1:1, 3:1) in C_6H_5Cl. It is important to premix the catalyst and co-catalyst before adding the monomer. If the monomer is added before the co-catalyst a small amount of cationic polymer is almost invariably formed. Other bases, such as pyridine, were also used to encourage the preference for metathesis, but complete suppression of cationic polymerization was not always achieved even in the presence of bases. It was found that the first system (WCl_6/Et_3Al) was quite reactive (e.g. 30% pure metathesis polymerization in 5 min.) therefore it was decided to use this catalyst to obtain a pure ring-opening polymerization of 5-methylenenorbornene, and to develop the author's technique. Many experiments were performed using different conditions, details of the individual experiment are given in Table 3.1 (experimental). In all the experiments the reaction was exothermic and the mixture became viscous immediately on addition of the monomer to the activated catalyst system in chlorobenzene. The reactions were terminated by the addition of a small quantity of methanol and then the viscous solution was added dropwise to a vigorously stirred five-fold excess of methanol. The precipitated polymer samples were dried and identified by their i.r. and ^1H n.m.r. spectra. From Table 3.1 it can be seen that the preference for metathesis polymerization increased with decreasing catalyst ageing time and the maximum was reached when the ageing time was about 5 minutes and when the activated catalyst was injected into the diluted monomer solution (run 6). With longer ageing time and more concentrated solutions the polymerization proceeded quickly but gave a mixture of cationic and metathesis polymer, the polymer sample collected from run 6 was fully characterized. I.r. spectroscopy (Appendix B, No. 22) of a film cast from chloroform, ^1H n.m.r., Table(3.2), and ^{13}C n.m.r. spectroscopy (Figure 3.1) provide clear unambiguous evidence that metathesis polymerization has occurred. The i.r. spectrum shows the presence of unsaturation, with $C_{sp}2$-H stretching vibrations at 3060 cm^{-1} and out of plane bending modes at 960 cm^{-1} (trans-vinylene), 880 cm^{-1} (vinylidene) and 730 (cis-vinylene) together with C=C stretching absorptions at ca. 1640 cm^{-1}. The ^1H n.m.r.

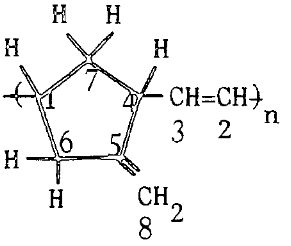


^{13}C N.m.r. spectrum of polymer 24 recorded at 90.56 MHz, upper spectrum DEPT

Figure 3.1

Table 3.2

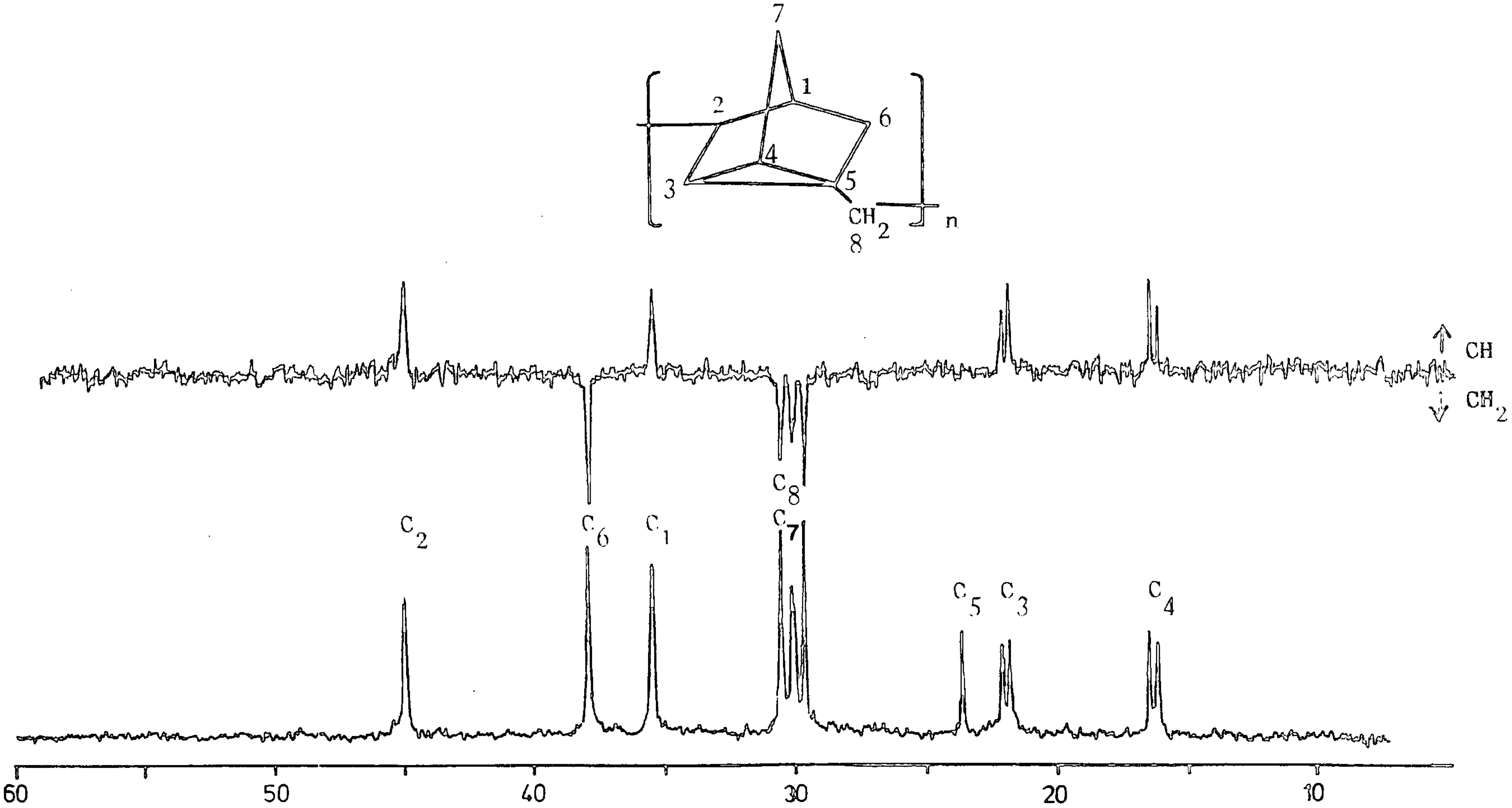
^{1}H N.m.r. shifts for polymer (24), measured at 90 MHz in $CDCl_3$ relative to internal T.M.S.

	shifts*	assignment of hydrogens at
	5.3	C_3, C_2
	4.7	C_8
	2.5	C_4, C_1
	2.0	C_6
	1.3	C_7

* broad unresolved bands centred at

shows clear evidence of vinyl protons and the ^{13}C n.m.r. spectrum is identical with that described by Ivin (Figure 3.1) and completely different to that of the cationic polymer (Figure 3.2). For purposes of reference and comparison a sample of the cationic polymer of 5-methylene-norbornene was prepared using CH_3AlCl_2 in chlorobenzene, the product was a white powdery material and had the expected infrared spectrum (Appendix B, No. 23) and ^{13}C n.m.r. spectrum (Figure 3.2).[176]

Since ^{13}C n.m.r. spectroscopy provides the most convincing evidence for the structures assigned to polymers (24) and (25) the data presented in Figures (3.1) and (3.2) is briefly discussed at this point. The spectra for the two polymers are each recorded in two ways, the lower trace shows a conventional broad band proton decoupled spectrum and the upper trace shows a Distortionless Enhancement by Polarization Transfer (DEPT) spectrum. The DEPT technique has become available to us only relatively recently and such spectra allow identification of carbon signals associated with CH_3, CH_2, CH and quaternary environments, the spectroscopist achieves this useful result by manipulation of the

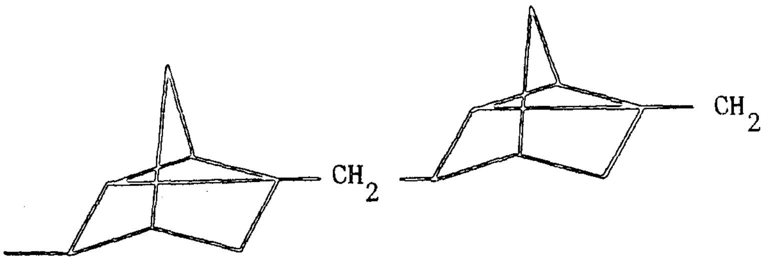


^{13}C N.m.r. spectrum of polymer 25 recorded at 90.56 MHz, upper spectrum DEPT

Figure 3.2

pulse sequence during the recording of the spectra. The DEPT spectra can be presented in a number of ways; the SERC service at Edinburgh, which provided these spectra, invariably presents the DEPT spectrum directly above the conventional broad band proton decoupled spectrum to aid assignment of resonances. Quaternary carbons do not appear in DEPT spectra, one DEPT pulse sequence allows only CH environments to be recorded, and another sequence allows CH_3 and CH environments to appear as positive peaks and CH_2 environments as negative peaks.

The first totally unambiguous observation in comparing the spectra of (24) (Figure 3.1) and (25) (Figure 3.2) is that none of the resonances in the spectrum of (24) appear in that of (25), and vice versa; therefore they have completely different structures. The assignment of the observed resonances has been discussed in detail by Ivin and co-workers and is recorded on these spectra. The spectrum obtained in this work for polymer (24) is identical with that published by Ivin, this has been assigned as having 66% cis-vinylene units and a roughly 50:50 distribution of Head-Head and Head-Tail units. The spectrum obtained for polymer (25), Figure 3.2 is essentially the same as that described earlier except that the peaks at 45 ppm and 30 ppm in these spectra are resolved somewhat better than those in the spectra published by the Belfast group; it is possible that this fine structure reflects stereochemically different dyad sequences; thus the repeat unit is chiral and meso dyads (adjacent units opposite chirality) and racemic dyads (adjacent units of the same chirality) are possible.

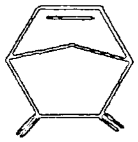


In light of this successful metathesis polymerization of 5-methylenenorbornene, and using exactly the same catalyst system and experimental procedure (run 6, experimental part), the polymerization of 5,6-dimethylenebicyclo[2.2.1]hepta-2-ene was repeated. After the monomer solution was injected to the activated dark brown catalyst solution, there was no evidence of any polymeric material being formed over a period of 2 days at room temperature. The solution started to gel after more than three days exposure to the catalyst. The polymer produced was isolated, dried and its i.r. spectrum (Appendix B, No. 24) was recorded. A sample of cationic polymer of monomer (14) was prepared using CH_3AlCl_2 and its i.r. spectrum (Appendix B, No. 25) was also recorded. The spectra of both these polymers showed no convincing evidence of unsaturation, the sample obtained from the WCl_6/Et_3Al initiated polymerization had a weak band at 3060 cm^{-1} which may indicate some residual $C_{sp}2$-H units, but there was no convincing evidence for -CH=CH- stretching or cis and/or trans vinylene units. Both samples were insoluble and unswollen by a variety of solvents and these attempts to polymerize (14) by metathesis were abandoned.

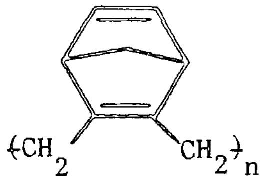
This failure to produce a metathesis polymer from monomer (14) was disappointing but the evidence presented above demonstrates that the failure was not due to the experimental procedure or the technique of the author. It seems unlikely that catalysts of the type examined in this study will provide a route to this metathesis polymer; however, in the general field of metathesis new catalysts have recently been described. Since monomer (14) is susceptible to cationic polymerization the best chance of success for any future investigation of this problem seems to require a catalyst with low Lewis acid acceptor character, and the monomeric catalyst recently reported by Grubbs[64] may be a promising candidate (see page <u>24</u>, Chapter 1).

3.3 Attempted Anionic Polymerization of 5,6-Dimethylenebicyclo[2.2.1]hept-2-ene

It was anticipated that monomer (14) might undergo cis-1,4-addition polymerization under anionic initiation:



(14)



The author had no previous experience of anionic polymerization and so as a first exercise styrene was polymerized using this technique following the instructions in a standard text book.[199] The initiator systems prepared and used were butyllithium in hexane and sodium naphthalide in THF; in both cases the polymerization of styrene was accomplished without difficulty. The same experimental procedures were then applied to the attempted polymerization of monomer (14), no polymer was obtained.

Using the sodium naphthalide initiator with styrene as monomer, it was observed that addition of catalyst solution resulted in a rapid colour change from dark green to red followed by a rapid polymerization (viscosity increase) and discharge of the red colour. In the case of monomer (14), addition of catalyst resulted in the same dark green to red to colourless sequence but no increase in viscosity, further portions of catalyst were added until a persistent red colour was obtained, even under these conditions there was no evidence of polymerization. The reaction was terminated by addition of methanol and after evaporation of solvent examination of the residue by infrared spectroscopy indicated that only monomer (14) and naphthalene were present. Very similar results were obtained using butyllithium in hexane as the initiator system. A possible interpretation of these observations was that the monomer was impure and the initial fading of the catalyst solution colour (Na Naphthalene case) was the result of a consumption of catalyst in a reaction with this impurity. When sufficient catalyst had been added the colour persisted but no polymerization occurred, this observation is consistent with the conclusion that monomer (14) is difficult to polymerize anionically. If this is true it is not immediately obvious why it should be so. Thus, we can consider the mechanism for styrene polymerization initiated by sodium naphthalene to be summarized as shown below.[199-201]

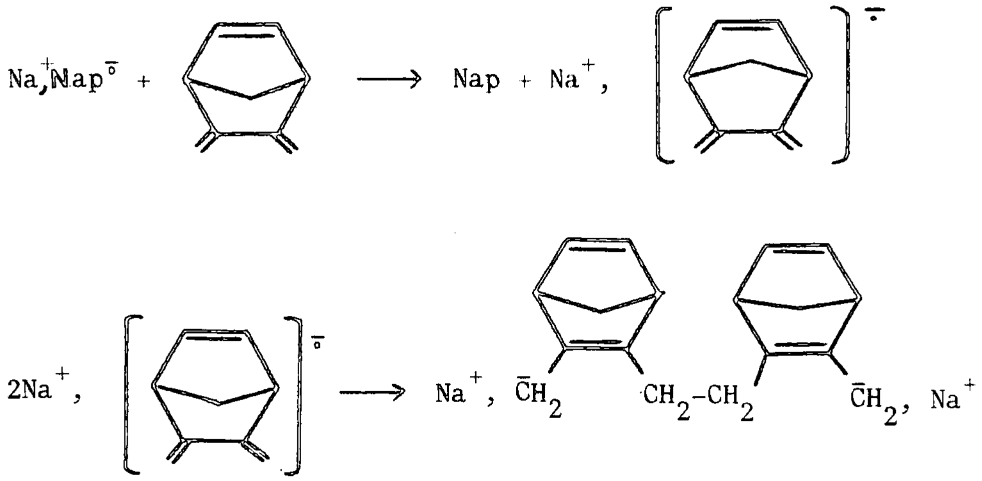
$$Na^+Nap^{\overset{-}{\circ}} + PhCH{=}CH_2 \longrightarrow Nap + Na^+PhCH{=}CH_2^{\overset{-}{\circ}}$$

$$2PhCH{=}CH_2^{\overset{-}{\circ}},\ Na^+ \longrightarrow Na^+, Ph\bar{C}H{-}CH_2CH_2\bar{C}HPh, Na^+$$

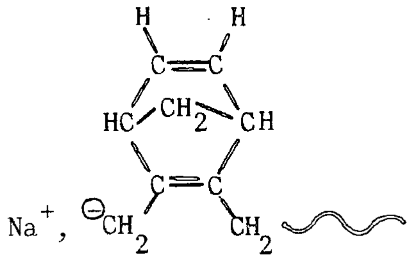
$$Na^+, Ph\bar{C}HCH_2CH_2\bar{C}HPh, Na^+ \xrightarrow{PhCH=CH_2} Na^+, \underset{\underset{Ph}{|}}{\bar{C}H}{-}polystyrene{-}\underset{\underset{Ph}{|}}{\bar{C}H}, Na^+$$

$$Na^+, \underset{\underset{Ph}{|}}{\bar{C}H}{-}polystyrene\ \underset{\underset{Ph}{|}}{\bar{C}H}, Na^+ \xrightarrow{H^+,\ donor} polystyrene$$

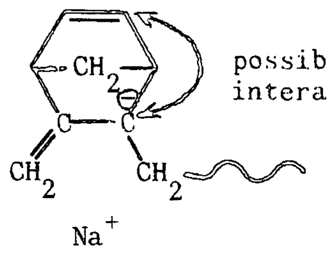
By analogy the steps for monomer (14) would be expected to be:



The anion which has to be formed for this process to happen lacks the stabilizing influence of the phenyl ring which is present in the styrene case, also the monomer (14) has other potential disadvantages. Stereochemically the desired polymerization may be hindered by interactions of the bicycloheptadiene unit being formed. The monomer may also be capable of undergoing other reactions at other sites, for example the bridging methylene may possibly be susceptible to abstraction of protons by the initiator species. A further hazard as far as the anionic polymerization of (14) is concerned may be seen by considering the structure of the anticipated propagating anion shown below.



This allyl anion probably lacks the expected allylic stabilization because charge on the ring carbon may experience an unfavourable transannular interaction with the other double bond, that is:-



possible unfavourable interaction

These initially discouraging results led the author to two further approaches. Firstly it was decided to repurify the monomer with the best available fractional distillation equipment and repeat the polymerization attempt with the reputedly more reactive initiator, butyllithium. Secondly, since there is not a large experience of anionic polymerization in the Durham group, it was decided to seek expert help. Dr. D.H. Richards and Dr. Malcolm Stewart at the

Ministry of Defence Research Establishment at Waltham Abbey kindly agreed to examine the polymerization of this monomer.

The author's final attempt using repurified 5,6-dimethylenebicyclo-[2.2.1]hept-2-ene and lithiumbutyl in hexane gave a low yield of a tacky material which rapidly became insoluble (see experimental). The i.r. spectrum of this product (Appendix B, No. 26) was consistent with its being an unsaturated hydrocarbon polymer; thus the CH stretching region showed bands at 3060 cm^{-1} ($C_{sp}2$-H) and 2860 - 2980 cm^{-1} ($C_{sp}3$-H), there were broad bands in the 1600 - 1700 cm^{-1} region which might in part be due to carbon-carbon double bond stretching absorptions, and bands in the 700 - 900 cm^{-1} which may be due to out of plane bending modes of vinylene C-H bands; however, this result is at best inconclusive.

The preliminary study carried out by Dr. Stewart led to very similar conclusions, which was to some extent gratifying, since it confirmed the difficulties experienced by the author, but was disappointing for the project as a whole. He concluded that this monomer does not undergo living anionic polymerization under any of the conditions examined and that the traces of polymeric material obtained under high catalyst concentration were of an irregular structure.

At this stage of the investigation successful polymerizations with other monomers were being obtained and it was decided to abandon further attempts to obtain polymers directly from 5,6-dimethylenebicyclo-[2.2.1]hept-2-ene.

3.4 Conclusions

The work reported in this chapter was disappointing. The failure to polymerize 5,6-dimethylenebicyclo[2.2.1]hept-2-ene by metathesis or anionic mechanisms so as to give a characterizable product illustrates the difficulty which can be encountered in translating plausible "paper chemistry" into practically useful results. If this project is re-examined in the future the author recommends that metathesis using catalysts of low Lewis acid character would seem likely to be the most fruitful approach. If anionic techniques are to be re-examined it would seem sensible to examine simpler model systems such as those shown below

before reinvestigating monomer (14), studies of these systems have not been reported previously.

Experimental

3.5 Ring-Opening Polymerization of 5-Methylenebicyclo[2.2.1]hept-2-ene

Using the general procedure of polymerization described in Chapter 2 (experimental section) 5-methylenebicyclo[2.2.1]hept-2-ene was polymerized with WCl_6/Et_3Al under the experimental conditions recorded in Table 3.1.

3.6 Unsuccessful Attempts to Polymerize 5,6-Dimethylenebicyclo[2.2.1] hepta-2-ene

Ring-opening polymerizations of 5,6-dimethylenebicyclo[2.2.1]hepta-2-ene were attempted using the general polymerization procedure described in Chapter 2 and the catalyst system and conditions described in Table 3.1, run 6. The monomer (0.50 g, 0.46 ml, 4.24 mmole) was dissolved in chlorobenzene (8 ml) and the active catalyst WCl_6 (1.7 ml, 0.008 g, 0.0214 mmole) and triethyl aluminium (7.3μ, 0.007 g, 0.064 mole) was added to the monomer solution. There was no evidence of a viscosity increase. The reaction was left under these conditions for two days, when the viscosity started to increase; after three days the reaction was quenched by addition of methanol and a white powdery material was isolated from which the i.r. spectrum (Appendix B, No. 24) was recorded. This product was not the anticipated ring-opened product, it was insoluble. The same result was achieved in all of five attempts.

3.7 Attempted Anionic Polymerization of 5,6-Dimethylenebicyclo[2.2.1]-hept-2-ene

3.7.a Reagent

Tetrahydrofuran was purified and dried by Mr. B. Hall, of this department by distillation from potassium. Hexane was purchased from Koch-Light Laboratories Ltd., it was dried by distillation and stored over sodium (shining metal); it was degassed before use.

Table 3.1

Ring-opening polymerization of 5-methylene norbornene using WCl_6/Et_3Al in chlorobenzene

Expt. no.	monomer amount (g)	catalyst system		molar ratio	T^{o}_{c}	solvent (ml)	ageing time (minutes)	reaction duration	wt. of the recovered material		note
		WCl_6 (g)	Et_3Al (μ)	WCl_6:Et_3Al:monomer					soluble	insoluble	
1	1.8738	0.028	35.5	1 : 4 : 250	RT	1	40	overnight	0.34	0.57	mixture
2	0.7271	0.0108	11.2	1 : 3 : 250	(-10 to -5)	3	20	3 minutes	0.3	0.2	mixture
3	0.727	0.016	11.2	1 : 2 : 250	RT	2	10	2 minutes	0.25	0.75	mixture
4	1.09	0.0163	16.8	1 : 3 : 250	RT	6	5	2 minutes	0.52	-	pure
5	1.00	0.0187	12.8	1 : 2 : 200	RT	2	7	1 minute	0.27	0.4	mixture
6	1.00	0.0187	16.1	1 : 3 : 200	RT	12	5	2 minutes	0.55	0.02	pure

RT = Room Temperature; Mixture = mixture of cationic and metathesis polymer as it was examined by i.r. and ^{1}H n.m.r.

3.7.b Preparation of a solution of n-butyllithium in anhydrous hexane

Hexane (100 ml) and lithium (4.3 g, 61.9 mole) were placed in a three-necked round bottomed flask (500 ml) equipped with a reflux condenser, a mercury-sealed stirrer, a thermometer and a gas inlet tube. The air was displaced by oxygen-free nitrogen, and a slow stream of nitrogen was maintained throughout the experiment. N-butylbromide (26.5 ml, 34.5 g) in anhydrous hexane (50 ml) was introduced via a dropping funnel supported by means of a grooved cork at the top of the reflux condenser, n-butylbromide solution (1 - 2 ml) was allowed to run into the reaction flask which was cooled to about -10°C (dry ice-acetone bath). When the reaction commenced bright spots appeared on the lithium surfaces and the reaction mixture became slightly cloudy. The remainder of the n-butylbromide solution was added over a period of 30 minutes whilst the internal temperature was maintained at about -10°C. Then the reaction mixture was allowed to warm up to 0 - 10°C over 1 hour, with stirring in order to complete the formation of n-butyllithium. A clear solution was collected by decanting the cloudy solution through a glass wool plug. An aliquot of the filtered solution was hydrolysed with distilled water and the hydrolysate was titrated with standard solution of HCl (0.1 N) using phenolphthalien as indicator. The hexane solution had a concentration of 99.3 g/l of butyllithium.

3.7.c Preparation of a solution of sodium naphthalide in dry tetrahydrofuran

Tetrahydrofuran (50 ml), resublimed dry naphthalene (1.5 g, 11.72 mmole) and metallic sodium (1.5 g, 62.25 mmole) cut into small pieces were placed in a two-necked round bottomed flask equipped with magnetic stirrer. The flask was purged with dry nitrogen and the nitrogen pressure was maintained at about atmospheric, the reaction mixture was stirred for two hours, dark green sodium naphthalide solution was formed.

3.7.d Attempted anionic polymerization of 5,6-dimethylenebicyclo[2.2.1]-hept-2-ene

One typical example of the reaction will be described here, the details of other syntheses being tabulated.

A clean 3-necked round bottomed flask (250 ml) containing a magnetic follower was used as a reaction flask, the first neck was fitted with a rubber serum stopper, the middle one was connected to the vacuum line and the third was closed with a thermometer pocket, the flask was connected to the vacuum system while hot from the oven and then flamed under vacuum. The required amount of purified dried solvent and monomer (the monomer was distilled under nitrogen from lithium aluminium hydride, and stored over $LiAlH_4$ under positive pressure of nitrogen and low temperature) were degassed using the freeze thaw procedure. They were vacuum transferred into the reaction flask, then the flask was purged with dry nitrogen, it was placed in an acetone/dry ice mixture bath, after stirring for about 10 minutes the monomer-solvent mixture was assumed to have reached the bath temperature (0 to -100°C) and the required amount of the catalyst was injected. No polymer was produced in any of several attempts, even when the monomer solution was stirred with active catalyst (the colour does not disappear for more than 24 hours). Repetition of this experiment under different conditions also failed to produce a polymer. Attempts to modify the reaction by addition of N,N,N',N'-tetramethylethylene diamine with n-butyllithium as catalyst system were also unsuccessful. Table 3.3 records the attempted anionic polymerization of 5,6-dimethylenebicyclo[2.2.1]-hept-2-ene. It should be noted that the author polymerized samples of styrene by this technique without any problems.

Table 3.3

Expt. no.	monomer m.mole	catalyst system	cat./co-cat. m.mole	solvent/ml	reaction temp.
1	29.323	n-C_4H_9Li	0.146	hexane/70	Room temp.
2	17.796	n-C_4H_9Li	0.09	hexane/50	-10°C
3	48.305	$C_{10}H_8^-Na^+$	0.234	T.H.F./50	-70°C
4	31.101	$C_{10}H_8^-Na^+$	0.154	T.H.F./32	-70°C
5	20.00	$C_{10}H_8^-Na^+$	0.098	hexane/25	-90°C
6	42.373	n-C_4H_9Li/T.M.E.D.	0.42/64	hexane/100	-70°C
7	40.678	n-C_4H_9Li/T.M.E.D.	0.39/61	hexane/40	-50°C
8	17.797	n-C_4H_9Li/T.M.E.D.	0.17/26.98	hexane/20	-10 - 0°C

3.7.e Repurification of monomer (14) and final attempt to anionically polymerize it using lithium butyl

The monomer (14) was repurified by fractional vacuum distillation (Fischer-Spaltrohr System 0200/01 with Vacuum Regulator) using the best equipment available. The fractionation uses a concentric tube fractionating column (HSM500) with a low fluid hold up and monomer (14) was distilled at 29°C/5 mm Hg, the fraction distilling at this temperature ± 0.1°C was collected and examined by gas chromatography where it appeared as a single sharp peak. This purified monomer was subjected to the polymerization procedure described above. 5,6-Dimethylenebicyclo[2.2.1]hept-2-ene (0.77 g, 6.53 mmole, 0.71 ml) and hexane (15 ml) were treated with n-butyllithium in hexane (0.0033 g, 0.05 ml) at room temperature. The solution was initially pale yellow but darkened slowly with time; there was no evidence of polymerization. After one day a further injection of catalyst was made (0.1 ml, 1.6M), the colour of the solution darkened further and a white product separated on the walls of the flask. The reaction was terminated by addition of methanol. The reaction solvents were removed by evaporation to leave (0.204 g, 26%) of a tacky semisolid which was soluble in $CHCl_3$. A film of this material was cast on a KBr disc and its infrared spectrum recorded (Appendix B, No. 26). This material was stored under a positive pressure of dry nitrogen but in 1 day it was no longer soluble in chloroform.

CHAPTER FOUR

Polymer Characterization

4.1 Introduction

In this chapter the characterization of the polymers prepared from monomers 26 - 32 and 40 is described. In the first part of the chapter (4.2.a - f) the analytical methods used are reviewed with respect to their application to ring-opened metathesis polymers, and in sections 4.3 and 4.4 the characterization of individual polymers prepared in this work is discussed.

4.2 Analytical Methods

4.2.a ^{13}C N.m.r. spectroscopy

^{13}C N.m.r. spectroscopy is perhaps the most powerful and informative technique available for studying the molecular structure of polymers. In this thesis we are primarily concerned with polymers produced by ring-opening metathesis. In such polymers it is possible to obtain the cis/trans double bond content and in favourable cases to establish other structural features, such as tacticity and Head-Head vs. Head-Tail monomer placements, together with the distribution of these variables. ^{13}C N.m.r. spectra obtained for polymers made by ring-opening polymerization were first observed by Ivin et al. These workers have investigated the ^{13}C n.m.r. spectra of many polymers prepared by ring-opening of cyclic and bicyclic olefins, including poly(1-pentenylene),[198] poly(1,3-cyclopentylene vinylene) and related norbornene derivatives.[198,203-209] The investigation of the spectra of poly(1,3-cyclopentylene vinylene) provides a good point to start a discussion of the method. The structure of the polymer repeat unit is shown in Figure 4.1., along with the numbering system adopted by Ivin. The ^{13}C n.m.r. spectra of three samples of poly(1,3-cyclopentene vinylene) were recorded and are shown in Figure 4.2, sample (a) had all cis vinylene units, sample (b) 50:50 cis/trans, and sample (c) had > 80% trans vinylenes.

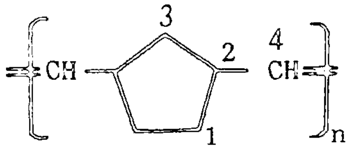


Figure 4.1

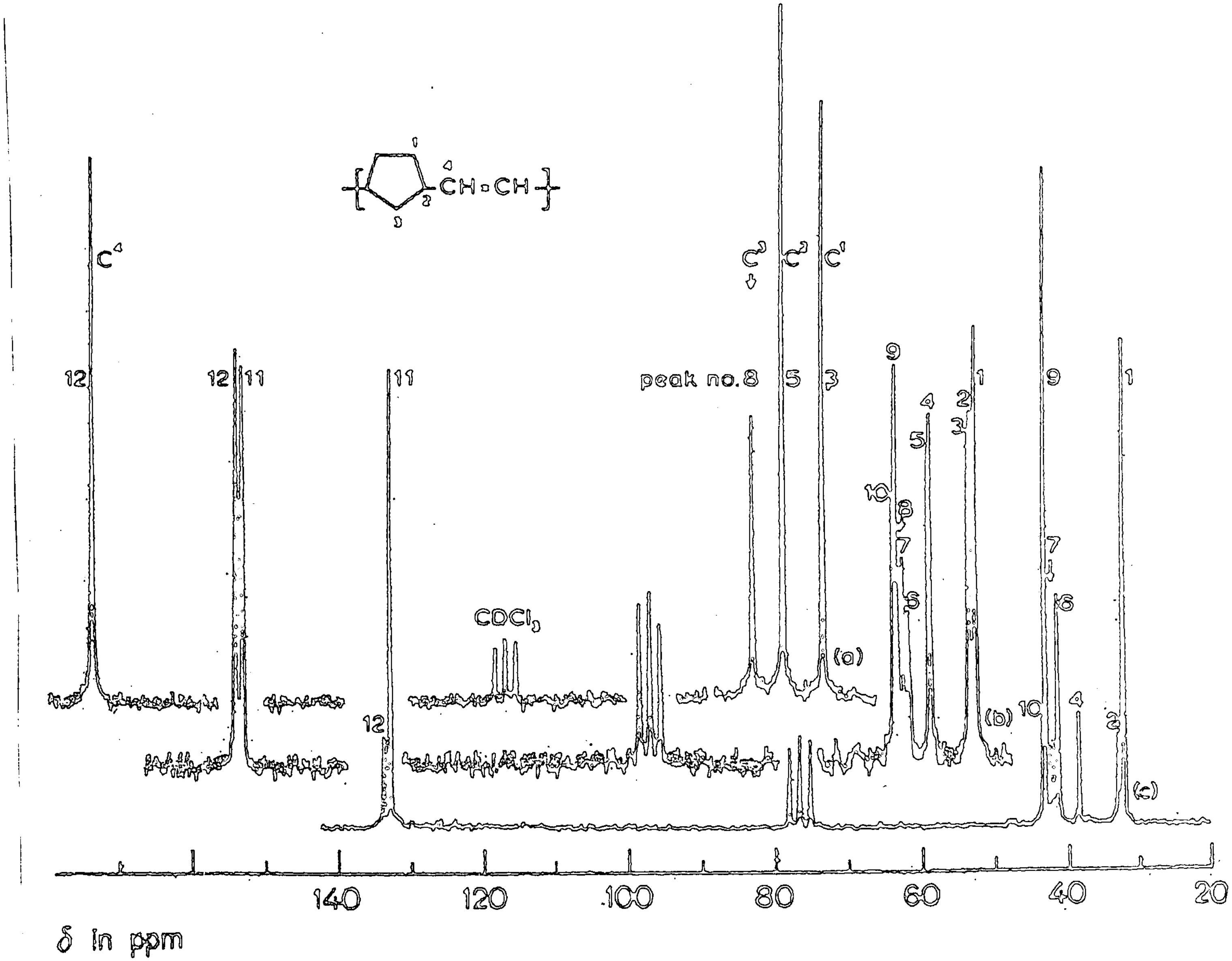
The spectra show multiple fine structure, the main splittings corresponding to a cis (upfield) and trans (downfield) peak for C_2(α-C), and a reverse line order for the other three carbons C_1, C_3, C_4. The chemical shifts of C_1, C_2 and C_3 carbon atoms are sensitive to the isomerism about the nearest double bond and also to that about the next nearest double bond, therefore in a poly(1,3-cyclopentylene vinylene) containing both cis and trans unsaturation four signals should be observed for C_2 and C_1 i.e. 2tc, 2tt, 2cc and 2ct; 1cc, 1ct, 1tc and 1tt respectively, in which the number denotes the carbon, the first letter, the cis (c) or the trans(t) structure at the nearest double bond the second letter that at the next nearest double bond. The methylene carbon, C_3, is symmetrically disposed between the two nearest double bonds so that we can expect three peaks corresponding to 3cc, 3ct ≡ 3tc and 3tt. The relative intensities of these signals may be used to calculate the amount of cis and trans-unsaturation in the polymer using the formulae for determination of the fraction of cis-unsaturation, σ_c, for each set of signals shown below and compared with the value obtained from the intensities of the signals due to cis-C_4 and trans-C_4 i.e. the vinylic carbons, where.-

$$\sigma_c = \frac{4c}{4c + 4t}$$

$$\sigma_c = \frac{1ct + 1cc}{1tt + 1tc + 1ct + 1cc}$$

$$\sigma_c = \frac{2ct + 2cc}{2tt + 2tc + 2ct + 2cc}$$

$$\sigma_c = \frac{3cc + 0.5(3ct + 3tc)}{(3tc + 3ct) + 3cc + 3tt}$$

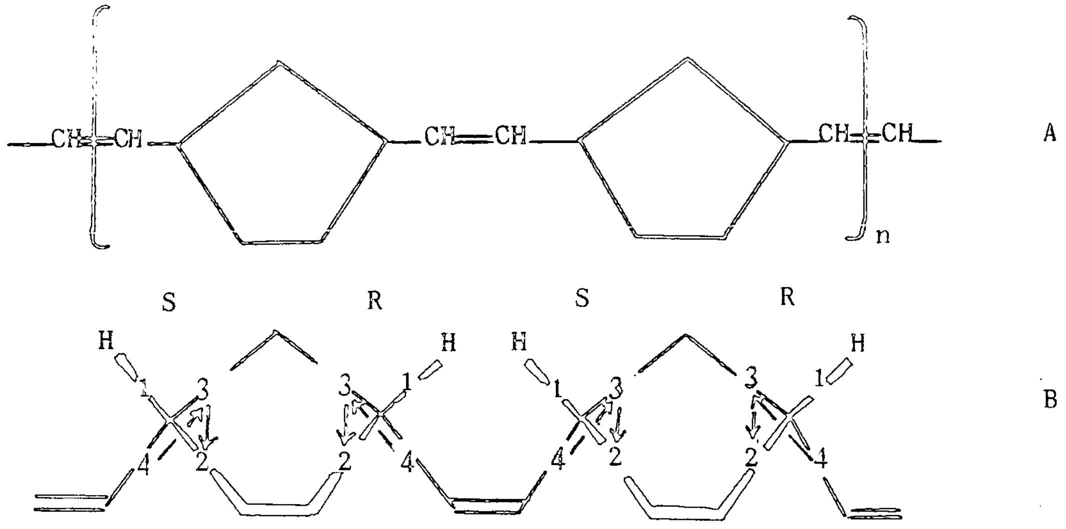


^{13}C N.m.r. spectrum of poly(1,3-cyclopentylenevinylene)

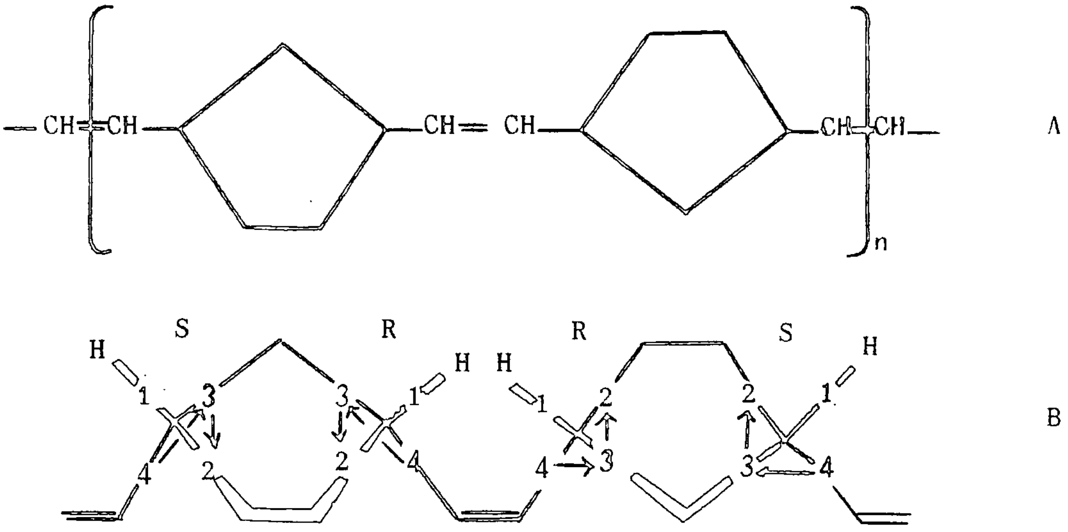
Figure 4.2

Ivin has also pointed out that a statistical analysis of the probability of having cc, ct≡tc and tt double bond sequences in the chain leads to the conclusion that the intensity ratio for C_3 should be given by $C_3(cc):C_3(ct{\equiv}tc):C_3(tt){\equiv}\sigma_c^2:2\sigma_c(1-\sigma_c):(1-\sigma_c)^2$ if the distribution is random. Any difference between the observed intensity ratio and the statistical prediction can be used to calculate the blockiness of the vinylene stereochemistry.

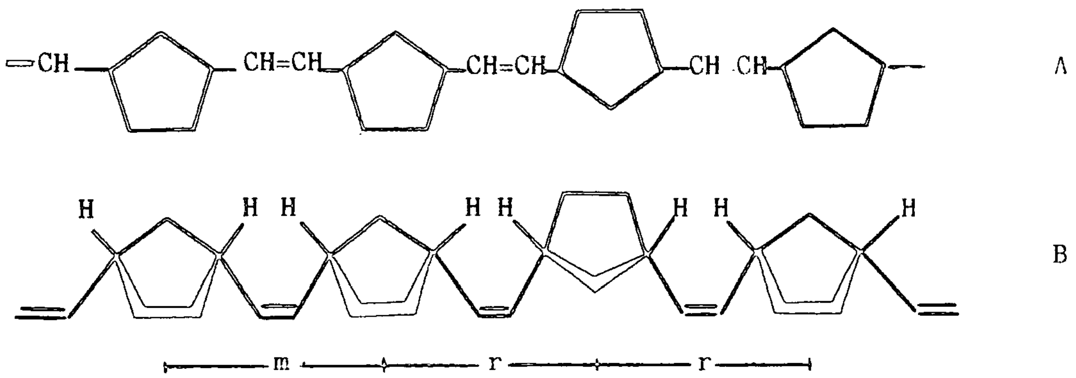
The cyclopentane rings in poly(norbornene) must be substituted in the form of a cis-1,3 structure, this means that such rings can be incorporated into the growing chain in two ways, giving rise to the possibility of ring tacticity as represented in Figure 4.3 for the polymers with all cis-vinylene units. At this point it is necessary to define the terms used in describing tacticity in polymers of this type. The terms are defined with respect to the configuration of the chiral centres adjacent to the vinylene units. A polymer with chiral centres of the same configuration is defined as r (racemic) and syndiotactic, with chiral centres adjacent to the vinylene unit of opposite configuration we have a meso dyad defined as an isotactic polymer. These definitions are illustrated in Figure 4.3 for the vinylene case and for completion the trans vinylene case is shown in Figure 4.4. The ^{13}C n.m.r. spectra of ring-opened polymers of norbornene recorded by Ivin and co-workers do not show any fine structure which can be attributed to a tacticity effect, it is not clear if the effect is absent because of stereoregularity or is present and unresolved. In order to investigate the question of stereoregulation in more detail Ivin and his co-workers have synthesized polymers by ring-opening of a variety of substituted monomers, they prepared (±) and (+)-exo-5-methylbicyclo[2.2.1]hept-2-ene, having cis double bond contents in the range 11 to 100%. They showed that the fine structure in the ^{13}C n.m.r.



meso or m-dyads
cis isotactic



racemic or r-dyads
cis syndiotactic

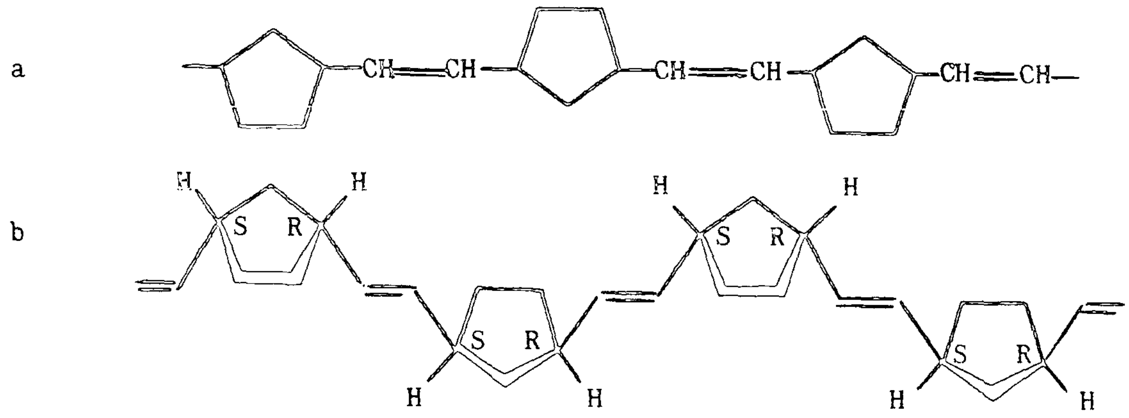


m/r
cis atactic

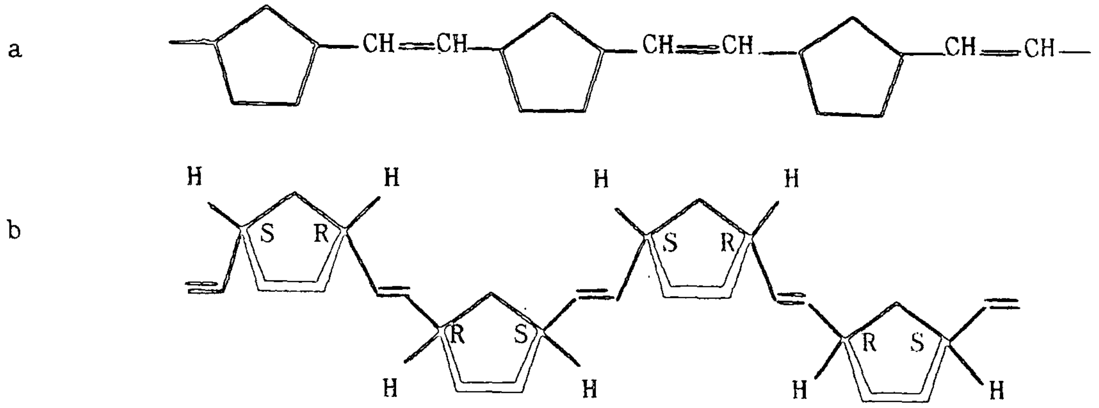
A - viewed from above
B - perspective drawing, heavy lines project towards the observer

Tacticity of poly(1,3-cyclopentylene cis vinylene)s

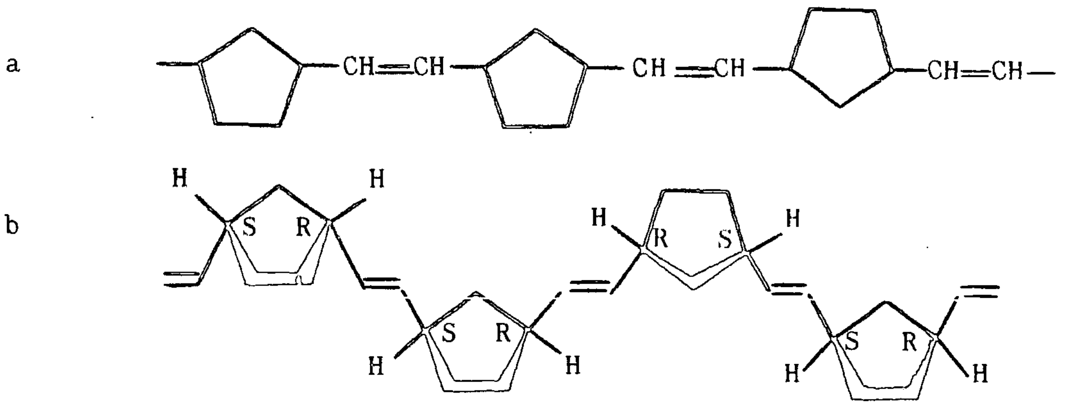
Figure 4.3



meso or m-dyads
trans isotactic



racemic or r-dyads
trans syndiotactic



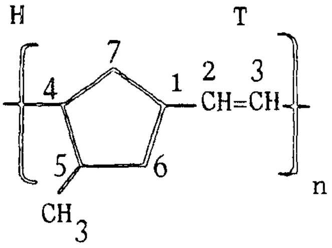
m/r dyads
trans atactic

a - viewed from above
b - perspective drawing, heavy lines project towards the observer

Tacticity of poly(1,3-cyclopentylene trans vinylene)s

Figure 4.4

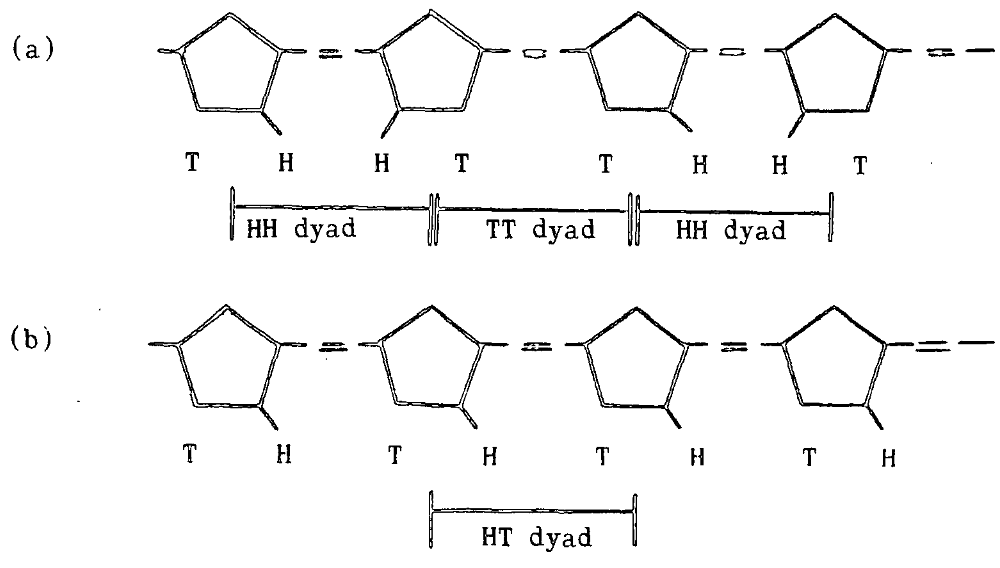
spectra of these polymers can be interpreted in terms of tt, tc, ct, cc effects analogous to norbornene polymers (see above) and TH, TT, HH, HT structures. These symbols (TH, TT, HH, HT) are used to designate the carbon atoms which constitute the head (H) or tail (T) of the polymer repeat unit, it should be noted that C_1, C_2, C_6 as shown in Figure 4.5 are always part of tail and C_3, C_4, C_5 and the methyl group are always part of a head structure. They showed that the spectra of these



Numbering and lettering for repeat units in 5-methylnorbornene polymers

Figure 4.5

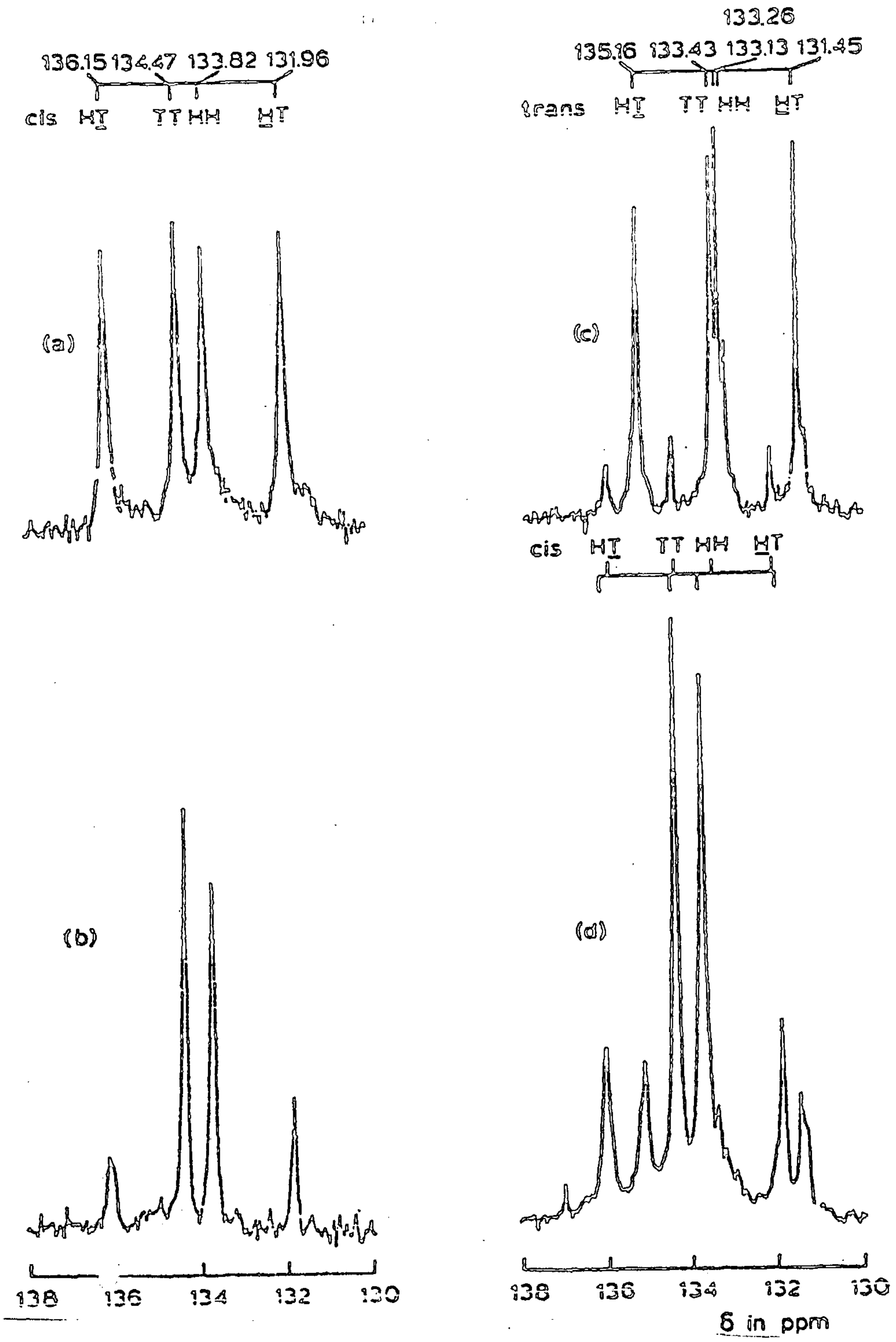
polymers have a group of olefinic carbon peaks (131 - 137 ppm), a group of ring peaks (35 - 53 ppm) and methyl carbon resonances (19 ppm). The ^{13}C n.m.r. chemical shifts are normally sensitive to substitution up to at least the δ position (i.e. over four bonds α, β, γ, δ) and it may therefore be predicted on the basis of known additive shift parameters that the structures shown in Figure 4.6 will have readily distinguishable



HH, TT and HT dyads in polymer of 5-methylenenorbornene

Figure 4.6

olefinic resonances. Thus, the vinylic carbons in the HH dyad shown in Figure 4.6.a will experience shift effects from both methyls ($\gamma + \delta$ effect), those in a TT dyad will experience only a single δ methyl effect; similarly the vinylic units in a HT sequence (Figure 4.6.b) will experience a single γ shift from one methyl in one case ($\underline{H}$T) and a 2 δ shift in the other ($\underline{T}$H). Detailed considerations show that (a) the expected line order for the individual olefinic carbons (downfield to upfield) is $\underline{T}$H (2δ), $\underline{T}$T (δ), $\underline{H}$H ($\gamma + \delta$), $\underline{H}$T (γ), (b) the chemical shift difference for $\underline{T}$H and $\underline{T}$T will be very similar to that for $\underline{H}$H and $\underline{H}$T and equivalent to a δ shift effect, and (c) cis and trans double bonds will each give a set of four lines since the substitution parameter may be expected to be different in the two cases. Figure 4.7 shows the olefinic region of the spectra recorded for four different polymers. Polymer (A) is an all cis sample made from (±) 5-exo-methylnorbornene, this gives four equally intense TH, TT, HH, HT lines resulting from a random arrangement of methyl groups. Polymer (b) is an all cis sample made from (+) 5-endo-methylnorbornene of estimated 73% optical purity. The inner $\underline{T}$T, $\underline{H}$H peaks are 3.3 times as intense as the outer $\underline{T}$H, H$\underline{T}$ peaks, and this pattern is consistent with a fully syndiotactic structure in which the outside peaks derive entirely from the presence of 13.5% (−)-enantiomer [Note 73% optical purity ≡ 88.5% (+) and 13.5% (−)-enantiomer]. The spectrum of a high trans polymer made from the same (+)-monomer is shown in Figure 4.7.c and is indistinguishable from the spectrum of a high trans polymer made from racemic monomer; this may be interpreted on the basis that the ring sequence is atactic even when the polymer is made from (+)-monomer. The spectrum consists essentially of four low intensity cis resonances (but in different positions from those in the spectrum of A because of their sensitivity to the cis or trans structure of the next nearest double bond) and four equal trans resonances (with

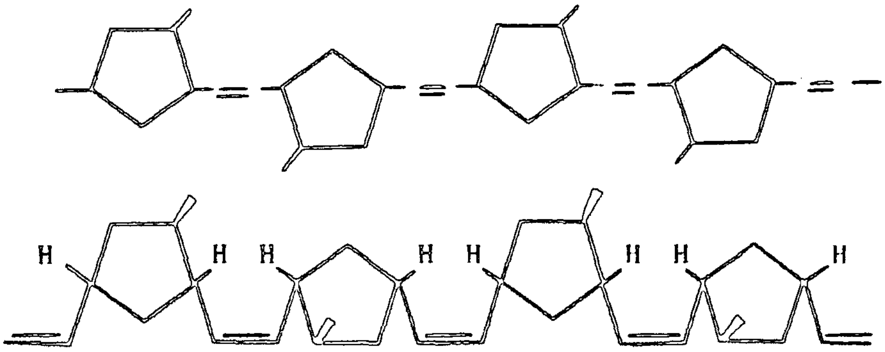


Olefinic carbon region in the $^{13}C(^{1}H)$ n.m.r. spectra of polymers made by ring-opening of exo-5-methylbicyclo[2.2.1]hept-2-ene. (a) All-cis polymer made from (±)-monomer; (b) all-cis polymer made from (+)-monomer (73% optical purity); (c) 11/89 cis/trans polymer made from (+)-monomer; (d) 74/26 cis/trans polymer made from (+)-monomer.

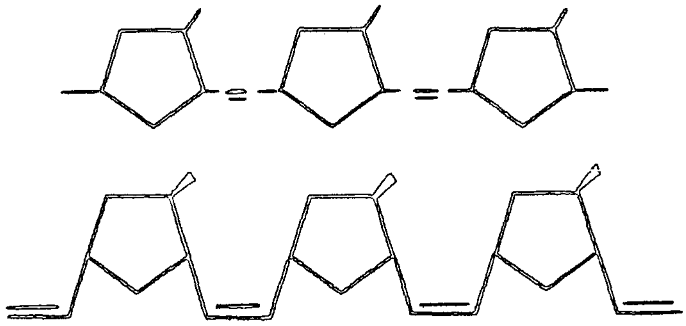
Figure 4.7

HH split into two). Spectrum D (Figure 4.7) is of a polymer with a 74/26 cis/trans ratio in which the polymer has mainly syndiotactic cis junctions and isotactic trans junctions.[204,206,209]

In summary we can say that in this case, for an optically pure monomer, a cis-isotactic polymer must necessarily have an all HT structure so that only the outer lines of each set of four will be observed. Conversely a cis-syndiotactic polymer must have an all HH, TT structure and only the inner lines of each set of four will be observed. For a polymer in which the ring sequence is completely random, two sets of four equally intense lines will be observed and the result will be the same as for the polymerization of racemic monomer. Figure 4.8 shows the tacticities of these polymers. Ivin and co-workers reported



r-dyads
cis-syndiotactic
head-head, tail-tail



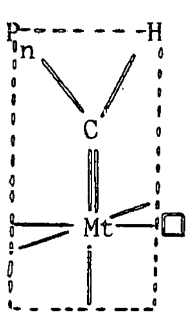
m-dyads
cis-isotactic
head-tail

Polymers from one enantiomer of exo-5-methylnorbornene, illustrating HH, TT or HT sequence required by cis-syndiotactic or cis-isotactic assembly

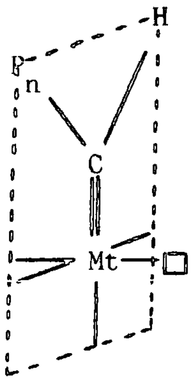
Figure 4.8

that the detailed analysis of ^{13}C n.m.r. spectra of polymers produced by metathesis gave information on stereochemistry and tacticity which could be related to the mechanism of formation of the polymers, since the polymer chain contains a record of all the steps in its formation.

These authors proposed, in agreement with the original suggestion of Chauvin and after analysis of the ^{13}C n.m.r. spectra of high cis and trans poly(endo/exo-5-methylbicyclo[2.2.1]hept-2-ene), that ring-opening polymerization using olefin metathesis catalysts proceeds by a chain mechanism in which the propagating species is a metallo-carbene generated by the catalyst system, sometimes with the assistance of the substrate olefin. They showed that in the ring-opening polymerization of cycloalkene the propagating metallo-carbene may be represented as $Mt{=}CHP_n$ where P_n is the polymer chain. In an octahedral complex the carbene ligand may have one of four possible orientations with respect to the vacancy □, as depicted in 1 - 4. Configurations 2 and 4 may be described as the mirror-image forms P_ℓ and P_r and 1 and 3 as the symmetrical forms (referring only to the geometry defined by C-P, C-H and □).[206]



(1)



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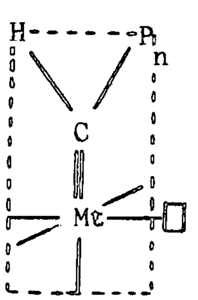

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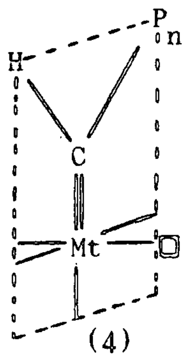
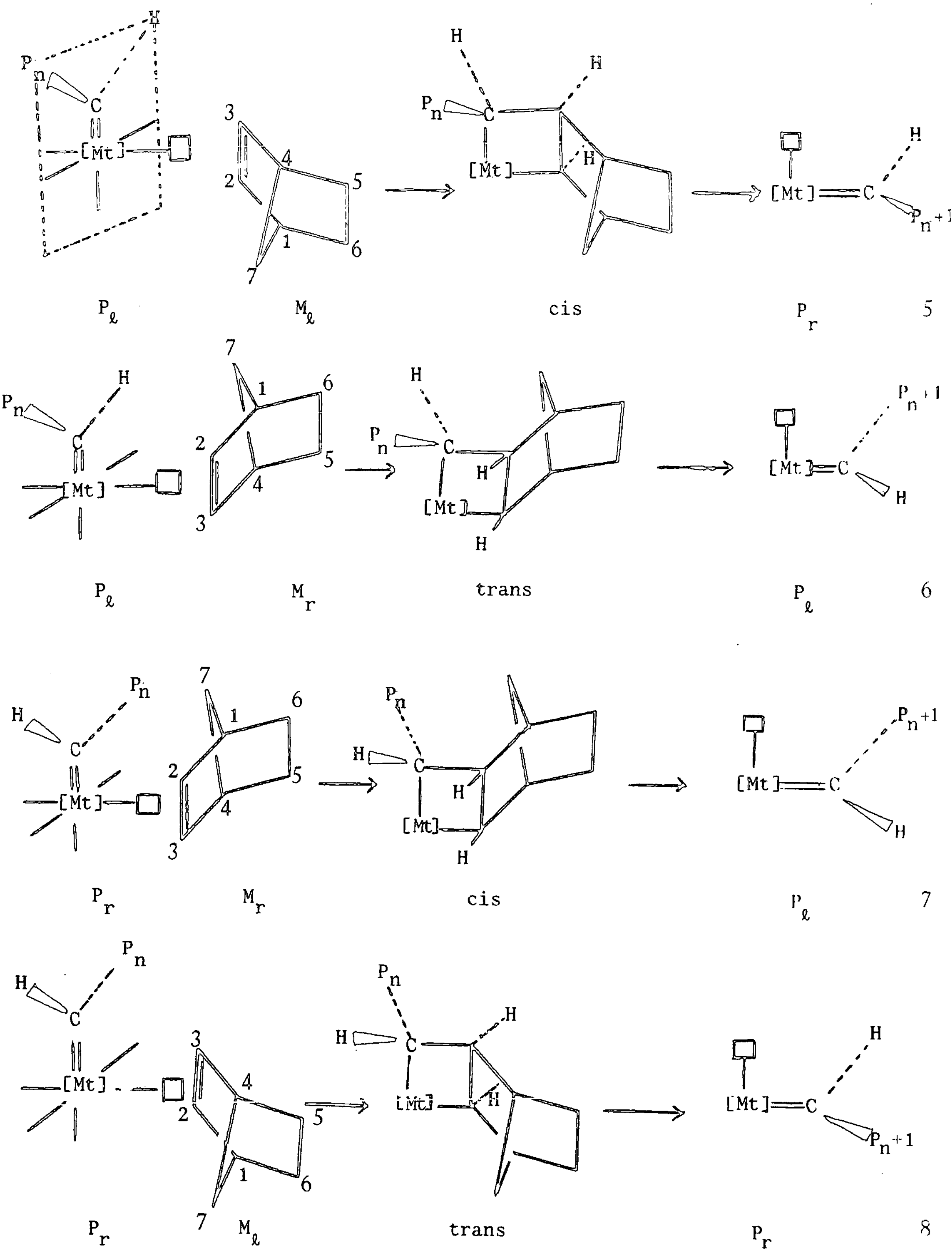


(4)



The four possible modes of addition of norbornene to a chiral conformationally immobile propagating species (after Ref. 210)

Figure 4.9

Now we can consider how the metallo-carbene mechanism applies to the ring-opening polymerization of norbornene. The simplest interpretation of the observations on the fully tactic polymers is provided in Figure 4.9, in this it is assumed:

(1) that the propagating species may have left or right handed forms P_ℓ or P_r as has been described above;

(2) that, as in other reactions, norbornene presents itself to the reaction site with the five membered unsaturated ring towards the metal, in other words the exo face of norbornene, which is the least hindered and is consequently favoured for the initial coordination;

(3) that it may do this in one of two ways (M_ℓ or M_r) according to the relative positions (anti or syn) of the bridging methylene (C_7) of the monomer and the polymer chain, P_n, so as to form cis or trans double bonds respectively on reaction with P_ℓ;

(4) that the configuration P_ℓ or P_r remains intact between successive propagating steps, i.e. there is no ligand migration or rotation about $Mt = C\langle$, or other significant change of geometry.

Then we can say that the metallo-carbenes first coordinate and then add olefin to give a transient metallocyclobutane which ruptures to yield a new metallo-carbene and a newly formed double bond.[210]

The configuration of enchained ring is defined as L when C_3 (see Figure 4.9) becomes attached to the carbene carbon and as D when C_2 becomes attached to the carbene carbon. Altogether there are four possible propagation steps 5,6,7 and 8, the stereochemical consequences, deduced by Ivin and co-workers, for all these possibilities are listed in Table 4.1.

Table 4.1

No.	Assembly modes	double bond form	ring
5	$P_\ell + M_\ell \rightarrow P_r$	cis	L
6	$P_\ell + M_r \rightarrow P_\ell$	trans	D
7	$P_r + M_r \rightarrow P_\ell$	cis	D
8	$P_r + M_\ell \rightarrow P_r$	trans	L

From Table 4.1 it is clear that an all cis polymer can be formed only by alternation of 5 and 7, leading to alternate incorporation of D and L rings i.e. to a syndiotactic polymer. This result can be shown best using molecular models, but has been represented diagrammatically in Figure 4.10. On the other hand an all trans polymer can be formed by a sequence of reactions (6) concurrently with a sequence of reactions (8), leading to an isotactic polymer. As an example of what happens when both cis and trans double bonds are formed, consider the sequence of reactions 5, 7, 6, 6, 5, 8, 7. This will yield the following chain of double bonds and rings cLcDtDtDcLtLcD. Every cis double bond is embraced by an r dyad (LD) and every trans double bond by an m dyad (DD or LL). This is exactly as observed for fully tactic polymers.[210,211]

At the other extreme, where the polymers are completely atactic it is clear that propagation must proceed either through a species P_s that is not chiral about the metal centre or through chiral species that rapidly interconvert between every propagation step, i.e. $P_\ell \rightleftharpoons P_s \rightleftharpoons P_r$. Ivin and Rooney have proposed that in the formation of high trans polymer there may be total relaxation of the metal-carbene to a structure which is not necessarily octahedral, probably square pyramidal or

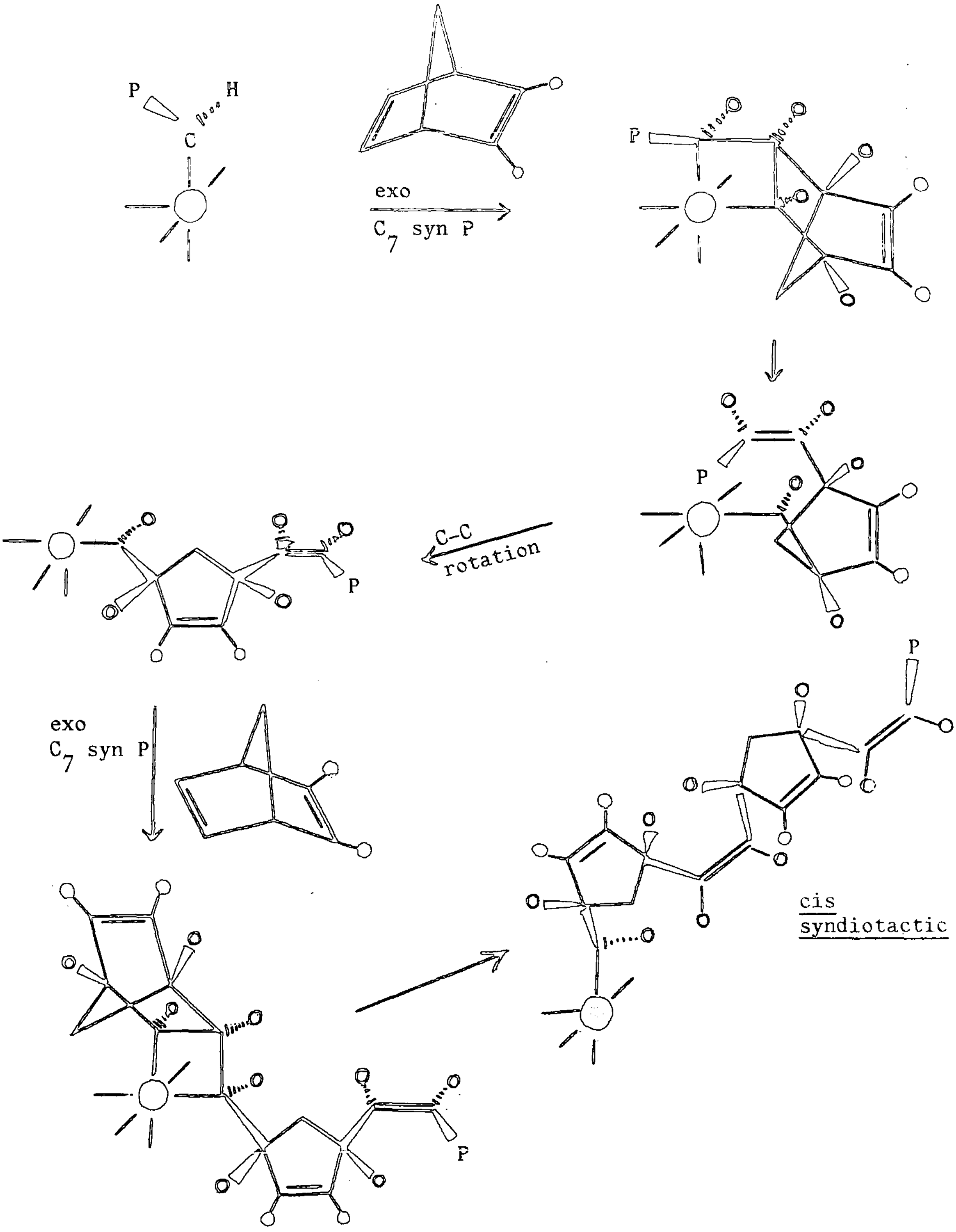


Diagram summarizing the conclusions reached by K.J. Ivin for the case of polymerization of a substituted bicyclo[2.2.1]hepta-2,5-diene with a conformationally immobile carbene as the chain carrying species

Figure 4.10

trigonal bipyramidal with no formal vacant position, and which has an equal chance of adding monomer as M_{ℓ} or M_r.

The foregoing discussion illustrates the very great detail which can be extracted from high resolution ^{13}C n.m.r. studies of polymers of the norbornene type. In section 4.3 and 4.4 the spectra obtained for polymers prepared in this work will be analysed in the light of the procedures established by Ivin and co-workers.

4.2.b ^1H N.m.r. spectroscopy

^1H N.m.r. spectroscopy is a widely used technique for structure determination in organic chemistry. The technique provides information concerning the number of different environments for hydrogen atoms in a molecule (chemical shifts) and the relative abundances of the different hydrogens (integration) and coupling constants in high resolution spectra can be interpreted in terms of structural and stereochemical relationships between hydrogen atoms. For the kind of systems of interest here information might be extracted at a variety of levels; consider as an example the polymers which can be derived from benzonorbornadiene (Figure 4.11).

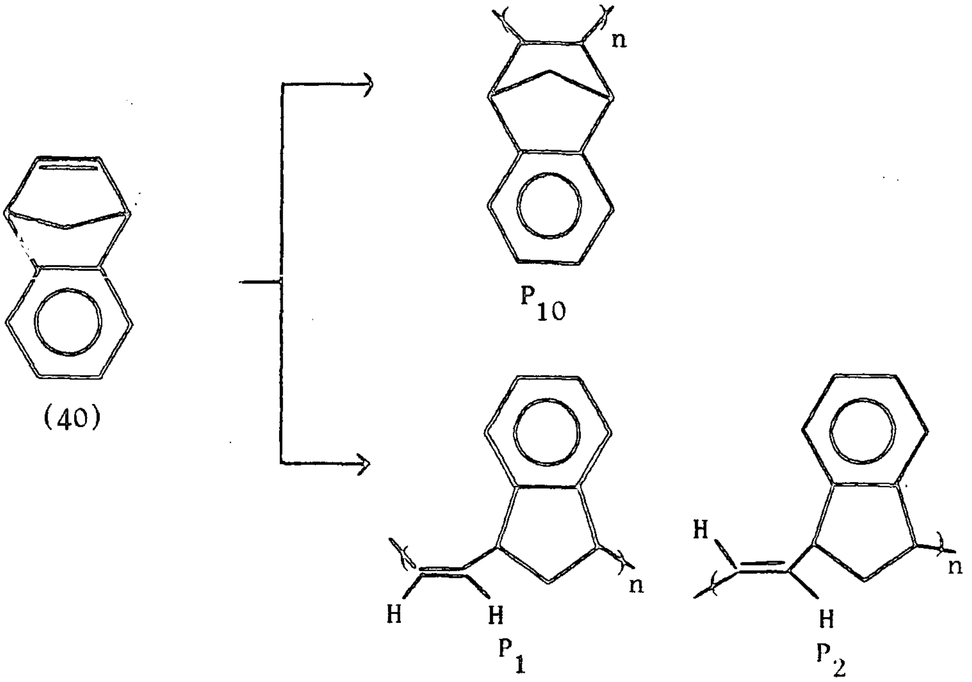


Figure 4.11

It would be expected that in monomer (40) the ^{1}H n.m.r. spectrum would show vinyl, bridgehead, bridging and aromatic resonances in the intensity ratio 1:1:1:2 and that the polymer P_{10} would show resonances associated with aliphatic protons and aromatic protons in a 3:2 ratio but no vinyl proton resonances, whereas either of the polymers P_1 and P_2 would be expected to show aromatic, vinylic and aliphatic protons in the ratio 2:1:2. Since the chemical shifts associated with these broad classifications are well known and quite distinct it is possible to distinguish between ring-opening polymers (P_1 and P_2) and the vinyl addition polymer P_{10} on the basis of low resolution ^{1}H n.m.r. spectroscopy; this has in fact been demonstrated previously.[102] In addition to the gross structural features of the polymer described above it is theoretically possible to obtain more detailed structural information from an analysis of coupling constants. Thus, for example, it should be possible to distinguish between cis and trans substituted double bonds on the basis of the vinyl H-H coupling constants; values of J_{HH} for cis -CH=CH- fall in the range 6 to 12 Hz whereas values of J_{HH} for trans -CH=CH- are typically 12 to 18 Hz.[185] Unfortunately all attempts to obtain well resolved ^{1}H n.m.r. spectra for polymers produced in this work were unsuccessful except for polymers derived from monomer (32). The ^{1}H n.m.r. data have been collected into the Table shown below.

Table 4.2

Polymer No.	$-CH_3$	$-CH_2-$	$>$CH	-CH=CH-	Aryl-H
(P_3, W)		1.3, 1.6	3.3, 3.4	5.4	7.15
(P_4, W)		2.8	4.1	5.8	7.62
(P_6, W)		1.5	2.97	5.39	
(P_7, W)		2.98	4, 4.5	5.85	7.65
(P_7, Mo)		2.99	4	6	7.8
(P_8, Mo)		3.9	4.76	5.62	
(P_9, W)	1.71		4.56	5.6, 5.14	
(P_9, Mo)	1.72		4.4	5.6	

As indicated in Table 4.2 the aromatic protons for polymers derived from monomer (26, 27, 30) were observed as a single broad peak . The allylic and methylene hydrogens for polymer (P_3, W) resolved into two peaks. Comparison of the spectra of (P_7, W) and (P_7, Mo), shows that (P_7, Mo) gives one signal due to an allylic proton, whereas (P_7, W) gives in addition to this signal at 4 ppm a signal at 4.5 ppm, the signal at 4 ppm may be assigned to an allylic proton adjacent to a cis double bond, and at 4.5 ppm an allylic proton adjacent to a trans double bond. The band assigned to the vinylic hydrogens had the appearance of two overlapping peaks of approximately equal intensity, whereas the vinylic hydrogens for polymer (P_7, Mo) show one broad band centred at 6 ppm.

Polymers (P_9, W) and (P_9, Mo) show well resolved bands in the vinylic region, Polymer (P_9, Mo) is a high cis stereoregular polymer, therefore the signal at 5.6 ppm was assigned to the cis vinylic proton. In the case of polymer (P_9, W), the vinylic protons resolved into two distinct bands with the cis vinylic H at 5.6 and the trans at 5.14 ppm. This observation is consistent with approximately equal amounts of cis and trans-double bond units for the polymers prepared from $WCl_6/(CH_3)_4Sn$ catalyst system,on the other hand the polymer prepared from $MoCl_5/(CH_3)_4Sn$ is consistent with the high cis double bond units in the main chain. This observation is in good agreement with that of ^{13}C n.m.r. spectra which will be discussed later in this chapter.

4.2.c Infrared spectroscopy

I.r. spectroscopy is associated with the absorptions of electromagnetic radiation in the wavelength range 2 to 25 microns (5000 - 40 cm^{-1}).[21] The absorbtions are associated with quantized transitions between vibrational or rotational states. The most useful absorbtions from the point of view of the organic chemist occur in the narrower range of

2.5μ to 15μ which most infrared spectrometers cover. The usual range of an infrared spectrum is, therefore, between 4000 cm^{-1} at high frequency end and 650 cm^{-1} at the low frequency end.

Functional groups have vibrational frequencies, characteristic of that of functional group , within well defined regions of the range. The fact that many functional groups can be identified by their characteristic vibration frequencies makes the infrared spectrum the simplest, most rapid and often most reliable means for assigning a compound to its class.

The normal modes of vibrations may be divided into two classes the skeletal vibrations and the characteristic group frequency vibration. Group frequencies are usually almost independent of the structure of the molecule as a whole and with a few exceptions, fall in the regions well above and well below that of the skeletal modes. The vibration of light atoms in terminal groups [e.g. C-H stretch (2970 - 2850 cm^{-1}), -OH ($\sim$ 3600 - 2500 cm^{-1}, free or H bonded), -C≡N ($\sim$ 2250 cm^{-1}), $>$C=O (1600 - 1750 cm^{-1}), $>$C=C$<$ (1650 cm^{-1}), etc.] are of high frequency; while those of heavy atoms [$>$C-Cl (725 cm^{-1}), $>$C-Br (650 cm^{-1}), metal-metal, etc.] are low in frequency.

In review, measurement of i.r. frequencies of a molecule can serve three useful purposes. Firstly the complete spectrum is unique for each molecule which serves to identify the molecule; the characteristic group frequencies can be used to define the organic functional groups within the molecule; and finally, in some cases a detailed analysis can be used to define the geometric relationships present in the molecule.[213]

I.r. spectroscopy has been widely used to identify polymers, to analyse their chemical composition quantitatively, and to specify steric and geometric isomerism, configuration, conformation, branching, end groups, and crystallinity. It is also used in the identification and analysis of additives residual monomers, fillers and plasticizers. For most polymers a thin self supporting film is ideal and procedures are available for preparing such samples. For solvent casting techniques care must be taken to remove residual solvents.[214,215] For insoluble polymer other methods must be used, the method of treatment is prescribed and based on the initial form of the material.[216] If the polymers melt without decomposition, degradation, or oxidation, heat processing or compression moulding can be used. Powders can be dispersed in KBr and pressed into pellets to give useful spectra, or can be mulled with liquid dispersion materials such as paraffin oil, and hexachlorobutadiene. Many polymeric materials such as fibres, rubbers, fabrics and paints cannot be produced in suitable form for transmission measurements but can be studied by attenuated total reflection (ATR).[217] With the development of FTIR, sampling requirements are less restrictive due to the higher sensitivity of the instrument.[218,219] The polymers produced from unsubstituted aromatic monomers (26, 27, 28, 40) and partially fluorinated aromatic monomers (29, 30, 31, 32), were characterized by their i.r. spectroscopy. The i.r. spectra were recorded on free standing films produced from volatile solvents, or as a KBr disk.

The spectra of the unsubstituted aromatic polymers showed the expected C-H aromatic absorptions above 3000 cm^{-1}, the aliphatic C-H absorptions in the region between 2800 - 2980 cm^{-1}, carbon-carbon stretching in the 1585 to 1400 cm^{-1} region. The out-of-plane C-H deformation modes have been used extensively to identify cis and trans -CH=CH- units, the trans unit giving rise to an absorption ca. (960 - 980 cm^{-1}) and the cis to an absorption ca. (665 - 730 cm^{-1}); thus, the presence of any of these bands indicates the geometry of the vinylene unit in the polymer chains. For example, superficial examination of the spectra of the polymers derived from benzonorbornadiene $P_1(WCl_6/Me_4Sn$

catalyst) and P_2 ($MoCl_5/Me_4Sn$ catalyst) which are recorded in Appendix B (No. 27 and 28) shows them to be very similar but a detailed examination of the out-of-plane bending region indicates that P_2 has a higher proportion of cis vinylene units than P_1, see Figure 4.12. Both polymers show bands at 970 cm^{-1} (trans vinylene) and 765 cm^{-1} (cis vinylene , unfortunately the situation is somewhat complicated by the fact that the cis vinylene absorption occurs as a shoulder on the out-of-plane bending mode of the aromatic C-H bonds at 743 cm^{-1} and that the absolute spectral intensities are quite different but comparison of the aryl CH absorption which should be constant for both P_1 and P_2 with the cis vinylene CH indicates that the molybdenum derived polymer has relatively more cis double bonds. This type of analysis is difficult to

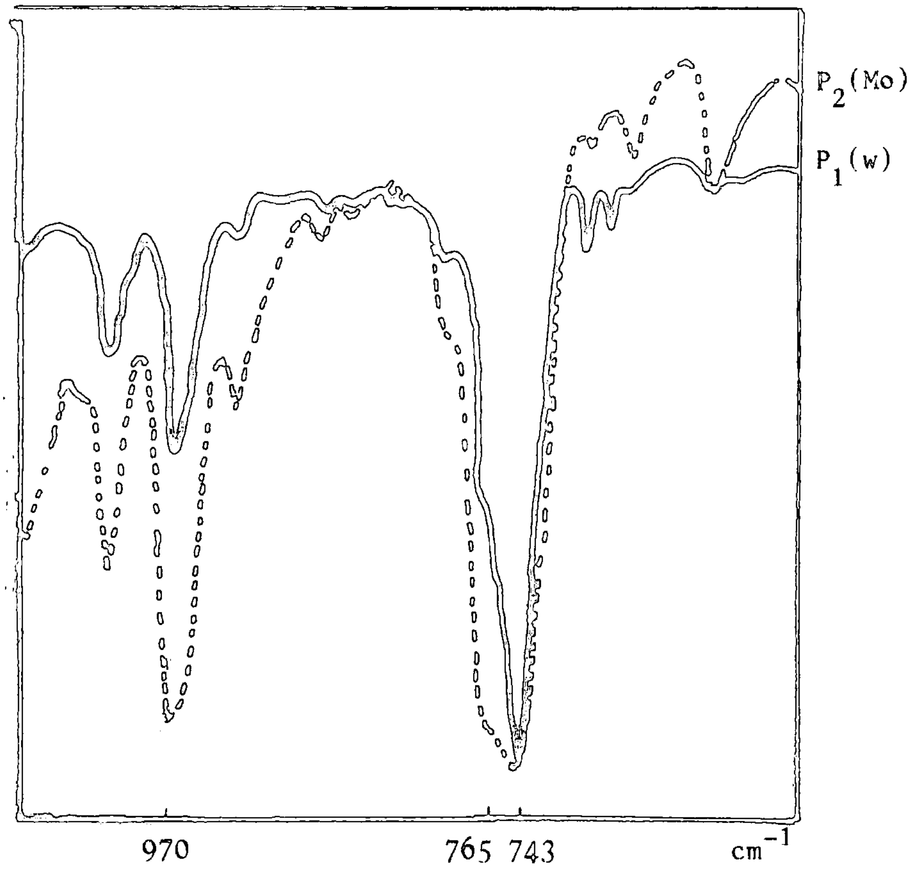


Figure 4.12

Infrared spectra for P_1(w) - P_2(Mo) in the vinylene C-H out-of-plane bending region quantify but, before ^{13}C n.m.r. methods were available it was extensively used to measure cis/trans ratios. The conclusions are as expected and in agreement with the ^{13}C n.m.r. data to be discussed later. There was a close similarity between spectra of polymers derived from monomers 29 and 30, these polymers show strong absorption bands in the region between 1350 - 1120 cm^{-1} assigned to the CF_3 groups, spectra in the region 975 - 730 cm^{-1} are very similar and there is no significant evidence which allows assignment of the cis and trans configurations in this case because of overlapping absorptions from other modes. Polymers derived from monomers 31 and 32 shows the aryl fluoride bands, these bands absorb in the 1250 - 1100 cm^{-1} region, with the same limitations as previously discussed.

In conclusion it can be said that the infrared spectra of the polymers produced in this work are consistent with the expected structures; but that since the structures are fairly complicated, detailed assignments of bands are less certain than with simpler systems such as polypentanemer or polynorbornene, consequently the technique has relatively little value in this work.

4.2.d Gel permeation chromatography

Gel permeation chromatography is a powerful separation technique which has found acceptance in the polymer field since its discovery in 1961.[220,221] Its basic principle depends on the fact that the molecules are separated on the basis of their hydrodynamic volume, which is the volume of the coiled chain of one polymer molecule. This is affected by the stiffness of the chain and the interactions of the polymer with solvent.

Chromatographic processes may be defined as those in which the solute is transferred between two phases, one of which is stationary and the other moving, often traversing along the tube called a column. In

GPC both phases are essentially the same (i.e. the solvent). The GPC column is filled with beads of a porous "gel"; usually made from a highly crosslinked copolymer of styrene and divinylbenzene or a porous glass. The pores in these gels are of the same size as the dimensions of polymer molecules. The stationary phase in the column is that part of the solvent which is inside the porous gel particles, while the mobile phase is outside. In GPC, the transfer of solute between the two phases takes place, as a result of diffusion, resulting from a difference in concentration of solute between the two liquid phases, and restricted by the molecule's ability (depending on its size) to penetrate the pore structure of the gel. This process is called permeation; a sample of a dilute polymer solution is introduced into a solvent stream flowing through the column. As the dissolved polymer molecules flow past the porous beads, they can diffuse into the internal pore structure of the gel to an extent depending on their size and the pore-size distribution of the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded from this stationary phase, the larger the molecule therefore, the less time it spends inside the gel, and the sooner it flows through the column (eluted quickly), the smaller the molecules are, the greater is the volume available to them, and therefore the longer is the time before they are washed out of the gel column (i.e. they elute less quickly).[222] Thus, the final trace obtained, by u.v. or refractive index detection will show a curve with the largest molecules represented at the front end of the trace; from this curve the average molecular weight of the polymer can be calculated. When polymolecular test samples are separated by this technique the peaks in the chromatogram may exhibit broadening which is due to two effects, on the one hand the effect of the molecular weight scatter in the components and on the other that of diffusion phenomena during the flow through the column. Mathematical corrections for the diffusion effect can be employed but are of importance only for polymers with a narrow molecular weight distribution. GPC has proved extremely valuable for both analytical and preparative work with a wide variety of systems ranging from low to very high molecular weights. The method can be applied to a wide variety of solvents and polymers, depending on the type of gel used. The experimental procedure used in this work consisted of preparing an approximately (0.4 to 0.5%) solution of the polymer in THF, the solution is filtered through a millipore filter to remove any particulate matter and injected into the solvent stream which is split into two, one stream is used as reference in the detector system and the other carries the sample through the GPC column and detector. The output from the instrument consists of a curve plotted on a potentiometric recorder. The area under this curve is divided into equally spaced points, by measuring from one of these points to the injection point. The elution volume to that point is obtained. The peak height h_i gives the relative number of molecules N_i with a molecular weight M_i, by the use of corresponding values of M_i from the calibration curve which was prepared by running standards of known molecular weight and narrow molecular weight distribution (polystyrene samples), and preparing of a plot of log molecular weight versus retention volume. The formulae shown below are then used to obtain $\bar{M}_w$ and $\bar{M}_n$ values for the polymer

$$\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad \bar{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad \text{polydispersity} = \frac{\bar{M}_w}{\bar{M}_n}$$

where $\bar{M}_w$ and $\bar{M}_n$ are the weight average and number average molecular weights and N_i is the number of molecules with molecular weight value M_i. $\bar{M}_w$ is sensitive to the amount of high molecular weight molecules present whilst $\bar{M}_n$ is affected by low molecular weight material in the sample.

The polydispersity value is an indication of the molecular weight distribution, for well characterized polymer systems where solution viscosity has been studied as a function of molecular weight, it is possible to use Mark-Howink k and α values to convert the polystyrene equivalent values of $\bar{M}_n$ and $\bar{M}_w$ to $\bar{M}_n$ and $\bar{M}_w$ values for the actual polymer. However, the constants k and α are not known for the samples measured in this work. The GPC output curves of elution volume versus peak height for polymer (P_6, W), (P_6, Mo), (P_7, W), (P_7, Mo), (P_8, Mo), (P_9, W) are shown in Figure 4.13. The weight average molecular weight $\bar{M}_w$, the number average molecular weight $\bar{M}_n$ and polydispersity $\bar{M}_w/\bar{M}_n$ were calculated for each sample. A typical example of the calculation is presented in Table 4.3.

Table 4.3

Calculation of $\bar{M}_n$ and $\bar{M}_w$ of polymer sample from GPC data, polymer P_6, Mo

Elution volume (mls)	peak height (cm)	M_i ($\times 10^6$)	$N_i = h_i/M_i$ ($\times 10^{-5}$)	$N_i.M_i$	$N_i.Mi^2$ ($\times 10^5$)
14.6	0.9	0.8912	0.1000987	0.9	8.0208
15.1	3.2	0.63095	0.507171	3.2	20.1904
15.6	7.2	0.44668	1.61189	7.2	32.16096
16.1	11.25	0.2985	3.76884	11.25	33.58125
16.6	13.95	0.21135	6.600	13.95	29.483325
17.1	14.6	0.14125	10.3362	14.6	20.6225
17.6	10.5	0.1	10.5	10.5	10.50
18.1	4.85	0.070794	6.78	4.85	34.293865
18.6	2.1	0.053088	3.9557	2.1	1.11489
19.1	1.1	0.033496	3.2838	1.1	0.368456
19.6	0.6	0.022387	2.68012	0.6	0.13434
20.1	0.1	0.05848	0.170998	0.1	0.05848
			50.2948	70.35	190.52926

$$\bar{M}_n = \frac{\Sigma N_i.M_i}{\Sigma N_i} = \frac{70.35}{50.2948 \times 10^{-5}} = 139875.29 \rightarrow 140 \times 10^3$$

$$\bar{M}_w = \frac{\Sigma N_i.M_i^2}{\Sigma N_i.M_i} = \frac{190.52926 \times 10^5}{70.35} = 270830.5 \rightarrow 271 \times 10^3$$

$$\text{polydispersity} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{270}{139} = 1.94$$

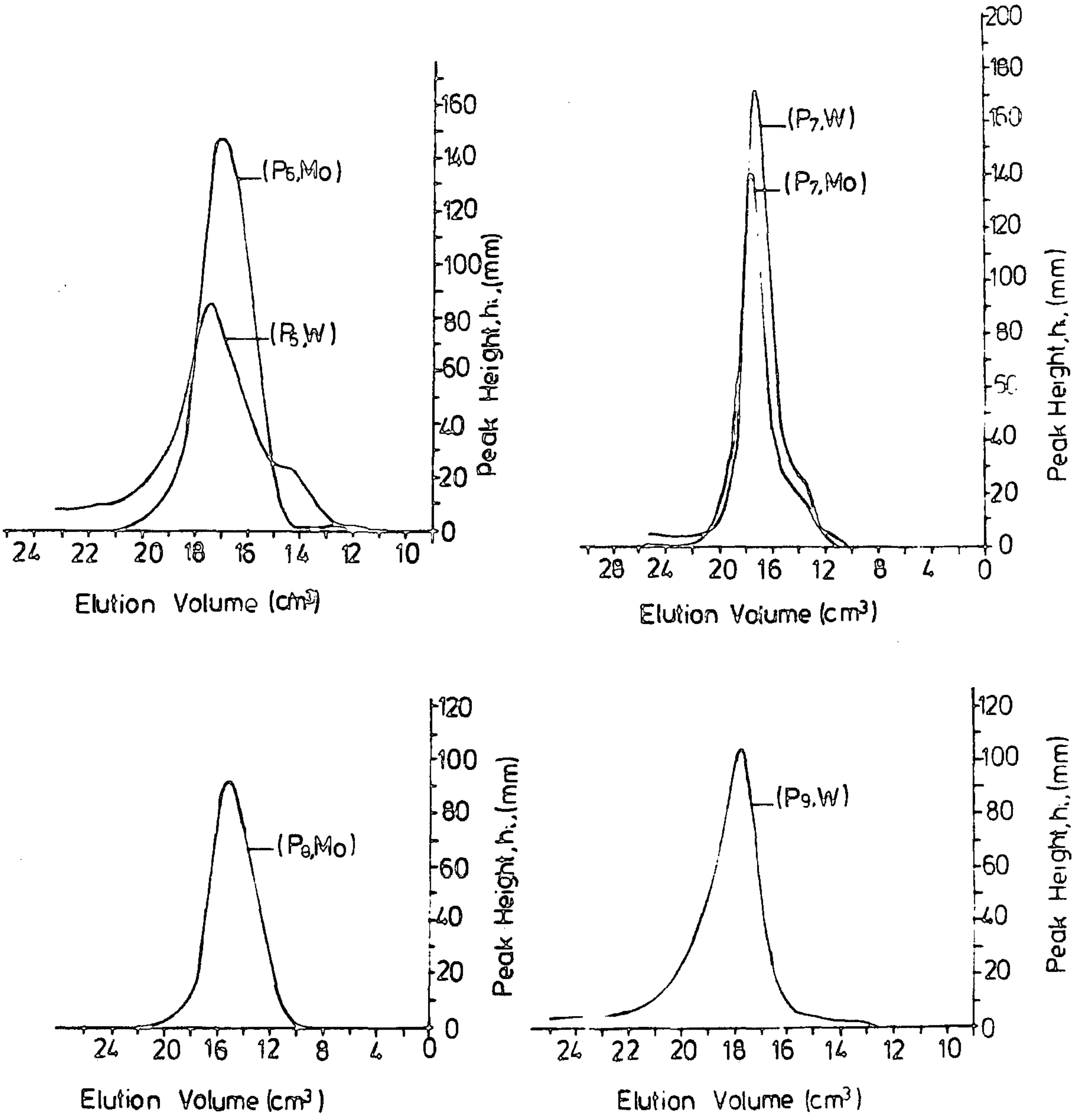

(P6,Mo)
(P6,W)
Peak Height, h., (mm)
0
20
40
60
80
100
120
140
160
24
22
20
18
16
14
12
10
Elution Volume (cm3)
(P7,W)
(P7,Mo)
Peak Height, h., (mm)
0
20
40
60
80
100
120
140
160
180
200
28
24
20
16
12
8
4
0
Elution Volume (cm3)
(P8,Mo)
Peak Height, h., (mm)
0
20
40
60
80
100
120
24
20
16
12
8
4
0
Elution Volume (cm3)
(P9,W)
Peak Height, h., (mm)
0
20
40
60
80
100
120
24
22
20
18
16
14
12
10
Elution Volume (cm3)

Figure 4.13

THF was the only GPC solvent available to the author during the course of this work, polymer (P_4, W) was only partially soluble in THF, and consequently no molecular weight data is available for this material, although, $CHCl_3$ solution viscosity indicates that it was a genuine high polymer. Polymer (P_9, W) gave a clear homogeneous solution in THF whereas polymer (P_9, Mo) was insoluble in THF and only soluble in C_6H_5Cl and $C_6H_5CH_3$; this difference in solubility may reflect a difference in chain microstructure (tacticity). For polymer (P_7, W), (P_7, Mo) and (P_8, Mo) the GPC traces were run twice under the same conditions but on different days, the analysis of these runs show different values for $\bar{M}_n$, $\bar{M}_w$ and polydispersity as shown in Table 4.4. The peak maxima for the two measurements of polymer (P_7, W) were the same but the values of $\bar{M}_n$, $\bar{M}_w$ and polydispersity obtained on analysis

Table 4.4

Gel permeation chromatography results calculated against polystyrene standards in THF

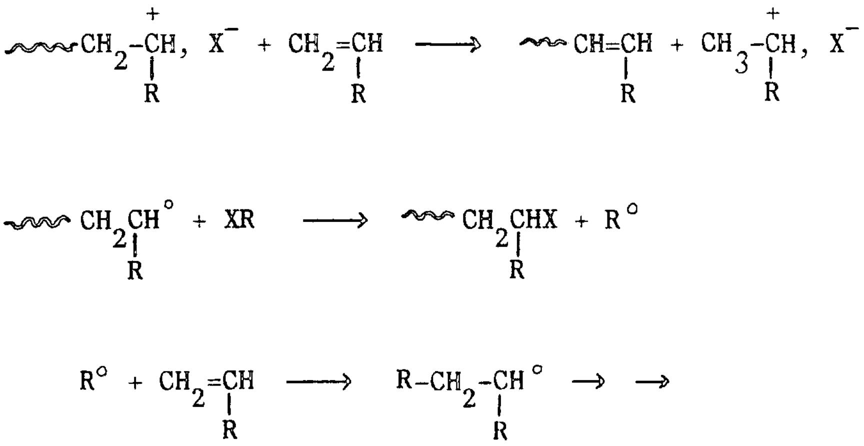
sample	$\bar{M}_w$ x 10^{-3}	$\bar{M}_n$ x 10^{-3}	polydispersity
P_6, W	400	218	1.8
P_6, Mo	271	140	1.9
P_7, W - run 1	438	129	3.4
- run 2	256	95	2.7
P_7, Mo - run 1	530	88	6.0
- run 2	216	74	2.9
P_8, Mo - run 1	1667	301	5.5
- run 2	1472	183	8.0
P_9, W	103	42	2.5

of the values are very different. There is, in this technique an element of subjectivity. When different people were presented with copies of the same trace, and carried out independent analysis as described above the $\bar{M}_n$ values obtained were in good agreement whereas the $\bar{M}_w$ values were in considerable less good agreement and consequently the $\bar{M}_w/\bar{M}_n$ values also showed some scatter, this is a consequence of the relatively large effect of the "wing" components of the peak and the subjectivity in the analysis arises from the definition of where the base line for the trace should be drawn. Runs repeated on the same day gave superimposable traces, so it seems likely that the differences between runs carried out on successive days are significant. In all these cases the molecular weight had dropped and this may indicate a relatively easy oxidative degradation of these polymers during storage in solution.

A general conclusion to be drawn from these results is that genuine high polymers have been produced, the molecular weights obtained are probably an over estimate since it is expected that these polymers will be stiffer than polystyrene and consequently for the same degree of polymerization a rather large hydrodynamic volume may be expected for the polymer coils. As discussed above, it seems that as a consequence of the sensitivity of the analysis of the curves to minor variations, the values obtained for $\bar{M}_w/\bar{M}_n$ should be treated with some reserve; the curves all have a very similar shape and consequently similar distribution would be expected.

4.2.e Control of molecular weight by transfer

In chain growth polymerizations the propagation reaction is responsible for the building up of the actual molecular backbone. This reaction can be stopped in two ways; either by termination or by chain transfer. Termination is the result of destruction of an active species whereas transfer is the result of termination of the growth of one chain concurrent with initiation of another molecular chain and there is therefore no reduction in the number of active centres, although such reactions limit the overall molecular weight of the polymers obtained. Examples of the process for cationic and radical polymerizations are shown below:[223-225]



$$\sim\sim CH_2-\underset{R}{\overset{+}{C}}H,\ X^- + CH_2=\underset{R}{C}H \longrightarrow \sim\sim CH=\underset{R}{C}H + CH_3-\underset{R}{\overset{+}{C}}H,\ X^-$$

$$\sim\sim CH_2\underset{R}{C}H^{\circ} + XR \longrightarrow \sim\sim CH_2\underset{R}{C}HX + R^{\circ}$$

$$R^{\circ} + CH_2=\underset{R}{C}H \longrightarrow R-CH_2-\underset{R}{C}H^{\circ} \rightarrow \rightarrow$$

When transfer becomes excessive, however, no high molecular weight units are formed only oligomeric products being obtained; in these circumstances the transfer reaction becomes, in effect, a termination reaction with respect to formation of high polymers. Compounds whose transfer constants are the order of unity or greater are especially useful in controlling the molecular weight of the polymer, only small quantities are required to depress the molecular weight to almost any desired level. The aliphatic mercaptans are widely used in radical polymerizations involving butadiene or other diolefins as for example in the preparation of synthetic rubbers, in order to reduce the polymer chain length to the range required for subsequent processing.[226,227]

In the present case, octene has been used as a chain transfer agent to reduce the molecular weight of polymer (P_9, W). Using the general polymerization procedure described on page 82, the activated catalyst solution WCl_6 (0.28 ml, 0.004 g, 0.01 mmole), $(CH_3)_4Sn$ (0.02

mmole) in chlorobenzene (0.3 ml) was injected to a mixture of monomer (0.5 g, 0.002 mmole) and octene in chlorobenzene (3 ml). This reaction was carried out four times using the same reaction procedure, the same monomer, catalyst and cocatalyst ratio and varying the amount of octene, the reactions were terminated by the addition of a small quantity of methanol and the product was added dropwise to a vigorously stirred five-fold excess of methanol. The product from experiments 2, 3 and 4 was precipitated as a fine powdery material, it was collected by filtration and dried under reduced pressure. In each experiment a yield of virtually 100% was obtained. The molecular weights of the polymeric samples collected from these reactions were determined using GPC. The GPC output curves of elution volume versus peak height for polymer (32, 1), (32, 2), (32, 3) and (32, 4) are shown in Figure 4.14. The effect of varying the molar ratio of octene on the number and weight average molecular weights is recorded in Table 4.5.

Table 4.5

Polymer no.	molar ratio Cat:Cocat:Mon:octene	M_n x 10^{-3}	$\bar{M}_w$ x 10^{-3}	polydispersity
(32, 1)	1 : 2 :200: 0	336	557	1.66
(32, 2)	1 : 2 :200: 2	17	61	3.6
(32, 3)	1 : 2 :200: 5	8.8	35.9	4.1
(32, 4)	1 : 2 :200: 10	3.6	21.0	5.9

As can be seen, the inclusion of octene has the expected effect in that the molecular weight is progressively reduced as the proportion of octene increases, it also appears from these results that the polydispersity M_w/M_n increases as the proportion of octene in the polymerization mixture is increased. It is established that unsaturated polymers can be degraded to smaller fragments by cross-metathesis and

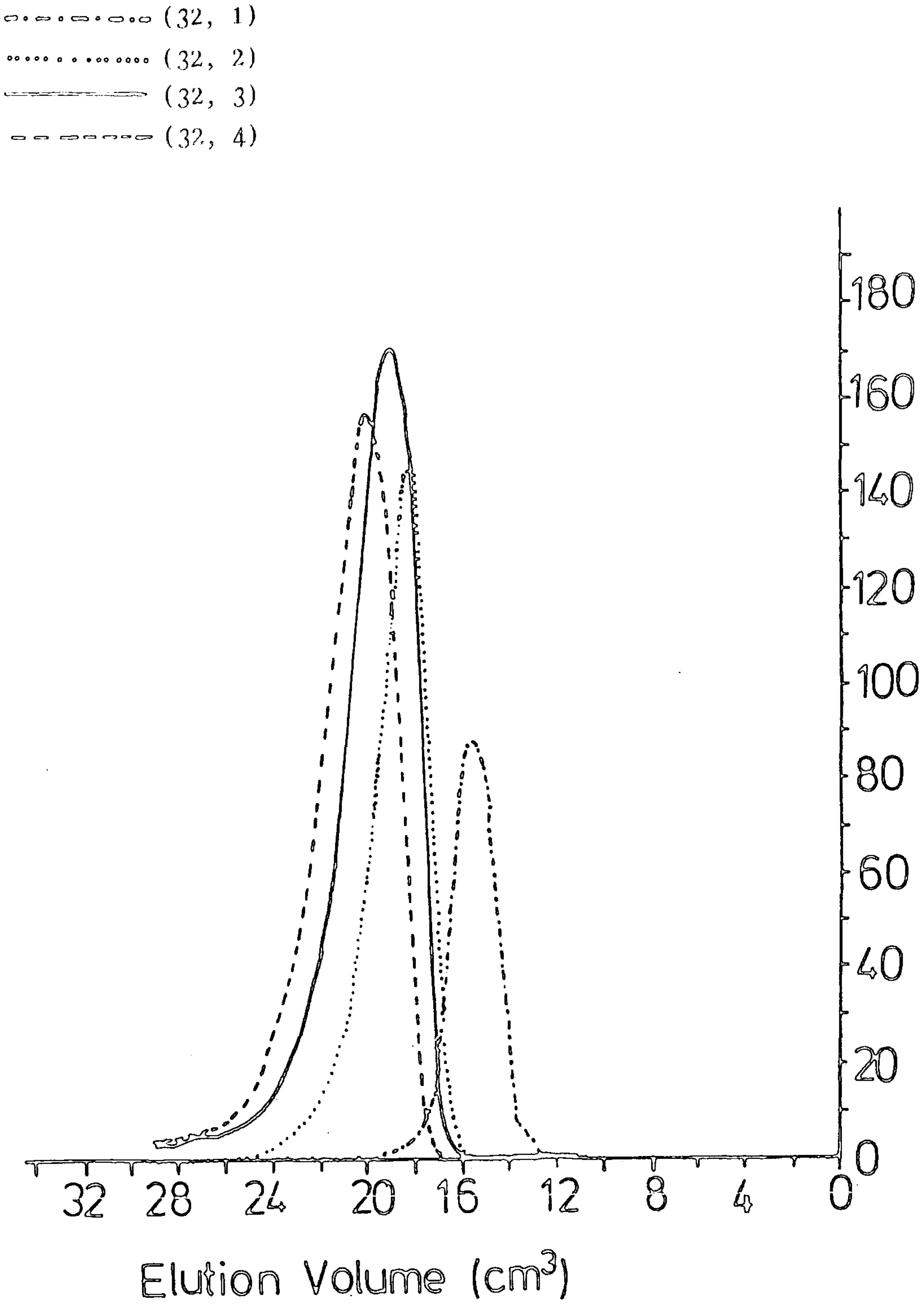

(32, 1)
(32, 2)
(32, 3)
(32, 4)
180
160
140
120
100
80
60
40
20
0
Peak Height, h_i, (mm)
32
28
24
20
16
12
8
4
0
Elution Volume (cm^3)

Figure 4.14

the observed reduction in molecular weight may result from a combination of polymer degradation as well as chain transfer. The purpose of these simple experiments was to establish if the molecular weights of polymers of this type could be satisfactorily regulated and this simple set of experiments demonstrates that this is true in practice. The reservations, expressed earlier, concerning the value to be placed on $\bar{M}_w/\bar{M}_n$ obtained by our GPC analyses and the possibility that two mechanisms of molecular weight regulation are operating means that no attempt to attach greater numerical significance to these results is justified. A practical consequence of these observations is that less soluble polymers can be produced in a low molecular weight (and hence more soluble) form in order to increase the chances of obtaining reasonable ^{13}C n.m.r. spectra.

4.2.f Elemental analyses

The results of elemental analysis for all the polymers prepared are summarised in Table 4.6.

Table 4.6

Elemental Analysis Results

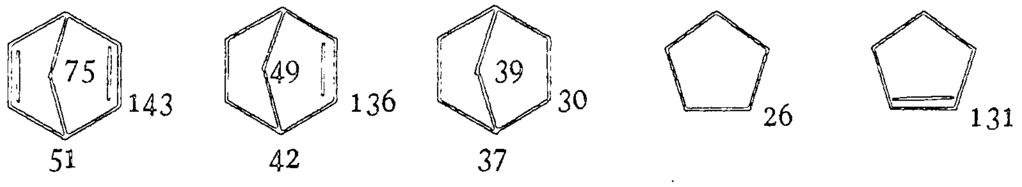
Polymer no.	Found			Calculated		
	C%	H%	F%	C%	H%	F%
P_3, W	90.16	9.22		92.78	7.21	
P_4, W	89.75	6.24		93.75	6.25	
P_6, W	55.57	3.58	39.44	52.72	3.6	40.70
P_7, W	55.96	3.21	40.54	56.13	2.88	40.99
P_8, Mo	62.50	2.7	30.40	61.69	2.8	35.5
P_9, W	67.16	3.77	28.06	66.15	3.937	29.91
P_9, Mo	67.11	3.53	29.40			

The analytical results are only really satisfactory for two of the samples, P_6, W and P_7, W; for the remaining samples there is some deviation from the calculated values. The fluorinated polymers (P_8, Mo), (P_9, W) and (P_9, Mo) are only marginally different from the calculated values for C and H but show some scatter for F; in practice these deviations are probably within the experimental error levels attainable by the analytical techniques used. The hydrocarbon polymers (P_3, W) and (P_4, W) are significantly low on carbon, this is attributed to oxidation of the samples prior to analysis.

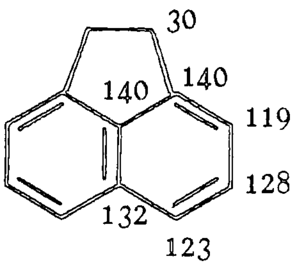
4.3 ^{13}C Nuclear Magnetic Resonance Spectroscopic Analyses of Hydrocarbon Polymers

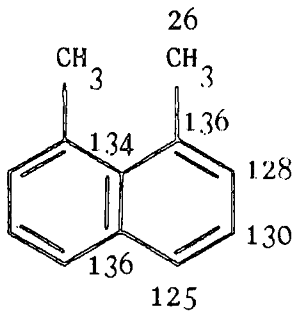
4.3.a Introduction

The application of ^{13}C n.m.r. spectroscopy to the investigation of polymers produced by metathesis ring-opening has been very highly developed by Ivin and co-workers (see pages 104 to 119); previous workers in these laboratories have also used the technique for investigations of polymers derived from fluorinated norbornenes,[100,101] arylnorbornenes,[102] polycyclic chloro- and fluoropolyenes[101] and functionalized norbornene monomers (esters,[228] carbonates[169] and imides).[229] Ivin's work on methyl substituted norbornenes has demonstrated the power of the technique in establishing overall molecular structure and, in favourable cases, details such as the proportion and distribution of cis and trans vinylene units; with unsymmetrically substituted monomers the proportion of head-tail versus head-head-tail-tail units; and details of tacticity. The basis of Ivin's analysis has been outlined earlier, however, prior to an analysis of the spectra of materials produced in this work it is necessary to consider the observed shifts for some molecules structurally related to the monomers used and polymers obtained. First consider the observed shifts for the structures shown below. The quoted chemical shifts are in p.p.m. downfield from



tetramethylsilane, and it can be seen that for all types of carbon decreasing ring strain results in an upfield shift. A similar effect is seen in the two structures shown below, thus all the signals for the carbons in the five membered ring are shifted to higher field in the unstrained analogue, 1,8-dimethylnaphthalene:

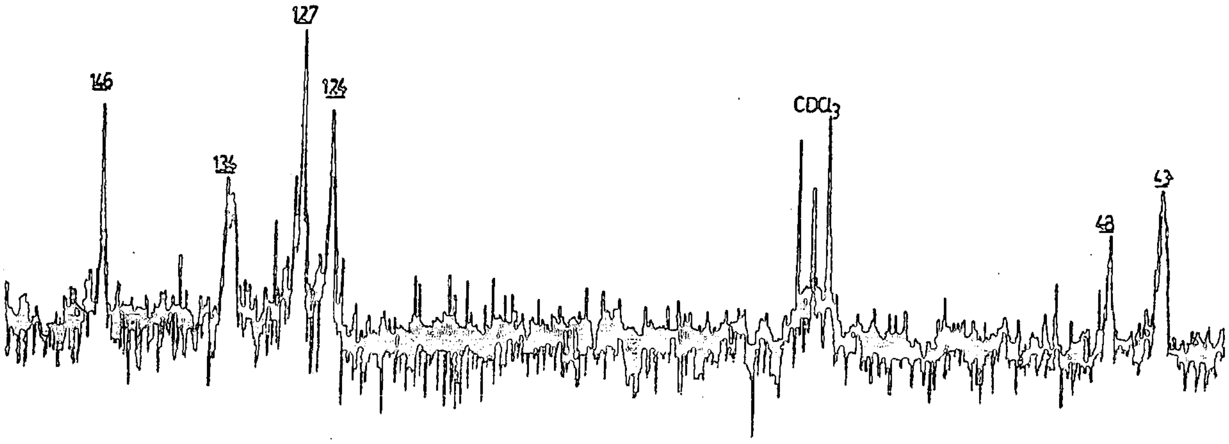




In this last example it is also interesting to note that the aromatic carbons which are not initially part of the five membered ring experience a downfield shift in the less strained system. The investigation of polymers by sophisticated techniques such as ^{13}C n.m.r. spectroscopy is very dependent on the availability and quality of instrumentation. In recent years there have been considerable improvements in both the attainable signal to noise and resolution, and it is clear that access to high quality instrumentation is very desirable. The spectra described below were obtained via the SERC High Field N.M.R. Service based in Edinburgh University and run by Dr. I. Sadler. Demand for this service is heavy and the time required to obtain good polymer spectra is sometimes very great, for example accumulation times in excess of 40 hrs. Considerations of this kind limit the number of spectra which can be obtained and certainly inhibit requests for repetition of measurements under slightly varied conditions; as a result, in this work a somewhat variable quality of resolution has had to be accepted since the resolution attainable is very sensitive to small variations in conditions of recording (purity, molecular weight, concentration, and instrumental variables).

4.3.b Polybenzonorbornadienes

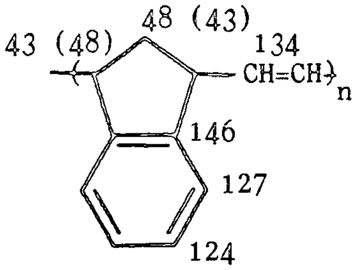
El-Saafin previously investigated this polymer and the spectral resolution obtained at that time is indicated in Figure 4.15. The spectrum was obtained for a freshly prepared sample, made using WCl_6/Ph_4Sn catalyst, and it can be seen that the signal to noise and resolution are not very good although they were fairly typical of data obtainable at that time. The six signals detected were assigned as shown below; those at 43 and 48 ppm were assigned to the methine and methylene carbons, signals at 124 and 127 were assigned to the aromatic carbons,



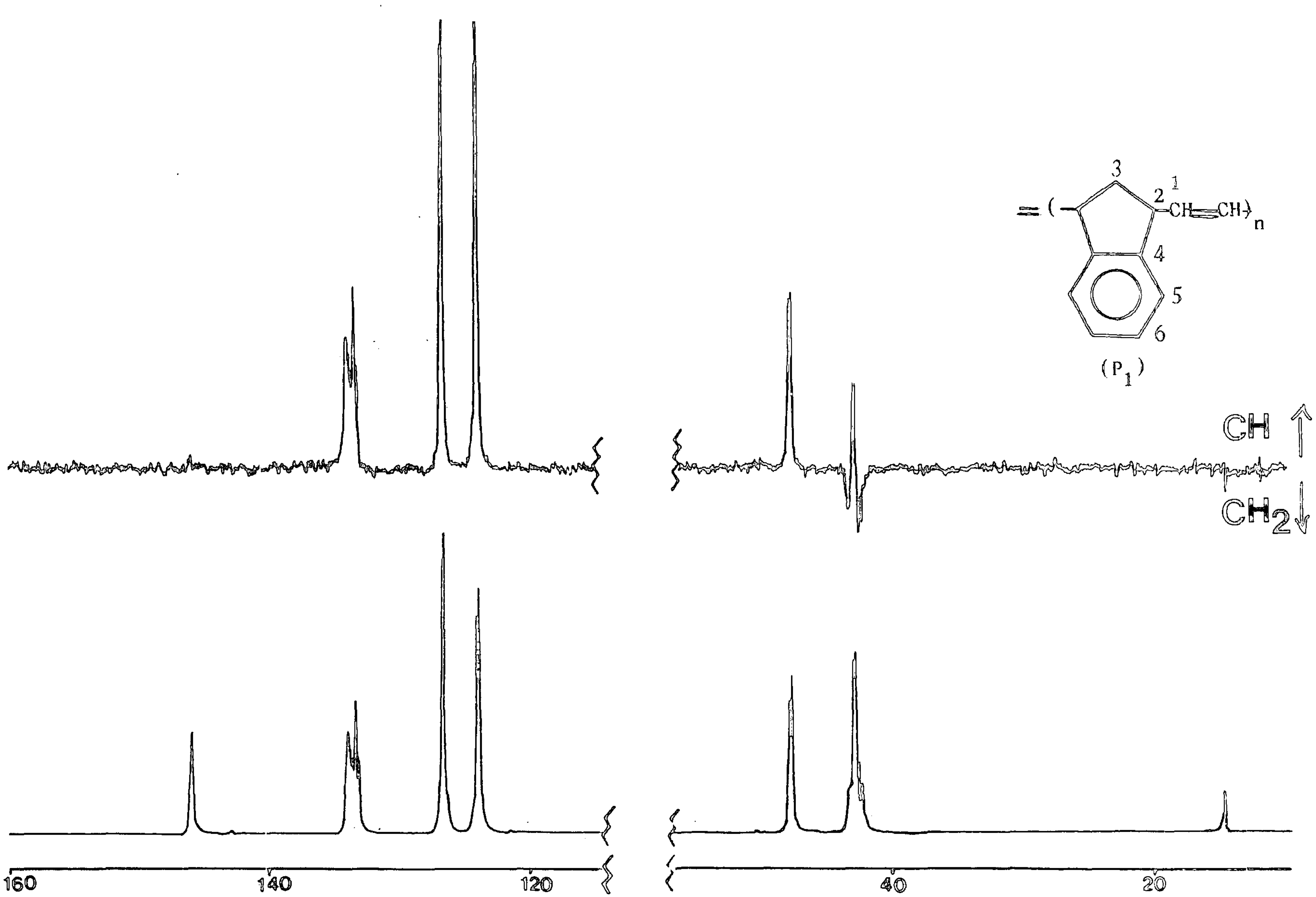
^{13}C N.m.r. spectrum of polybenzonorbornadiene, from the Ph.D. Thesis of I.F.A.F. El-Saafin (Durham 1981)

Figure 4.15

the low intensity signal at 146 ppm was assigned to the aromatic carbons which do not carry a hydrogen atom and the vinylic carbon signal at 134 appeared to be a partially resolved doublet corresponding to cis (downfield) and trans units expected for polymers prepared using this catalyst system. This work has been repeated using WCl_6/Me_4Sn and

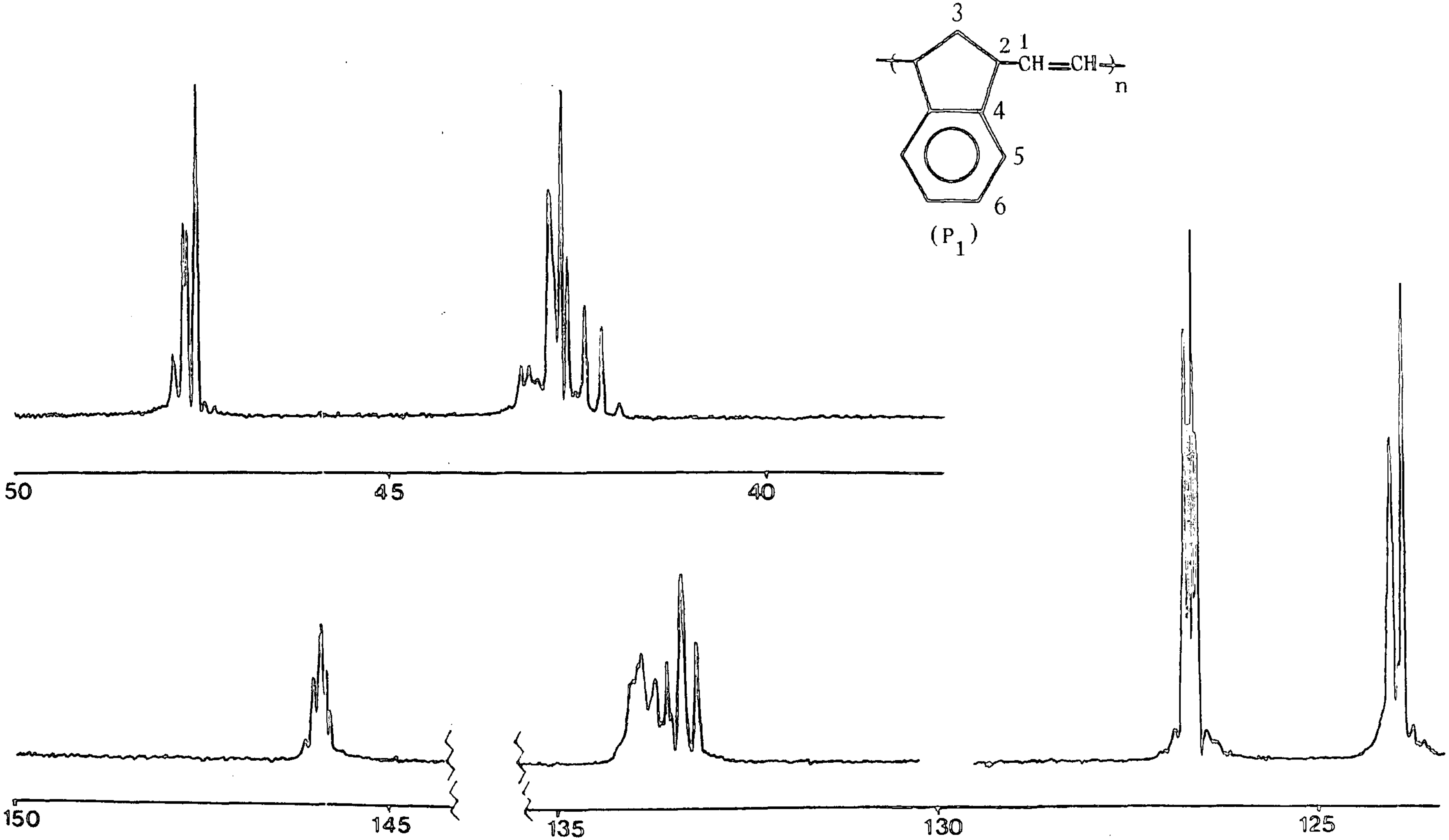


$MoCl_5/Me_4Sn$ catalysts to give polybenzonorbornadienes P_1 and P_2 respectively. These syntheses were described earlier and the different solubilities for P_1 and P_2 noted (see pages 65 to 66); the spectra obtained for these polymers are recorded in Figures 4.16a, 4.16b, 4.17a and 4.17b. The resolution and signal to noise in these spectra are much improved with respect to what was obtained previously. The first point to emerge is that El-Saafin's assignments were generally correct, but the DEPT spectrum (Figure 4.16a) shows that the methine carbon occurs as two multiplet signals at ca. 43 and 47 ppm and that the methylene signal overlaps with the methine signal at 43 ppm. The possible assembly modes for polybenzonorbornadienes were discussed earlier (see page 64) and it is clear from these spectra that a lot of information concerning the chain microstructure is contained in the complicated multiplicities observed, unfortunately the spectrum obtained for P_2 is not as good as that obtained for P_1. The assignments shown on the spectra follow in a straightforward manner from those made for norbornene by Ivin and co-workers. The cis content of these two polymers can be determined from the vinylene carbon intensities given



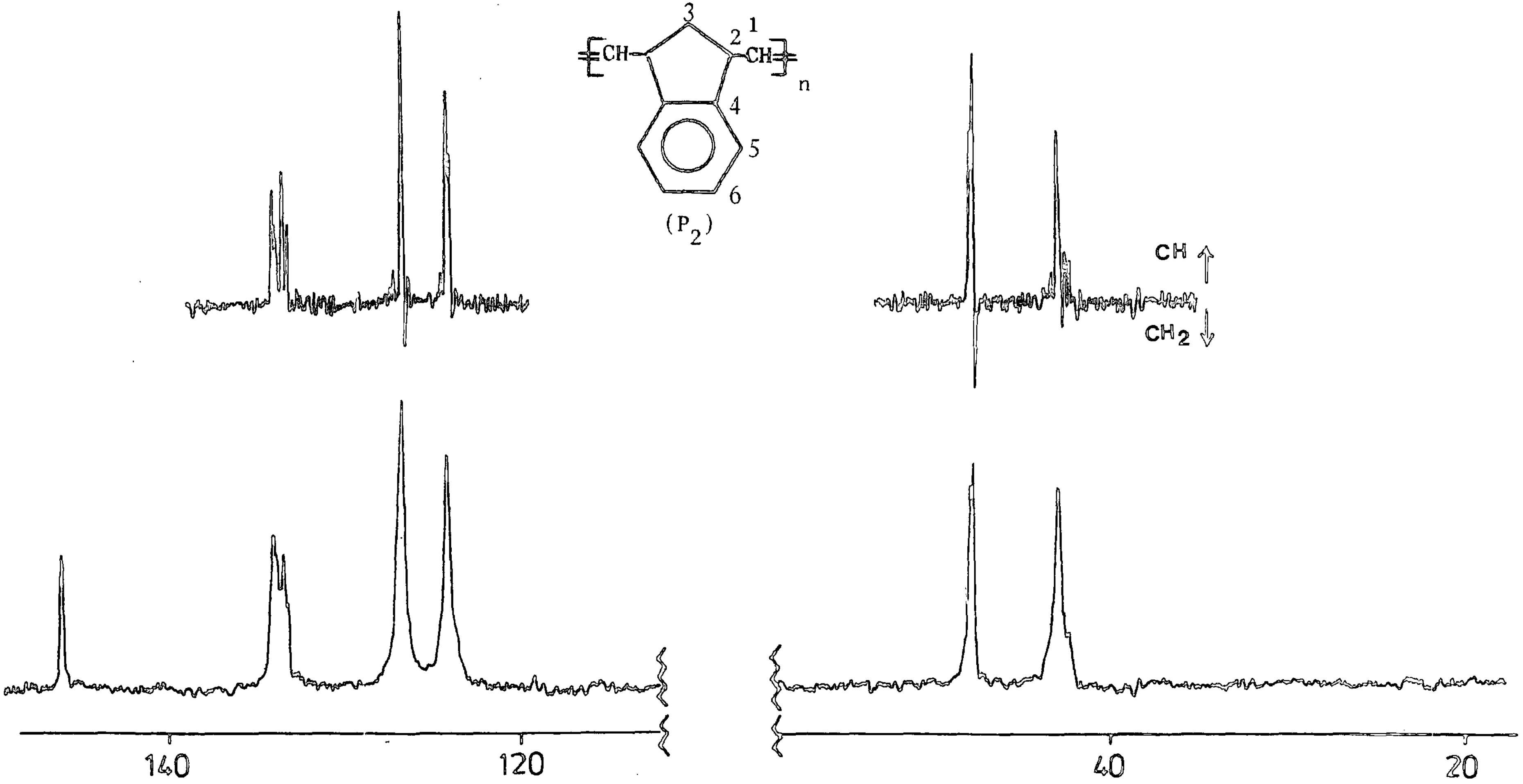
^{13}C N.m.r. spectrum of P_1 recorded at 90.56 MHz, upper spectrum DEPT

Figure 4.16(a)



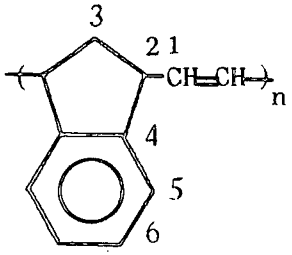
^{13}C N.m.r. spectrum of P$_1$ after line narrowing and expansion

Figure 4.16(b)

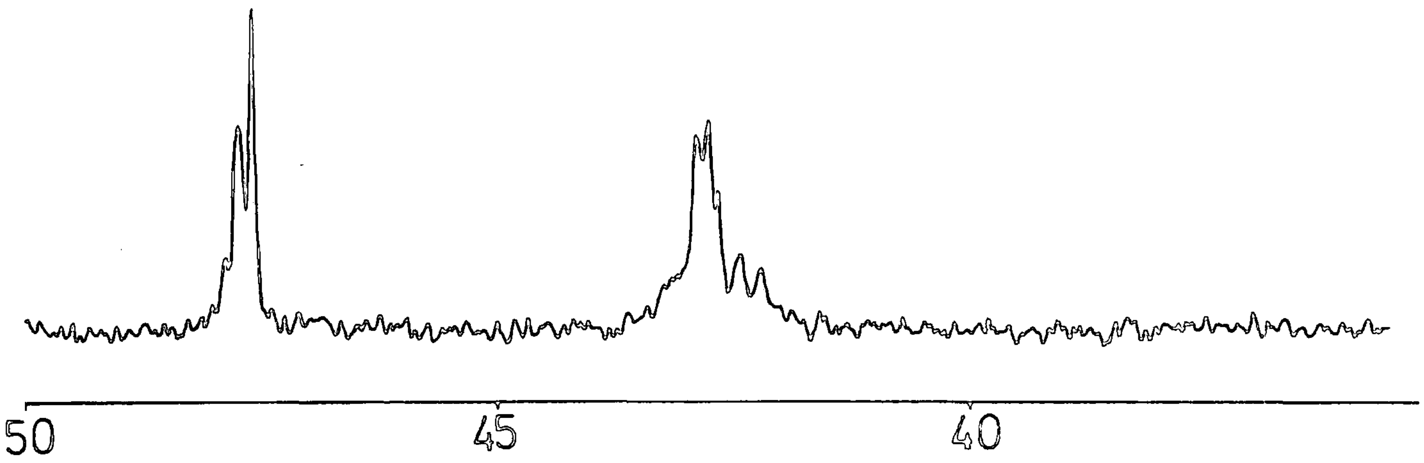


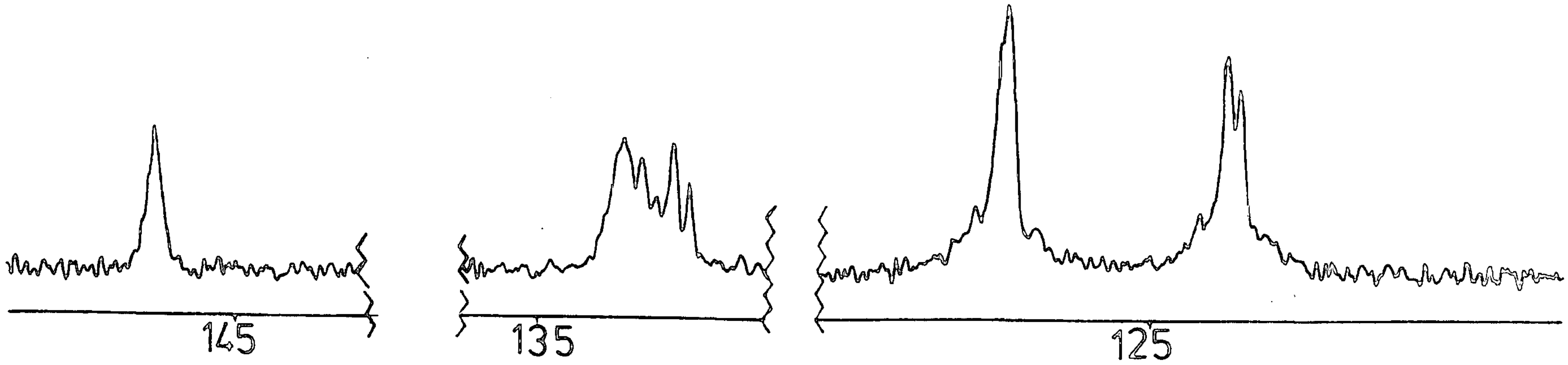
^{13}C N.m.r. spectrum of P_2 recorded at 90.56 MHz, upper spectrum after line narrowing

Figure 4.17(



(P$_2$)





^{13}C N.m.r. spectrum of P$_2$ after expansion and line narrowing

Figure 4.17(b)

in the computer printout, see Table 4.7. The assignment of the vinylene carbon lines recognized by the computer is not entirely unambiguous and

Table 4.7

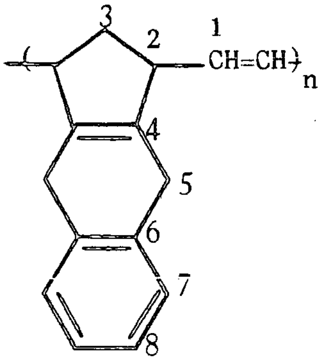
	Shift	Assignment	Integral	
P_1	133.90	cis	29.44	$\sigma_c = 0.52$
	133.72		12.00	
	133.55	trans	9.32	
	133.36		19.20	
	133.16		12.00	
P_2	133.96	cis	44.07	$\sigma_c = 0.67$
	133.76		23.19	
	133.40	trans	20.47	
	133.20		9.80	

it is usual practice to calculate σ_c from several different signals, in this case the overlapping methine and methylene signals make a calculation from either impossible. However, the aromatic signal at ca. 124 which is assigned to C-5 is split into a doublet and the computer recorded the two lines as 124.03 (36.50) and 123.88 (39.08) if the lower field line is assigned to environments adjacent to cis double bonds the value of σ_c calculated is 0.48 which is in reasonably good agreement with the 0.52 values derived from the vinylene signals; unfortunately, although the line narrowed spectrum shows that the analogous signal from C-5 in the spectrum of P_2 (Figure 4.17b) is split in a similar way, the computer did not recognize this resolution and although it is clear that the lower field line assigned to cis C-5 is more intense than the trans C-5 line no numerical value can be derived.

Thus, it can be concluded that polybenzonorbornadiene P_1 has roughly a 50:50 distribution of cis and trans units whereas P_2 has a preponderance of cis units. The spectrum of P_1 has considerable fine structure detail in all signals, which unfortunately is not matched in the spectrum of P_2 and as a consequence it is not possible to make any unambiguous stereochemical assignments of microstructure, although it is clear that the two samples are different. In P_1 the fine structure in the C-6 aryl carbon signal at 126.6 ppm and in the methine signal at 47.6 ppm (see expanded spectra, Figure 4.16b) indicate that this polymer cannot be high stereoregular since a high degree of stereoregularity results in essentially unique environments and single narrow lines. This observation is consistent with many other examples where WCl_6/Me_4Sn produces essentially atactic polymer, with roughly equal proportions of cis and trans vinylenes.

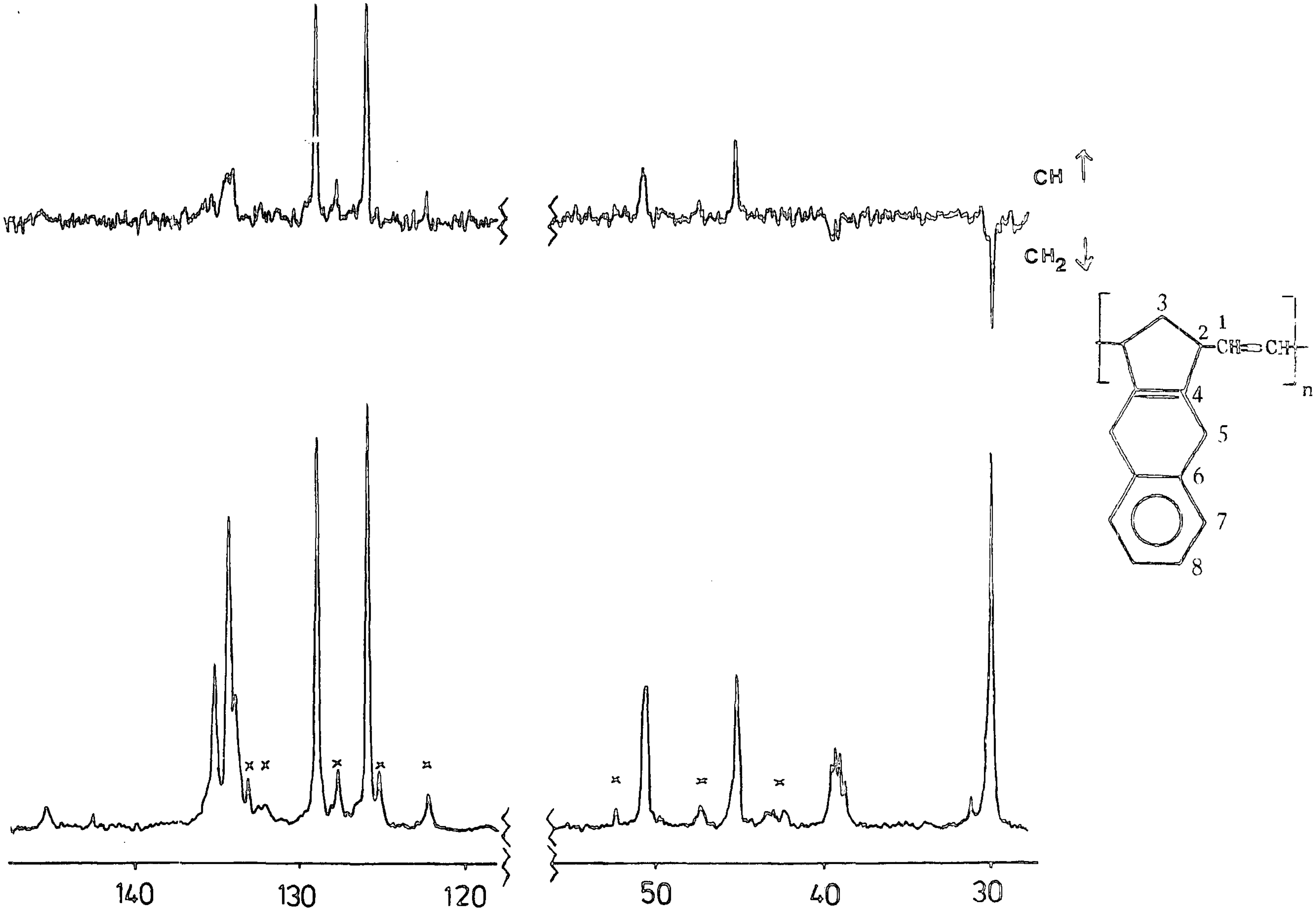
4.3.c Poly(4,5-benzotricyclo[6,2,1,$0^{2,7}$]undeca-2(7),4,9-triene), P_3

Polymer P_3 was prepared using WCl_6/Me_4Sn in chlorobenzene, a fairly well resolved spectrum was obtained, Figure 4.18. The assignments for polymer P_3 follow fairly straightforwardly from the background data presented in the discussion of polybenzonorbornadiene and the analysis of the spectra of norbornene polymers presented by Ivin and co-workers.



P_3

If we look at the spectrum of polymer P_3, Figure 4.18, we see that there are two regions in which resonances occur, namely the aliphatic carbon resonances from ca. 25 to 55 ppm and the olefinic and aromatic carbon resonances from ca. 120 - 150 ppm. The DEPT spectrum, in which

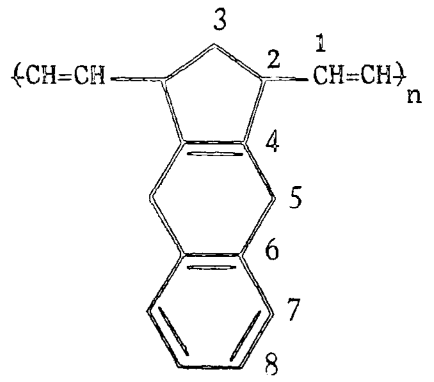


^{13}C N.m.r. spectrum of P_3 recorded at 90.56 MHz, upper spectrum DEPT

Figure 4.18

Table 4.8

Chemical shift in the ^{13}C n.m.r. of poly(4,5-Benzotricyclo[6,2,1,$0^{2,7}$]-undeca-2(7),4,9-triene), P_3

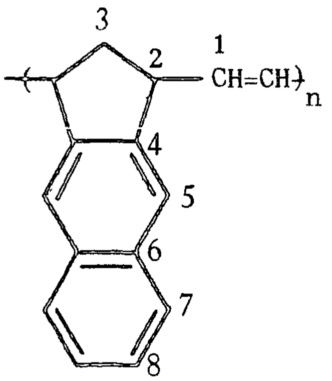


Peak no.	Chemical shift	Assignment	Integral	σ_c
1	29.88	5t	35.39	0.36
	30.1	5c	19.95	
2	38.68	3tt	4.96	0.41
	39.0	3tt	7.939	
	39.26	3ct≡3tc	7.62	
	39.5	3cc	7.743	
3	45.19	2cc	24.117	0.45
4	50.52	2tt	11.497	
	50.59	2tc	17.280	
5	125.78	8	8.736	
6	128.87	7	49.966	
7	133.86 134.27	4,6, 1(c+t)	overlap between vinylic and quaternary carbons	
8	135.1			

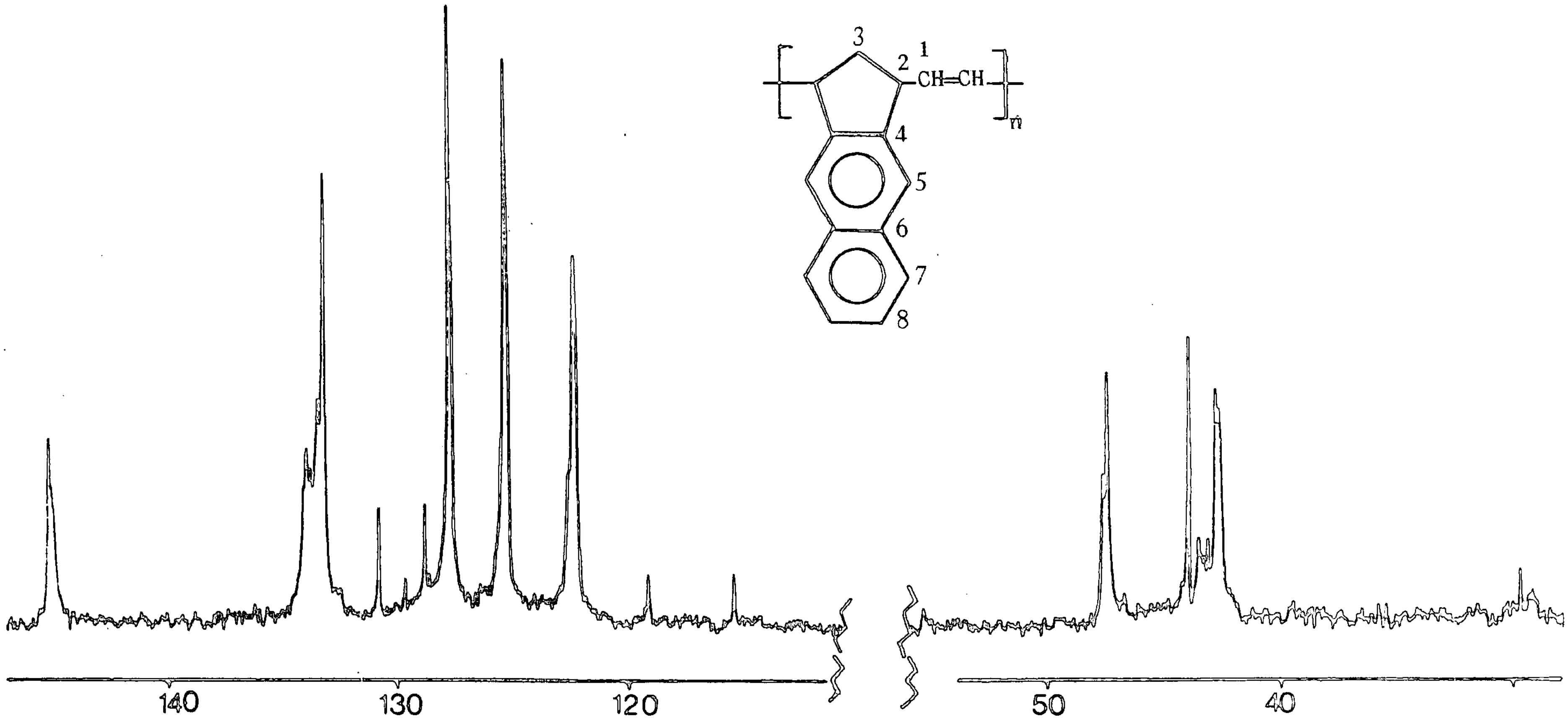
CH_2 carbons are inverted, CH remains unchanged and quaternary signals vanish, allows us to assign the resonances at ca. 30 and ca. 39 ppm to the methylenes labelled C_5 and C_3 respectively, some fine structure is almost resolved but the resolution is insufficient to make unambiguous assignments. The other aliphatic carbon resonances are due to the α-carbon, C_2 and occur at 45.19 (C_2 (c)) and 50.52 and 50.59 (C_2 (tt and tc)) giving a $\sigma_c = 0.45$; although it is not clear to the naked eye, the methylene resonance at ca. 30 is assigned by the computer to two signals at 29.88 and 30.10 ppm and if we allocate these signals to 5t and 5c respectively, the computer integration generates a value of $\sigma_c = 0.36$ which is in rather poor agreement with the α_c derived value. The methylene at C_3 would normally be expected to appear as a three line signal (3(tt):3(tc=ct):3(cc)), however, four lines are observed in the recorded spectrum. A provisional assignment of these lines is based on the assumption that the 3(tt) line is split, possibly as a result of syndio and isotactic sequences; and using this assignment a σ_c value of 0.41 was computed which is intermediate between the two previous computed values. It seems reasonable to assume that this polymer has roughly 42% cis vinylene units which would be in reasonable accord with many other results obtained with this catalyst system. The computer printout also splits the α-carbon adjacent to trans vinylenes into two resonances at 50.59 and 50.52 although to the naked eye this looks like a broad unresolved band, whereas α_c adjacent to cis vinylenes at 45.19 appears as a fairly narrow line, the significance of these differences with respect to microtacticity is not readily apparent, but it may indicate that cis dyads have only one tacticity (presumably syndiotactic) whereas trans dyads have both syndio and isotacticity, this might be reasonable on steric grounds. Comparison with the spectrum of polymer P_4 (see below) identifies the low intensity resonances in this spectrum as being due to traces of P_4. These impurity peaks are marked X, and it is entirely reasonable from the mode of formation and the ease of dehydrogenation of polymer P_3, that some contamination by polymer P_4 should have occurred. The aromatic, C_7 and C_8, carbon resonances are assigned by analogy as shown in Table 4.8; unfortunately the quaternary carbons at C_4 and C_6 overlap with the vinylene resonances as is clearly demonstrated by comparison of the normal and DEPT spectra in which quaternary carbon resonances vanish. In the DEPT spectrum the vinylene resonances are split into two roughly equal signals which is consistent with the earlier computations of σ_c. In conclusion we can say that the polymer P_3 produced by WCl_6/Me_4Sn catalyst appears to have the expected structure and approximately 50:50 distribution of cis and trans vinylenes, but unfortunately S/N and resolution is insufficient to say anything positive concerning the tacticity of the polymer, although the indications are that the polymer is essentially atactic.

4.3.d Poly(2,3-naphthotricyclo[2.2.1]hept-2,5-diene), P_4

The ^{13}C n.m.r. spectrum of polymer P_4 produced using $WCl_6/2(CH_3)_4Sn$ is shown in Figure 4.19, the shifts and assignments are given in Table 4.9.



P_4

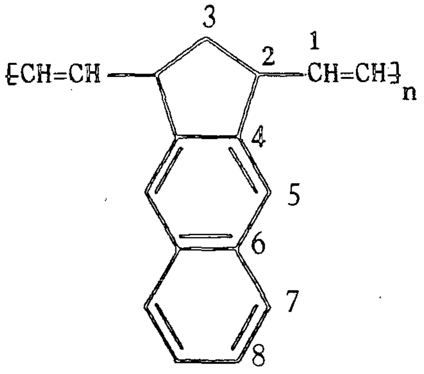


^{13}C N.m.r. spectrum of P$_4$ recorded at 90.56 MHz

Figure 4.19

Table 4.9

Chemical shifts in the ^{13}C n.m.r. of poly(2,3-naphtho-tricyclo[2.2.1]hept-2,5-diene), P_4



Peak no.	Chemical shift	Assignment	Integral	σ_c
1	42.61	3tt	22.08	0.34
	42.7485	3tc≡ct	18.42	
	43.08		6.49	
	43.51	3cc	13.93	
2	43.92	2c	17.022	0.36
	47.33		19.97	
	47.51	2t	11.24	
3	122.27	C_8	65.57	–
4	125.25	C_7	78.33	
5	127.67	C_5	68.13	
6	128.79	4t	13.66	0.41
	130.74	4c	9.48	
7	145.11	C_6	30.358	–
8	133.15	1t	49.63	0.37
	133.39		21.76	
9	133.68	1c	10.01	
	133.86		31.03	

Polymer P_4 was difficult to dissolve, it was purified using a dilute solution of chloroform, the viscous solution was precipitated in methanol. The limited solubility of this polymer required a very long accumulation time (≈ 66 hours), and this made it impossible to obtain a DEPT spectrum. By comparison with the assigned ^{13}C n.m.r. spectrum of polymer P_3, the two bridging quaternary aromatic carbons, C_4 and C_6, are associated with the lower intensity signals in the low field part of the spectrum. The signal at ca. 145 ppm is assigned to C_6, and the signals due to C_4 appear as a doublet with cis C_4 (130.74 ppm) downfield from the trans C_4 (128.79 ppm). Both vinylene carbon signals occur as two overlapping multiplets at 133.86 and 133.15 ppm possibly due to cis/trans sequence effects or tacticity effects. In the aromatic region we can observe three fairly sharp signals at ca. 122.27, 125.25 and 127.67 ppm due to the aromatic carbon C_8, C_7, C_5 respectively. The methine and methylene signals at higher field allowed calculation of the cis/trans content of the polymer (see below). The methine carbons are both allylic and naphthylic and consequently their resonances occur at lower field than the methylene resonances. In the spectrum of polymer P_4, the methine carbons appear as an unresolved signal at 43.92 assigned to the cis while the trans signal appears as a doublet at 47.33 and 47.51 ppm. The methylene peaks at 43.51 and 43.08 ppm are assigned to C_3 (cc), while the peaks at 42.75 and 42.61 are assigned to the 3ct≡3tc and 3tt respectively. The justification for these assignments is that the proportion of cis double bonds calculated using the various sets of signals assigned as above are in quite good agreement. Thus, from the vinylene carbons σ_c was computed as 0.37, from the methine carbons a value of $\sigma_c = 0.36$ was obtained and from methylene carbons the σ_c value was 0.34. Using the bridging aromatic carbon at C_4 $\sigma_c = 0.41$, the discrepancy between this value and those derived from C_1, C_2 and C_3 may well be due to the fact that the spectrum phase appears to be marginally out in the C_4 region.

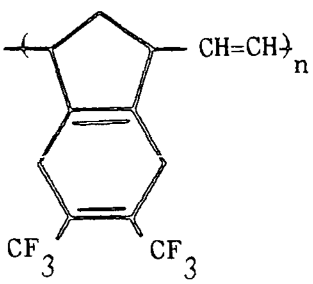
4.3.e Summary

The results presented above demonstrate that the aryl norbornene derivatives 26, 27 and 40 are readily polymerized via ring-opening at the vinylene bond in the presence of metathesis catalysts such as $WCl_6/(CH_3)_4Sn$. It appears that in the case of benzonorbornadiene $WCl_6/(CH_3)_4Sn$ and $MoCl_5/Me_4Sn$ catalysts produce different polymers, and it is likely that the polymer derived from the tungsten catalyst is essentially atactic whereas that derived from the molybdenum catalyst has an element of stereoregularity as is reflected in differences in the solubilities and spectra of the two polymers.

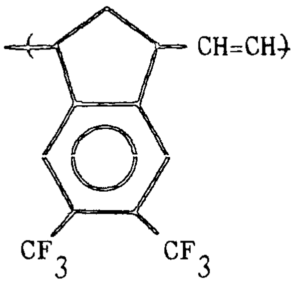
The monomer (28), containing a pendent anthracyl unit also polymerizes in the presence of the WCl_6/Me_4Sn catalyst, but the product was insoluble and was not amenable to detailed investigation.

4.4 ^{13}C N.m.r. Spectra for Fluorinated Polymers (P_6, W), (P_6, Mo), (P_7, W), (P_7, Mo), (P_8, W), (P_8, Mo), (P_9, W) and (P_9, Mo)

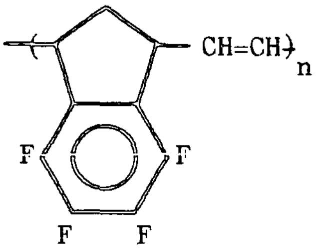
In this section we discuss the metathesis polymerization of four new fluorinated monomers (29, 30, 31 and 32), the polymer structures are shown below. In each case two catalyst systems have been examined;



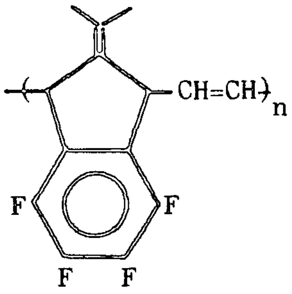
(P_6, W) (P_6, Mo)



(P_7, W) (P_7, Mo)



(P_8, W) (P_8, Mo)



(P_9, W) (P_9, Mo)

these were, (a) the generally very active non-discriminating WCl_6/Me_4Sn system, and (b) the relatively less active $MoCl_5/Me_4Sn$ system. Although the detailed stereochemical outcome of metathesis reactions is determined by a combination of monomer structure, catalyst composition, solvent, temperature and concentration it has been generally found that WCl_6 derived catalysts have a tendency to produce a random 50:50 distribution of cis and trans vinylene units in an essentially atactic backbone, whereas $MoCl_5$ derived catalysts display a tendency towards producing polymers with a high cis content and a preference for syndiotactic assembly.

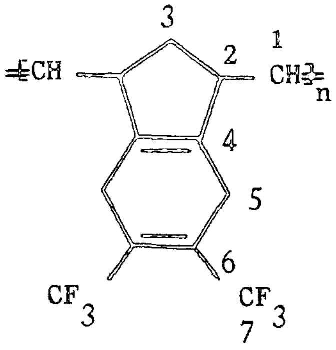
4.4.a Poly(4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene)

Figures 4.20 and 4.21 show the ^{13}C n.m.r. spectra of polymers (P_6, W) and (P_6, Mo) respectively. Table 4.10 records the chemical shifts and integrated intensities of the peaks recognized by the computer. These two spectra were kindly recorded by Professor K.J. Ivin (Queen's University, Belfast). The peak assignments recorded in Table 4.10 must be regarded as rather uncertain; it proved very difficult to obtain a good set of agreeing σ_c values from the signals in different regions of the spectrum and overlapping or poorly resolved multiplets, particularly in the vinylene region, make it very difficult to provide an unambiguous assignment of the observed resonances. For these samples DEPT or off resonance spectra were not available which also makes elimination of ambiguity difficult.

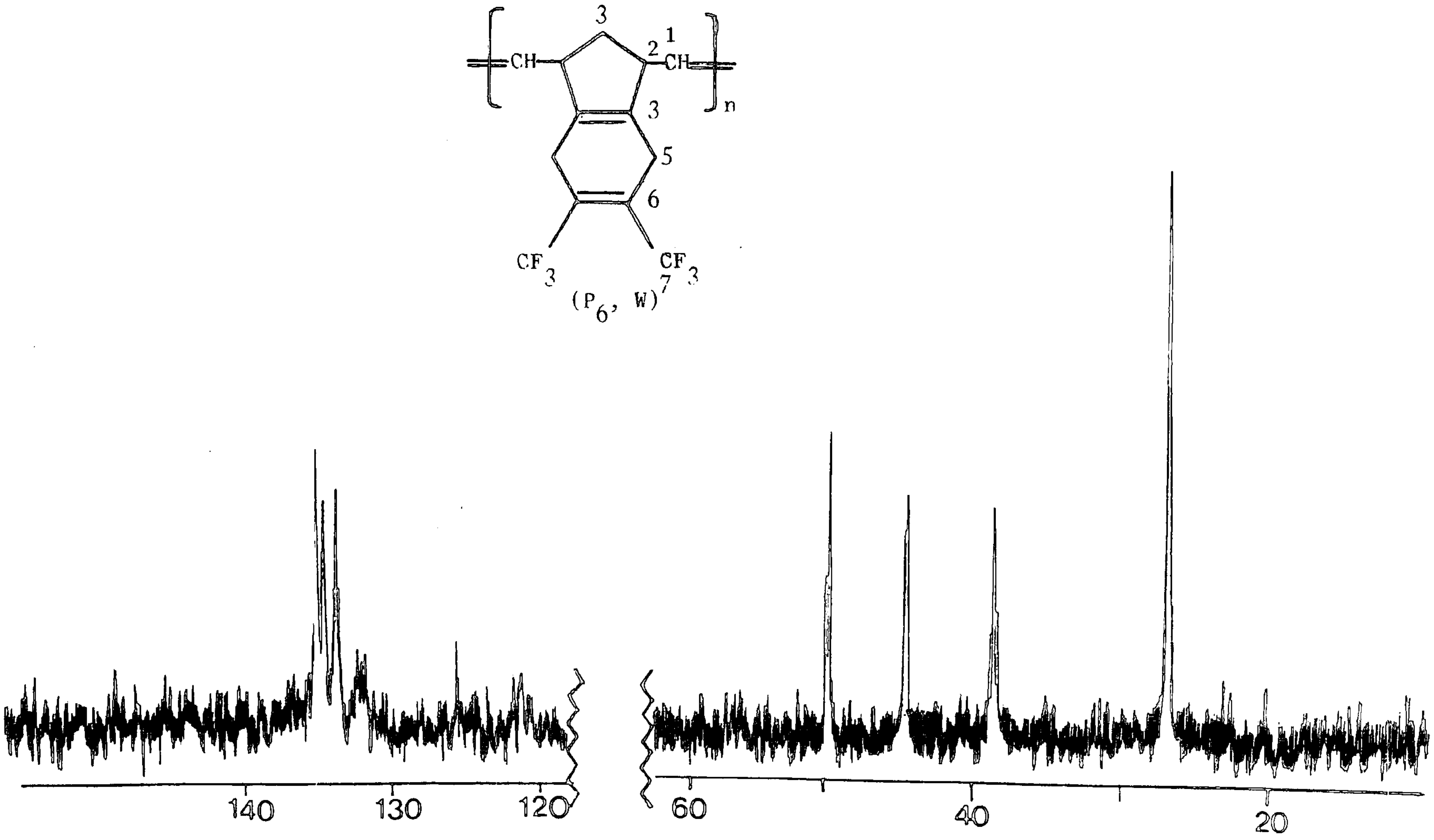
The overall features of the spectra provide evidence that the polymer obtained has the expected structure. In order to obtain even the poor agreement of σ_c values for (P_6, W) and (P_6, Mo) shown in the table it has been necessary to assume that the line orders of the signals for the allylic methine carbon C_2 and the methylene at C_3 are the reverse of those normally found in hydrocarbon substituted

Table 4.10

Chemical shifts in the ^{13}C n.m.r. spectra of poly(4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,9-triene) initiated by $WCl_6/(CH_3)_4Sn$ (A) and $MoCl_5/(CH_3)_4Sn$ (B)

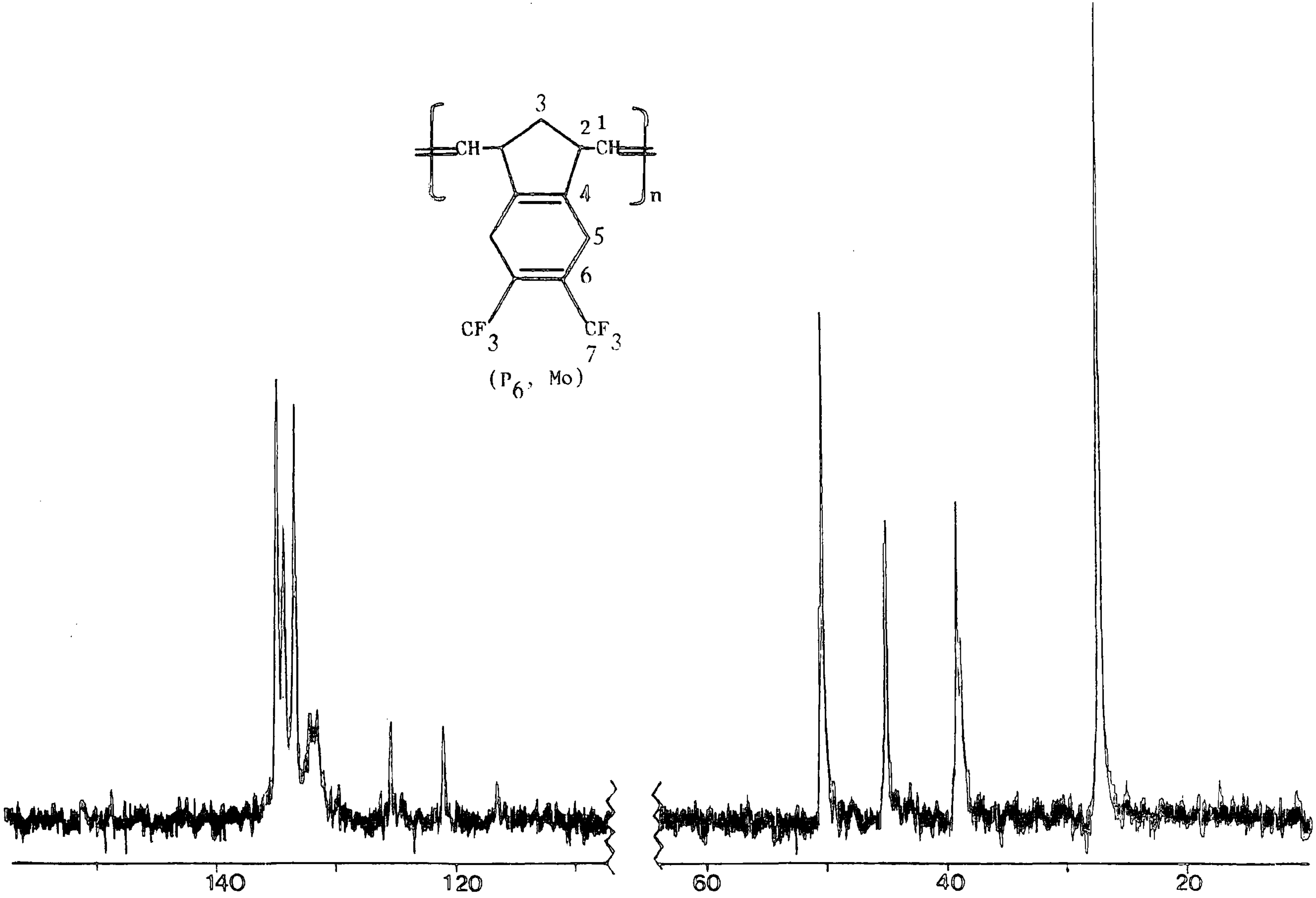


chemical shifts		assignment	integral		σ_c	
A	B		A	B	A	B
27.23	27.25	C_5	8.01	17.33		
38.68 38.94 39.14	38.62 38.91 -	3cc 3ct≡tc 3tt	1.24 2.26 0.66	2.61 5.71 -	0.57	0.66
44.78 44.87 50.00 50.23	44.74 44.89 50.00 50.26	2tt 2tc 2ct 2cc	1.90 1.84 2.90 1.30	4.12 2.56 9.40 2.08	0.53	0.63
	124.78 130.93 131.51	C_6 and C_7		1.25 1.48 2.06		
132.75 132.91 133.01	132.72 132.87 133.26	4cc 4ct≡tc 4tt	0.71 1.89 1.14	2.07 7.02 0.88	0.44	0.56
133.77 133.87	133.63 133.76 133.90	1t	3.17 1.16	2.43 3.86 2.15	0.53	0.56
134.27 134.34	134.20 134.31 134.38	1c	3.18 1.65	2.75 3.98 4.11		



^{13}C N.m.r. spectrum of (P_6, W) recorded at 62.77 MHz

Figure 4.20



^{13}C N.m.r. spectrum of (P$_6$, Mo) recorded at 62.77 MHz

Figure 4.21

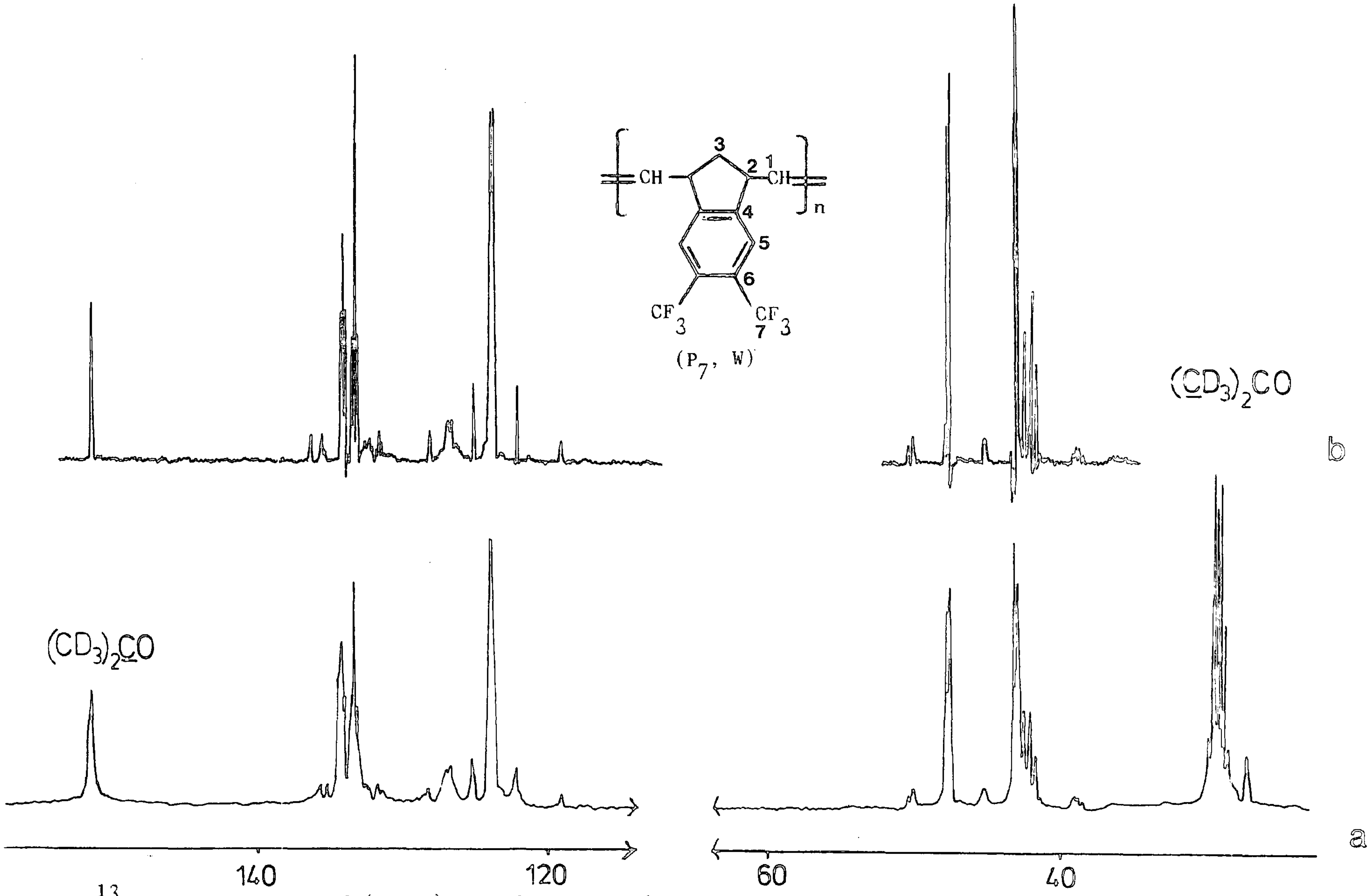
norbornene polymers; while this is not impossible, and we shall encounter more convincingly unambiguous cases later, it is not clear why this should be so. The assignment of bands in the vinylene region to C_1 and C_4 is difficult and is based largely on the best fit of σ_c values for the whole spectrum, in our assignment the quaternary vinylic carbon C_4 appears to have an unusually high signal intensity; however, it is difficult to avoid the conclusion that one of the three multiplets in the vinylic region must be associated with C_4. The signals due to C_7 (CF_3) are clearly seen in the spectrum but not recorded by the computer, the same comment applies to C_6; the CF_3 quartet has a J_{CF} value of ca. 274 Hz in agreement with expectation.

Unfortunately these spectra are not sufficiently good to make a detailed analysis but it can be concluded that (P_6, W) and (P_6, Mo) have the structure assigned, and surprisingly there is relatively little difference in the proportion of cis vinylene units or, as judged by the close similarity of the spectra, in the polymer microstructure. Although these assignments lack real certainty alternative assignments result in much greater fluctuations in computed σ_c values.

4.4.b Poly(4,5-bis-trifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraene) (P_7, W) and (P_7, Mo)

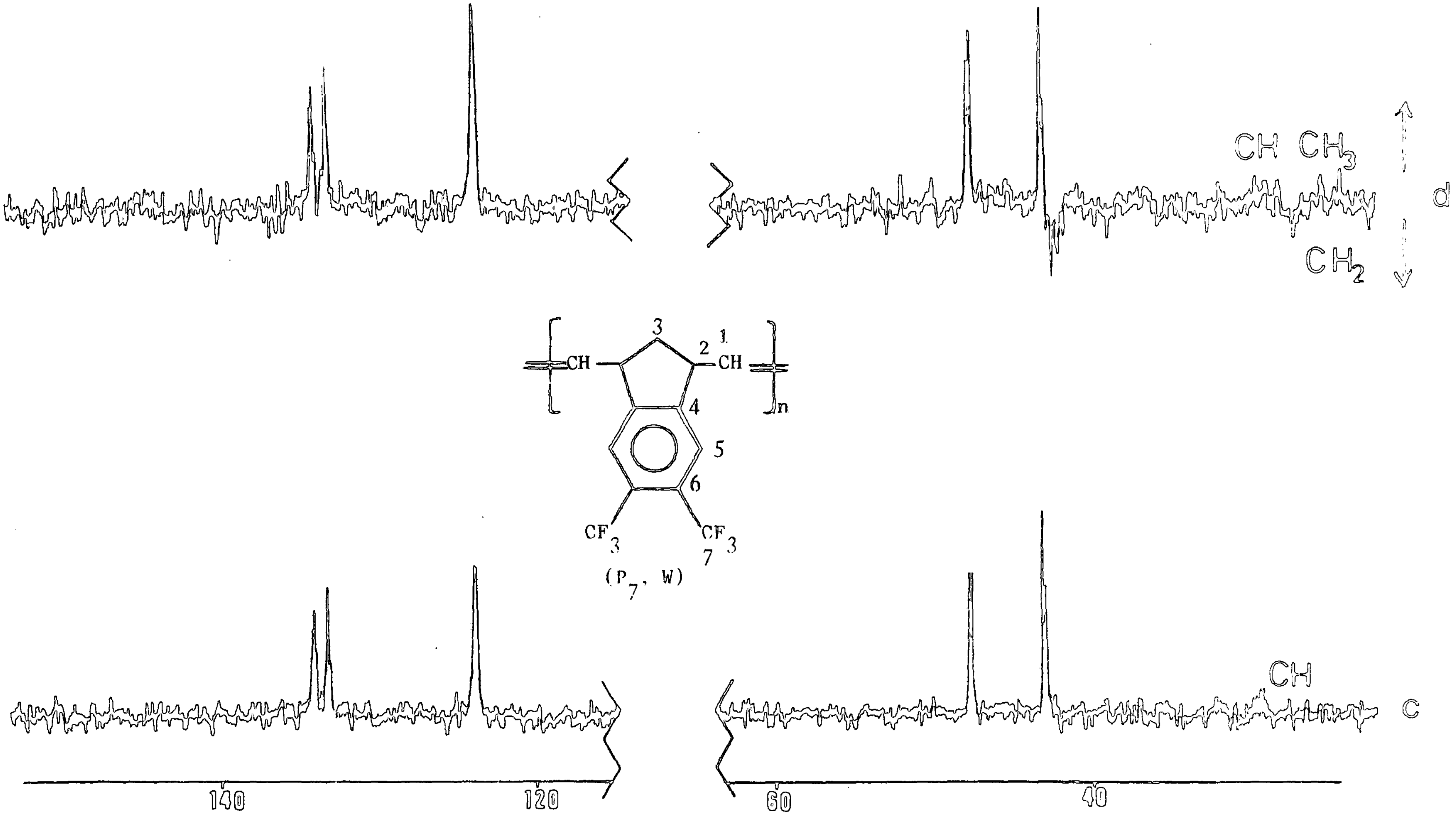
The ^{13}C n.m.r. spectrum of polymer (P_7, W) prepared by using $WCl_6/(CH_3)_4Sn$ is shown in Figure 4.22(a), Figure 4.22(b) shows the line narrowed spectrum; two forms of DEPT spectra are shown in Figures 4.22(c) and (d). The spectrum of the polymer (P_7, Mo) prepared using $MoCl_5/(CH_3)_4Sn$ is shown in Figure 4.23. The chemical shifts and assignments are collected in Table 4.11.

If we first examine Figure 4.22 (a) - (d), that is the ^{13}C n.m.r. spectra of polymer (P_7, W), we see that the lower intensity signals in the low field region are clearly due to the quaternary carbons, C_4



^{13}C N.m.r. spectrum of (P_7, W) recorded at 90.56 MHz, upper spectrum after line narrowing

Figure 4.22(a) and (b)

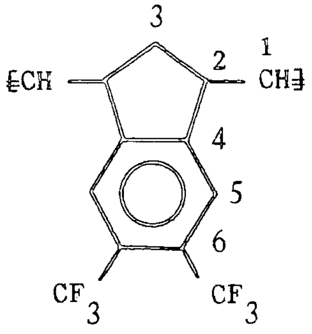


DEPT spectra of (P_7, W)

Figure 4.22(c) and (d)

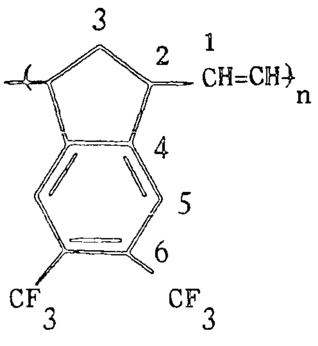
Table 4.11

Chemical shifts in the ^{13}C n.m.r. spectra of poly[4,5-bistrifluoromethyltricyclo[6,2,1,$0^{2,7}$]undeca-2,4,6,9-tetraene] (P_7, W) (P_7, Mo)



(P_7, W) (P_7, Mo)

chemical shift		assignment	integral		σ_c	
A	B		A	B	A	B
41.75	41.76	3tt	3.540	2.760	0.65	0.41
42.06	42.06	3tc≡ct	9.113	2.405		
42.54	42.54	3cc	10.192	1.591		
43.02	43.00	2tt	22.732	3.050	0.41	0.74
43.20	not resolved	2tc	19.371	–		
47.60	47.59	2ct	13.038	5.155		
47.76	47.74	2cc	16.061	3.606		
123.65 qu J_{CF} = 280 Hz	123.66 qu J_{CF} = 280 Hz	7				
123.94		5t	25.474			
124.09	124.10	5c	29.242	10.713	0.53	
126.74 J_{CCF} 33 Hz	126.64 J_{CCF} 33 Hz	6				
ca. 131		4tc				
131.67		4tt	1.061			
133.24			6.069			
133.40	133.41	1t	14.651	2.346		
133.56			7.978		0.49	0.75
134.03			6.465			
134.20	134.19	1c	21.203	7.174		
135.56		4ct	1.763			
136.29	136.26	4cc	1.818	1.405		

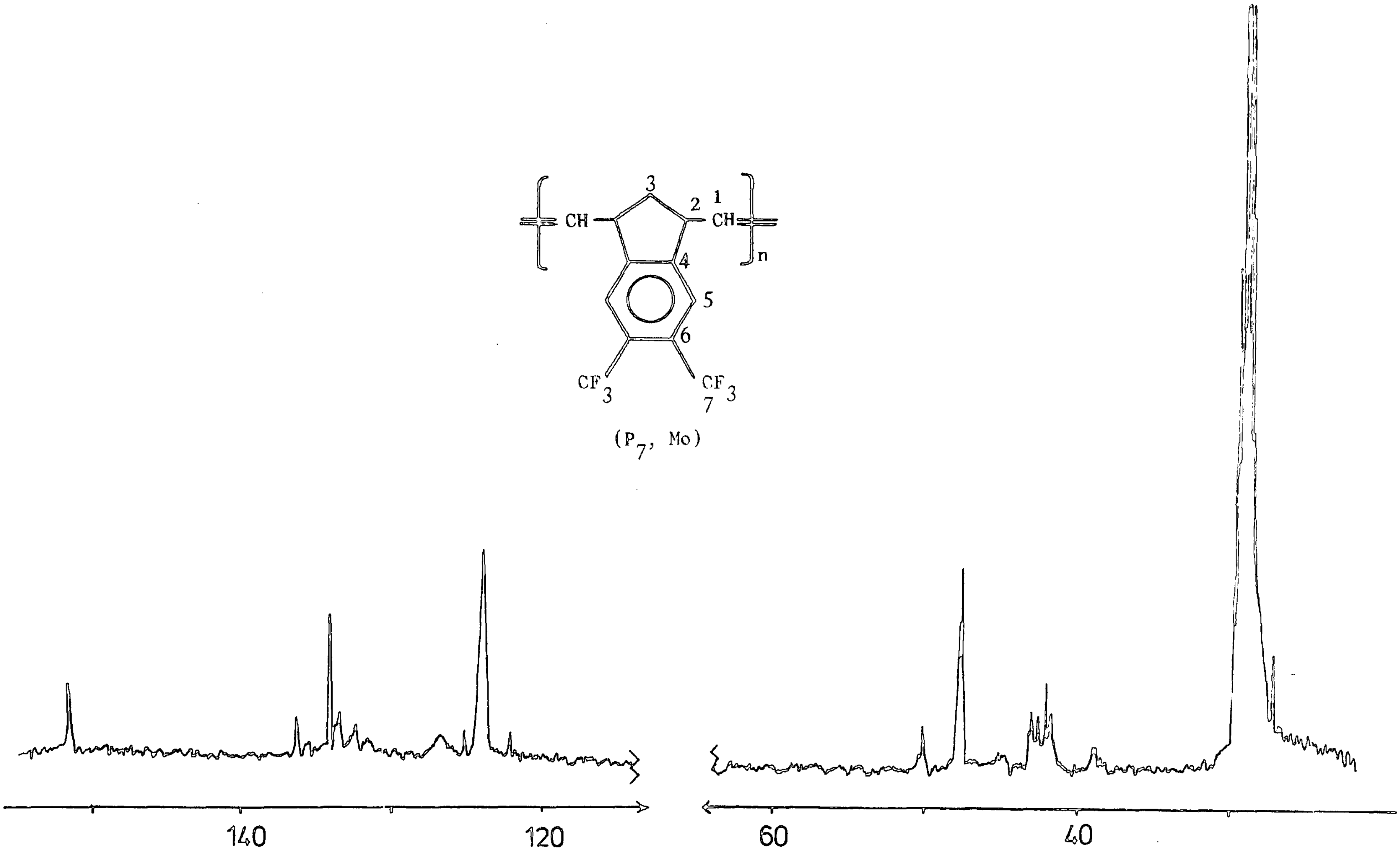


(P_7, W), (P_7, Mo)

and C_6, and the CF_3 group. The carbon atom of the trifluoromethyl group C_7, was assigned to the quartet centred at δ = 123.65 ppm (J_{CF} = 280 Hz). The aromatic carbon C_6 couples to the fluorine atoms of the trifluoromethyl group and hence appears as a quartet at δ = 126.74 ppm ($J_{CCF} \simeq 33$ Hz). The other low intensity signals, recorded at 136.29, 135.56 and 131.67 ppm are assigned to the aromatic quaternary carbon atom C_4, and correspond to the 4cc, 4ct and 4tt environments respectively. The peak corresponding to the 4tc environment is not recognized by the computer, but can be seen at ca. 131 ppm; the integration of these poorly resolved low intensity peaks is not sufficiently reliable to calculate a σ_c value but indicates a roughly 50:50 cis:trans distribution. These low intensity signals disappeared in the two DEPT spectra confirming their quaternary nature. The olefinic resonance is split into two sets of overlapping resonances centred at 134.10 ppm (cis) and 133.4 ppm (trans). The fine structure of these two signals shows that they are partially resolved into triplets, although the computer again did not recognize one of these peaks. This triplet splitting may arise from olefinic tryad (ccc etc.) effects and/or tacticity effects, but unfortunately none of these splittings can be unambiguously assigned, σ_c for the vinylic carbons was calculated as 0.49. The aromatic carbon at C_5 is split into two signals at 123.94, 124.09 ppm assigned as trans and cis respectively;

the cis content calculated from these absorptions is $\sigma_c = 0.53$. When we turn to the aliphatic region the signals at 43.02, 43.20, 47.60 and 47.76 ppm corresponding to the methine carbon are assigned as 2tt, 2tc, 2ct and 2cc respectively; it will be seen that in this case the line order for this carbon is reversed when compared with that observed in the spectra of polynorbornadiene given by Ivin and co-workers and discussed at the beginning of this chapter. This assignment is confirmed in the spectrum of the $MoCl_5$ derived "high cis" polymer (see below), the reversed line order possibly being a consequence of the adjacent aromatic unit. From the intensities of the C_2 absorptions the calculated cis content is $\sigma_c = 0.41$. The CH_2 carbon, C_3, appears as a clear triplet, the assignment being confirmed by the DEPT spectrum (d), where the methylene carbon signals are inverted. The resonances are observed at 41.75, 42.06 and 42.54 ppm assigned to 3tt, 3tc/3ct and 3cc environments. The calculated cis content from these absorptions is 0.65, however, computation of σ_c from C_2 and C_1 can not be regarded as reliable because the groups of resonances due to these two carbons overlap making accurate integration impossible. Thus, for the WCl_6/Me_4Sn derived polymer we assign a structure having approximately equal amounts of cis and trans vinylene units randomly distributed; tacticity can not be assigned from this data.

The ^{13}C n.m.r. spectrum of the polymer prepared using the $MoCl_5/(CH_3)_4Sn$ catalyst system is shown in Figure 4.23. Comparison between this spectrum and spectra shown in Figure 4.22 shows that most of the signals are greatly altered in relative intensity but the shifts are virtually unaltered. In the low field region the peaks corresponding to the cis-vinylene at 134.19, cis aromatic C_5 at 124.1 ppm and the aromatic bridging carbon C_4 (cc) at 136.26 ppm become relatively more intense than the analogous trans signals. The calculated cis content



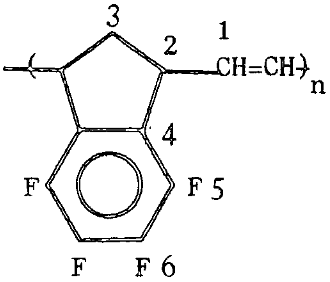
^{13}C N.m.r. spectrum of (P_7, Mo) recorded at 90.56 MHz

Figure 4.33

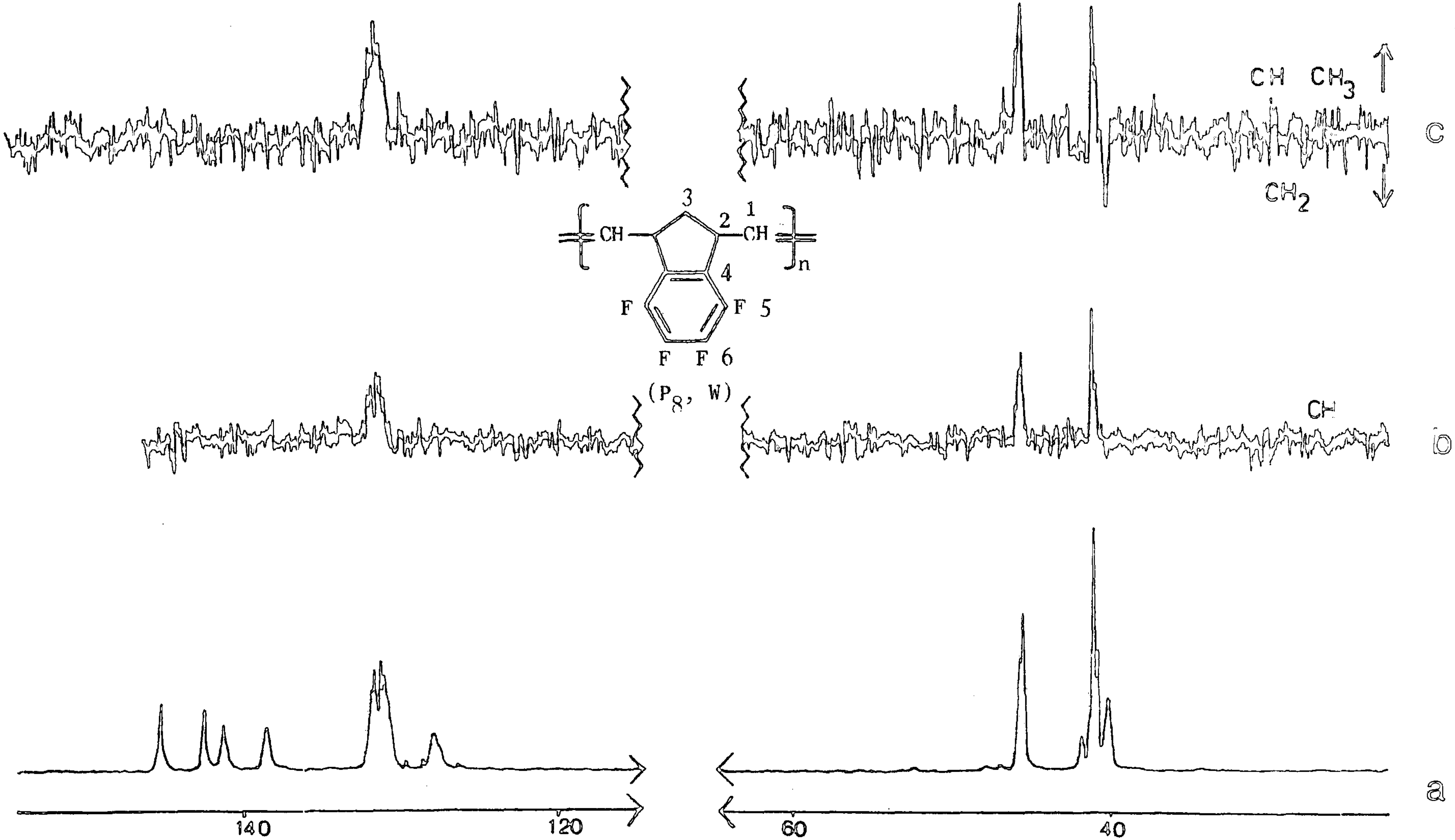
from the vinylic carbons (C_1) is $\sigma_c = 0.75$, this is confirmed by the methine resonances at 47.74 (2cc), 47.59 (2ct) and 43.00 (2tt) which give $\sigma_c = 0.74$, the methylene signals at 42.54 ppm, 42.06 ppm and 41.76 ppm are assigned as 3cc, 3cc≡3tc and 3tt respectively and the calculated cis content from these absorptions is 0.41, this poor agreement between the σ_c for the methylene and the other values is due to the relatively poor resolution in this region of the spectrum and the limitations of the computer in recognizing relatively low intensity signals. The carbon atom of the CF_3 group appears at ca. 123.65 ppm and the aromatic carbon carrying the CF_3 group appears at ca. 126.63 ppm. Thus, for the $MoCl_5/Me_4Sn$ derived polymer it is clear that cis vinylene units predominate (ca. 75%), again no information concerning tacticity can be unambiguously deduced, but the somewhat greater simplicity of the spectra of (P_7, Mo) is consistent with its expected greater stereoregularity.

4.4.c Poly(5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene) (P_8, W), (P_8, Mo)

The ^{13}C n.m.r. spectrum of polymer (P_8, W) prepared using $WCl_6/(CH_3)_4Sn$ is shown in Figure 4.24(a), Figure 4.24(b) shows its DEPT spectrum in which only the CH carbons appear, and Figure 4.24(c) shows the DEPT spectrum in which CH_2 carbons are inverted, whereas CH and CH_3 remain unchanged, the quaternary carbon atoms disappear in both DEPT spectra. The peak shifts and their assignments are given in Table 4.12, column (A).



(P_8, W), (P_8, Mo)

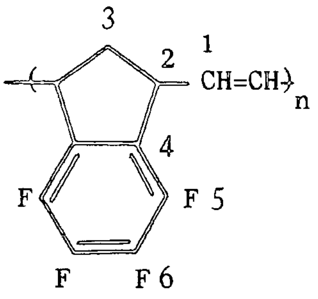


^{13}C N.m.r. spectrum of (P$_8$, W) recorded at 90.56 MHz, upper spectra DEPT

Figure 4.24(a), (b) and (c)

Table 4.12

Chemical shifts in the ^{13}C n.m.r. spectra of poly-(5,6,7,8-tetrafluoro-1,4-dihydro-1,4 methano naphthalene)



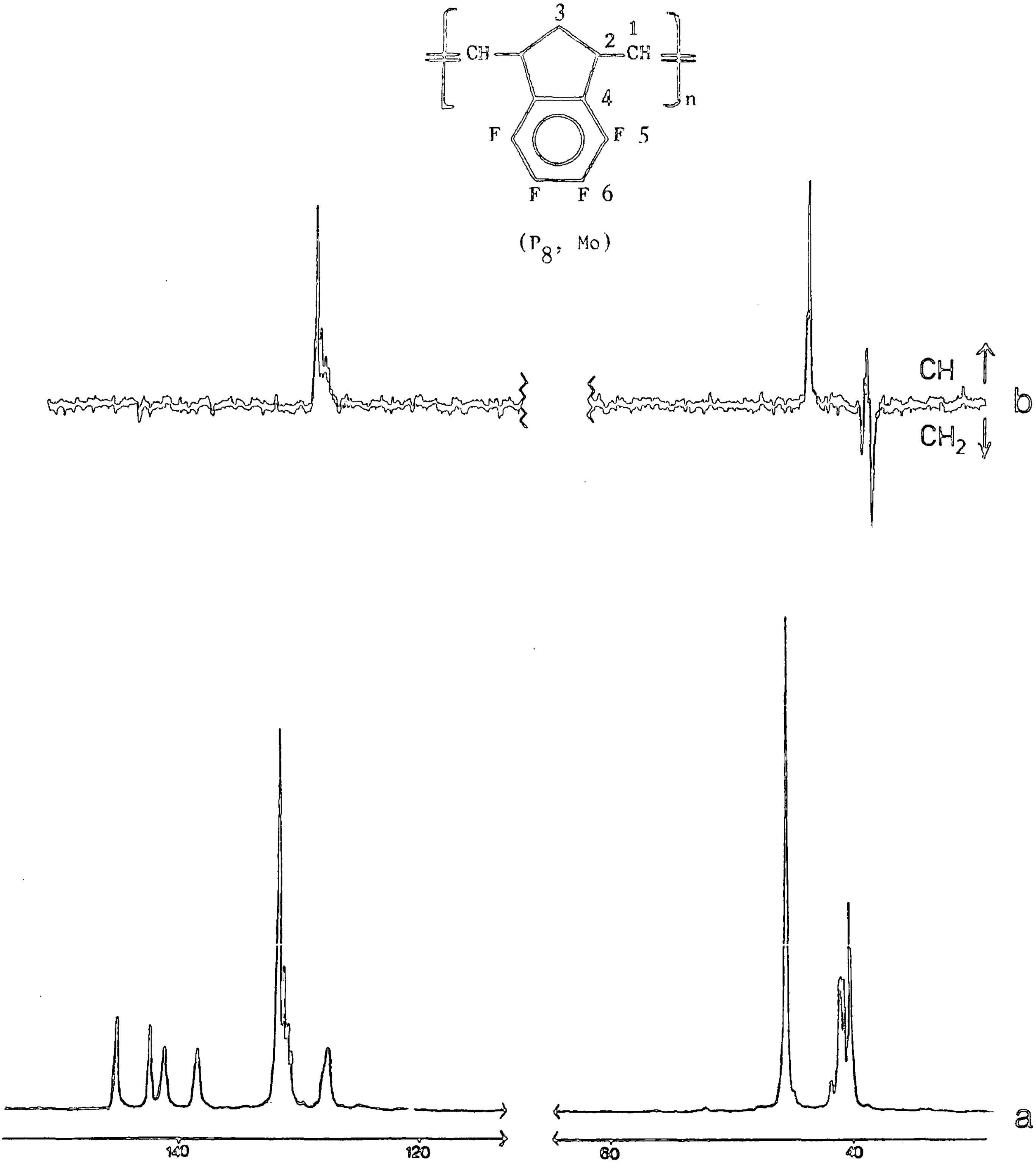
(P_8, W) (P_8, Mo)

chemical shifts		assignment	integral		σ_c	
A	B		A	B	A	B
40.04 40.18 40.31 41.72 41.83	40.21 40.32 41.14	3tt 3tc≡3ct 3cc	11.964 9.58 5.429 5.989 3.682	17.177 20.423 13.788	0.33	
40.75 40.99 43.39 45.57	40.75 41.02 45.40	2tt 2tc 2ct 2cc	21.964 52.105 28.994 21.401	13.94 13.937 81.468	0.40	0.75
127.71 127.87	127.53 127.62	C_4	6.521 10.035	8.525 14.78		
130.61 130.96 131.18 131.55 131.76	130.62 130.84 130.98 131.21 131.56 131.74	t c	10.847 27.51 18.23 22.34 20.998	7.137 7.876 6.98 15.687 42.014 25.696	0.43	0.64
139.86 d J_{CF} = 250 Hz	139.86 d J_{CF} = 250 Hz	C_6				
143.83 d J_{CF} = 250 Hz	143.83 J_{CF} = 250 Hz	C_5				

The resonances due to carbon 3 (methylene) and carbon 2 (methine) overlap but it is possible to differentiate between them using DEPT spectra which allows assignment which would otherwise be difficult. Hence the absorptions due to carbon 3 at (40.04, 40.18), 40.31, and (41.72, 41.8) ppm are due to 3tt, 3tc≡3ct and 3cc environments, and the signals due to carbon 2 at 40.74, 40.99, 45.39 and 45.57 ppm due to the 2tt, 2tc, 2ct and 2cc environments respectively; as in earlier examples the line orders for this aryl norbornadiene polymer are reversed as compared to norbornene. The σ_c values calculated from C_3 and C_2 resonances, respectively 0.40 and 0.33 must be regarded as only approximate values because of the uncertainty introduced on integration of overlapping resonances. Moving downfield we find that the olefinic resonance is split into two components at 130.9 ppm (trans) and 131.6 ppm (cis). The calculated cis content σ_c is 0.43. The peak centred at 127.8 ppm disappears in the DEPT spectrum and is therefore assigned to a quaternary aryl carbon C_4, presumably it is broadened by long range CCF coupling and the effects of adjacent cis/trans vinylene isomerism. The aryl carbons carrying fluorine atoms appear as doublets easily identified by the large CF coupling.

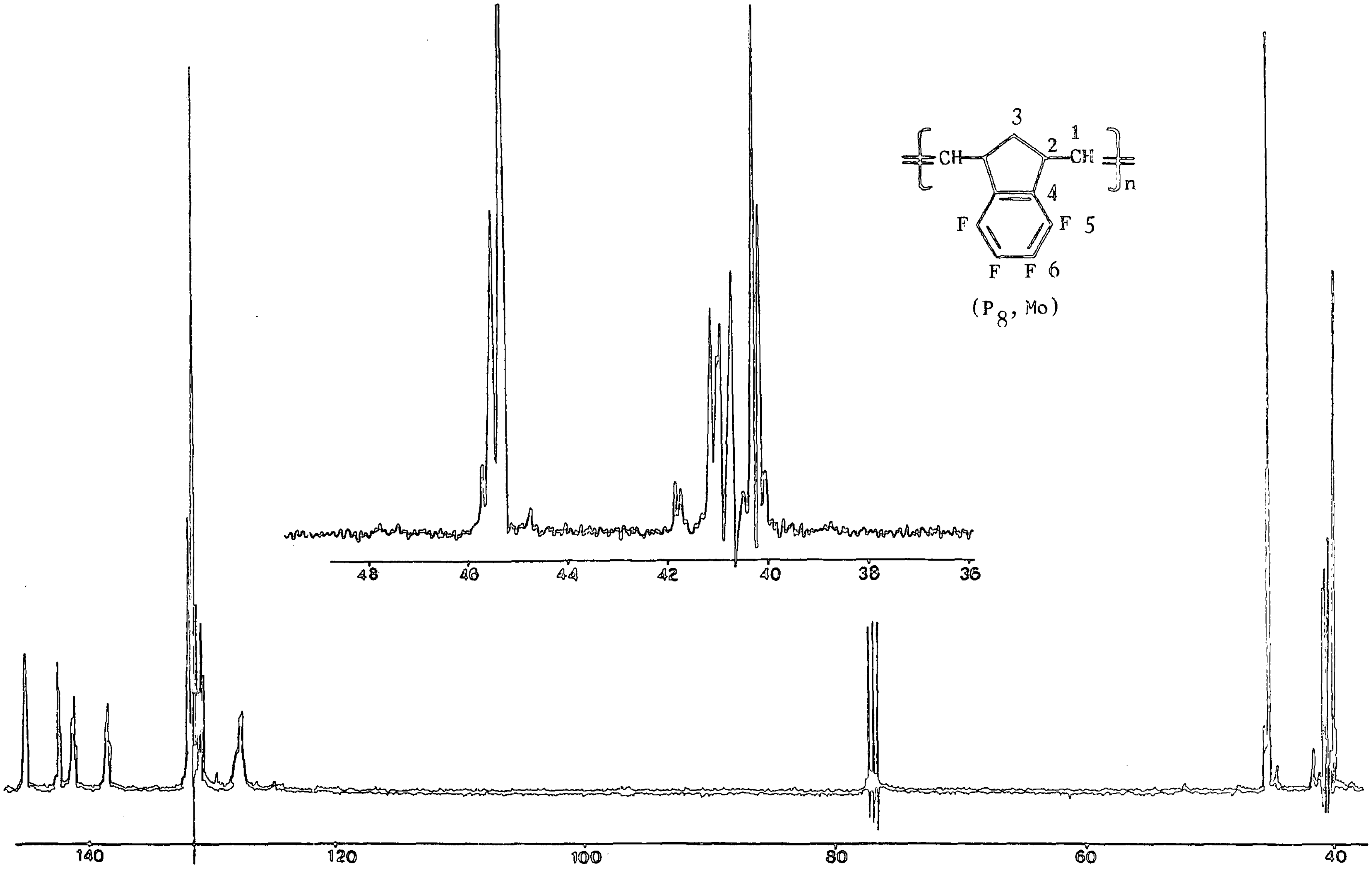
The ^{13}C n.m.r. spectrum of polymer (P_8, Mo) produced using $MoCl_5/(CH_3)_4Sn$ is shown in Figure 4.25(a), Figure 4.25(b) shows its DEPT spectrum, while Figure 4.25(c) shows the line narrowed and expanded spectrum. The ^{13}C n.m.r. shifts and assignment are given in Table 4.12, column (B).

It is expected that this catalyst system will give a polymer with a high cis content and therefore the high field signal at 45.40 ppm should be assigned to the methine carbon C_2 adjacent to cis vinylenes, with the other signals at 40.74 and 41.02 ppm are assigned to the methine adjacent to trans vinylenes. This line order is the reverse of



^{13}C N.m.r. spectrum of (P$_8$, Mo) recorded at 90.56 MHz, upper spectrum DEPT

Figure 4.25(a) and (b)



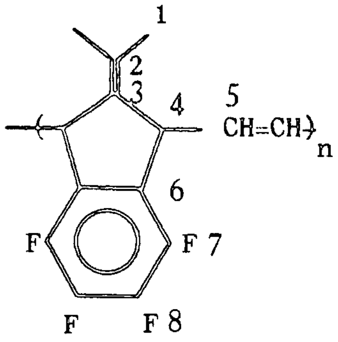
^{13}C N.m.r. spectrum of (P$_8$, Mo) after expansion and line narrowing

Figure 4.35(a)

that found from polynorbornadiene given by K.J. Ivin, inspection of the expanded spectrum in the region between 36 - 48 ppm shows that both methylene and methine carbon signals consist of complex multiplets and that the methylene signal overlaps with the methine signal at 41.6 ppm. The signals in the range 40 - 42 ppm are very complicated, but the signal between 45 and 46 ppm is relatively simple, consisting of three lines; this resonance has been assigned to carbons C_2 adjacent to cis vinylenes and we might have expected two lines arising from C_2 (cc) and C_2 (ct). The observation of three lines may indicate tacticity effects are being resolved in this resonance and that, for example, C_2 (ct) in syndiotactic and isotactic assemblies occurs in different environments; it is worth noting that the major part of this signal occurs as a single sharp line as would be expected from a stereoregular cis-syndiotactic sequence. Absorptions due to the vinylic carbon C_1 at 130.98 and 131.6 ppm have been assigned to the trans and cis respectively as shown in Table 4.12. The signals due to the quaternary carbon atom and the fluoroaryl carbons occur in approximately the same position as in (P_8, W) and the assignment is recorded in Table 4.12(B). The line narrowed spectrum of (P_8, Mo) allows assignment of the fluoroaryl carbons since the higher field signal occurs as a doublet of triplets and must therefore be C_6, the doublet being due to C-F coupling and the triplet resulting from two C-C-F couplings from the two ortho fluorines; in agreement with this argument the lower field signal is split (in one limb) into a doublet and this is reasonable since C_5 has only one ortho fluorine. The σ_c values computed from the vinylic and methine carbons indicate a significant preference for cis-vinylene formation although the agreement between the two values is not particularly good.

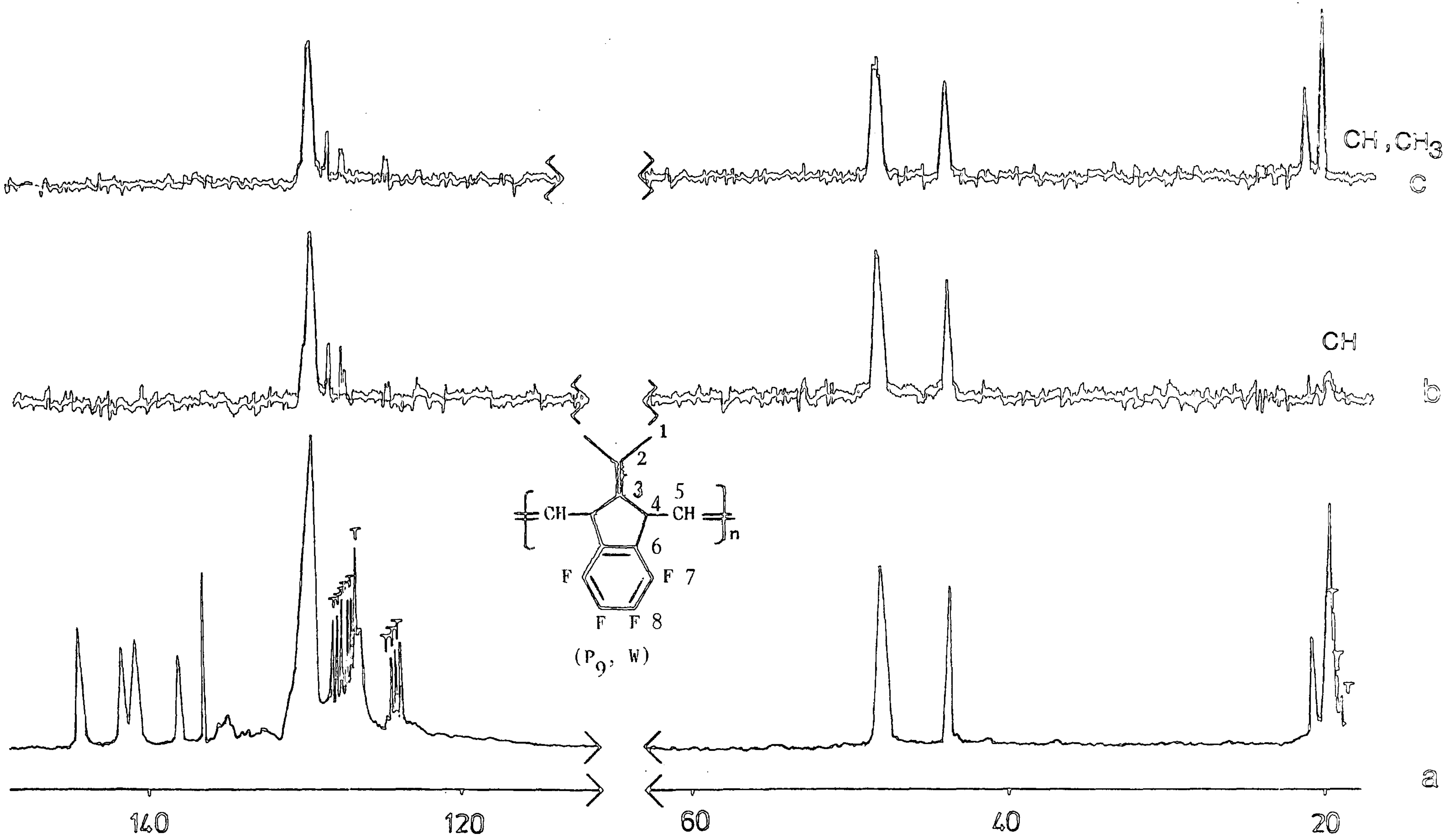
4.4.d Poly(5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene) (P_9, W) (P_9, Mo)

The ^{13}C n.m.r. spectrum of polymer (P_9, W) produced using WCl_6/$(CH_3)_4Sn$ is shown in Figure 4.26(a), Figure 4.26(b) records its DEPT spectrum in which only CH signals are recorded, Figure 4.26(c) shows the DEPT spectrum in which both methyl and methine signals are recorded, in both DEPT spectra quaternary carbon atoms do not show; Figure 4.26(d) shows the line narrowed spectrum. The ^{13}C n.m.r. shifts and their assignments for this polymer are given in Table 4.13.



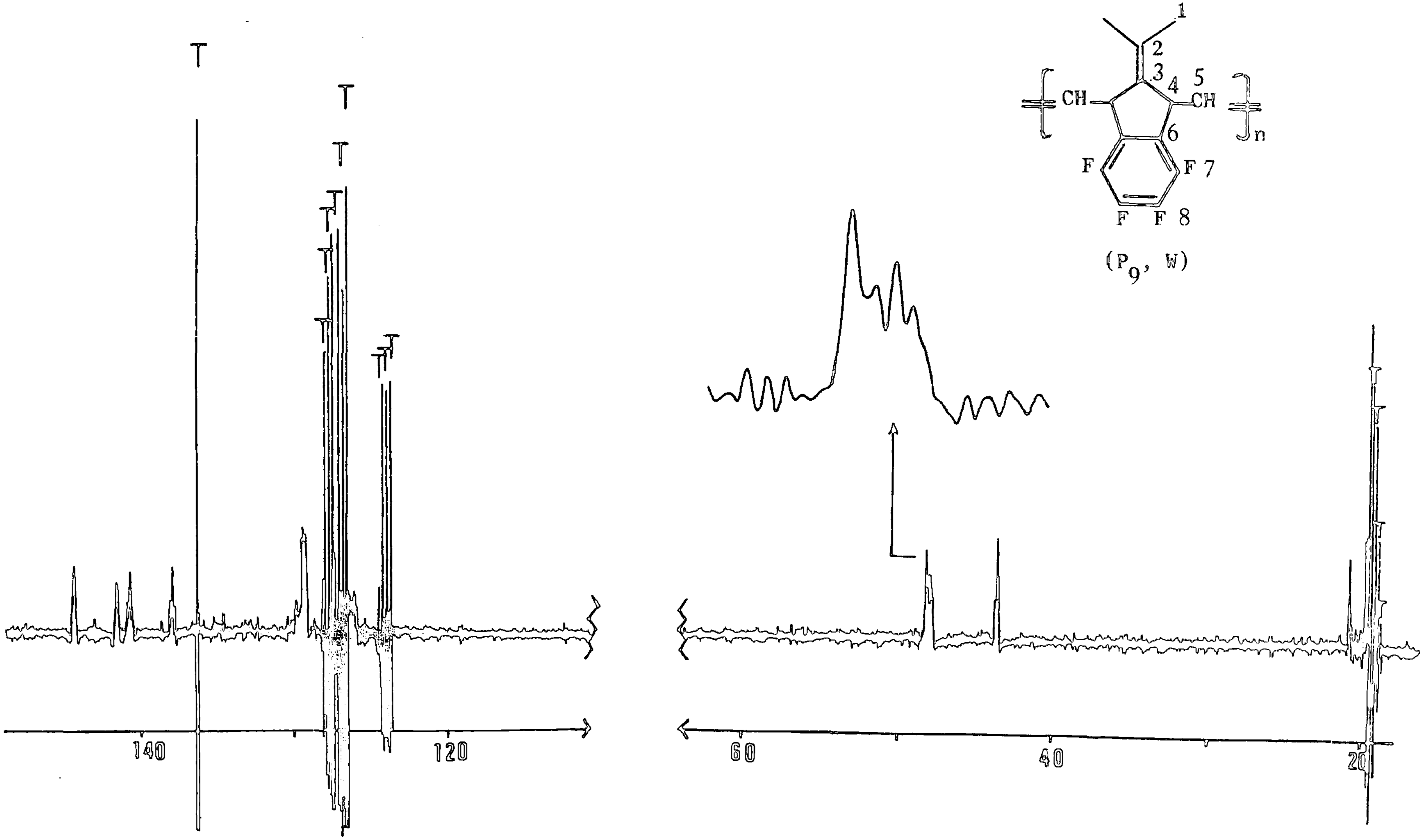
(P_9, W), (P_9, Mo)

These spectra were recorded in D_8 toluene and the sharp lines marked T are due to solvent. The signals at about 20 ppm can be assigned to methyl carbons on the basis of the DEPT spectra. There are two distinct resonances and these are attributed to methyls adjacent to cis (higher field) and trans vinylene units respectively; the integrated intensities lead to a value of σ_c = 0.63. The methine carbon signals are situated at 43.63 ppm when adjacent to the trans vinylene unit and at 47.99 and 48.08 ppm when adjacent to a cis vinylene unit, and these resonances lead to a σ_c value of 0.67. The expanded spectrum shows that the methine signal adjacent to cis vinylene units, is split into at least four lines, this may reflect vinylene sequence effects or tacticity but it is difficult to assign unambiguously. The olefinic



^{13}C N.m.r. spectrum of polymer (P$_9$, W) recorded at 90.56 MHz, upper spectra DEPT

Figure 4.26(a), (b) and (c)

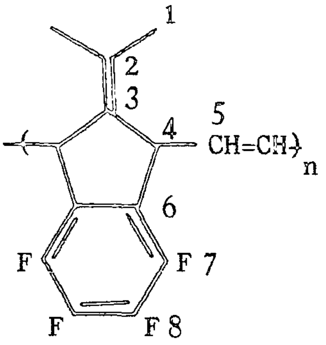


^{13}C N.m.r. spectrum of (P_9, W) after line narrowing

Figure 4.26(d)

Table 4.13

Chemical shifts in the ^{13}C n.m.r. spectra of poly-(5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methano naphthalene

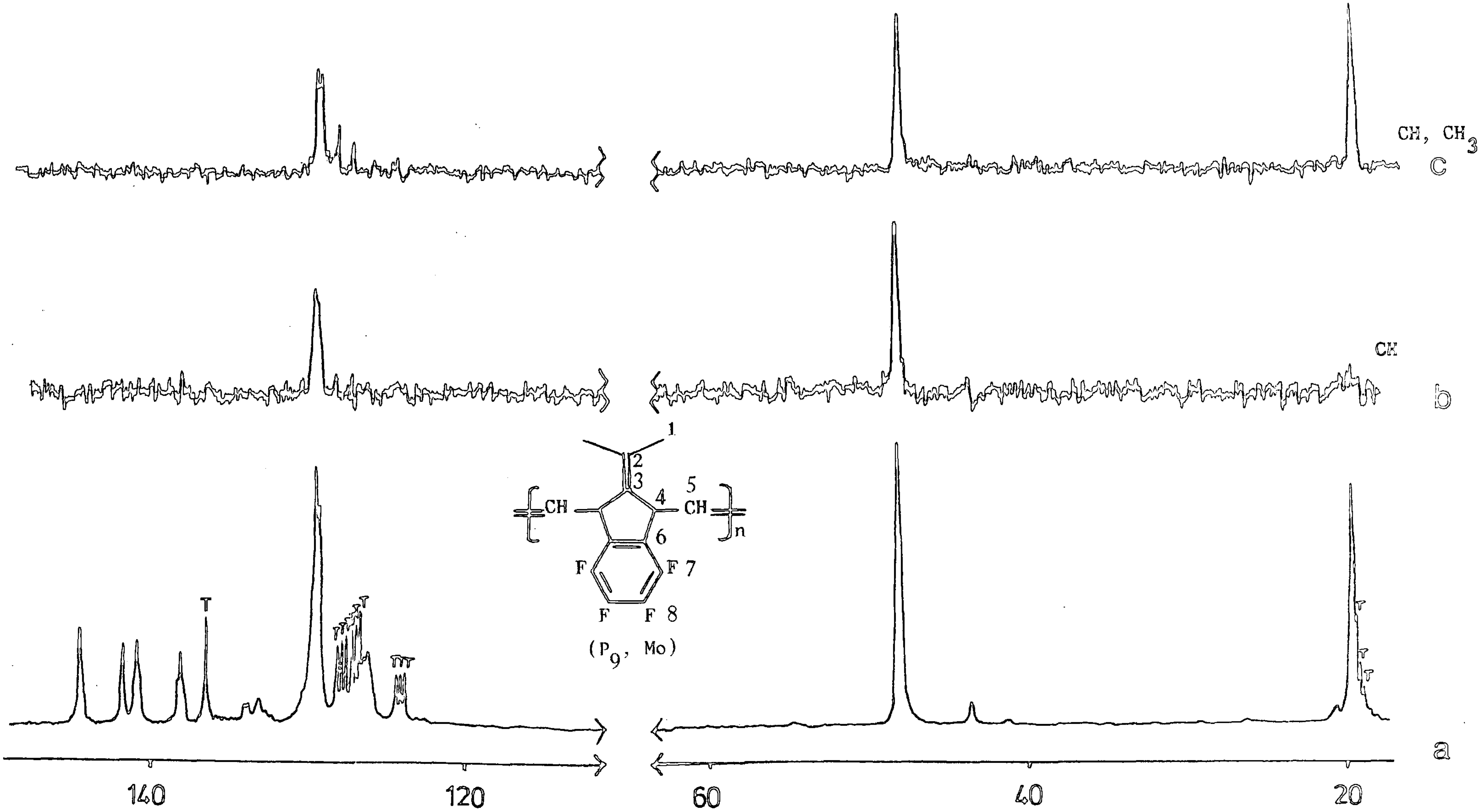


(P_9, W), (P_9, Mo)

chemical shifts		assignment	integral		σ_c	
A	B		A	B	A	B
19.63 19.83 20.04 20.85	19.71 not recorded by computer	1c 1t	50.138 15.673 5.389 32.786	51.45 -	0.63	
43.63 47.99 48.08	43.58 48.12	4t 4c	50.302 52.033 50.286	3.519 78.59	0.67	0.96
126.24 126.35	126.14 126.39	C_6	32.490 24.516	18.89 10.85		
129.44	129.24 129.54	5t 5c		34.84 75.61		
133.0 133.75 136	133.08 133.71 133.95	C_2 and C_3		7.101 3.316 1.88		
139.51 d J_{CF} = 250 Hz 143.16 d J_{CF} = 250 Hz	139.51 d J_{CF} = 250 Hz 143.16 d J_{CF} = 250 Hz	C_8 C_7				

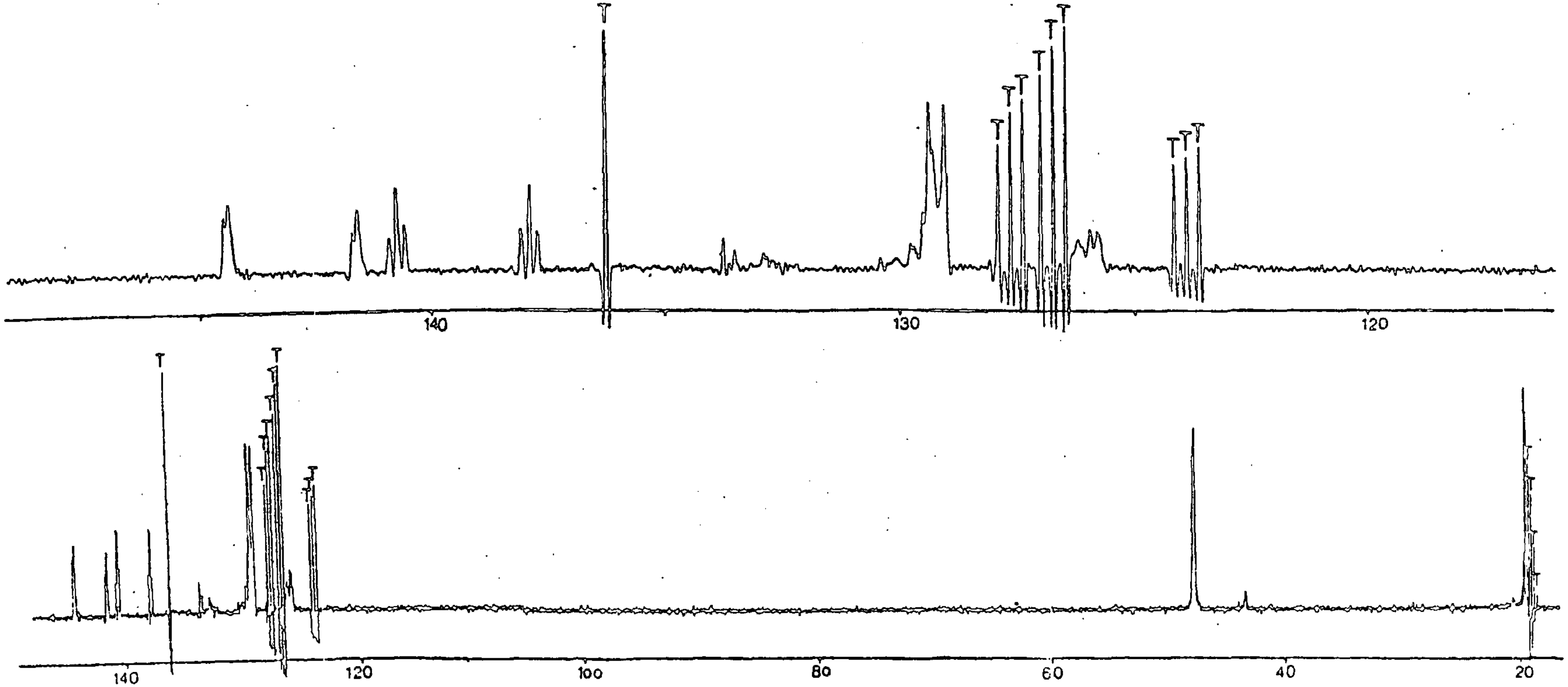
resonances (C_5) and the aryl resonances at C_6 appear as broad unresolved bands in the low field region of the spectrum, no σ_c values could be sensibly computed although the computer did resolve separate lines for C_6. The weak triplet and doublet at ca. 133 and ca. 136 ppm are assigned to the quaternary carbons C_3 and C_2 respectively. The aryl carbons carrying a fluorine atom appear as doublets with the expected large J_{CF} coupling.

The spectrum of the sample prepared using $MoCl_5/(CH_3)_4Sn$ catalyst is shown in Figure 4.27(a), Figure 4.27(b) and (c) show its DEPT spectra which allows identification of the tertiary, methyl and methine carbons; ^{13}C n.m.r. shifts and assignments are given in Table 4.13, column B. Comparison of this spectrum with the spectrum of the polymer sample prepared using $WCl_6/(CH_3)_4Sn$ as a catalyst, shows that most of the signals assigned to the trans unit are very greatly reduced. Only the high field signals are really clearly resolved and the computer failed to recognize the signal from the methyl carbon adjacent to trans vinylene C_1 at ca. 20.8 ppm, consequently only the signals due to the methine carbons C_4 can be used to calculate σ_c and these generate a very high value of 0.96. The absorptions in the low field part of the spectrum parallel those observed for (P_9, W) and the assignments shown in Table 4.13 are based on the same arguments. In the line narrowed and expanded spectrum 4.27(d) the assignment of the aryl CF carbons is confirmed by the clear doublet of triplets (J_{CF} = 250 Hz, J_{CF} 250 Hz) associated with C_8. The significance of the multiplicity observed for the vinylene carbon at ca. 129 ppm in the line narrowed and expanded spectrum is not immediately clear, but since this polymer has a very high cis content, it may be a reflection of tacticity effects.



^{13}C N.m.r. spectrum of polymer (P$_9$, Mo) recorded at 90.56 MHz, upper spectra DEPT

Figure 4.27(a), (b) and (c)



^{13}C N.m.r. spectrum of (P_9, Mo) after expansion and line narrowing

Figure 4.27(d)

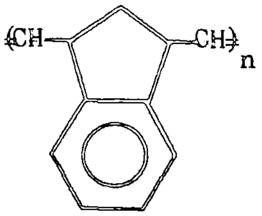
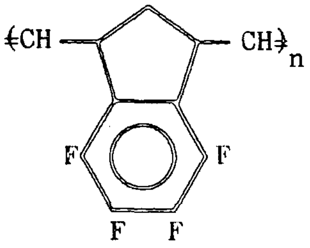
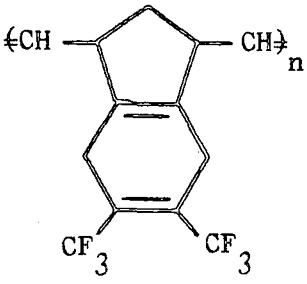
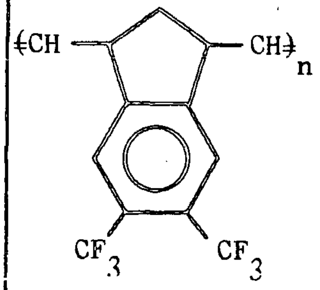
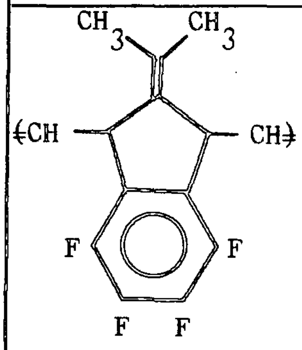
4.5 Conclusions

At the start of this work it was known that aryl substituted polycyclic alkenes could undergo metathesis ring-opening polymerization with catalysts derived from WCl_6/Ph_4Sn or $WCl_6/(CH_3)_4Sn$.[102] The objectives of this work were to extend the range of monomers which could be polymerized by this technique and to see if stereoregulation could be established with different catalysts. Seven monomers have been examined (26, 27, 28, 29, 30, 31 and 32) and two catalyst systems, i.e. WCl_6/Me_4Sn and $MoCl_5/Me_4Sn$.

The first conclusion to be drawn is that all these monomers undergo the expected ring-opening polymerization. Gel permeation chromatography results demonstrated that the products are genuine high polymers and spectroscopic analysis, especially ^{13}C n.m.r. spectroscopy, establishes that the product polymers have the expected structures. It has also been demonstrated that for these polymerizations the molecular weight of the polymer can be regulated by carrying out the polymerization in the presence of oct-4-ene.

The second main conclusion is that stereoregulation is possible in polymers of this type. Although this work has not resulted in the preparation of completely stereoregular polymers the detailed analysis of ^{13}C n.m.r. spectroscopic data for pairs of polymers derived from the same monomer using either tungsten or molybdenum based catalysts shows clear differences in microstructure with a tendency for a greater degree of stereoregulation with molybdenum based catalysts. The details of stereoregulation are clearly very complicated and Ivin's work has demonstrated that monomer structure, catalyst composition and reaction conditions, all influence the way the polymerization goes. In this work some broad trends can be seen, for example the average values for σ_c are collected together in Table 4.14, and in general the

Table 4.14

Polymer repeat unit	Average σ_c values	
	WCl_6/Me_4Sn	$MoCl_5/Me_4Sn$
 P_1, P_2	0.5	0.7
 P_8	0.4	0.7
 P_6	0.6	0.6
 P_7	0.5	0.8
 P_9	0.7	0.9

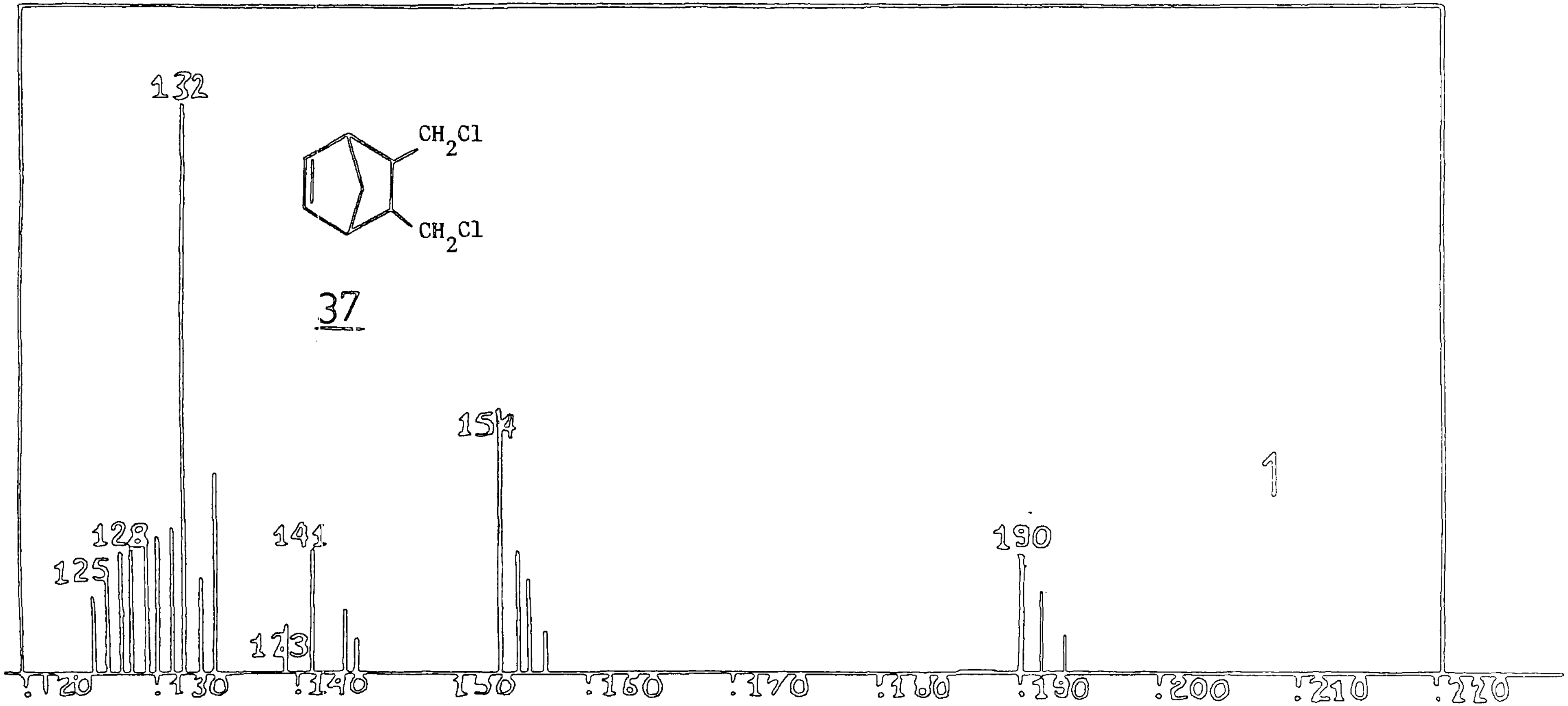
$MoCl_5/Me_4Sn$ derived polymers have a higher cis content than the analogous polymers derived from WCl_6/Me_4Sn. The only exception to this generalization is P_6 where the two catalysts appear to give essentially the same polymer; this observation is in such clear disagreement with the general trend seen with these monomers and several other systems investigated in Durham and elsewhere that it would seem desirable to repeat this part of the work. The detailed examination of the ^{13}C n.m.r. spectra (see above) also leads to the conclusion that the $MoCl_5/Me_4Sn$ derived polymers have a greater degree of stereoregularity than the WCl_6/Me_4Sn derived materials. Stereoregular polymers and their atactic analogues are expected to have markedly different physical properties, this work has been concerned with monomer synthesis, polymerization and structure elucidation and the author has not studied bulk properties of the product polymers. However, some observations do appear to agree with the conclusion that a significant degree of stereoregulation is caused by the molybdenum catalyst; thus, the solubility of the polymers which are believed to have significant stereoregularity is found to be much lower than that of their atactic analogues and this solubility difference appears to be independent of molecular weight.

4.6 Suggestions for Further Work

It is clear that there are many aspects of the work described in this thesis which could be expanded in future studies. In the first instance it seems desirable to investigate the possibility of making totally stereoregular polymers by choice of appropriate catalysts, rather than the partially stereoregular materials prepared so far. A paper by Ivin and co-workers, which appeared during the preparation of this thesis, describes the polymerization of 1-methylnorbornene by a very wide range of catalysts which allowed the preparation of materials of various microstructures (for example 100% trans-isotactic ($OsCl_3$), 100% trans-atactic ($RuCl_3.3H_2O$) and 100% cis-syndiotactic ($ReCl_5$));[230] it would be interesting to find out if the monomers described in this work can be polymerized in the same manner by these newer catalysts which appear to offer complete stereoregulation. The work carried out in this study establishes that the ^{13}C n.m.r. analytical method will work best with monomers 30 and 32 since for these systems the problem of overlap between methine and methylene carbon resonances in the product polymer spectra is avoided. If this is possible a number of further studies would follow based on investigations of how physical properties vary with microstructure. One particular disadvantage of polymers described in this work is their oxidative instability, this might be decreased if the vinylene units were hydrogenated and this also seems worth the attention of future workers in the field.

APPENDIX A

MASS SPECTRA



37

132
CH$_2$Cl
CH$_2$Cl
154
1
125
128
141
143
190
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130
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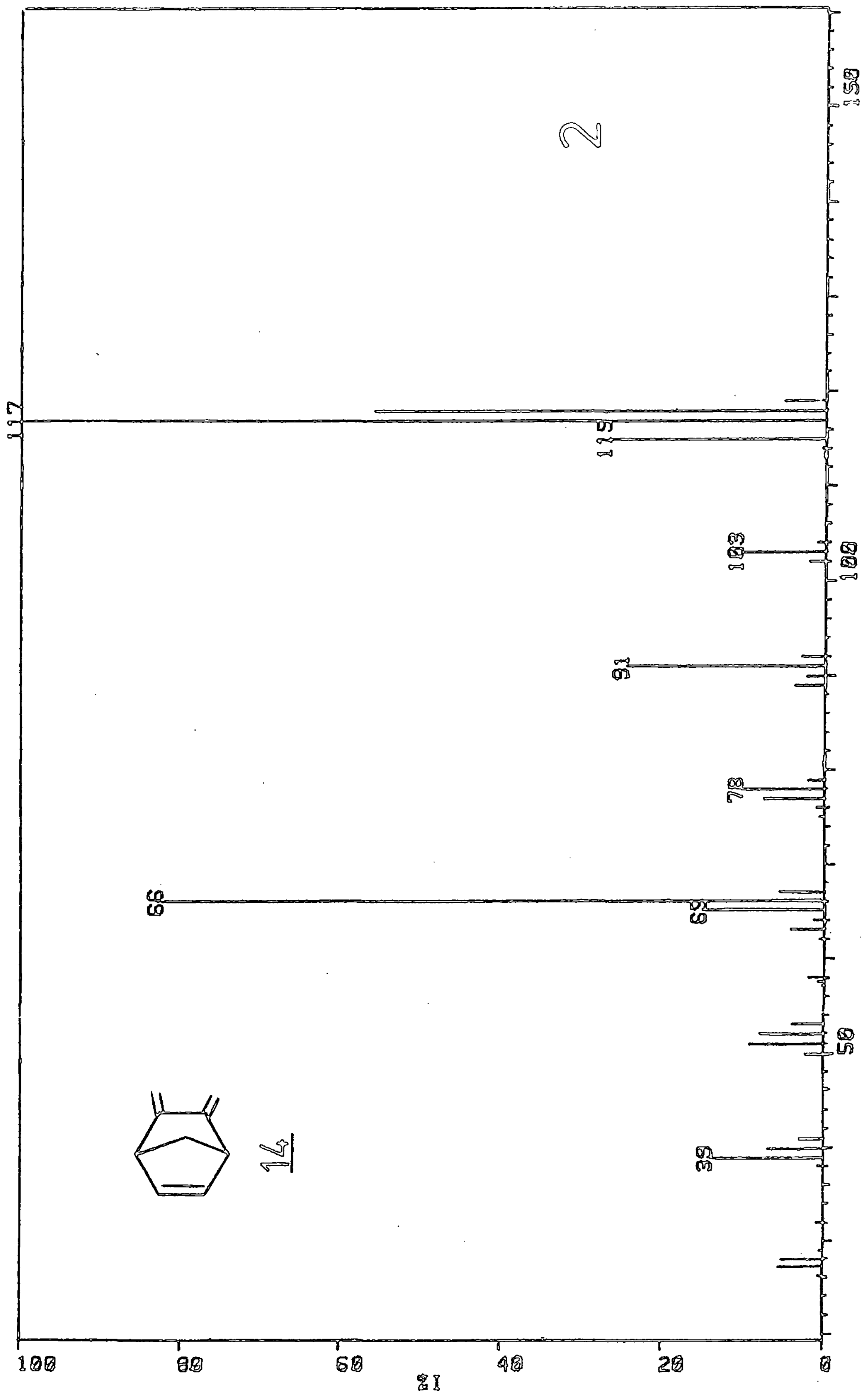
170
180
190
200
210
220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117
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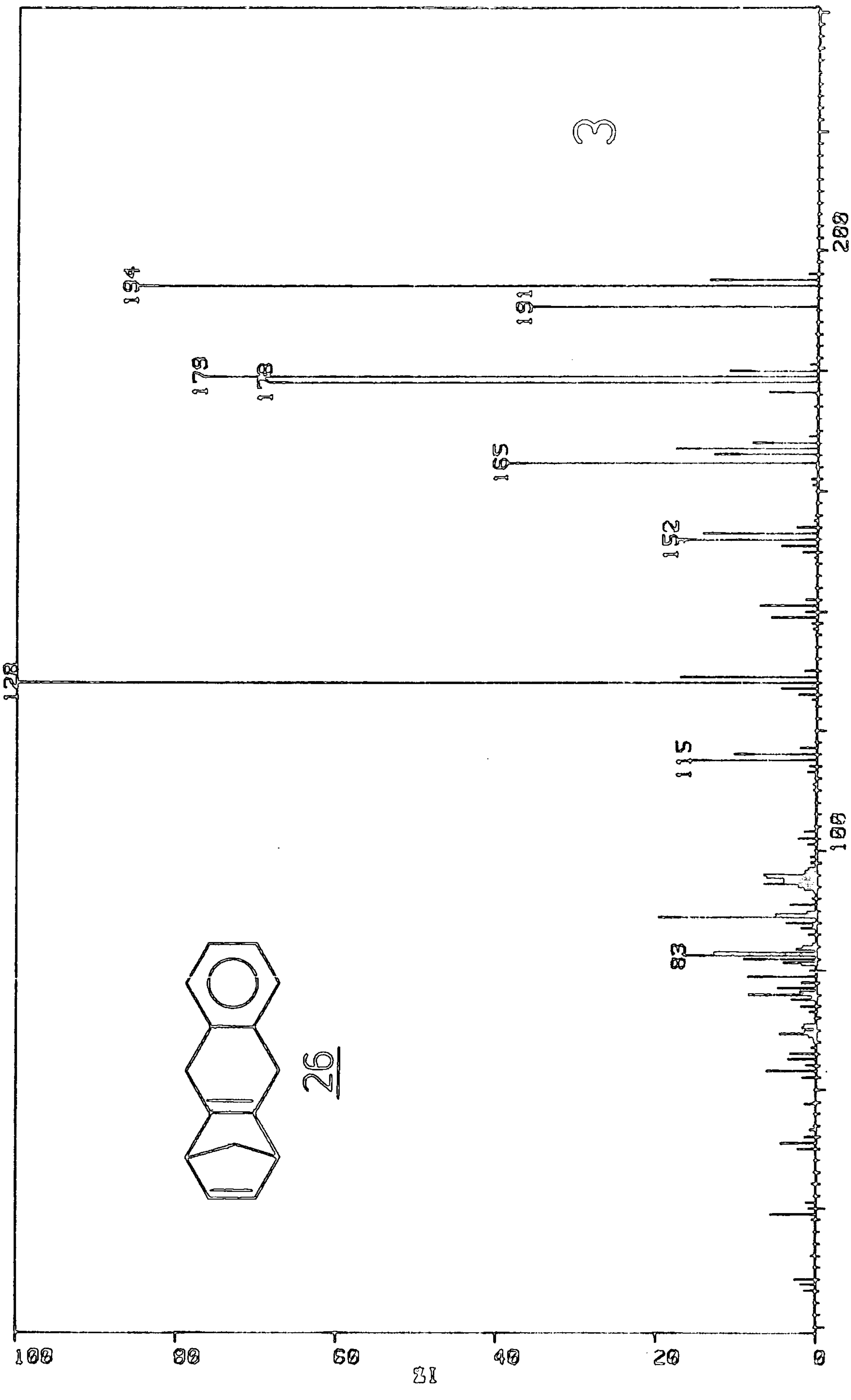
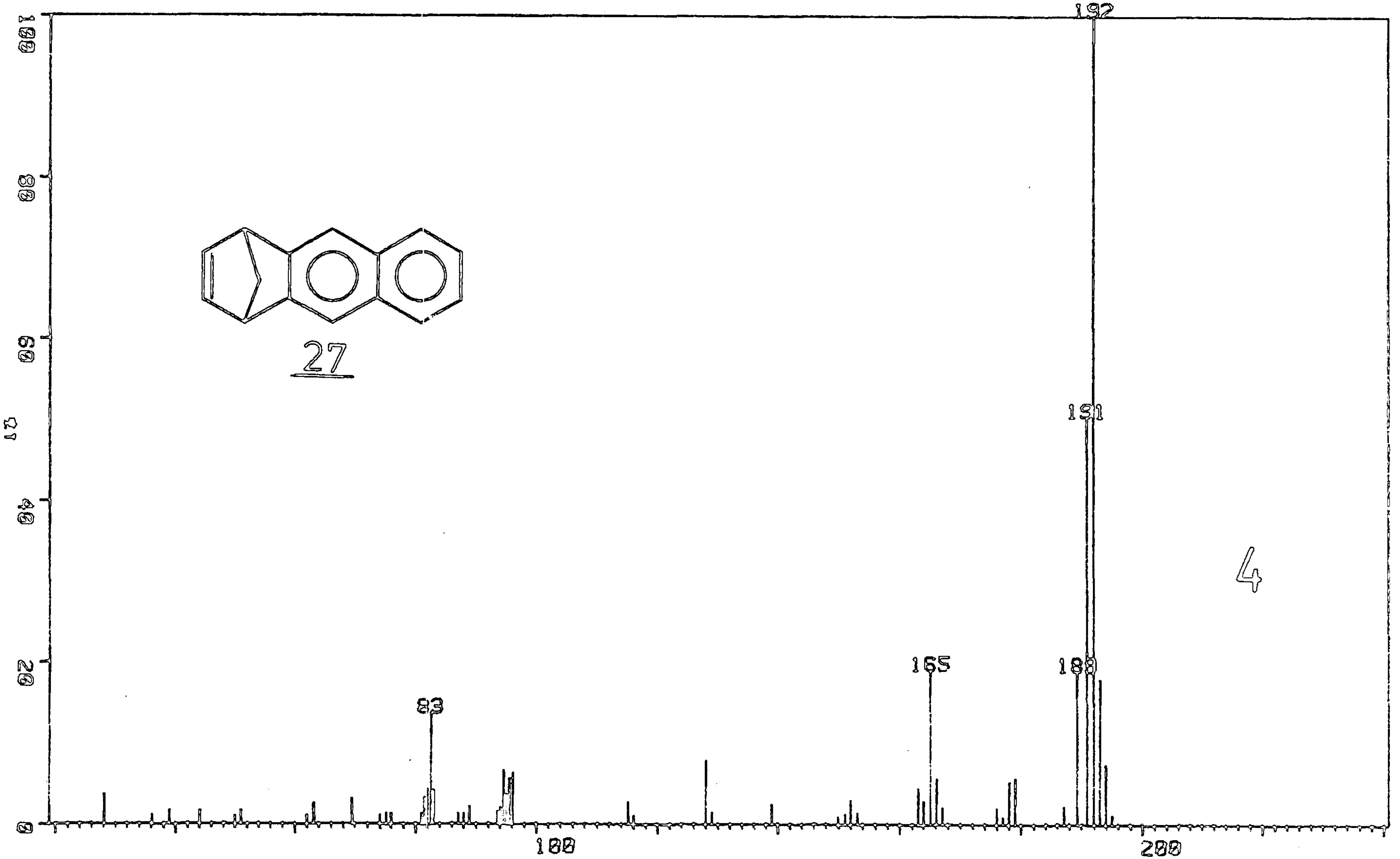


26



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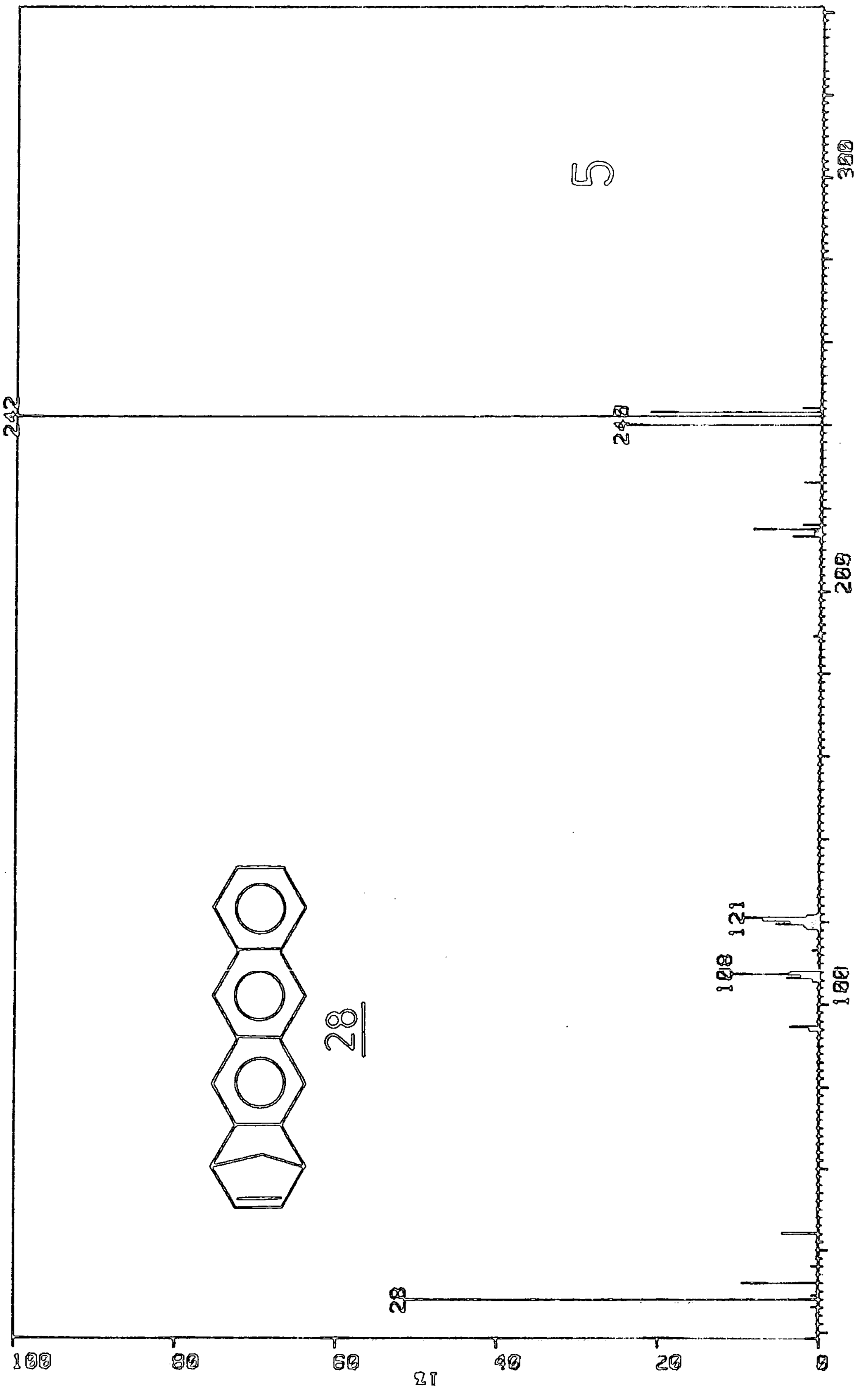
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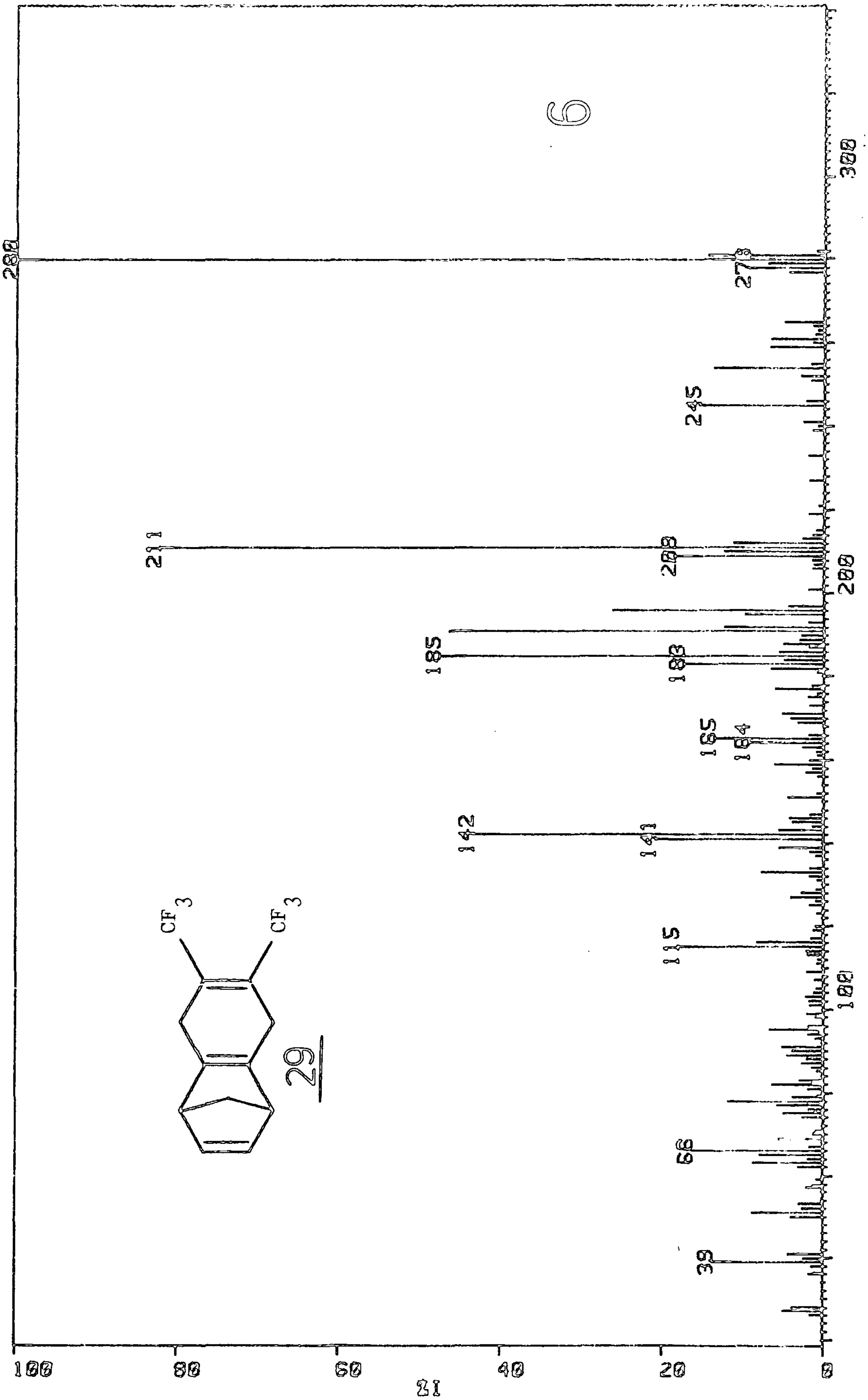

29

6

CF3
CF3
288
278
245
211
208
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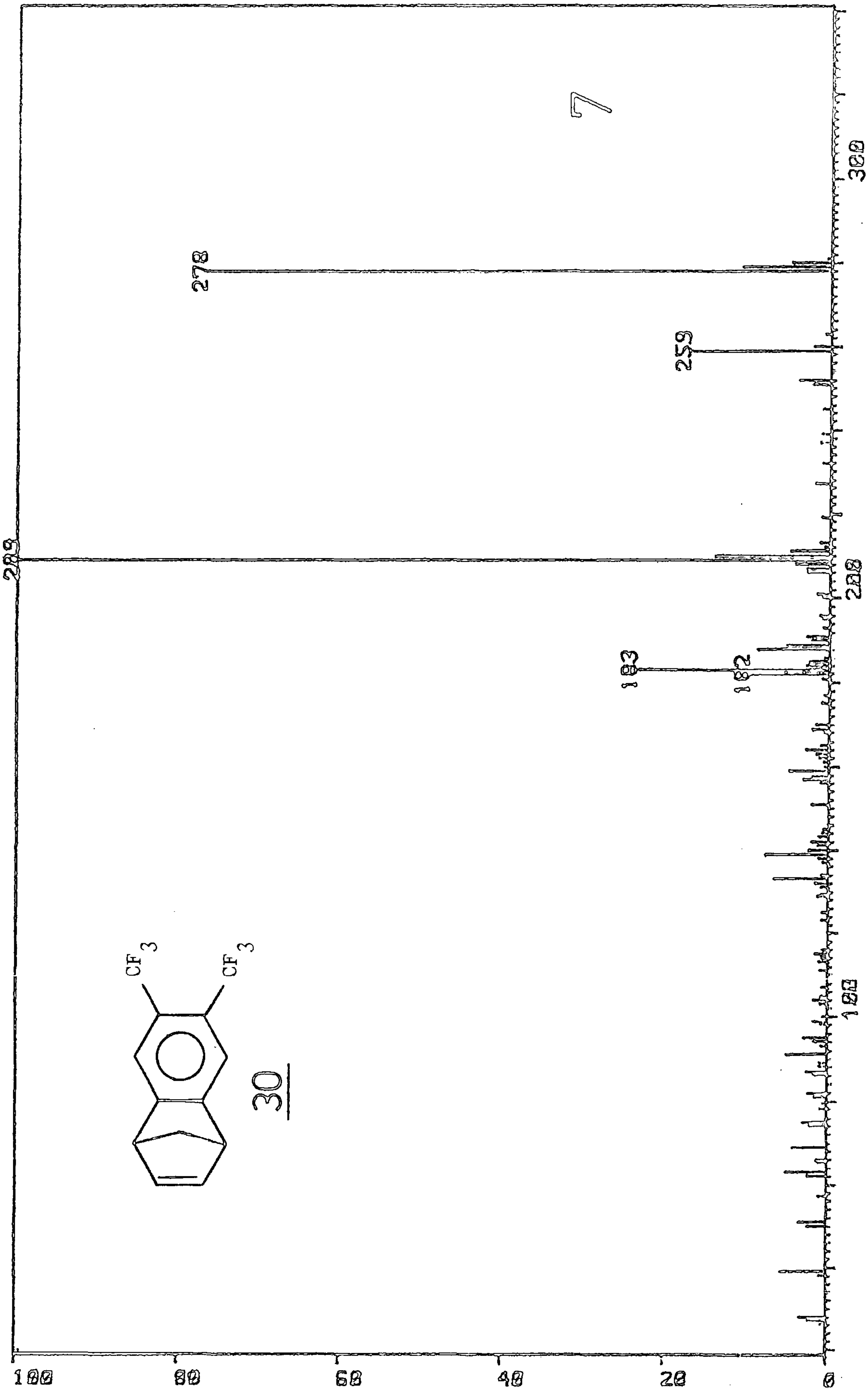
7
278
259
209
183
182
CF3
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100
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APPENDIX B

I.R. SPECTRA

All spectra were recorded using KBr plates, pressed discs or thin films and were run under condition designation by:-

A: KBr disc

B: Thin Liquid film (KBr plates)

C: Thin polymer film

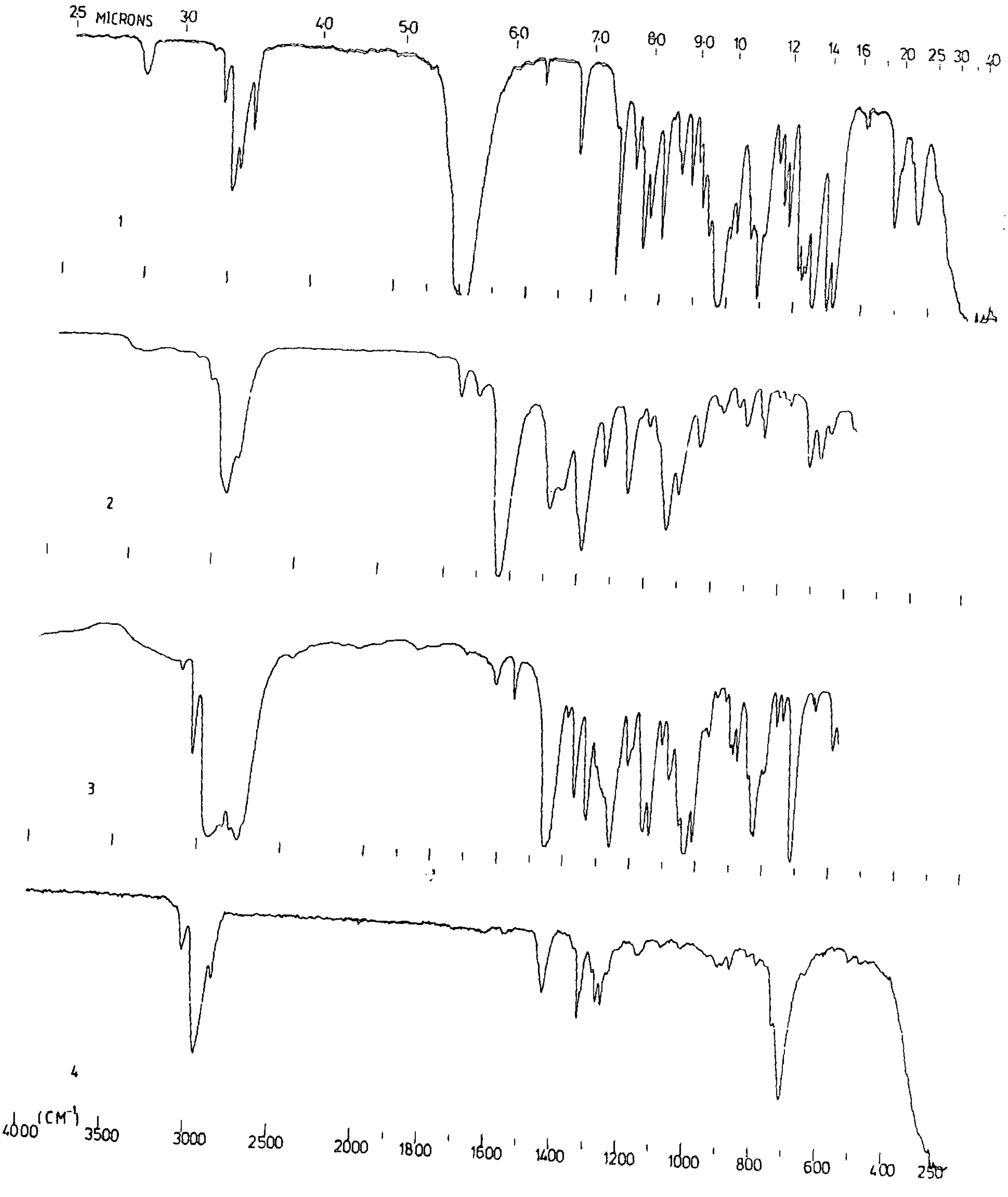
D: Thin polymer film (cast on KBr plate).

Infrared spectra are tabulated below.

Spectrum No.	Name of Compound	Sample No.
(1)	endo, exo-5,6-dicarboxychloridebicyclo[2.2.1]hept-2-ene	(33)
(2)	bicyclo[2.2.1]hept-2-ene-5,6-dicarboxydimethylamide	(34)
(3)	5,6-bis(dimethylaminomethyl)bicyclo[2.2.1]hept-2-ene	(35)
(4)	5,6-dichloromethylbicyclo[2.2.1]hept-2-ene	(37)
(5)	5,6-dimethylenebicyclo[2.2.1]hept-2-ene	(14)
(6)	4,5-benzotricyclo[6,2,1,$0^{2,7}$]undeca,2(7),4,9-triene	(26)
(7)	poly(4,5-benzotricyclo[6,2,1,$0^{2,7}$]undeca,2(7), 4,9-triene)	(P_3)
(8)	2,3-naphthotricyclo[2.2.1]hept-2,5-diene	(27)
(9)	poly(2,3-naphthotricyclo[2.2.1]hept-2,5-diene)	(P_4)
(10)	2,3-anthraceno[2.2.1]hept-2,5-diene	(28)
(11)	poly(2,3-anthraceno[2.2.1]hept-2,5-diene)	(P_5)
(12)	4,5-bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$] undeca-2,4,9-triene	(29)
(13)	poly(4,5-bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$] undeca-2,4,9-triene) from $WCl_6/(CH_3)_4Sn$	(P_6, W)
(14)	poly(4,5-bis(trifluoromethyltricyclo[6,2,1,$0^{2,7}$] undeca-2,4,9-triene) from $MoCl_5/(CH_3)_4Sn$	(P_6, Mo)
(15)	4,5-bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$] undeca-2,4,6,9-tetraene	(30)
(16)	poly(4,5-bis(trifluoromethyl)tricyclo[6,2,1,$0^{2,7}$] undeca-2,4,6,9-tetraene) from $WCl_6/(CH_3)_4Sn$	(P_7, W)

/cont......

Spectrum No.	Name of Compound	Sample No.
(17)	poly(4,5-bis(trifluoromethyl)tricyclo[6,2,1,0^{2,7}] undeca-2,4,6,9-tetraene from $MoCl_5/(CH_3)_4Sn$	(P_7, Mo)
(18)	poly(5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methano naphthalene from $WCl_6/(CH_3)_4Sn$	(P_8, W)
(19)	poly(5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methano naphthalene) from $MoCl_5/(CH_3)_4Sn$	(P_8, Mo)
(20)	poly(5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methano naphthalene) from $WCl_6/(CH_3)_4Sn$	(P_9, W)
(21)	poly(5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methano naphthalene) from $MoCl_5/(CH_3)_4Sn$	(P_9, Mo)
(22)	poly(4-methylene-1,3-cyclopentylenevinylene)	(24)
(23)	poly(tricyclo[3,2,1,0^{2,3}]oct-1,4-ylene methylene)	(25)
(24)	poly(5,6-dimethylenebicyclo[2.2.1]hept-2-ene	(16)
(25)	poly(6-methylenetricyclo[3,2,1,0^{2,3}]oct-1,4-ylene methylene	(17)
(26)	poly[8,9-(5,6-dimethylenebicyclo[2.2.1]hepta-2-ene	(15)
(27)	poly(benzonorbornadiene) from $WCl_6/(CH_3)_4Sn$	(P_1)
(28)	poly(benzonorbornadiene) from $MoCl_5/(CH_3)_4Sn$	(P_2)



2.5 MICRONS 3.0
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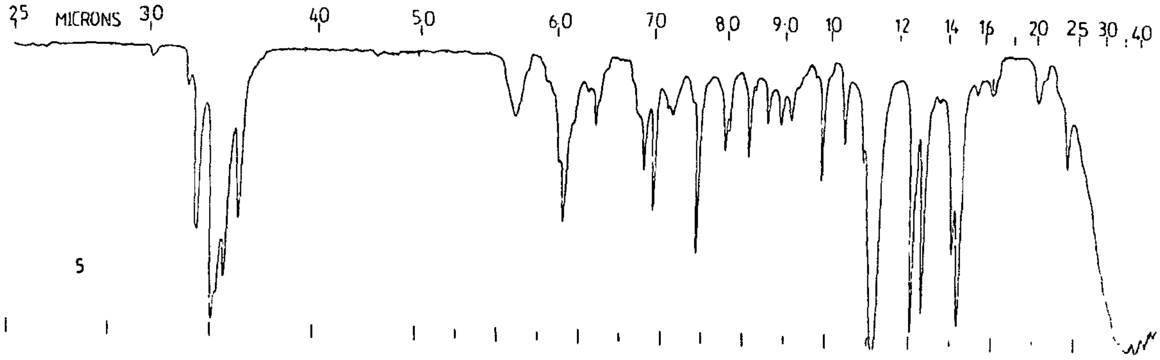
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MICRONS
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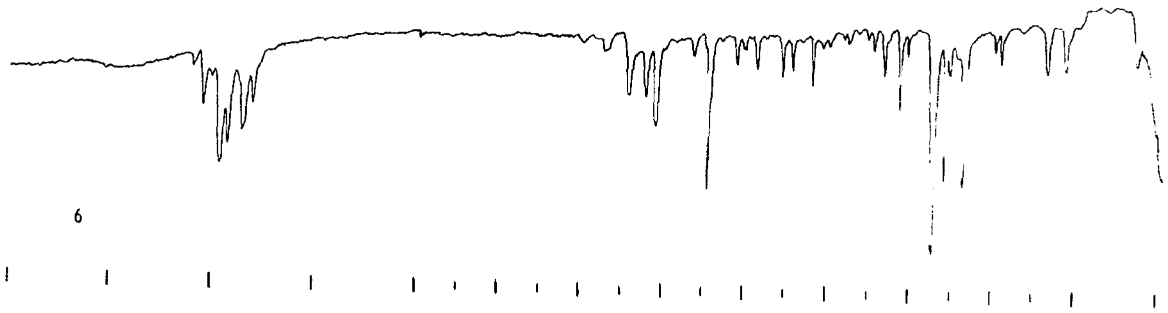

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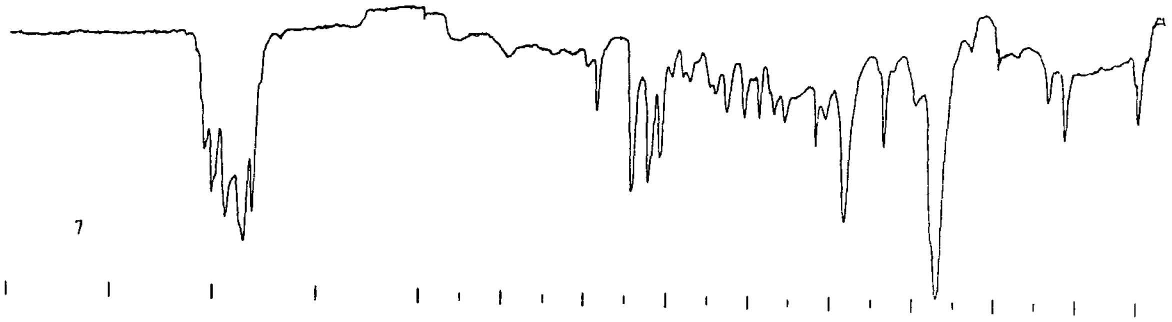

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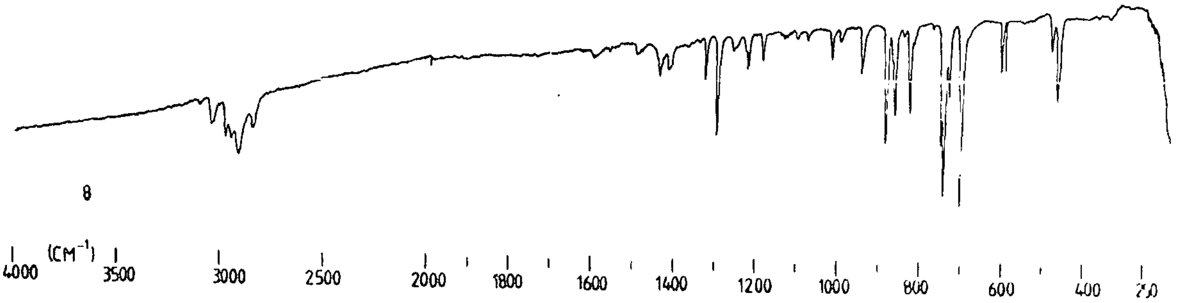
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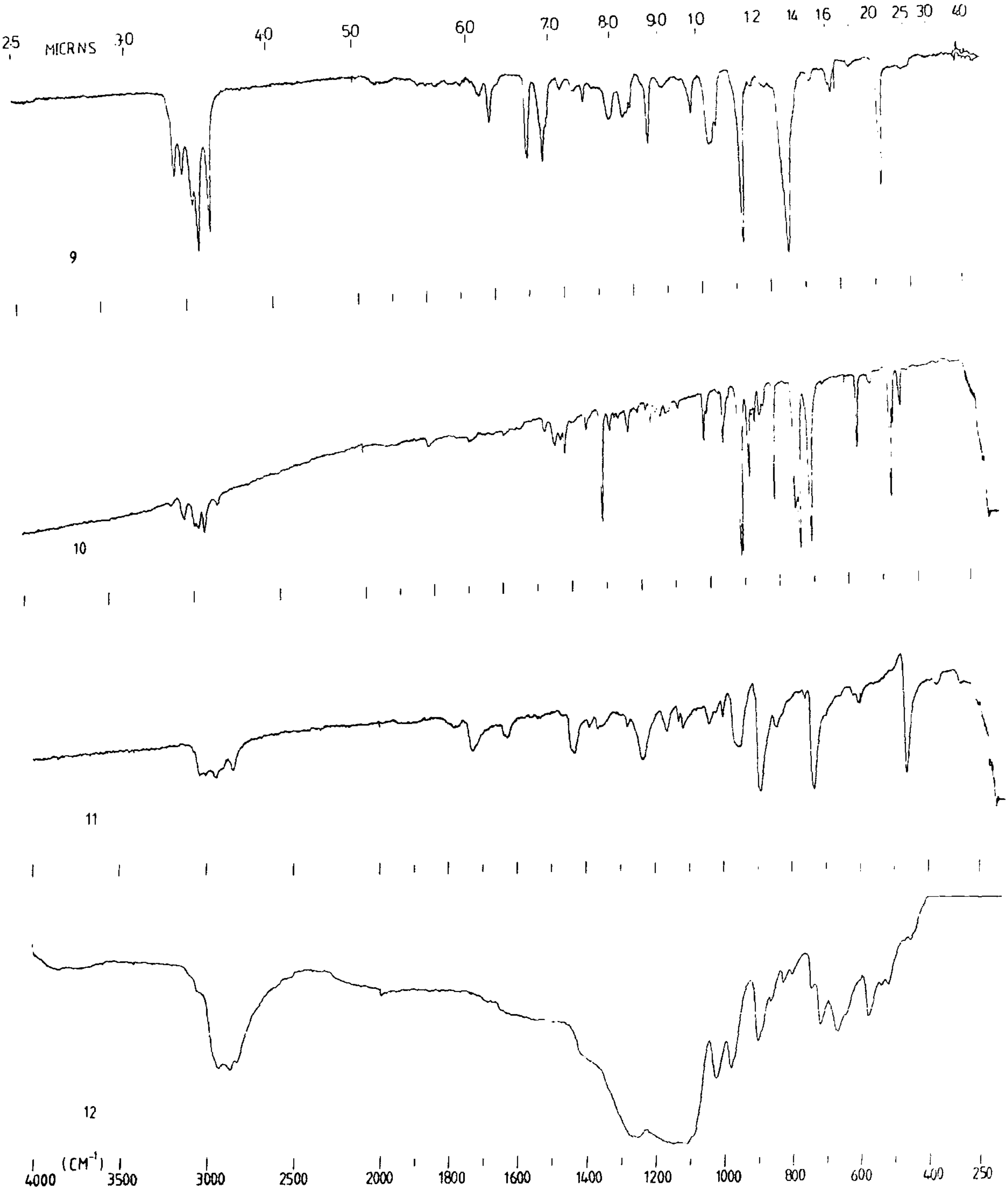
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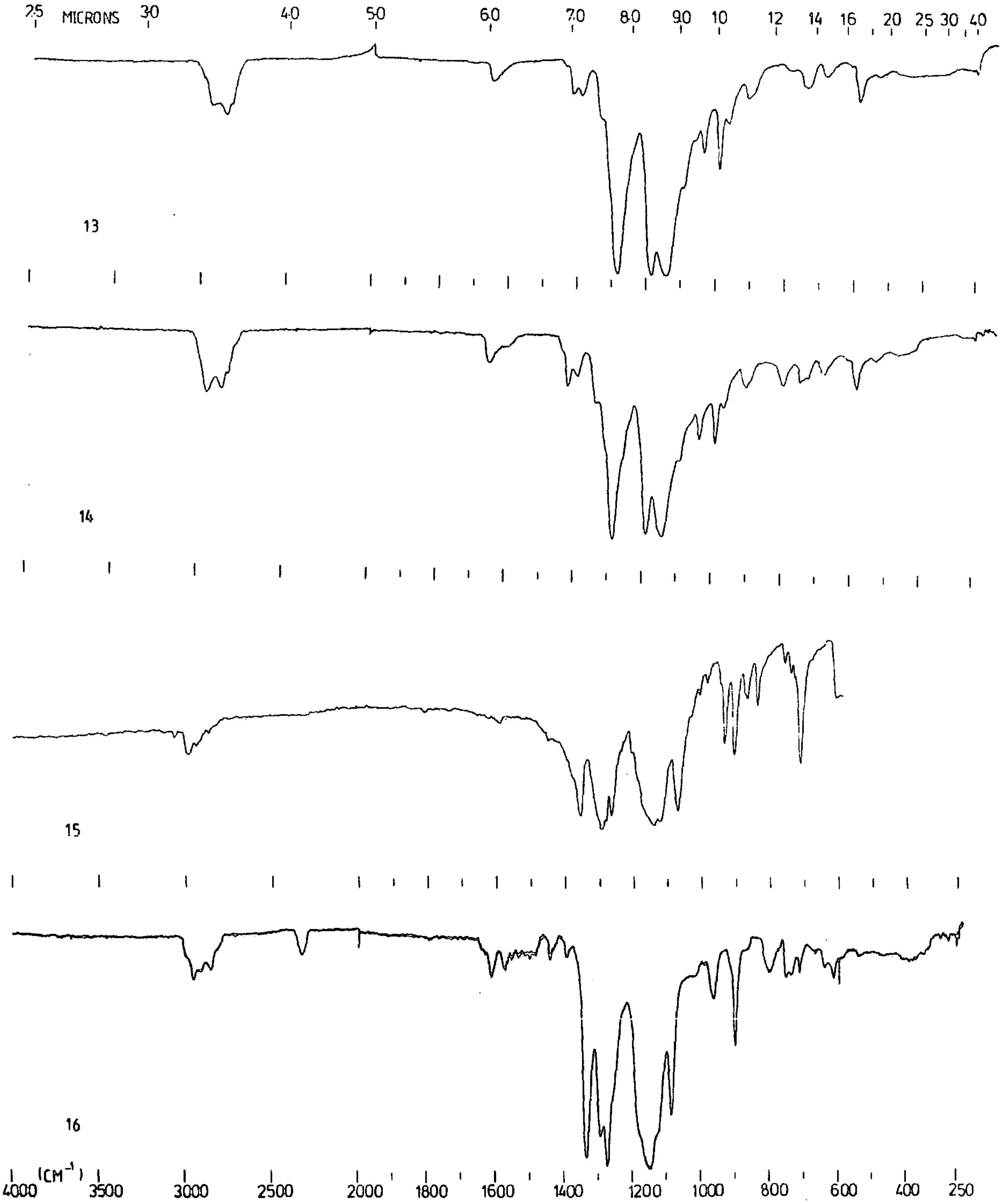
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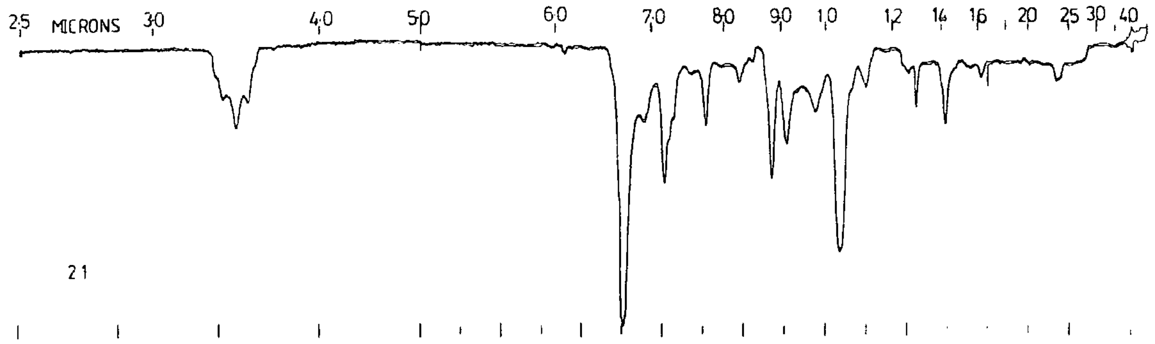
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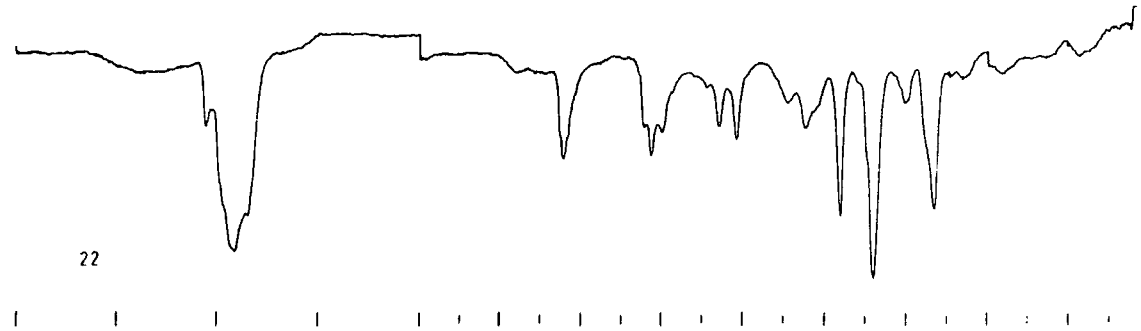

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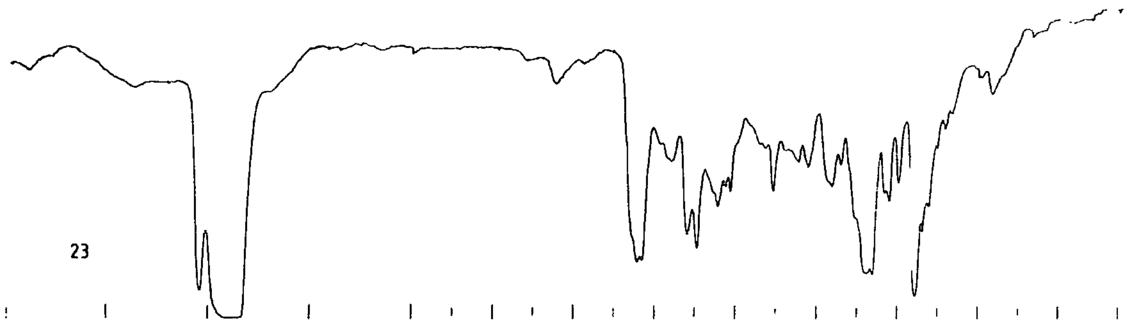

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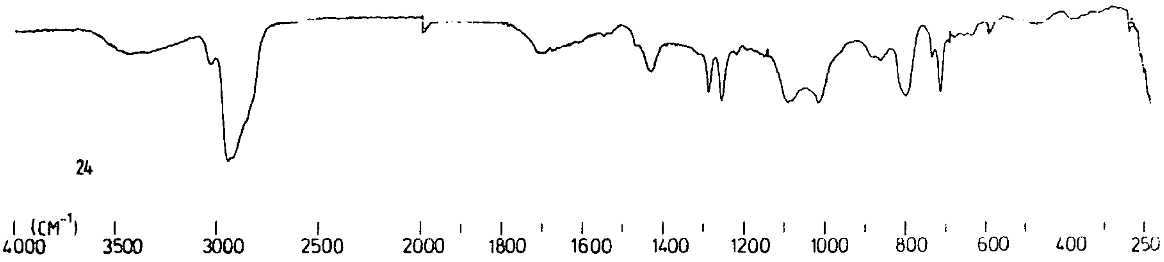
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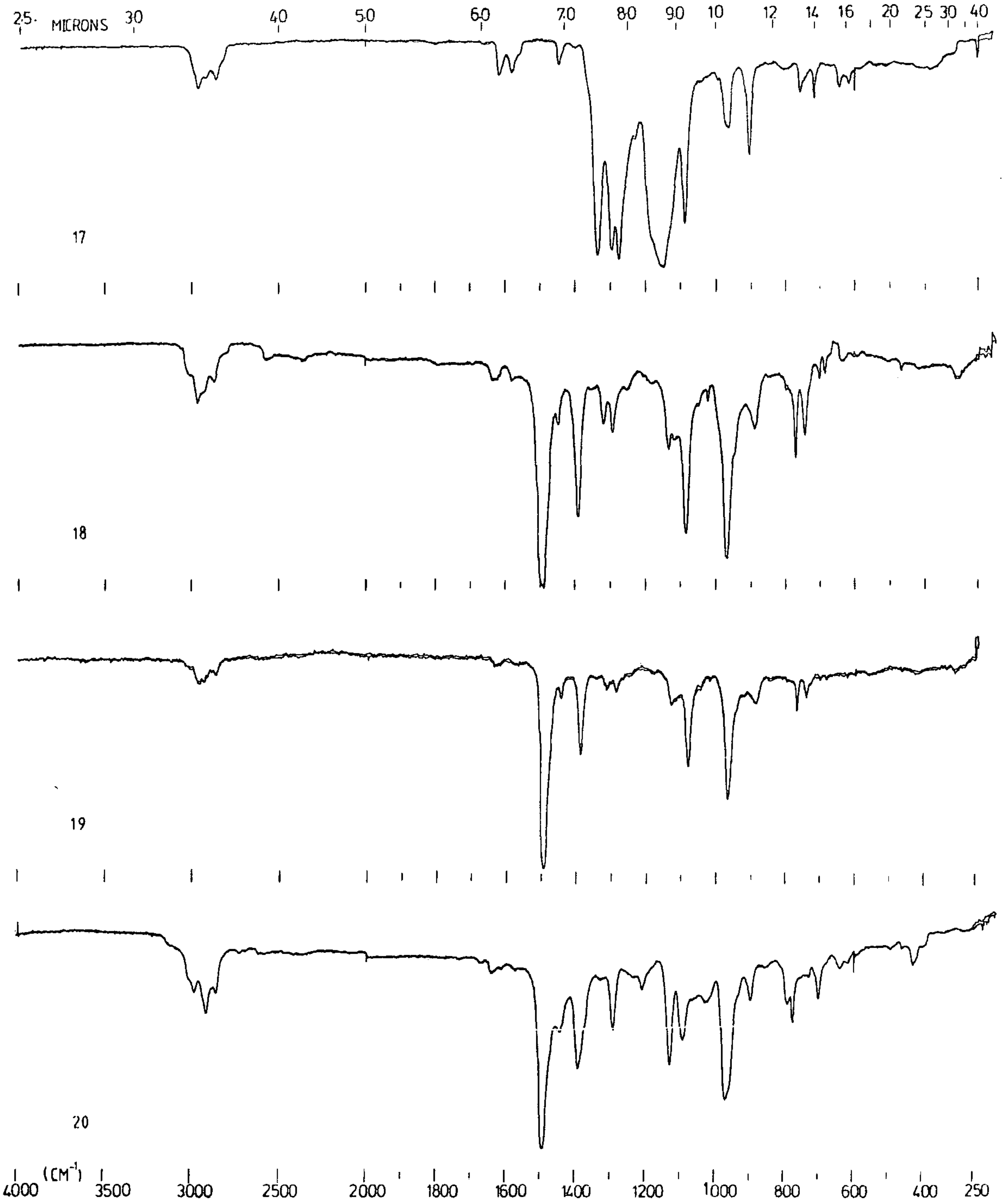
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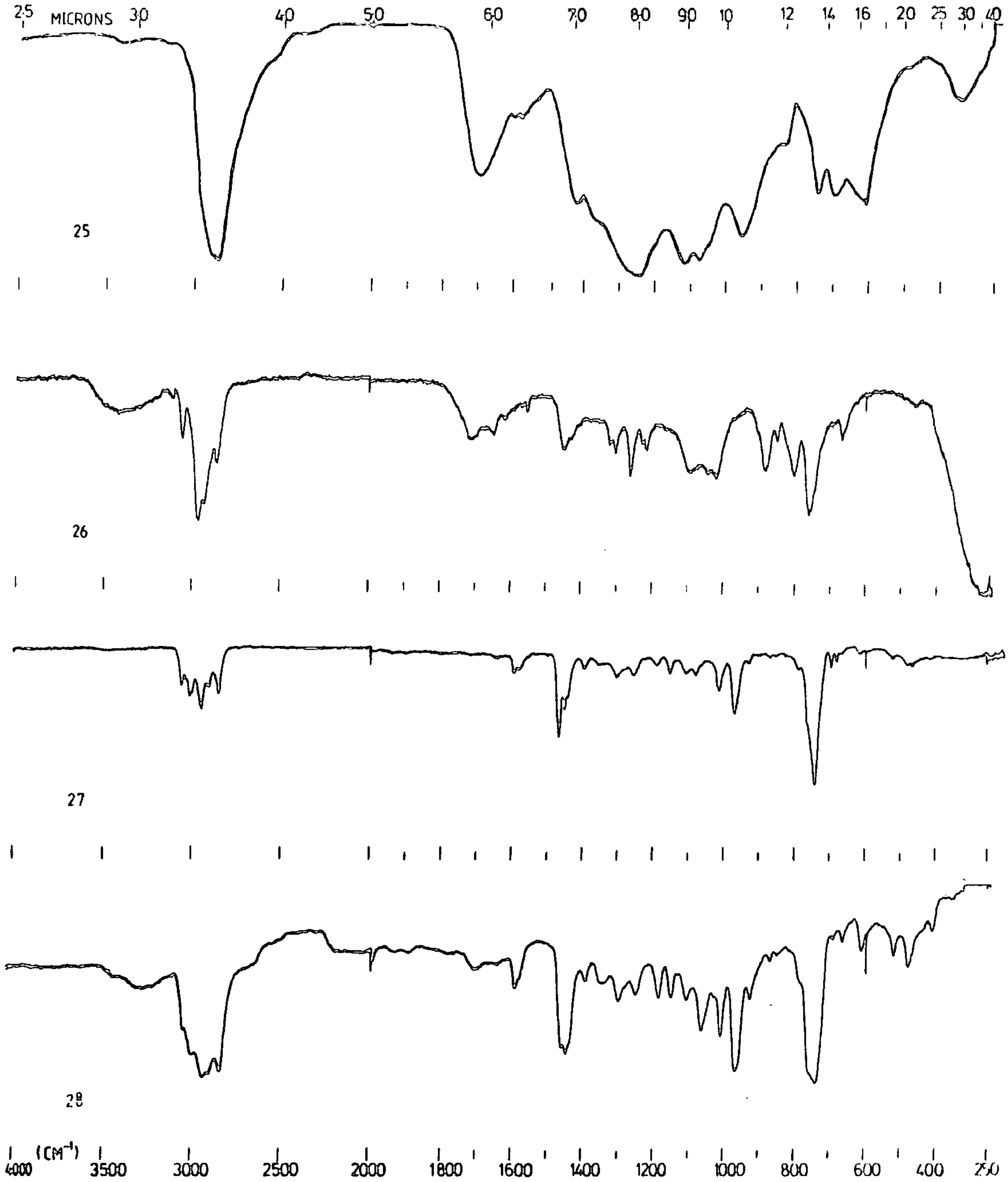
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REFERENCES

1. A.W. Anderson and N.G. Merckling, U.S. Patent, 2, 721, 189 (1955).
2. N. Calderon et.al., Chem. Eng. News, 45, 51 (1967).
3. R.L. Banks and G.C. Bailey, Ind. Eng. Chem., Prod. Res. Develop., 3, 170 (1964).
4. W.L. Truelt, D.R. Johnson, I.M. Robinson and B.A. Monlague, J. Amer. Chem. Soc., 82, 2337 (1960).
5. H.S. Eleuterio, U.S. Patent, 3, 074, 918 (1957).
6. G. Dall'Asta, G. Mazzanti, G. Natta and L. Porri, Makromol. Chem., 56, 224 (1962).
7. G. Dall'Asta, G. Mazzanti, G. Natta and G. Mortoni, Makromol. Chem., 69, 163 (1963).
8. G. Dall'Asta, G. Mazzanti and G. Natta, Angew. Chem., 76, 765 (1964).
9. N. Calderon, H. Yu Chen and K.W. Scott, Tetrahedron Lett., 3327 (1967).
10. K.W. Scott, N. Calderon, E.A. Ofstead, W.A. Judy and J.P. Ward, J. Amer. Chem. Soc., 90, 4133 (1968); Adv. Chem. Ser., 91, 399 (1968); A.C.S. Meeting Abs., 155, 154 (1968).
11. R.L. Banks, Topics in Current Chem., 25, 39 (1972).
12. G.C. Bailey, Catalysis Rev., 3, 37 (1969).
13. C.P.C. Bradshaw, E.D. Howman and L. Turner, J. Catal., 7, 269 (1967).
14. T.P. Kobylinksi and H.E. Swift, J. Catal., 26, 416 (1972).
15. A.F. Ellis and E.T. Sabourin, U.S. Patent, 3, 595, 920 (1971).
16. F. Pennella, U.S. Patent, 3, 544, 647 (1970).
17. R.L. Banks and F. Pennella, J. Catal., 31, 304 (1943).
18. W.H. Davenport, V. Kollonitsch and C.H. Kline, Ind. Eng. Chem., 60, 10 (1968).

19. N. Calderon, Accounts Chem. Res., 5, 127 (1972).

20. P. Gunther, F. Hass, G. Marwedw, K. Nutrel, W. Oberkirch, G. Pampus, N. Schon and J. Witte, Angew. Makromol. Chem., 14, 87 (1970).

21. G. Natta, D. Dall'Asta and G. Mazzanti, Italy Patent, 733, 857 (1965); Chem. Abs., 65, 3996 (1966).

22. T.J. Katz, J. McGinnis and G. Altus, J. Amer. Chem. Soc., 98, 606 (1976).

23. G. Natta, G. Dall'Asta, I.W. Bassi and G. Corella, Makromol. Chem., 91, 87 (1966).

24. G. Natta, G. Dall'Asta and G. Mazzanti, Angew. Chem. Int. Ed., 3, 723 (1964).

25. G. Dall'Asta and G. Mortoni, Angew. Makromol. Chem., 16, 117, 51 (1971).

26. P.R. Hein, J. Polym. Sci. Polym. Chem. Ed., 11, 163 (1973).

27. A.J. Amass, T.A. McGourtey and C.N. Tuck, Eur. Polym. J., 14, 817 (1978).

28. A.J. Amass and T.A. McGourtey, Eur. Polym. J., 16, 235 (1980).

29. K.J. Ivin, B.S.R. Reddy and J.J. Rooney, J. Chem. Soc. Chem. Commun., 1062 (1981).

30. K. Finter, G. Wegner, E.J. Nagel and R.W. Lenz, Makromol. Chem., 181, 1619 (1980).

31. J.C. Mol, J.A. Moulijn and C. Boelhouwer, J. Chem. Soc. Chem. Commun., 633 (1968).

32. F.L. Moody, M.J. Lewis and G.B. Wills, J. Catal., 14, 389 (1969).

33. G. Dall'Asta, Makromol. Chem., 154, 1 (1972).

34. G. Dall'Asta and G. Mortoni, Eur. Polym. J., 7, 707 (1971).

35. G. Dall'Asta, G. Mortoni and L. Motta, J. Polym. Sci., A1, 10, 1601 (1972).

36. A. Mortreux and M. Blanchard, Bull. Soc. Chim. France, 1641 (1972).

37. A. Mortreux, F. Petit and M. Blanchard, Tetrahedron Lett., 4967 (1978).

38. K.W. Scott, N. Calderon, E.A. Ofstead, W.A. Judy and J.P. Ward, Rubber Chem. Technol., 44, 1341 (1971).

39. S.E. Bresler, J.I. Mosevitskii, I.Ya. Poddubnji and I. ShiGuan, Rubber Chem. Technol., 34, 986 (1961).

40. G. Mango, J. Amer. Chem. Soc., 89, 2484 (1967); J. Amer. Chem. Soc., 93, 1123 (1971).

41. R. Hoffmann and R.B. Woodward, J. Amer. Chem. Soc., 89, 2486 (1967).

42. P.G. Gassman and T.H. Johnson, J. Amer. Chem. Soc., 98, 861 (1976); P.G. Gassman and T.H. Johnson, J. Amer. Chem. Soc., 98, 6055, 6057 and 6059 (1976).

43. W.J. Feast and B. Wilson, J. Mol. Catal., 8, 277 (1980).

44. Private Communication, W.J. Feast, R.R. Grubbs and T. Katz. Discussions at ISOM 5, Graz, (1983).

45. G.S. Lewandas and R. Pettit, Tetrahedron Lett., 789 (1971).

46. R.H. Grubbs and T.K. Brunck, J. Amer. Chem. Soc., 94, 2538 (1972).

47. J.P. Herisson and Y. Chauvin, Makromol. Chem., 141, 161 (1970).

48. D.J. Cardin, M.L. Doyle and M.F. Lappert, Chem. Commun., 927 (1972).

49. B.A. Dolgoplosk, K.L. Makovetskii, E.I. Tinyakova, T.G. Golenko and I.A. Oreshkin, Izv. Akad. Nauk SSSR, Ser. Khim., 4, 1084 (1976).

50. P. Casey and T.J. Burkhardt, J. Amer. Chem. Soc., 96, 7808 (1974).

51. T.J. Katz, S.J. Lee, M. Nair and E.B. Savage, J. Amer. Chem. Soc., 102, 7940 (1980).

52. T.J. Katz and N. Acton, Tetrahedron Lett., 4251 (1976).

53. T.J. Katz, S.J. Lee and M. Ashippey, *J. Mol. Catal.*, 8, 219 (1980).

54. T.J. Katz, S.J. Lee and N. Acton, *Tetrahedron Lett.*, 4247 (1976).

55. (a) R.R. Schrock, *J. Amer. Chem. Soc.*, 96, 6796 (1974);
(b) R.R. Schrock, *J. Amer. Chem. Soc.*, 98, 5399 (1976).

56. M. Ephritikhine, M.L.H. Green and R.E. Mackenzie, *J. Chem. Soc., Chem. Commun.*, 619 (1976).

57. B.A. Dolgoplosk, K.L. Makovetskii, J.G. CoLenk, Yu.V. Korshak and E.T. Tinyakova, *Eur. Polym. J.*, 10, 901 (1974).

58. E.O. Fischer and W. Held, *J. Organometallic Chem.*, C59, 112 (1976).

59. M.T. Mocella, R. Rouner and E.L. Mueltertus, *J. Amer. Chem. Soc.*, 98, 4689 (1976).

60. E.L. Muetterties and M.A. Bush, *J. Chem. Soc. Chem. Commun.*, 754 (1974).

61. E.L. Muetterties, *Inorg. Chem.*, 14, 951 (1975).

62. R.H. Grubbs and M.L.H. Green, *J. Chem. Soc. Chem. Commun.*, 639 (1977).

63. M.L.H. Green, G.J.A. Adam, S.G. Davies, K.P. Ford, M. Ephritikhine and P.F. Todd, *J. Mol. Catal.*, 8, 15 (1980).

64. R.H. Grubbs, The Fifth International Symposium on Olefin Metathesis, Graz, Austria, August (1983).

65. K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, *J. Chem. Soc. Chem. Commun.*, 604 (1978).

66. E.O. Fischer and S. Riedmuller, *Chem. Ber.*, 107, 915 (1974).

67. P.B. Van Dam, M.C. Mittelmeijer and C. Boelhouwer, *J. Chem. Soc. Chem. Commun.*, 1221 (1972).

68. E. Verkuijlen and C. Boelhouwer, *J. Chem. Soc. Chem. Commun.*, 793 (1974).

69. E. Verkuijlen and C. Boelhouwer, Felte, Seifen, Anstrichm., 78, 444 (1976).

70. J. Tsuji and S. Hashiguchi, Tetrahedron Lett., 2955 (1980).

71. J. Tsuji and S. Hashiguchi, J. Organomet. Chem., 69, 218 (1981).

72. C. Boelhouwer and E. Verkuijlen, Int. Metathesis Symp. Mainz, 28, 1976 (1976).

73. R. Nakamura, S. Fuvuhara, S. Matsumoto and K. Komatsu, Chem. Lett., 253 (1976).

74. R. Nakamura, S. Matsumoto and E. Echigoya, Chem. Lett., 1019 (1976).

75. K. Hummel and Y. Imamoglu, Coll. Polym. Sci., 253, 225 (1975).

76. W. Ast, G. Rheinwald and R. Kerber, Recueil, 96 (279-292), M 127 (1977).

77. J.P. Lavel, A. Lattes, R. Mutin and J.M. Basset, J. Chem. Soc. Chem. Commun., 502 (1977).

78. G. Foster, German Patent, 2, 063, 150 (1971).

79. Charbonnages de France, French Patent, 1, 594, 934 (1970); Chem. Abs., 74, 65280 (1971).

80. Charbonnages de France, French Patent, 1, 550, 351 (1968); Chem. Abs., 71, 30827 (1969).

81. R.E. Rinehart and H.P. Smith, J. Polym. Sci., Part B, 1049 (1965).

82. F. Michelotti and W. Keaveney, J. Polym. Sci., Part A, 895 (1965).

83. Charbonnages de France, French Patent, 1, 543, 497 (1968); Showa Denko, Japan Kokai, 74/77, 999 (1974).

84. Imperial Chemical Industries, German Patent, 2, 231, 995 (1973); Chem. Abs., 78, 98287 (1973).

85. Japan Synthetic Rubber, Japan Kokai, 75/22, 100 (1975); Chem. Abs., 83, 44047 (1975).

86. Japan Synthetic Rubber, German Patent, 2, 447, 687 (1975); Chem. Abs., 83, 44046 (1975).

87. Showa Denko, German Patent, 2, 441, 742 (1973); Chem. Abs., 83, 29199 (1975).

88. A.G. Bayer, German Patent, 2, 334, 606 (1975); Chem. Abs., 83, 28844 (1975).

89. S. Matsumoto, K. Komatsu and K. Igarashi, A.C.S. Symp. Ser., (Ring-opening Polym., Int. Symp.), 59, 303 (1977).

90. S. Matsumoto, K. Komatsu and K. Igarashi, Polym. Prepr., 18, 110 (1977).

91. Mitsubishi Petrochemical Co. Ltd., Japan Kokai, 81, 65, 018 (1981); Chem. Abs., 95, 151435 (1981).

92. Showa Denko, Japan Kokai, 77/63, 298 (1977).

93. Showa Denko, German Patent, 2, 316, 087 (1973); Chem. Abs., 80, 83, 932 (1974).

94. Japan Synthetic Rubber, German Patent, 2, 442, 181 (1975); Chem. Abs., 83, 132, 321 (1975).

95. Showa Denko, Japan Kokai, 76, 112, 867 (1976); Chem. Abs., 86, 90947 (1977).

96. Showa Denko, German Patent, 2, 452, 461 (1975); Chem. Abs., 83, 132, 320 (1975).

97. R. Nakamura, M. Kohuma and S. Kokuryo, Japan Kokai, 76, 712, 866 (1977); Chem. Abs., 86, 56162 (1977).

98. Y. Kobayashi, T. Ueshima, Y. Tanaka, S. Kurosowa and S. Kobayashi, German Patent, 2, 590, 553 (1976); Chem. Abs., 86, 156, 245 (1977).

99. F. Imaizumi, H. Nubuyo and M. Kakake, Japan Kokai, 88, 87, 499 (1977); Chem. Abs., 88, 7691 (1978).

100. (a) W.J. Feast and B. Wilson, Polymer, 20, 1182 (1979).

(b) B. Wilson, Ph.D. Thesis, Durham University, Durham (1978).

101. A.B. Alimuniar, Ph.D. Thesis, Durham University, Durham (1982).

102. (a) W.J. Feast and I.F.A.F. ElSaafin, J. Mol. Catal., 15, 61 (1982);

(b) I.F.A.F. El-Saafin, Ph.D. Thesis, Durham University, Durham (1981).

103. T.J. Katz and R.J. Rothchild, J. Amer. Chem. Soc., 98, 2519 (1976).

104. S.J. Lee, J. McGinnis and T.J. Katz, J. Amer. Chem. Soc., 98, 7818 (1976).

105. F.W. Kupper and R. Streck, Makromol. Chem., 175, 2055 (1974).

106. E.A. Ofstead, 4th Int. Synth. Rubber Symp., London, Paper S42, (1969).

107. A.I. Syatkowsky, T.T. Denisova, E.L. Aranenko, A.S. Katchaturov and B.D. Babitsky, Polymer, 22, 1554 (1981).

108. L.I. Red'Kina, K.L. Makovetskii, I.L. Kershenbaum, U.M. Dzhenilev and G.A. Tolstikov, Izu. Akad. Nauk SSSR, Ser. Khim., 133 (1981).

109. L.I. Red'Kina, K.L. Makovetskii and B.A. Dolgoplosk, Vysokomol Soedin, B23, 227 (1981).

110. E.A. Ofstead, U.S. Patent, 3, 597, 403 (1969).

111. W. Ast, G. Rheinwald and R. Kerber, Makromol. Chem., 177, 1349 (1976).

112. R. Streck, J. Mol. Catal., 15, 3 (1982).

113. W. Ast, G. Rheinwald and R. Kerber, Makromol. Chem., 177, 1341 (1976).

114. G. Dall'Asta, Rubber Chem. Technol., 47(3), 511 (1974).

115. H. Hocker, Angew. Makromol. Chem., 100, 87 (1981).

116. N. Calderon, U.S. Patent, 3, 439, 056 (1969); Chem. Abs., 71, 38438 (1969).

117. N. Calderon, U.S. Patent, 2, 439, 657 (1969); Chem. Abs., 71, 80807 (1969).

118. L.G. Wideman, J. Org. Chem., 33, 4541 (1968).

119. K. Wolovsky, J. Amer. Chem. Soc., 92, 2132 (1970).

120. D.A. Ben-Afrain, C. Batich and E. Wasserman, J. Amer. Chem. Soc., 92, 2133 (1970).

121. E.A. Zeuch, W.B. Hughes, D.H. Kubik and E.T. Kittleman, J. Amer. Chem. Soc., 92, 528 (1970).

122. G.P. Pinazzi, I. Guilmet and D. Reyx, Tetrahedron Lett., 989 (1976).

123. J. Lal and R.R. Smith, J. Org. Chem., 40, 775 (1975).

124. R. Rossi, P. Diversi, A. Lucherini and L. Porri, Tetrahedron Lett., 879 (1974).

125. R. Baker and M.J. Crimmin, Tetrahedron Lett., 441 (1977).

126. J. Otton, Y. Colleuilleand and J. Voragnat, J. Mol. Catal., 8, 313 (1980).

127. C. Pinazzi, I. Campistron, M.C. Croinssandeau and D. Reyx, J. Mol. Catal., 8, 325 (1980).

128. R. Rossi, Chimica Industria, 57, 242 (1975).

129. D.M. Siglenton, U.S. Patent, 3, 530, 196 (1970).

130. E.A. Zuech, U.S. Patent, 3, 558, 518 (1971).

131. W.B. Hughes, Ann. N.Y. Acad. Sci., 295, 271 (1977).

132. W.B. Hughes, Chem. Tech., 486 (1975).

133. J.K. Walter and C. Nissim, Ionic Poly. Unsolved Poobl. Jon. U.S. Semin. Polym. Synth., 1, 271 (1974).

134. R. Ross, P. Diversi, A. Lucherini and L. Porri, Tetrahedron, 989 (1976).

135. K. Hummel, F. Stelzer, P. Heiling, O.A. Wedan and K. Griesse, J. Mol. Cat., 8, 253 (1980).

136. E. Canji and H. Perner, Recl. Trav. Chim., Pays.Bas., 96, M70 (1977).

137. F. Stelzer, C. Graiman and K. Hummel, *Colloid Polym. Sci.*, 260, 829 (1982).

138. D. Wewerke and K. Hummel, *Colloid Polym. Sci.*, 254, 116 (1976).

139. W. Kathan, O.A. Wedon and K. Hummel, *Makromol. Chem.*, 178, 1693 (1977).

140. K. Hummel, O.A. Wedon, W. Kathan and H. Demel, *Makromol. Chem.*, 179, 1159 (1978).

141. F. Stelzer, R. Thummer and K. Hummel, *Colloid Polym. Sci.*, 225, 664 (1977).

142. F. Stelzer, K. Hummel and R. Thummer, Prog., *Colloid Polym. Sci.*, 66, 411 (1979).

143. R.L. Banks, D.S. Banasiak, P.S. Hudson and J.R. Norell, *J. Mol. Catal.*, 15, 21 (1982).

144. R.S. Logan and R.L. Banks, *Oil Gas J.*, 66, 131 (1968).

145. D.L. Crain and R.E. Reusser, *Am. Chem. Soc., Div. Petrol. Chem. Prepr.*, 17, E80 (1972).

146. K.L. Anderson and T.D. Brown, *Hydrocarbon Processing*, 119 (1976).

147. F.W. Kupper and R. Streck, *Chem. Ztg.*, 99, 464 (1975).

148. P. Le Delliou, *Caout. Plast.*, 77 (1977).

149. R.F. Ohm, *Chem. Tech.*, 183 (1980).

150. T. Ueshima and S. Kobayashi, *Jpn. Plast.*, 8, 11 (1974).

151. N. Calderon and R.L. Hinrichs, *Chem. Tech.*, 627 (1974).

152. W. Graulich, *Kautsch, Gummi, Kunstst.*, 26, 380 (1973).

153. K. Alder, S. Hartung and O. Netz, *Chem. Ber.*, 90, 1 (1957).

154. B. John and H. Anthony, *Brit.*, 796, 133 (1958).

155. M.A.P. Bow, R.G.J. Miller, J.R. Rose and D.G.M. Wood, *J. Chem. Soc.*, 1541 (1960).

156. R.B. King and F.G.A. Stone, *J. Amer. Chem. Soc.*, 83, 3590 (1961).

157. P.E. Hoch, U.S. Patent, 3, 220, 988 (1965).

158. J.A. Claisse and D.I. Davies, J. Chem. Soc., C. Org., 11, 1045 (1966).

159. S.W. Tinsley and D.L. Macpeek, U.S. Patent, 3, 238, 227 (1966).

160. D.N. Butler and R.A. Snow, Can. J. Chem., 50, 795 (1972).

161. P. Asmus and M. Klessinger, Tetrahedron, 30, 2477 (1974).

162. D.N. Butler and R.A. Snow, Can. J. Chem., 53, 256 (1975).

163. W.R. Roth, H. Humbert, G. Wegener, G. Erken and H.D. Exner, Chem. Ber., 108, 1655 (1975).

164. M. Hardy, P.A. Carrupt and P. Vogel, Helv. Chim. Acta, 59, 1685 (1976).

165. L.A. Paquette, D.H. Cottrell and R.A. Snow, J. Amer. Chem. Soc., 99, 3723 (1977).

166. J.M. Sonney and P. Vogel, Tetrahedron Lett., 9, 829 (1978).

167. D.E. Axelson and C.E. Holloway, Can. J. Chem., 58, 1679 (1980).

168. M.C. Böhm, R.V.C. Carr, R. Gleiter and L.A. Paquette, J. Amer. Chem. Soc., 102, 7218 (1980).

169. J.H. Edwards and W.J. Feast, Polymer, 21, 595 (1980).

170. K. Harper, Ph.D. Thesis, Durham University, Durham (1982).

171. M.M. Ahmad and W.J. Feast, submitted for publication.

172. T. Ito, H. Shirakawa and S. Ikeda, J. Polym. Sci., Polym. Chem., 12, 11 (1974).

173. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, J. Chem. Soc. Chem. Commun., 578 (1977).

174. C.K. Chiang, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis and A.G. MacDiarmid, Phys. Rev. Lett., 39, 1098 (1977).

175. C.K. Chiang, M.A. Druy, S.C. Gau, A.J. Heeger, E.J. Louis, A.C. MacDiarmid, Y.W. Park and H. Shirakawa, J. Amer. Chem. Soc., 100, 1013 (1978).

176. K.J. Ivin, D.T. Laverty, B.S.R. Reddy and J.J. Rooney, Makromol. Chem., Rapid Commun., 1, 467 (1980).

177. M. Thakur and J.B. Lando, Macromolecules, 16, 143 (1983).

178. M. Stiles and R.G. Miller, J. Amer. Chem. Soc., 82, 3802 (1960).

179. R.S. Berry, G.N. Spokes and M. Stiles, ibid., 82, 5240 (1960); 84, 3750 (1962).

180. M. Stiles, R.G. Miller and U.R.S. Burckhardt, J. Amer. Chem. Soc., 85, 1792 (1963).

181. L. Friedman and F.M. Logullo, J. Amer. Chem. Soc., 85, 1549 (1963).

182. G. Wittig and E. Krauss, Ber., 91, 895 (1958).

183. R. Huisgen and P. Knorr, Naturwissenschaften, 48, 716 (1961).

184. T.F. Mich, E.J. Nienhouse, T.E. Farina and J.J. Tufariello, J. Chem. Edu., 45, 272 (1968).

185. R.M. Silverstein, C.G. Bassler and T.C. Morrill, Spectrocopic Identification of Organic Compounds (1974).

186. American Petroleum Research Institute, Research Project 44, Catalogue of Selected U.V. Spectra.

187. G.M. Brooke, R.S. Matthews and A.C. Young, J. Chem. Soc. Perk. Trans. I, 1411 (1977).

188. D.D. Callander, P.L. Coe, J.C. Tatlow and A.J. Uff, Tetrahedron, 25, 25 (1969).

189. G.M. Brooke and A.C. Young, Journal of Fluorine Chemistry, 223 (1976).

190. B. Hankison, H. Heaney, A.P. Price and R.M. Sharma, J. Chem. Soc. Perk. Trans. I, 2569 (1973).

191. G. Natta, P. Pino, F. Corradini, E. Manteca, G. Mazzanti and G. Moragi, J. Amer. Chem. Soc., 77, 1708 (1955).

192. K.J. Ivin, Olefin Metathesis, Academic Press, London, 228 (1983).

193. E.A. Ofstead, J.P. Lawrence, M.L. Senyek and N. Calderon, J. Mol. Cat., 8, 227 (1980).

194. A.P. Sheinker, M.K. Yakovleva, N.P. Bessonova, Z.F.I. Iicheva, Y.K. Godovskii and A.D. Abkin, Dokl. Chem., 247, 602 (1979).

195. A. Wasserman, Diels-Alder Reactions, Elsevier, New York (1965).

196. J.P. Kennedy, H.S. Makowski, J. Macromol. Sci., Chem. I, 345 (1967).

197. G. Sartori, A. Valvassori, V. Turba, M.P. Lachi, Chim. Ind. (Milan), 45, 1529 (1963).

198. K.J. Ivin, D.T. Laverty, J.J. Rooney, Makromol. Chem., 178, 1545 (1977).

199. E.A. Collins, J. Bares and F.W. Billmeyer, Experiments in Polymer Science, John Wiley and Sons, 357 (1973).

200. J.F. Henderson and M. Szwarc, Macromol. Revs., 3, 317 (1968).

201. M. Szwarc, in "Living Polymers", pp. 303-325 in Herman, F. Mark, N.G. Gaylozd and N.M. Bikales eds., Encyclopaedia of Polymer Science and Technology, Vol. 8, Interscience Div., John Wiley and Sons, New York (1968).

202. K.J. Ivin, D.T. Laverty and J.J. Rooney, Makromol. Chem., 179, 253 (1978).

203. K.J. Ivin, D.T. Laverty, J.J. Rooney and P. Walt, Recl. Trav. Chim. Pays. Bas., 26, M54 (1977).

204. K.J. Ivin, G. Lapienis and J.J. Rooney, Polymer, 436 (1980).

205. K.J. Ivin, G. Lapienis and J.J. Rooney, J. Chem. Soc. Chem. Commun., 1068 (1979).

206. K.J. Ivin, Pure and Appl. Chem., 52, 1907 (1980).

207. K.J. Ivin, J.J. Rooney, L. Bencze, J.G. Hamilton, L.M. Lam, G. Lapienis, B.S.R. Reddy and H.T. Ho, Pure and Appl. Chem., 54, 447 (1982).

208. K.J. Ivin, L.M. Lam and J.J. Rooney, Makromol. Chem., 182, 1847 (1981).

209. K.J. Ivin, G. Lapienis, J.J. Rooney and C.D. Stewart, J. Mol. Catal., 8, 208 (1980).

210. K.J. Ivin, Olefin Metathesis, Academic Press, London, 216 (1983).

211. H.T. Ho, K.T. Ivin and J.J. Rooney, J. Mol. Catal., 15, 245 (1982).

212. W.S. Potts, Chemical Infrared Spectroscopy, John Wiley and Sons, New York (1964).

213. J.L. Koenig, Chemical Microstructure of Polymer Chains, John Wiley and Sons, New York, 182 (1980).

214. C.J. Henniker, Infrared Spectroscopy of Industrial Polymers, Academic Press, London (1967).

215. J. Haslam, H.A. Willis and M. Squirrell, Identification and Analysis of Plastics, 2nd ed., Ileffe, London (1972).

216. J. Higgins and P. Miller, in "Laboratory Methods in Infrared Spectroscopy", 2nd ed., Miller and Stace, Heyden, Philadelphia (1972).

217. N.J. Harnick, Internal Reflection Spectroscopy, Wiley-Interscience Publishers, New York (1967).

218. P.R. Griffiths, Chemical Infrared Fourier Transform Spectroscopy, John Wiley and Sons, New York (1975).

219. J.L. Koenig, Appl. Spectrosc., 29, 293 (1975).

220. J.C. Moore, J. Polym. Sci., A2, 835-843 (1964).

221. J. Cazes, J. Chem. Educ., 47, A461 (1970); A505 (1970).

222. H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J.-G. Zilliox, J. Chem. Phys., 63, 1507 (1966).

223. Z. Zlanal, "Kinetics and Mechanism of Polymerization", 1, 11 ed. G.E. Ham, Marcel Dekker, New York (1969).

224. P.H. Plesch, Progress in High Polymers, 2, 137 (1968).

225. P.J. Flory, *J. Amer. Chem. Soc.*, 59, 241 (1937).

226. R.H. Snyder, J.M. Stewart, R.E. Allen and R.J. Dearbon, *J. Amer. Chem. Soc.*, 68, 1422 (1946).

227. F.T. Vall, F.W. Banes and G.D. Sands, *ibid.*, 68, 1429 (1946).

228. I. Millichamp, Ph.D. Thesis, Durham University, Durham (1983).

229. P.M. Blackmore, unpublished results (1984).

230. J.G. Hamilton, K.J. Ivin and J.J. Rooney, *Brit. Pol. J.*, 16, 21 (1984).