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SOME STUDIES IN STEP-GROWTH PHOTOREDUCTIVE POLYMERIZATIONS

A thesis submitted for the degree of Master of Science

by

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(Graduate Society)

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1978

TO MY PARENTS

SUMMARY

This thesis describes some studies in the area of step-growth photoreductive polymerization.

The monomers used were meta-dibenzoylbenzene and meta - and para - bisbenzhydrols. Equimolar mixtures of diketone and diol were irradiated under a variety of conditions in an attempt to attain the optimum degree of polymerization for the product polypinacols.

The polypinacols obtained were isomerized to polypinacolones, which were reduced and then dehydrated in an attempt to synthesize a totally conjugated system. This aspect of the work was only partially successful and the problems encountered are discussed in the last chapter of the thesis.

I would like to thank Dr. W.J. Feast for his encouragement and unfailing support throughout the supervision of this work.

I am indebted to all the technical and laboratory staff for their constructive advice and assistance, as well as to the staff and partners of Mann Judd.

MEMORANDUM

The work of this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1977 and September 1978. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

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CHAPTER 1

STEP-GROWTH PHOTOPOLYMERIZATION

1.1 INTRODUCTION

In this chapter the context and objectives of the work to be described subsequently are set out. It seems appropriate to start with a brief discussion of the classification of polymer forming reactions and the associated terminology, since the process of classification has played an important role in clarifying our understanding of the subject and the terminology used in this area has been the subject of recent redefinition.

1.2 POLYMER CLASSIFICATION

In 1929, Carothers[1] formulated the first important though rather general classification of polymers and polymer forming reactions. He classified the subject into two broad sections, addition polymerizations leading to addition polymers and condensation polymerizations leading to condensation polymers. In the former process the products have repeating units containing the same number and sequence of constituent atoms as those of the monomers and the polymer molecular weight ($\bar{M}$) is a simple summation of the monomer molecular weights. Condensation polymers, on the other hand, have repeating units containing fewer atoms than the monomers from which the polymer was formed and consequently $\bar{M}$ for these products is less than the sum of molecular weights of the reacting monomers.

The shortcoming of Carothers classification arises from the fact that polymers having the same chemical structure may be made via either route, and the physical properties of the resulting polymers are found to be independent of the type of polymerization. For example, polymethylene formed by a Wurtz reaction from 1,10 - dibromodecane (condensation polymerization) is a low melting wax whereas samples of polymethylene formed by the copper catalysed decomposition of diazo-methane[2] (condensation) or the polymerization of ethylene (addition) both yield the familiar plastic material, polyethylene[3]. Several other examples of the same type are known and these observations led to a reconsideration of polymer classifications. The whole subject of polymer classification has been discussed at length by Lenz[4] who advocates a classification based on three considerations. Firstly the addition/condensation classification outlined above, secondly whether the polymer chain grows by a step-growth or chain-growth process and thirdly the effectiveness of the process as measured by the high or low molecular weight attained. Three criteria, each having two options leads to eight main classes. The important point emphasised by this new classification is the nature of the process by which polymer molecules may be built up and this aspect is discussed in more detail below.

1.3 POLYMER GROWTH MECHANISMS

a) Chain-Growth Polymerization

This type of reaction proceeds via the following steps; initiation, propagation and termination, each involving a different mechanism and rate of reaction. The overall rate is usually faster than that of a typical step-growth polymerization and the product tends to have a high molecular weight. The essential feature of this type of process is that monomer units react only with the reactive chain ends and consequently high molecular weight products can be formed in the presence of monomer.

b) Step-Growth Polymerization

In this case the polymer chain grows at a relatively slow rate over a much longer period of time compared with chain-growth polymerization.

In step-growth polymerization the functional group of the monomer has the same reactivity as the functional group on the end of a growing polymer chain, consequently monomer units can react with other monomer units or polymer chains with equal ease.

Table 1-1[5] lists the important differences between the two growth processes.

TABLE 1-1

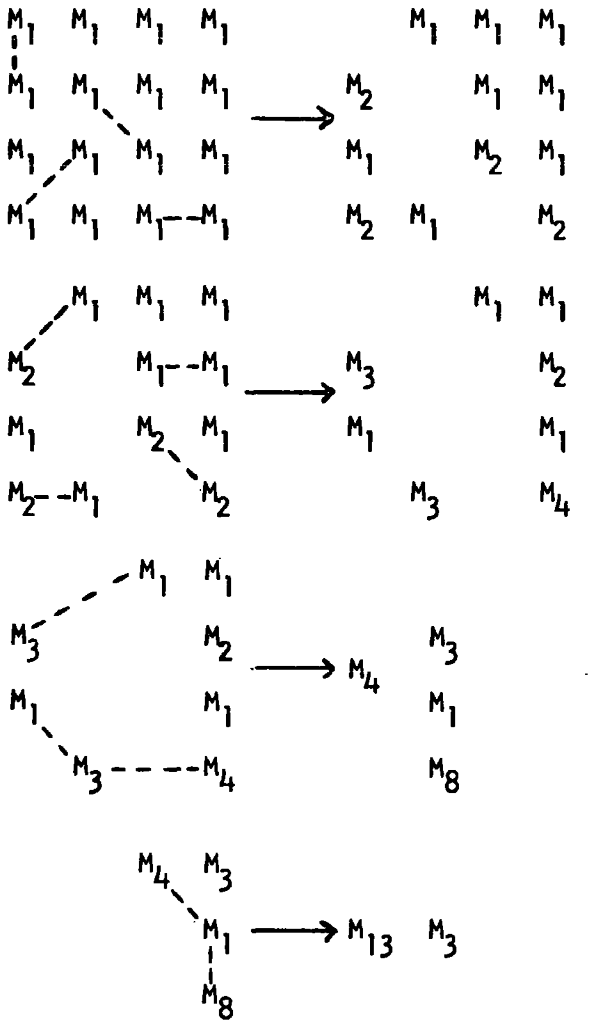
Characteristics of the Limiting Types of Polymerization Reactions

Characteristic	Step-Growth Polymerization	Chain-Growth Polymerization
Component Reactions	Initiation, propagation and termination reactions essentially identical in rate and mechanism.	Initiation, propagation and termination reactions significantly different in rate and mechanism.
Polymer Growth	Slow, random growth of polymer with high reaction conversion required for a high degree of polymerization.	Rapid, preferential growth of each polymer chain, once initiated, with high degrees of polymerization attained at the start of the reaction.
Reactivity of Monomer	Monomer capable of combining with itself or with any other species present with equal facility, resulting in rapid disappearance of monomer at early stages of the polymerization reaction.	Monomer capable of reacting only with an active end-group on a polymer chain, resulting in steadily decreasing but significant concentrations of monomer throughout the polymerization reaction.

Carothers showed that the attainable $\overline{D.P.}$ for a step-growth polymerization could be related to the reaction conversion by the simple expression -

$$\overline{D.P.} = \frac{1}{(1-p)}$$

- where p is the fractional conversion. The implication of this expression is that high $\overline{D.P.}$'s for step-growth processes can only be achieved at very high reaction conversions. This point is illustrated in the Fig. 1.1[4], in which it is evident that the random growth of the polymer permits only a gradual increase in molecular size. Applying Carothers' equation, assuming no side reactions occur it is easy to show that a $\overline{D.P.}$ of 16 requires a conversion of 93.75% and a $\overline{D.P.}$ of 50 requires 98% conversion.



25% reacted, $\overline{D.P.}$ = 2

50% reacted, $\overline{D.P.}$ = 3

75% reacted, $\overline{D.P.}$ = 5

87.5% reacted, $\overline{D.P.}$ = 8

1.4 PHOTOPOLYMERIZATION

Before the turn of the century Blythe and Hoffman made a polymer by irradiating styrene[5]. The whole process is initiated by U.V. light, which interacts with the monomer to produce radicals; propagation of the chain by addition of monomer to radical chain ends follows. Other compounds besides the monomer, may be used as initiators, for example organic sulphur compounds, azo compounds, metal carbonyls and peroxides[6]. The quantum yields for the above type of photopolymerizations can be of the order of 10^3 or more. The important point is that the light used creates the initiator in this type of photopolymerization, which then proceeds by a chain growth process.

Another important photochemical process that may take place is the cross-linking of polymers. The work of Minsk[7] was of prime importance in the development of this field, with his preparation of poly (vinyl cinnamate) and the use of dyes as a means of photosensitizing the cross-linking process. Examples of light sensitive units which may be incorporated into polymers are olefins, azides and diazonium salts.

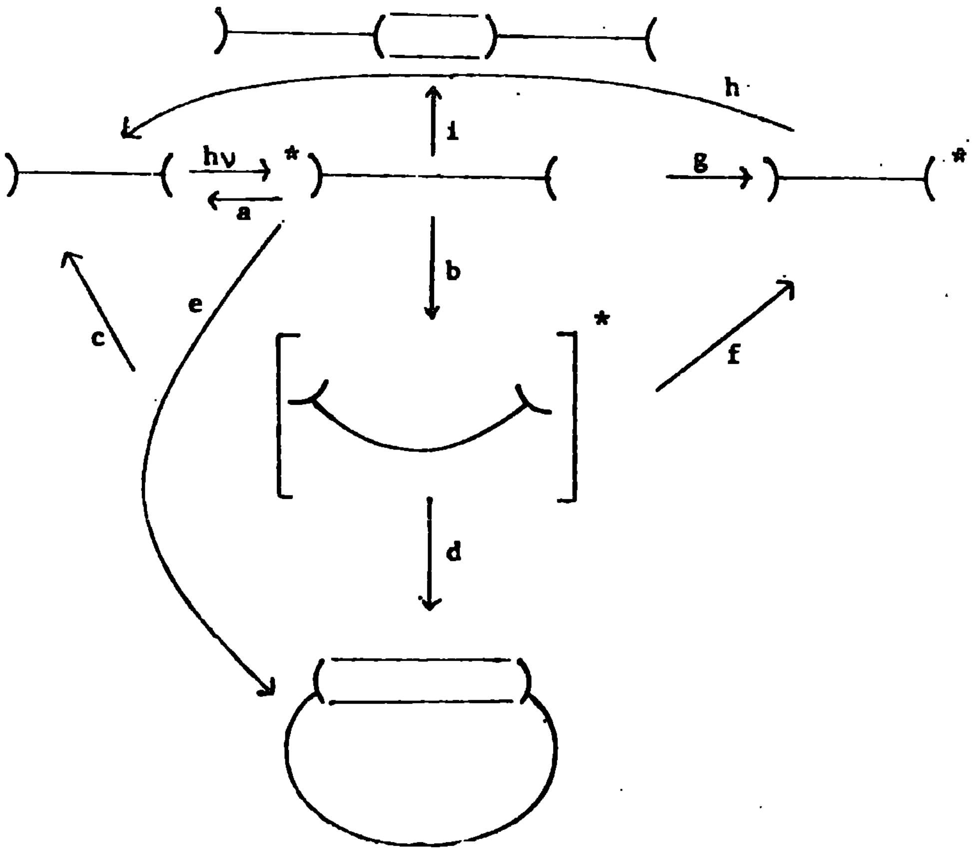
The two processes described above have commonly been referred to as photopolymerizations, both processes have been the subject of intensive research and commercial exploitation, particularly in the surface coatings, printing and electronic industries.

More recently examples have been published of polymerizations in which each new bond in the polymer backbone is formed as the result of a photochemical process and this has led Smets and De Schryver to suggest that the term photopolymerization should be redefined as a step-growth polymerization in which each propagating step requires the absorption of a quantum of light[8]. They go further and propose three classes within this redefined subject, depending on the species involved in the propagation step. This species may be a reactive ground state following a photochemical reaction, a singlet excited state or a triplet excited state.

The published examples of photopolymerization as redefined above, have involved irradiation of non-conjugated bichromophoric monomers (see later)[9]. However, it is worth pointing out that in the design of new photopolymerizations it is not sufficient to simply plan a synthesis of a new non-conjugated bichromophoric system which will then be irradiated, since a number of processes other than photopolymerization can occur, these are illustrated in Figure 1.2[9].

FIGURE 1.2

Possible reaction pathways in non-conjugated bichromophores



Key) = chromophoric group; * = photoexcited group.

The possible reaction pathways indicated in Figure 1.2 are:-

a) deactivation of the excited state returning the monomer to the ground state,

b) delocalization of the excited state over the two chromophores,

c) deactivation of the product resulting from b) to give starting material,

d) and e) formation of cyclomer,

f) and g) intramolecular energy transfer (when chromophores are not identical),

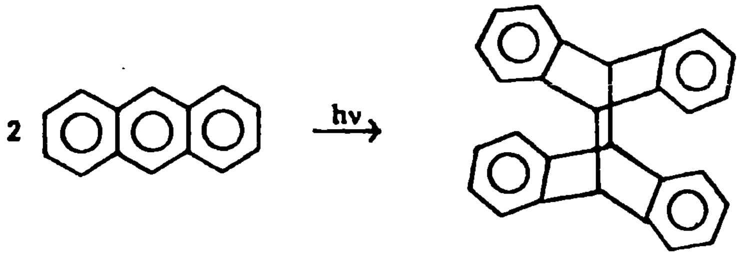
h) deactivation of the complex arising from intramolecular energy transfer,

i) All the above processes are an alternative to this path, which represents photopolymerization.

1.5 SOME EXAMPLES OF STEP-GROWTH PHOTOPOLYMERIZATION

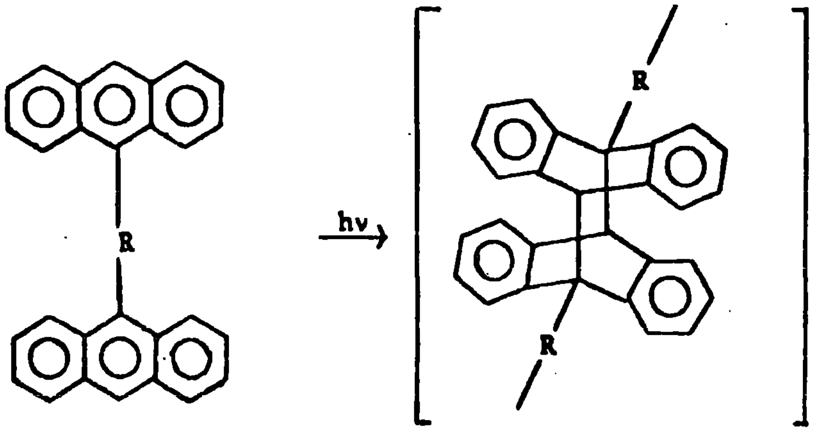
a) Photopolymerization via the Singlet State

When irradiated, anthracene undergoes photodimerization at the 9, 10 positions, and at the same time it looses its aromaticity and planarity, due in part to electrostatic repulsion[10] (1.1).



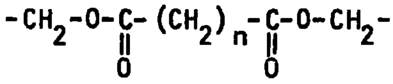
(1.1)

Extending the use of this reaction to the polymerization of bisanthracene has produced several polymers of the general structure indicated in Figure 1.3[11] (1.2)



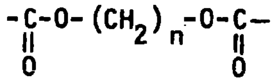
(1.2)

Polymers have been made where R =



$$-CH_2-O-\underset{\underset{O}{\|}}{C}-(CH_2)_n-\underset{\underset{O}{\|}}{C}-O-CH_2-$$

and R =

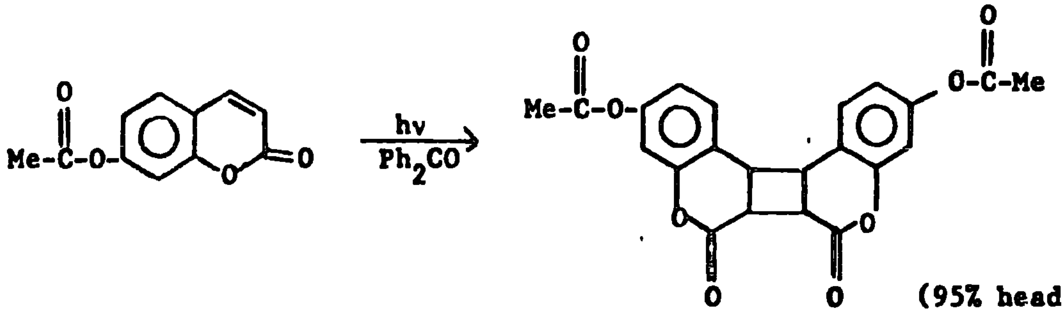


$$-\underset{\underset{O}{\|}}{C}-O-(CH_2)_n-O-\underset{\underset{O}{\|}}{C}-$$

An important point to note in relation to these results is that the polymers derived from bisanthracenes with R = $-CH_2-O-\underset{\underset{O}{\|}}{C}-(CH_2)_n-\underset{\underset{O}{\|}}{C}-O-CH_2-$ were invariably of significantly lower molecular weight than those derived from monomers where R = $-\underset{\underset{O}{\|}}{C}-O-(CH_2)_n-O-\underset{\underset{O}{\|}}{C}-$. This observation illustrates the potential importance of possible side reactions since in the former case a 1,5 - sigmatropic hydrogen shift (from the methylene at C-9 to the C-10 position) can act as a chain terminating competitor to the chain propagating anthracene dimerization. The result illustrates the particular importance of a detailed understanding of the model reaction in designing a photopolymerization.

b) Photopolymerization via the Triplet State

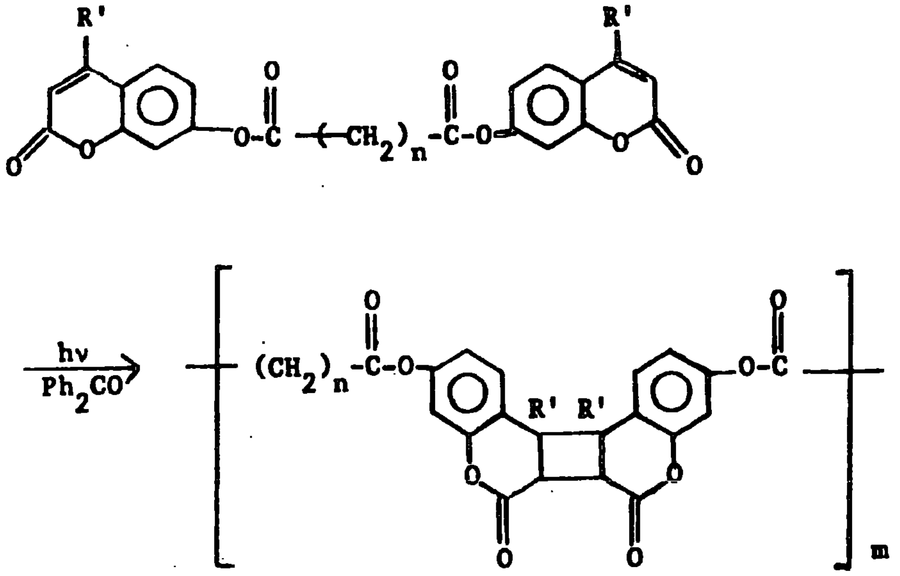
Coumarins may be dimerized via a benzophenone sensitized reaction as indicated below[12] (1.3)



(1.3)

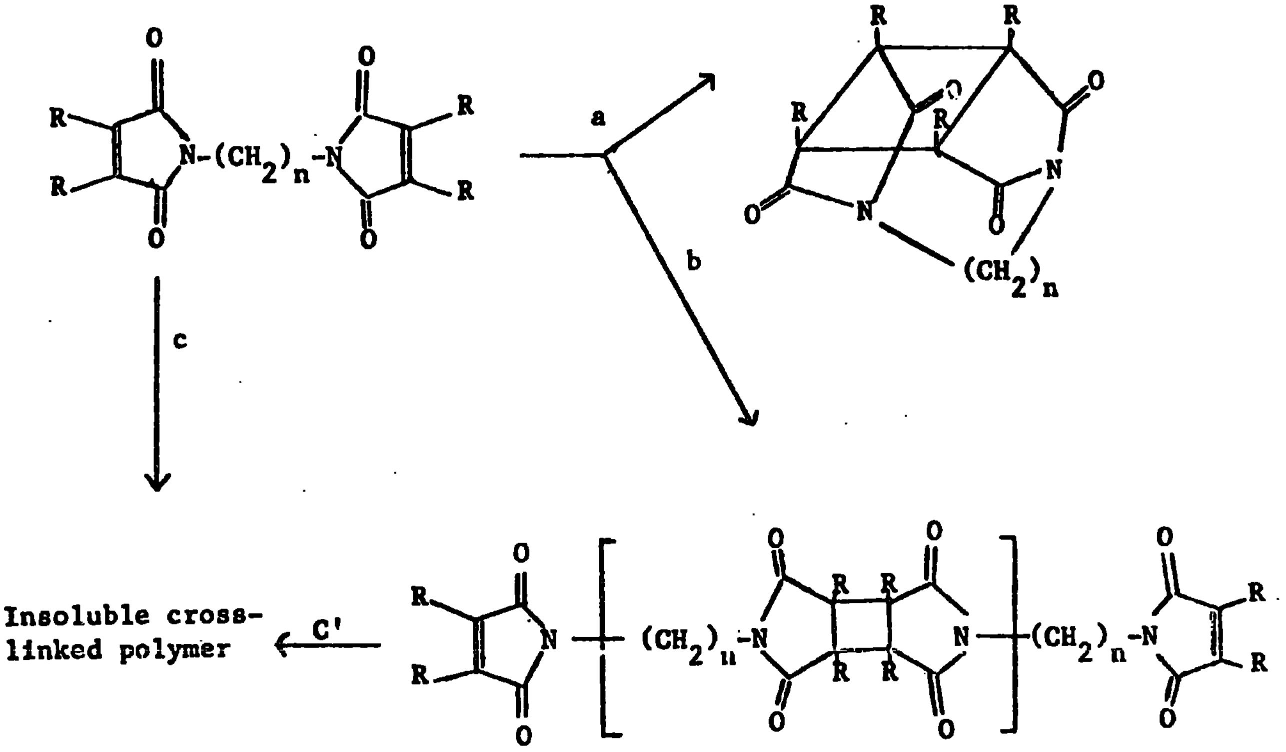
(95% head-to-head exo).

By analogy, biscoumarins have yielded polymers according to equation (1.4).[13]



(1.4)

Another example of this type of reaction is the 2 + 2 photocycloaddition of tetrachlorobismaleimides (sheme 1.5; route b; R=Cl).

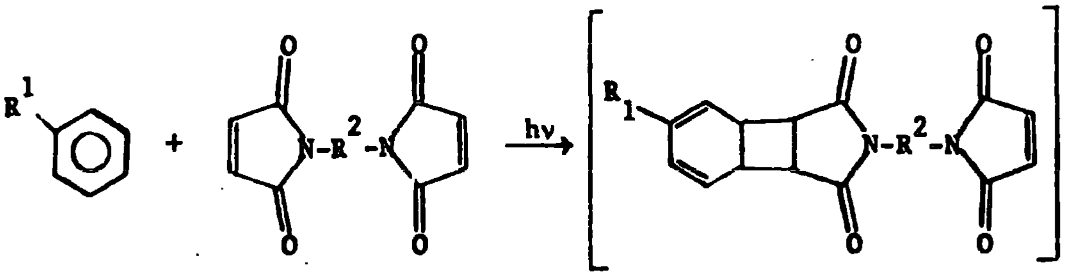


(1.5)

In the latter example, the authors emphasised the critical importance of monomer purity to successful polymerization. In practice, two samples of monomer purified by different techniques were apparently identical in all respects except that one yielded a genuine polymer on irradiation in the presence of benzophenone as triplet sensitizer whereas the other was recovered as unchanged monomer after the same treatment, the difference in behaviour being attributable to a low concentration of an unidentified but effective triplet quencher.

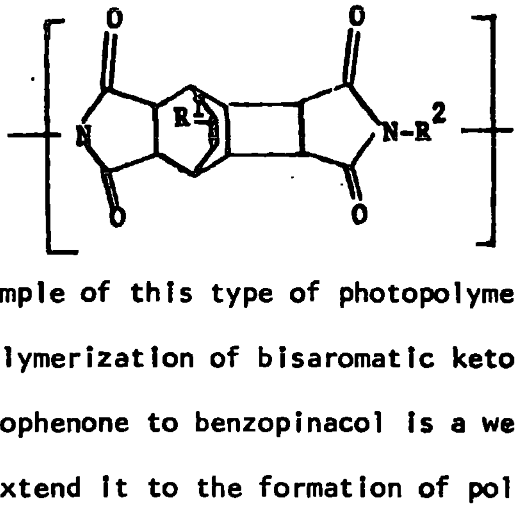
c) Photopolymerization via a Reactive Intermediate Formed in an Initial Photochemical Process

When bis-maleimides are irradiated in the presence of benzene or an alkyl benzene linear polymers are formed in a two stage process. In the first stage a maleimide unit adds photochemically to the aromatic ring (1.6).



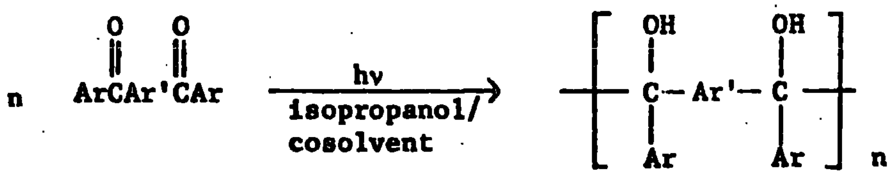
(1.6)

In the second stage this initial product reacts via a ground state Diels-Alder Cycloaddition reaction to give the final polymer (1.7).



(1.7)

Another example of this type of photopolymerization is the photoreductive polymerization of bisaromatic ketones. The photoreduction of benzophenone to benzopinacol is a well known reaction[14,15], and attempts to extend it to the formation of polybenzopinacols (1.8) have been described by several groups of workers[16-20].



$$n\ \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ar'}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ar}\ \xrightarrow[\text{isopropanol/ cosolvent}]{h\nu}\ \left[-\overset{\mathrm{OH}}{\underset{\mathrm{Ar}}{\mathrm{C}}}-\mathrm{Ar'}-\overset{\mathrm{OH}}{\underset{\mathrm{Ar}}{\mathrm{C}}}-\right]_n$$

(1.8)

This reaction will be discussed in greater detail in the next chapter, since attempts to utilize and extend its applicability form a substantial part of the work reported in this thesis.

CHAPTER 2

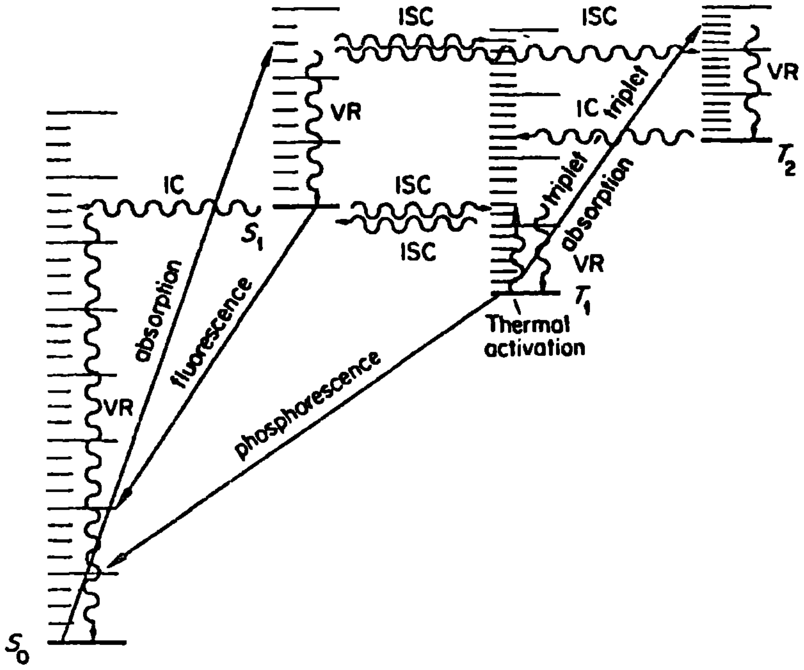
PHOTOREDUCTIVE POLYMERIZATION

2.1 PHOTOCHEMICAL PROCESSES

In most organic molecules the absorption of a quantum in the ultraviolet/visible region of the spectrum leads to a singlet excited state, which is slightly higher in energy than the triplet of the same electronic configuration. Fig 2.1 shows the major possible states for the molecule; their relative energies and the pathway between them as depicted in schematic form by Jablonski[21]. Before any emission of radiation or photochemical reaction, the two radiationless processes may occur:

i) Internal Conversion is a radiationless transition between degenerate states of the same multiplicity. Such transitions are extremely rapid, hence the negligible emission from upper states. Internal conversion from the first excited singlet state ($S_1 \rightarrow S_0$) is so much slower, that fluorescence can compete.

ii) Intersystem Crossing is a radiationless transition between states of different multiplicity. Deactivation of the lowest triplet by this route is a process in competition with normal phosphorescence. The intersystem crossing ($S_1 \rightarrow T_1$ or $S_1 \rightarrow T_n$) is competitive with fluorescence and is the process by which the triplet manifolds are normally populated. The transition $T_1 \rightarrow S_1$ is endothermic. Radiative transitions on the other hand involve an excited species passing from a higher excited state to a lower one with emission of a photon. The three processes described below can occur:



The Jablonski Diagram

Figure 2.1

iii) Fluorescence results from a radiative transition between states of the same multiplicity and is a rapid process ($K_f \sim 10^6 - 10^9 s^{-1}$). For polyatomic molecules encountered in organic chemistry the transition is usually $S_1 \rightarrow S_0$,

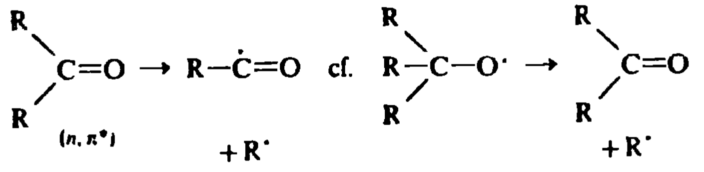
iv Phosphorescence is the result of a transition between states of different multiplicity typically $T_1 \rightarrow S_0$; $T_n \rightarrow S_0$ is very rare. The process, being spin forbidden, has a much smaller rate constant ($K_p \sim 10^{-2} - 10^4 s^{-1}$) than that for fluorescence.

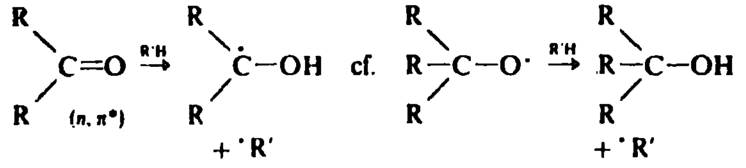
v) Delayed fluorescence differs from ordinary fluorescence in that the measured rate of decay of emission is less than that expected from the transition giving rise to the emission. The process is usually observed when excited singlets are populated via endothermic intersystem crossing from the corresponding triplets, or via triplet-triplet annihilation.

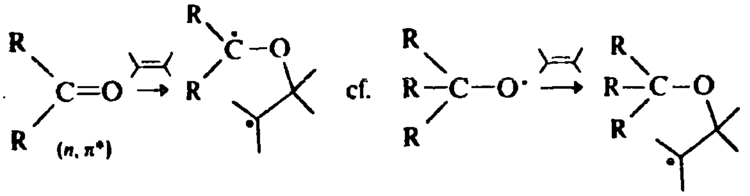
2.2 THE CARBONYL CHROMOPHORE

Compounds containing the carbonyl chromophore are among the most thoroughly investigated in photochemistry. Aliphatic ketones and aldehydes show a weak absorption band around 280 - 300 n.m. arising from the forbidden n, π^* transition. Strong absorption occurs in the vacuum ultraviolet region at 195, 170 and 155 n.m. associated with π, π^* transitions. The lowest triplet is an n, π^* state and this state is mainly responsible for the observed photochemistry of carbonyl compounds. Exceptions to this generalisation can occur where the carbonyl group is conjugated; in such compounds both the n, π^* and π, π^* states are lowered in energy. The detailed effect depends on the structure of the particular compound and the polarity of the solvent used. In some cases the π, π^* triplet can become the lowest energy excited state and in such cases the photochemical behaviour is not that typically associated with carbonyl compounds.

Upon excitation of the carbonyl chromphore an electron is transferred from a non-bonding orbital localized mainly on the oxygen atom to an anti-bonding π^* orbital which is associated with both the carbon and oxygen nuclei. As a consequence of this redistribution of electron density, nucleophilic attack at the carbon atom which typifies carbonyl chemistry, is no longer important; the electronic feature of the excited species of greatest significance is its resemblance to an alkoxy radical, and indeed its chemical reactivity is closely allied to that of alkoxy radicals. The major reactions of excited carbonyl compounds are cleavage of the C-C bond α to the carbonyl (Norrish Type 1), hydrogen abstraction reactions (Norrish Type 11) and addition reactions to olefins which find their parallels in the well known reactions of alkoxy radicals (2.1 - 2.3).

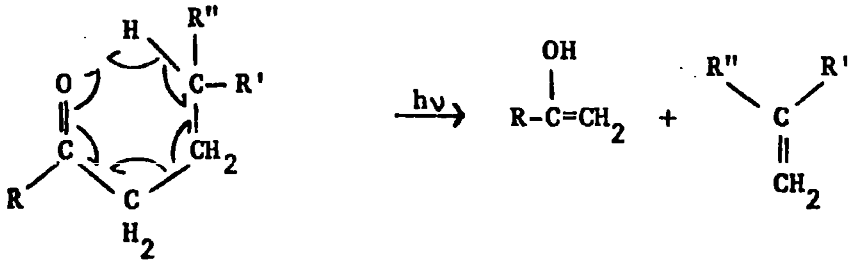

(2.1)


(2.2)


(2.3)

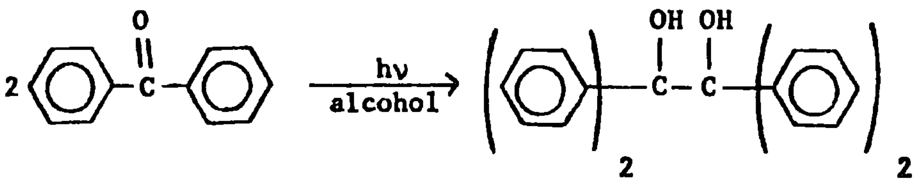
Norrish Type I cleavage may occur via either the excited triplet or singlet state and its extent is dependent on substitution at the carbon. This process is unimportant when considering solution phase photochemistry of diaryl ketonessuch as benzophenone, when an unstable phenyl radical would be produced.

Norrish Type II processes occur with carbonyl compounds possessing γ hydrogens which may be abstractable by the carbonyl group upon n,π excitation (2.4).


(2.4)

2.3 PHOTOREDUCTION OF CARBONYL COMPOUNDS

The photoreduction of carbonyl compounds in suitable hydrogen donating solvents has been investigated since the turn of the century[22]. The early work of Ciamician and Silver[23] indicated that benzophenone was reduced to benzopinacol on exposure of an alcoholic solution of the ketone to sunlight (2.5).



(2.5)

In the presence of alkali it was found that benzhydrol was formed[24]. Bachmann showed that in the presence of a sodium-2-propanolate a series of photoreductions of benzophenone and substituted benzophenones in isopropanol gave benzhydrols in high yields. The mechanism for the formation of benzhydrol from benzophenone in the presence of alkali is a matter in dispute[24,25].

The most intensively studied reaction is the actual photoreductive coupling yielding 1,2-ethanediols. Aldehydes and ketones both undergo the reaction[22], ketones having received by far the most attention. Benzophenone is the most thoroughly studied ketone, yielding benzopinacol in quantative yield. The quantum yield for the formation of acetone in the photoreduction of benzophenone in isopropanol is nearly constant using irradiation at several different wavelengths between 366 and 254 n.m. suggesting that both n, π^* excitation and π, π^* excitation may bring about the reaction[26,27]. Various solvents have been used as hydrogen donors, in particular alcohols and alkylbenzenes[28,29]. Many comparisons of solvents have been made with benzophenone as reacting ketone. Some quantum yields of benzophenone disappearance in various solvents are tabulated below (Table 2.1)[30].

SOLVENT	MOLAR CONCENTRATION OF BENZOPHENONE	QUANTUM YIELD OF DISAPPEARANCE
Water	10^{-4}	0.002
Benzene	10^{-2}	0.05
Toluene	10^{-2}	0.45
Hexane	10^{-2}- 10^{-4}	1.0
Ethanol	10^{-4}- 10^{-1}	1.0
Isopropanol	10^{-5}- 10^{-1}	0.8 to 2.0

If the bond energies for hydrogen abstraction are high enough ($>$ 100 K cal mole^{-1}) to prevent hydrogen abstraction by the triplet with anything other than very low collisional efficiency[29], the quantum yields of benzophenone disappearance will tend to zero. For hexane, toluene and ethanol, quantum yields are less than or equal to unity and independent of concentration, and it is suggested that all benzophenone triplets abstract a hydrogen atom, the appropriate C-H bond energies in hexane and toluene being approximately 85 and 80 Kcal mole^{-1} respectively. The thermal reactions of the radical R$^\cdot$ formed on abstraction from the solvent RH will affect the overall quantum yield. The reversal of the abstraction reaction can result in and overall quantum yield of less than unity (2.6).

$$Ph_2\dot{C}OH + R^\cdot \longrightarrow Ph_2CO + RH \qquad (2.6)$$

Whereas quantum yields in isopropanol tend to a limiting value of 2, since the solvent radical ($(CH_3)_2\dot{C}OH$) may transfer a hydrogen to a ground state benzophenone with the production of acetone and a diphenyl ketyl radical (2.7).

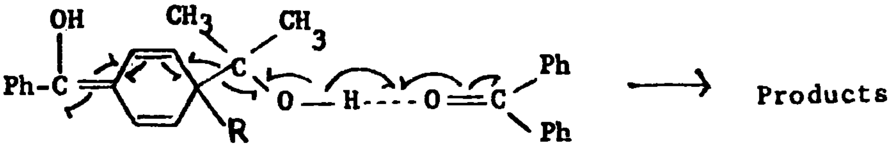
$$(CH_3)_2\dot{C}OH + Ph_2CO \longrightarrow (CH_3)_2CO + Ph_2\dot{C}OH \qquad (2.7)$$

Such transfer reactions are energetically improbable in the benzyl or hexyl radicals derived from toluene or hexane. The in-cage dimer, derived from the ketyl and solvent radicals was detected in early investigations of photoreduction in toluene, but failure to detect the in-cage dimer for photoreductions in isopropanol led to considerable dispute and discussion of the mechanism of this process.

The structure of the possible intermediates involved has been the subject of much controversy; for example Filipescu has proposed that the yellow colour frequently observed during irradiation of solutions of aromatic ketones is caused by an intermediate of structure (I) in the case of benzophenone and 4-alkyl substituted benzophenones. He suggested the reaction scheme (2.8).

$$\begin{aligned}
&Ph_2CO(T_1) + (CH_3)_2CHOH \longrightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH \\
&Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH \longrightarrow (I)\ (R{=}H) \\
&I + Ph_2CO \longrightarrow 2Ph_2\dot{C}OH + (CH_3)_2CO \\
&2Ph_2\dot{C}OH \longrightarrow Ph_2C(OH)C(OH)Ph_2
\end{aligned} \tag{2.8}$$

It was proposed that (I) yielded products via a ground state reaction (2.9).



(2.9)

Recent work by Weiner[31] appears to have established the mechanism of photoreduction of benzophenone in isopropanol beyond reasonable doubt and he also isolated the elusive in-cage dimer. The mechanism is summarized in scheme (2.10).

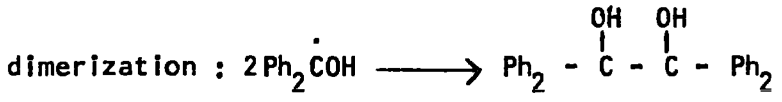
$$Ph_2CO(T_1) + (CH_3)_2CHOH \longrightarrow \underset{(c)}{\overline{Ph_2\dot{C}OH \quad (CH_3)_2\dot{C}OH}}$$

$$\text{Spin flip, in-cage combination (c)} \longrightarrow Ph_2C(OH)C(OH)(CH_3)_2$$

$$\text{In cage H - transfer (c)} \longrightarrow Ph_2CHOH + (CH_3)_2CO \qquad (2.10)$$

$$\text{migration out of cage (c)} \longrightarrow Ph_2\dot{C}OH + (CH_3)_2\dot{C}OH$$

$$\text{H - transfer } (CH_3)_2\dot{C}OH + Ph_2CO \longrightarrow (CH_3)_2CO + Ph_2\dot{C}OH$$



$$\text{dimerization : } 2Ph_2\dot{C}OH \longrightarrow Ph_2 - \overset{\overset{OH}{|}}{C} - \overset{\overset{OH}{|}}{C} - Ph_2$$

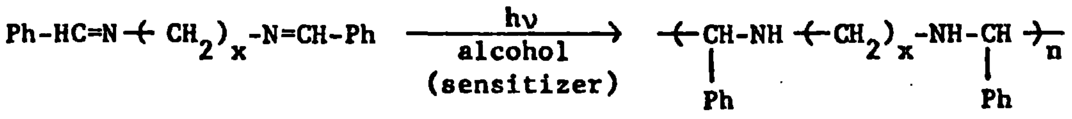
The significant proportion of cage reaction (11%) requires that in the pair of radicals comprising (C) (where the electron spins are initially parallel), spin flipping must occur in some radical pairs prior to diffusion out of the solvent cage.

The majority of photoreductive processes with quantum yields approaching unity occur when the n, π^* triplet is the lowest lying excited state. The effectiveness of the reaction has been attributed to the highly localised n electron on the oxygen. In cases where the π, π^* triplet is the lowest excited state the unpaired electrons are more delocalized and hydrogen abstraction is usually endothermic and relatively inefficient[32,33].

A third type of possible lowest lying triplet state is a charge-transfer state[34]. Such states have been extensively investigated and occur in aromatic ketones where an electron donor substituent (such as hydroxyl, amino, methoxy, etc.) is situated para with respect to the carbonyl group.

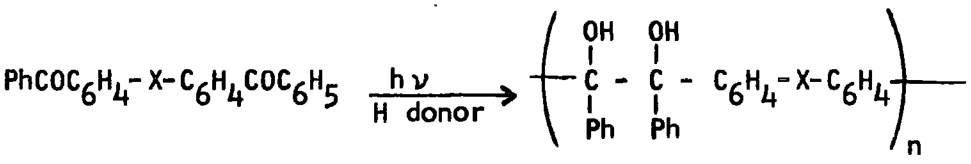
2.4 PHOTOREDUCTIVE POLYMERIZATION

The photochemical reductive coupling of a bisimine has been utilised in polymer synthesis (2.11).



$$Ph\text{-}HC{=}N(CH_2)_x\text{-}N{=}CH\text{-}Ph \xrightarrow[\text{alcohol (sensitizer)}]{h\nu} \left(\underset{\underset{Ph}{|}}{CH}\text{-}NH(CH_2)_x\text{-}NH\text{-}\underset{\underset{Ph}{|}}{CH} \right)_n \qquad (2.11)$$

However, considerably more work has been reported on the photoreductive coupling of aromatic diketones, and this work is directly relevant to the main objectives of the work reported here. The process can be summarized as shown below, bisbenzophenone being photoreduced to a polybenzopinacol (2.12).

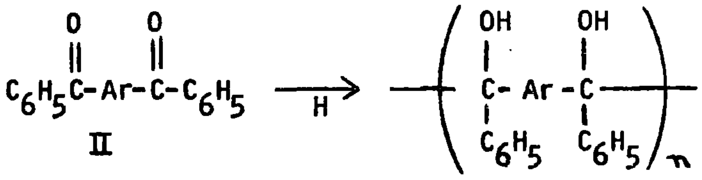


$$PhCOC_6H_4-X-C_6H_4COC_6H_5 \xrightarrow[\text{H donor}]{h\nu} \left(\overset{OH}{\underset{Ph}{C}} - \overset{OH}{\underset{Ph}{C}} - C_6H_4-X-C_6H_4 \right)_n \qquad (2.12)$$

The idea is simple and it is not too surprising to find that two of the first papers on the subject of step-growth photopolymerization described attempts to realise the synthesis indicated above.

2.4 a) Early results on photoreductive polymerizations of diketones

The first being by Higgins et al[16] who obtained low molecular weight polybenzopinacols on irradiation of benzene-isopropanol solutions of aromatic diketones (IIa—c), their results are summarized below (2.13) and in Table 2.2.

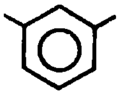


$$C_6H_5\overset{O}{\overset{\|}{C}}-Ar-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[H]{} \left(\overset{OH}{\underset{C_6H_5}{C}}-Ar-\overset{OH}{\underset{C_6H_5}{C}} \right)_n \qquad (2.13)$$

II

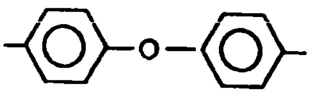
III

a, Ar =



b, Ar =

c, Ar =



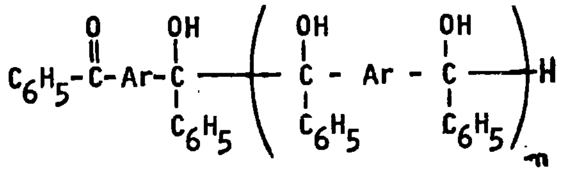
Polymer Properties

Polymer	Viscosity	M.Pt.	$\overline{M}$	$\overline{D.P.}$
IIIa	0.12	140	825	~3
IIIb	0.06	135	435	~1·5
IIIc	0.14	160	805	~2

Table 2.2

From the data (table 2.2) it is evident that only dimers and trimers were obtained. The infrared spectra of the products showed a small peak remaining at 1650 cm^{-1} indicating unreacted carbonyl groups were present.

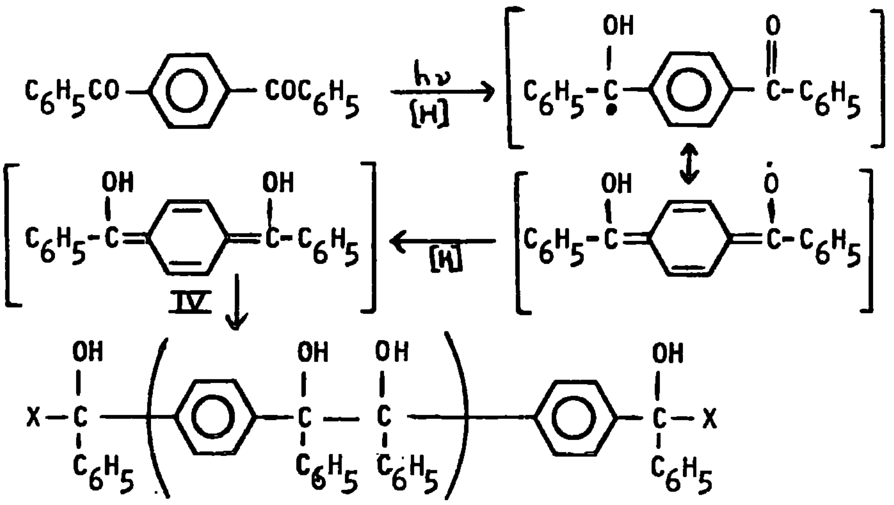
The authors suggested possible explanations for the above observations. The low $\overline{D.P.}$'s obtained were attributed to complete reduction of the carbonyl function to a benzhydrol like chain end, as illustrated in structure 2.14. The residual



$$C_6H_5-\overset{O}{\overset{\|}{C}}-Ar-\underset{C_6H_5}{\overset{OH}{C}}\left(\underset{C_6H_5}{\overset{OH}{C}}-Ar-\underset{C_6H_5}{\overset{OH}{C}}\right)_n H \qquad (2.14)$$

carbonyl function was accounted for in terms of chain ends (see 2.1) and unreacted monomer. However, the explanation of low $\overline{D.P.}$'s in terms of benzhydrol like units seems unlikely to be valid in view of results obtained subsequently by other workers (see later). They concluded by stating that the reactivities of the radical intermediates involved in this attempted polymerization appeared to be different to those involved in the model reaction, namely benzophenone photoreduction.

At about the same time Pearson and Thiemann[17] worked on just one of the monomers investigated by Higgins. They irradiated p-dibenzoylbenzene in an isopropanol-benzene mixture and obtained a product with a molecular weight of 1570 whereas Higgins had reported a value of 435. The solvent compositions differed for these two experiments, on a volume basis Higgins' work used a 1 : 1 benzene : isopropanol mixture whereas Pearson's work used a 3 : 1 ratio; the importance of solvent composition will be referred to again later. Pearson and Thiemann proposed the reaction sequence shown in scheme (2.15).



(2.15)

Where X, the capping group is partly $(CH_3)_2$-COH, partly H and partly where the ends of the polymer are cyclised at the X positions. They also attributed the yellow colouration typical of these reactions to the structure IV, because of the long wavelength absorption and the relative stability of the intermediate, though it is observed to decay with time. Although as the authors point out, the yellow colouration is also observed for the m-dibenzoylbenzene case where such a structure is not possible.

These early attempts were not very successful; degrees of polymerization of 4 to 5 being obtained. The major reasons why they were not successful may be summarised as follows :-

a) the materials used were insufficiently purified (in Chapter 1 the importance of monomer purity was emphasised), and

b) insufficient effort was made to optimise solution compositions from the point of view of reaching a satisfactory compromise between the demands of monomer and polymer solubility and the provision of sufficient H donor capacity.

Some of this work was subsequently repeated in these laboratories using the same conditions as reported by the earlier workers

(Higgins group), they had stated that a 50/50 V/V mixture of benzene : isopropanol provides the optimum solvent system for these reactions, yet when Andrews[19] repeated their work under apparently identical conditions, a substantial improvement in $\overline{\text{D.P.}}$ was observed, indicating perhaps a better momomer purity. For example the irradiation of m-dibenzoylbenzene in a 1 : 1 benzene : isopropanol mixture gave Andrews a product with a $\overline{M}_n$ = 4800, whereas the earlier workers had obtained a product with $\overline{M}_n$ = 825. In an attempt to optimise the attainable $\overline{\text{D.P.}}$'s for such systems, Andrews investigated the effect of varying the solution compositions. He observed that use of a benzene/isopropanol ratio between 3 : 1 and 4 : 1 resulted in a marked improvement, in that no precipitation occurred during irradiation and a faster rate of disappearance of carbonyl in those solutions with the higher ratio of benzene. Generally there was also a significant improvement in molecular weight (Table 2.3). This improvement may be due in part to a reduction in the importance of termination via coupling with the isopropanol radicals.

Molecular Weights, Degrees of Polymerization of Polybenzopinacols Prepared in 1 : 1 and 3 : 1 - 4 : 1 Benzene-Isopropanol Mixtures[19]

Table 2.3

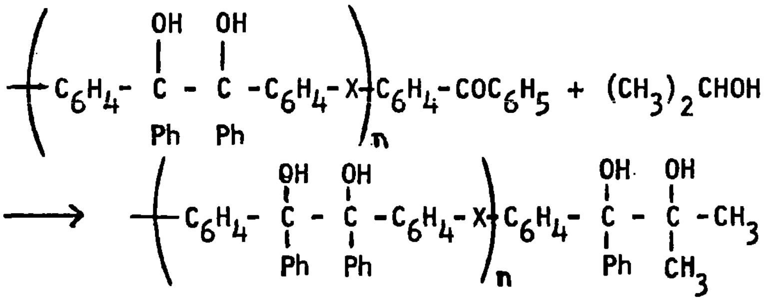
Polymer	Molecular Weight (D.P.)	
	1:1	3:1 - 4:1
Polypinacol M	4800	-
" P	1300	-
" E	3400	-
" 1	950	14700
" 2	2700	3700
" 3	2300	4400
" 4	3500	-
" 5	9100	7900
" 6	10300	-
" 10	12600	-

Where the following momomers used were :-

	Abbreviation
m - dibenzoylbenzene	M (ie IIa)
p - dibenzoylbenzene	P (ie IIb)
4,4' dibenzoyldiphenyl ether	E (ie IIc)
4,4' dibenzoyldiphenyl methane	1 (ie IId)
1,2 - (4,4' - dibenzoyldiphenyl) ethane	2
1,3 - (4,4' - dibenzoyldiphenyl) propane	3
1,4 - (4,4' - dibenzoyldiphenyl) butane	4
1,5 - (4,4' - dibenzoyldiphenyl) pentane	5
1,6 - (4,4' - dibenzoyldiphenyl) hexane	6
1,10 (4,4' - dibenzoyldiphenyl) decane	10 (ie IIe)

Andrews' results showed the potential of this approach to the synthesis of high molecular weight polypinacols although he did not carry out a detailed optimization of the experimental variables.

The best results to date in this field were obtained by De Schryver and co-workers[18] after careful consideration of the details of benzophenone photoreduction as elucidated by Weiner and discussed in Section 2.3. It is clear that any in-cage combination of the diphenyl ketyl radical and the radical derived from the hydrogen donor molecule is chain terminating as far as step-growth photopolymerization is concerned (2.16).



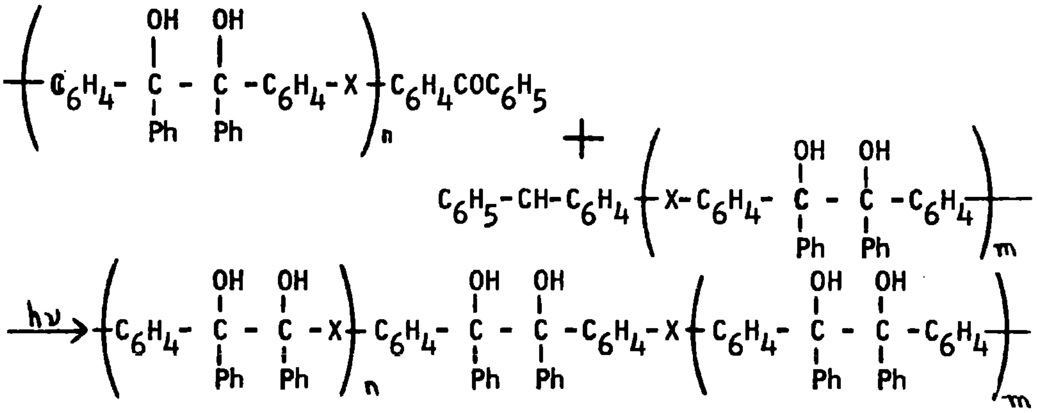
$$\left(-C_6H_4-\underset{Ph}{\overset{OH}{C}}-\underset{Ph}{\overset{OH}{C}}-C_6H_4-X-\right)_n C_6H_4-COC_6H_5 + (CH_3)_2CHOH$$
$$\longrightarrow \left(-C_6H_4-\underset{Ph}{\overset{OH}{C}}-\underset{Ph}{\overset{OH}{C}}-C_6H_4-X-\right)_n C_6H_4-\underset{Ph}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

(2.16)

Chain termination with isopropanol as donor

The Belgian's solution to this problem was the simple and elegant step of making the hydrogen donor a monomer for the polymerization.

Thus, when an appropriate diketone and a bisbenzhydrol are irradiated, the triplet carbonyl abstracts a hydrogen atom from a benzhydrol unit to generate a solvent caged pair of diaryl ketyl radicals (2.17). These results are discussed below.



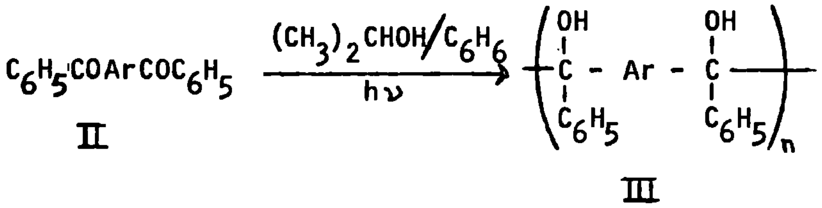
(2.17)

Chain extension resulting from use of bisbenzhydrol as H-donor and monomer

2.4 b) Results of De Schryver and co-workers on the photoreductive polymerization of diketones

De schryver and co-workers studied two types of aryl ketones, namely bisbenzophenones and bisketotriazoles. They also used two types of H-donor system, namely isopropanol, and bisbenzhydrols derived from the bisketones; in the latter case the donor is also a comonomer for the polymerization. Their results with the conventional isopropanol H-donor system will be considered first.

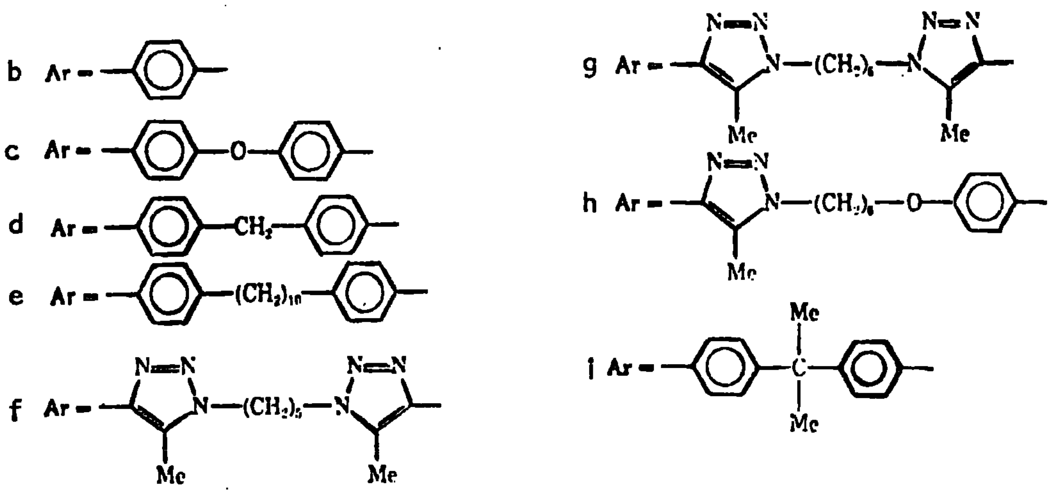
The monomers used in the investigations of the Belgian group are shown below (2.18).



$$C_6H_5COArCOC_6H_5 \xrightarrow[h\nu]{(CH_3)_2CHOH/C_6H_6} \left(\begin{array}{c} OH \\ | \\ C \\ | \\ C_6H_5 \end{array} - Ar - \begin{array}{c} OH \\ | \\ C \\ | \\ C_6H_5 \end{array} \right)_n$$

II III

(2.18)



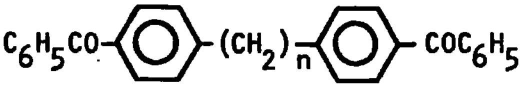
(2.18)

Photoreductive polymerization with diketone-isopropanol-benzene systems

Some of their results are summarized in Table 2.4.

Table 2.4

Monomer	[M] mole/l	Me_2CHOH C_6H_6	Irradiation time	$\bar{M}$	$[\eta]$
b	0.23	1:5	7 days	-	0.06
c	0.054	1:5	4 days	-	0.27
d	0.3	1:3	4 days	-	0.23
f	0.17	1:3	4 hours	82,200	0.32
g	0.17	1:3	5 hours	-	0.26
h	0.1	1:3	5 hours	-	0.19
i	0.5	1:3	2 days	69,000	0.28

Several points are worthy of note in these results. The $\bar{M}_n$ values quoted are for high molecular weight fractions obtained after fractional precipitation of the initial product; thus, for example, the polypinacol derived from monomer IIf had a molecular weight of 12,000 as initially isolated and after reprecipitation gave a fraction with a molecular weight of 82,000. This group confirm the observation of Pearson and Andrews that solvent systems rich in benzene give higher molecular weight products than the 1 : 1 solvent system advocated by Higgins; also it is clear that with appropriate monomers products can be isolated of reasonably high molecular weight which confirms Andrews' results using monomers of the type  where n = 1 ($\bar{M}_n$=14,700), n = 6 ($\bar{M}_n$=10,300) and n = 10 ($\bar{M}_n$=12,600). Unfortunately, direct comparisons between the results of the different groups of workers are difficult since some have used mainly solution viscosity and some mainly molecular weight to characterize their various products. However, consideration of the results available from all the workers in the field shows that the highest molecular weight samples were invariably obtained using momomers where the two aromatic ketone chromophores were separated from each other by the presence of at least one saturated carbon atom; in the one example common to all four groups there was complete agreement that a high molecular weight polymer was not formed on photoreduction of p-dibenzoylbenzene, the results for irradiation of this momomer in benzene-isopropanol solution are summarized below. In this particular example the two carbonyl functions are completely conjugated with each other, it is also likely that the lowest triplet is π, π^* in character for this system.

Worker	Benzene: Isopropanol	$\bar{M}$	η
Higgins	1:1	435	0.06
Pearson	3:1	1570	-
Andrews	1:1	1300	-
De Schryver	5:1	-	0.06

One further point of importance emerged from the ^{1}H n.m.r. examination of the low molecular weight fractions obtained by the Belgian group, this was the clear demonstration of the presence of end groups derived from the in-cage reaction of acetone ketyl radicals with the diphenyl ketyl radicals, this confirms that this minor reaction does act as a chain termination process in these systems.

The irradiation of a diketone-dibenzhydrol mixture in benzene yielded high molecular weight polypinacols. The great advantage of this system is the avoidance of a cage reaction, with $Me_2\dot{C}OH$, which constitutes chain termination.

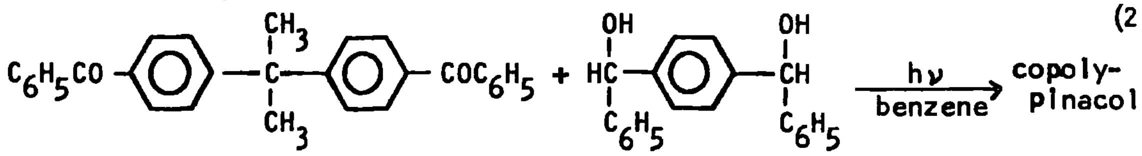
Where the dibenzhydrol used for this type of photoreduction polymerization is the product of the diketone monomer homopolymers are obtained, whereas when the dibenzhydrol is derived from a different diketone regular alternating copolymers are formed. This contrasts with the situation obtaining when mixtures of diketones are irradiated in benzene-isopropanol solution which gives rise to statistical copolymers. Some results of the Belgian group with this system are presented in Table 2.5., the benzhydrols V listed in the table are derived by reduction of the diketones discussed above (see 2.17). The quoted $\overline{M}_n$ values were measured for the high molecular weight

Photopolymerization of Bisaryl Ketone-Bishydrol Solution

Table 2.5

Ketone	Hydrol	$[M]$, mole/l	Irradiation time	$\overline{M}$	$[\eta]$
IIi	Vb	0.1	4 days	-	0.08
IIi	Vc	0.17	5 days	-	0.21
IIi	Vd	0.17	5 days	-	0.18
IIi	Ve	0.013	4 days	93,500	0.33
IIi	Vi	0.3	4 days	174,000	0.36
IIf	Vi	0.17	4 hours	141,000	0.43
IIg	Vi	0.17	5 hours	140,000	0.43

fractions obtained by fractional precipitation of the initial product. Satisfactorily high molecular weights and/or viscosities were obtained for all cases except that where the benzhydrol was the product resulting from reduction of p - dibenzoylbenzene; that is the reaction (2.19).



(2.19)

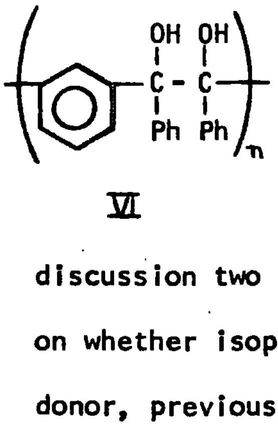
- yielding a product of very much lower solution viscosity than all other cases investigated.

2.5 OBJECTIVES OF PRESENT RESEARCH

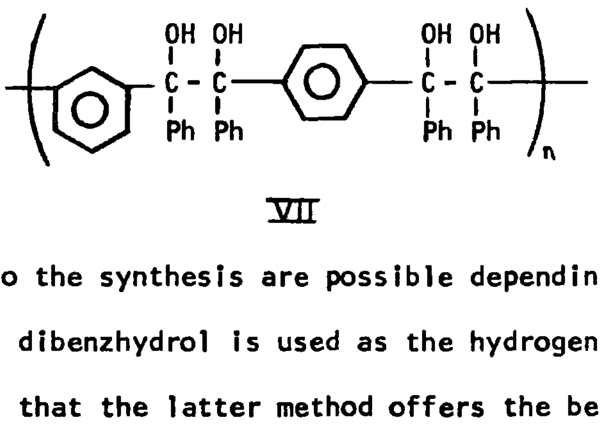
In this work it was intended to use step-growth photoreductive polymerization as the first stage in the synthesis of novel aromatic polymers. The overall objectives of the work are summarized below.

Stage 1 Preparation of Polybenzopinacol Starting Materials.

The first step in the projected work involved the synthesis of the following polybenzpinacols (VI & VII) from the foregoing

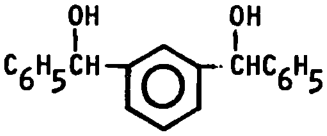


VI

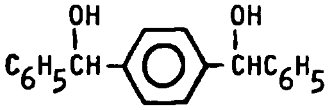


VII

discussion two approaches to the synthesis are possible depending on whether isopropanol or a dibenzhydrol is used as the hydrogen donor, previous work imples that the latter method offers the best chance of obtaining high molecular weight products and this approach was investigated first. The diketone, m - dibenzoylbenzene, was irradiated with the meta-and p - dibenzhydrols VIII and IX. Due to the poor solubility of the m- and p-bisbenzhydrols,



VIII



IX

three sets of conditions were used in this previously uninvestigated reaction.

i) m-Dibenzoylbenzene dissolved in benzene at room temperature in the presence of either undissolved m- or p-bisbenzhydrol was irradiated with the intention of allowing the diol to dissolve as the reaction proceeded. This technique was used successfully by the Belgian group with different monomers.

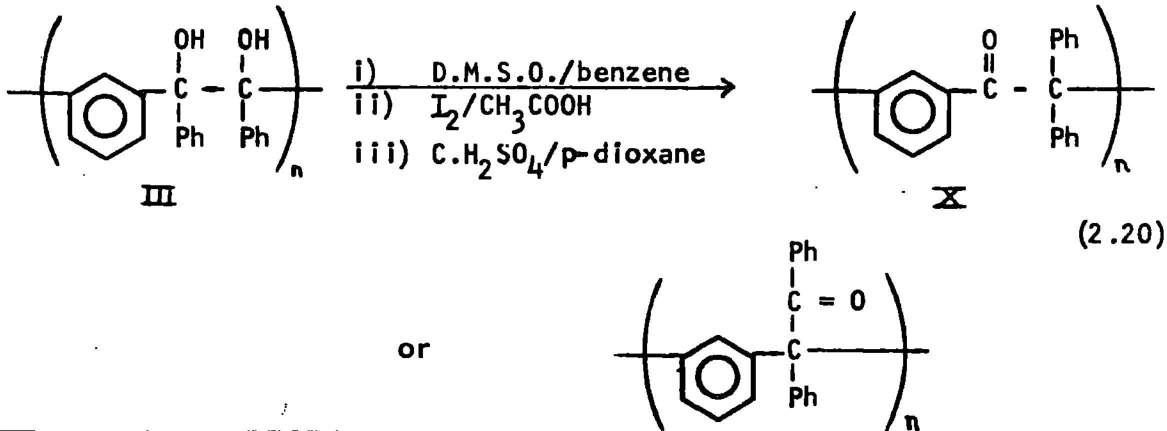
ii) m-Dibenzoylbenzene dissolved in hot benzene with either m- or p-bisbenzhydrol was irradiated. The use of a filter solution was later incorporated into this experiment to ensure that unwanted radiation at wavelengths lower than 350 n.m. was excluded.

iii) Irradiation of m-dibenzoylbenzene dissolved in acetonitrile at room temperature with m- or p- bisbenzhydrol; both monomers being readily soluble.

Since none of these procedures yielded high molecular weight polymers the photoreductive polymerization of m-dibenzoylbenzene in isopropanol-benzene solution was investigated in an attempt to optimise $\overline{M}$ for polymer VI .

Stage 2 Catalytic Dehydration of Polybenzopinacol Starting Material.

Having made a polybenzopinacol with a reasonable molecular weight the next intended step was the acid catalyzed dehydration of the polybenzopinacol involving a pinacol-pinacolone rearrangement (2.20).

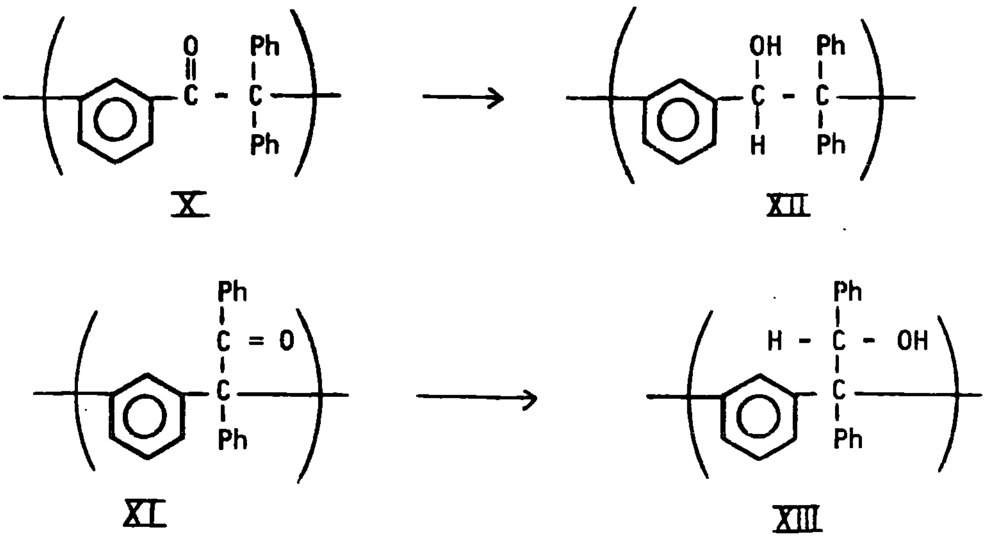


(2.20)

Two possible products may be produced depending on whether chain migration or phenyl migration takes place. The difficulty encountered with this reaction is degradation of the polymer and whether dehydration takes place at all despite the fact that the model monomer can be readily converted to the ketone: hence several methods were tried.

Stage 3 Reduction of Polybenzopinacolone (X or XI) using NaBH$_4$.

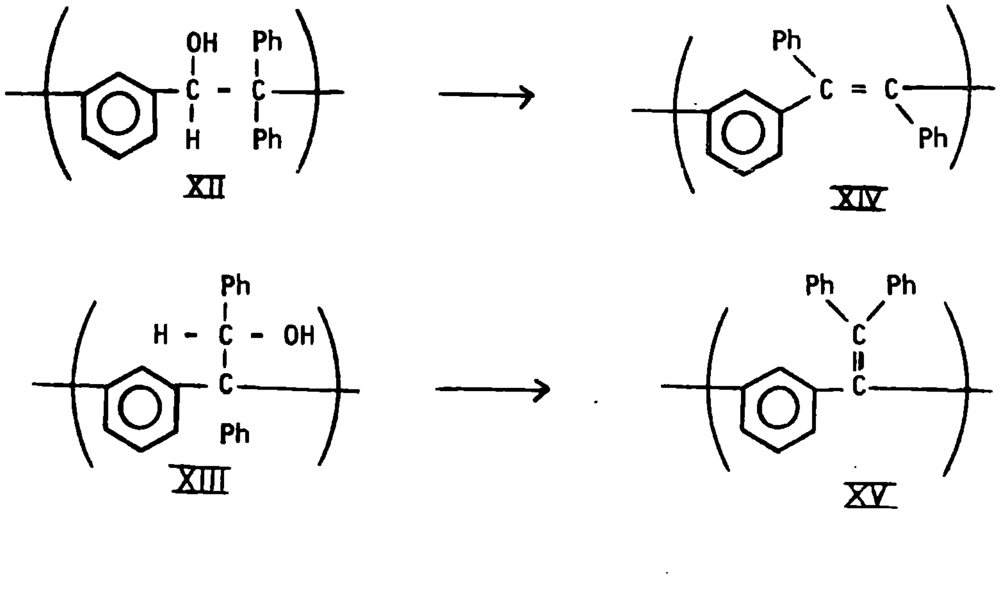
This reaction could be carried out in either toluene or 1,4-dioxan (2.21).



(2.21)

Stage 4 Dehydration of Polymers XII and/or XIII .

Finally, acid catalyzed dehydration of the products to give polymers XIV and/or XV (2.22).



(2.22)

The likely properties of polymers with the novel structures XIV and XV are difficult to predict; but in recent years considerable efforts have gone into attempts to synthesise totally conjugated aromatic and heteroaromatic polymers.

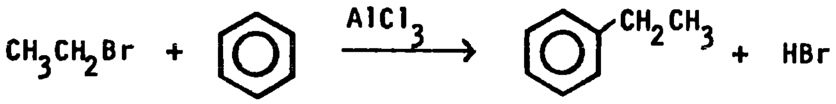
CHAPTER 3

SYNTHESIS OF MONOMERS, THEIR PHOTOPOLYMERIZATION AND SUBSEQUENT REACTIONS

PART 1. MONOMERS

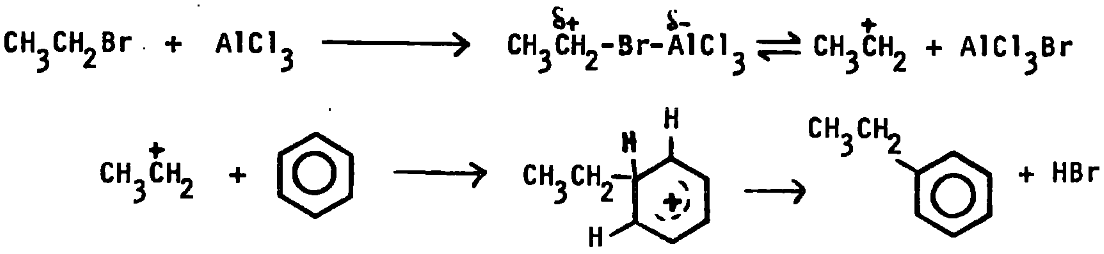
3.1 The Friedel-Crafts Reaction

This reaction was used in the preparation of m-dibenzoylbenzene, the principal monomer required for this work. Friedel-Crafts reactions can be divided into two general types namely alkylation and acylations. An example of a Friedel-Crafts alkylation is the following (3.1).



(3.1)

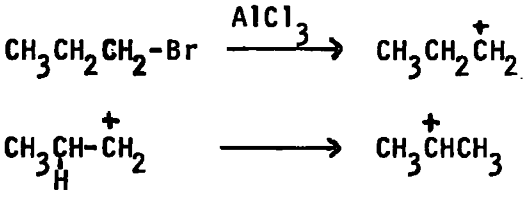
On treatment with a lewis acid the ethyl bromide is converted to a free carbonium ion ($CH_3CH_2^+$) which being a strong electrophile attacks the benzene ring (3.2).



$$CH_3CH_2Br + AlCl_3 \longrightarrow CH_3\overset{\delta+}{C}H_2\text{-}Br\text{-}\overset{\delta-}{Al}Cl_3 \rightleftharpoons CH_3\overset{+}{C}H_2 + AlCl_3Br$$

(3.2)

One of the main disadvantages of the Friedel-Crafts alkylation is that carbonium ion rearrangements may occur, as shown for example in 3.3.

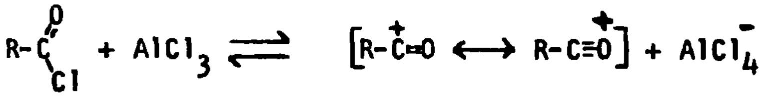


$$CH_3CH_2CH_2\text{-}Br \xrightarrow{AlCl_3} CH_3CH_2\overset{+}{C}H_2$$

$$CH_3\underset{H}{\overset{+}{C}}H\text{-}CH_2 \longrightarrow CH_3\overset{+}{C}HCH_3$$

(3.3)

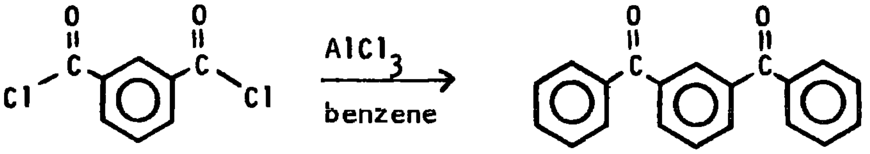
Hence the n-propyl cation rearranges to the more stable isopropyl cation. Even if rearrangement does not occur, polyalkylation may and these factors put restrictions on the synthetic utility of the reaction. An improvement on this type of reaction is the Friedel-Crafts acylation in which an acylium ion is generated (3.4).



$$R\text{-}C(=O)Cl + AlCl_3 \rightleftharpoons [R\text{-}\overset{+}{C}{=}O \longleftrightarrow R\text{-}C{\equiv}\overset{+}{O}] + AlCl_4^- \qquad (3.4)$$

This reaction, however, requires more than one equivalent of catalyst ($AlCl_3$) because the ketone is basic enough to form a salt with the lewis acid which reduces the catalytic activity of the latter. The most commonly used catalyst is aluminium chloride because it is cheap and it possesses high catalytic activity. Other catalysts may be employed such as $AlBr_3$, $FeCl_3$, $FeBr_3$, $TiCl_4$, $NbCl_5$, $ZrCl_4$, metal powders, iodine etc.

With particular reference to the preparation of m-dibenzoylbenzene the method adopted was an acylation using isophthaloyl chloride with $AlCl_3$ in the presence of benzene as both reagent and solvent (3.5).

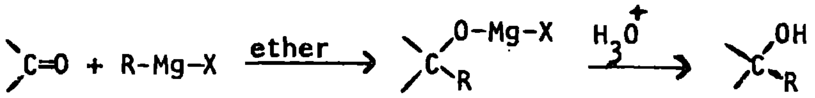


(3.5)

This reaction has been extensively used by other workers who reported yields in the region 20-45%, recent work in this department has allowed yields of pure material to be considerably increased, the experimental details are reported later.

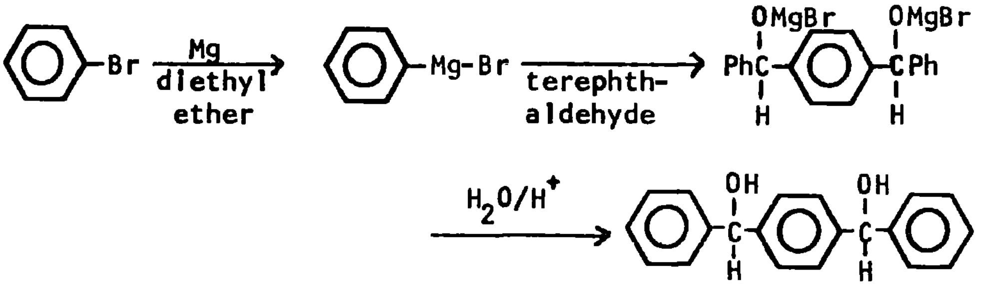
3.2 Grignard Reagents

Grignard reagents (organomagnesium compounds, prepared from organic halides and magnesium) are amongst the most useful reagents available. A common method for the preparation of an organometallic compound is by reaction of an organic halide with a metal. The reactivity of the resulting organometallic compound increases with the percent of ionic character of the carbon to metal bond. An organic halide and magnesium react in ether to form what is often represented as R-Mg-X though this formula is a simplified form of the complex. Tetrahydrofuran is also commonly used in the preparation of Grignard reagents. Since the carbon to magnesium bond is polarised with partial negative charge on R or X, rearrangements of the carbonium ion type are not common. The advantage of making a Grignard reagent is its ability to react with a carbon-heteroatom multiple bond, for example an aldehyde or ketone, whereby a complex magnesium alkoxide is formed from which the alcohol may be liberated by the addition of dilute acid (3.6).



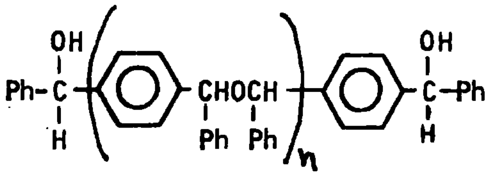
(3.6)

In the case of preparing p-bisbenzhydrol intended for use in the photoreduction of m-dibenzoylbenzene, the Grignard reagent was first prepared by reacting bromobenzene with magnesium turnings in diethyl ether, terephthaldehyde was then added to give (after hydrolysis) the final product (3.7).



(3.7)

The first attempt at this synthesis gave a yellow oily wax which may be ascribed to a dehydration product of structure



Subsequent preparations gave the expected product.

3.3 Sodium Borohydride Reduction of meta-Dibenzoylbenzene

Complex metal hydrides offer the most convenient method for the reduction of aldehydes and ketones to the corresponding alcohols. The most commonly used reagents are lithium aluminium hydride and sodium borohydride. The latter is a much milder reducing agent used in ethanol or aqueous ethanol, under which conditions it will rapidly reduce aldehydes and ketones, but is inert towards most other functional groups. The preparation of m-bisbenzhydrol (1,3-bis(α-hydroxybenzyl) benzene) was carried out in this way to give the third and final monomer. The reaction was straightforward and experimental details are presented below.

3.4 Experimental

a) Preparation of m-dibenzoylbenzene (Friedel-Crafts)

To a stirred solution of isophthaloyl chloride (55 grms., 0.271 moles) in dry benzene (400 mls), anhydrous aluminium chloride (80 grms., 0.6 moles) was added in small portions as a crushed powder. Initially the reaction proceeded spontaneously due to exothermicity, after which the isomantle was used to maintain the solvent at reflux. The solution went from a light brown colour to a dark brown-green. The reaction occurred over a period of approximately two hours.

After cooling the mixture was removed from the flask (2 litre., 3 necked R.B.) and added to a large 5 litre conical flask containing ice, water and a 5% aqueous solution of sodium carbonate, rather than the HCl solution usually advocated. The resulting mixture in the conical flask consisted of two layers, the lower one being the aqueous layer which contained a milky white precipitate of aluminium hydroxide. The top layer containing benzene plus product was orange in colour. At this stage dilute hydrochloric acid was added which did little to the reaction mixture except allowing the aluminium hydroxide to go into solution. The two layers were separated and the benzene evaporated, leaving a milky white precipitate. This was dissolved in cyclohexane and dried (anhydrous $MgSO_4$), after filtration the hot solution was allowed to cool slowly in a 3 litre round bottomed flask wrapped in cotton wool. The process or recrystallization was repeated several times, each time two types of crystal being produced; a prismatic soft white crystal and a harder tabular crystal which was tinged yellow. Eventually the white finer crystalline form became more dominant than the yellow coarse crystals.

A larger scale preparation was later necessary where the following amounts of reactant were used : 250 grms. (1.23 moles) isophthaloyl chloride, 2 litres (1756 grms) benzene and 400 grms of $AlCl_3$ (freshly ground). With this preparation the additional precaution was taken by boiling the product with decolourizing charcoal for 1 hour, this was then removed by filtration using Hyflo in a Buchner funnel. This time all the crystals recovered were of one crystalline form, i.e. flaky and white (Yield : 73%, m.p. 102°-104° C, (literature[16] 103°, 100°, 110°). Found : C, 84.19%; H, 5.26%. Calculated for $C_{20}H_{14}O_2$: C, 83.90%; H, 4.93%. I.r. - Appendix A; 1).

b) Preparation of 1,3-bis(α hydroxybenzyl) benzene

Sodium borohydride (33.3 grms.) was added slowly to an ethanol-water mixture containing m-dibenzoylbenzene (125 grms., 0.44 moles). The whole system was purged with N_2 in order to disperse the large amounts of hydrogen produced in a reaction of this type. After all the borohydride had been added the solution was refluxed for approximately 45 minutes and, after cooling, excess borohydride was destroyed by careful addition of dilute hydrochloric acid. This required 600 mls of approximately 8-10% aqueous HCl and gave a milky solution. The product was precipitated by evaporation of part of the ethanol and then recrystallized from ethanol/water. (Yield: 82%, Found: C, 82.62%; H, 5.96%. Calculated for $C_{20}H_{18}O_2$: C, 82.731%; H, 6.248% with correct infrared spectrum Appendix A; 2).

c) Preparation of 1,4-bis(α hydroxybenzyl) benzene (Grignard route)

All apparatus was dried in the oven and assembled hot while being flushed with dry nitrogen. The magnesium turnings (97.28 grms.) were covered by approximately 1.5 litres of T.H.F. in a 3 litre, 3 necked R.B. flask. The dropping funnel was then filled with 314 grms. (2 moles) of bromobenzene, which was added slowly. An iodine crystal was necessary to intitate the reaction which proceeded smoothly. The temperature range was maintained at approximately 65° - 75° C by the reaction exothermicity and control of the rate of addition. This operation lasted approximately 2 hours.

After the solution cooled to below 30° C, the terephthaldehyde (65.0 grms. dissolved in approximately 0.5 litres of T.H.F.) was added dropwise, giving a dark orange solution which was viscous at room temperature. The mixture was refluxed for 2 hours after which it was added to a large excess of acidified cold water. Stirring of this mixture produced a white solution containing $Mg(OH)_2$ which dissolved when more acid was added. The solubility of T.H.F. in water made it necessary to extract with ether until finally the extract was transparent orange. Evaporation of T.H.F. and ether gave an orange precipitate which failed to recrystallize in a 1 : 1 ethanol-water mixture. After several attempts to purify this product it was assumed that the diol had not been recovered and that possibly an excess of acid had been introduced during the work-up which may have facilitated an acid catalyzed dehydration. The preparation was repeated; this time taking particular care to add the acid in small quantities and keep the mixture at ambient temperature during the work up; recrystallization in a water : ethanol mixture (1 : 4) gave fine white crystals. (Yield: 67%; Found: C, 82.60 %; H, 6.2%; Calculated for $C_{20}H_{18}O_2$: C, 82.73%; H, 6.25 % with correct i.r. - Appendix A; 3).

PART 2. POLYMERIZATIONS

3.5 Preparation of the Solutions to be Irradiated

The monomers used in the following experiments were dried on the vacuum line (ca. 1 day at 10^{-3} m.m. Hg) and the benzene was refluxed over sodium and then distilled prior to use. The following procedures were adopted in the attempted photoreduction of m-dibenzoylbenzene.

I. Irradiation of meta-dibenzoylbenzene and either 1,3 or 1,4 - bis (α hydroxybenzyl) benzene in benzene solution

Equimolar quantities of diketone and bisbenzhydrol were weighed out into irradiation vessels (long pyrex tubes ca. 1 cm. diameter) and sufficient dry benzene added to make solutions 0.1 M in each monomer. Only the diketone dissolved completely under these conditions. The mixture was streamed with nitrogen to remove the possibility of residual oxygen quenching the carbonyl triplets; the tubes were stopped and irradiated in a Rayonet Photochemical Reactor (350 n.m. lamps). It was hoped, following the precedent of the reported Belgian work, that as the reaction proceeded the diol monomer would dissolve; however, after several days the only observable change was the yellowing of the solution. An analysis by infrared spectroscopy of the solid recovered after evaporation of solvent indicated that no reaction had occurred; it was concluded that the diol monomers were too insoluble to allow the gradual dissolution process reported by the Belgian group to operate in this case.

In an attempt to obtain homogeneous solutions of both monomers in benzene progressively higher dilutions were examined; however, the dilutions required for solubility (ca 0.008 M) involved inconveniently small quantities of monomer and large volumes of benzene. Even then there was no detectable reaction after irradiating for prolonged (ca 1 week) periods; for example, the infrared spectrum of the solid recovered after irradiation of a 0.0077 M solution of meta-dibenzoylbenzene and 1, 3-bis (α hydroxybenzyl) benzene in benzene is shown in Appendix A, No. 4 and indicates no appreciable consumption of carbony.

II. <u>Irradiation of meta-dibenzoylbenzene and 1, 3 bis (α hydroxybenzyl) benzene in benzene solution at reflux</u>

Since both monomers were found to be soluble in hot benzene, it was decided to attempt the reaction by irradiating the refluxing solution. The apparatus used for experiments described here is shown in diagram 3.1 with accompanying reference table. The use of a filter solution (see (b) below) prevents unwanted radiation reaching the reactants. The solution enters the reactor at 5. and leaves at 18., when no filter was used this space was purged with dry nitrogen. To the two B.19 cones (21.) two double walled condensers were fitted; one of them having a N_2 bleed passing through the centre to the bottom of the reaction flask. Circulation of the filter solution was achieved by a peristaltic pump which also pumped the solution through a spiral condenser for the purpose of keeping it cool. Finally the major part of the reactor was enclosed in aluminium foil so preventing the escape of harmful U.V. radiation.

a) The first attempt involved irradiating 1, 3 - bis (α hydroxybenzyl) benzene (1.45 grms.) and m- dibenzoybenzyl) benzene (1.43 grms.) in 250 mls of benzene at reflux for several days. On cooling the crystals which precipitated were pure unreacted 1, 3 - bis (α hydroxybenzyl) benzene (i.r. - Appendix A; 5) whereas the material isolated by evaporation of solvent appeared to be a mixture of monomers (i.r. - Appendix; 6).

b) The above experiment was repeated under identical conditions except for the incorporation of a filter solution which contained NaBr (74.09 grms.) and $Hg(NO_3)_2$ (0.25 grms.) dissolved in 250 mls. This solution cuts out most of the lamp output of wavelength less than ca 310 n.m. Although the t.l.c. showed the presence of two components other than the monomers, an infrared spectroscopic analysis of the solid product from this reaction (Appendix A; 7) indicated an almost insignificant consumption of carbonyl. Attempts to separate the components of the product by column chromatography proved unsuccessful because a suitable solvent could not be found. The reaction between m-dibenzoylbenzene and 1,4 - bis (α hydroxybenzyl) benzene was not attempted in view of the failure of the attempt with the meta isomer.

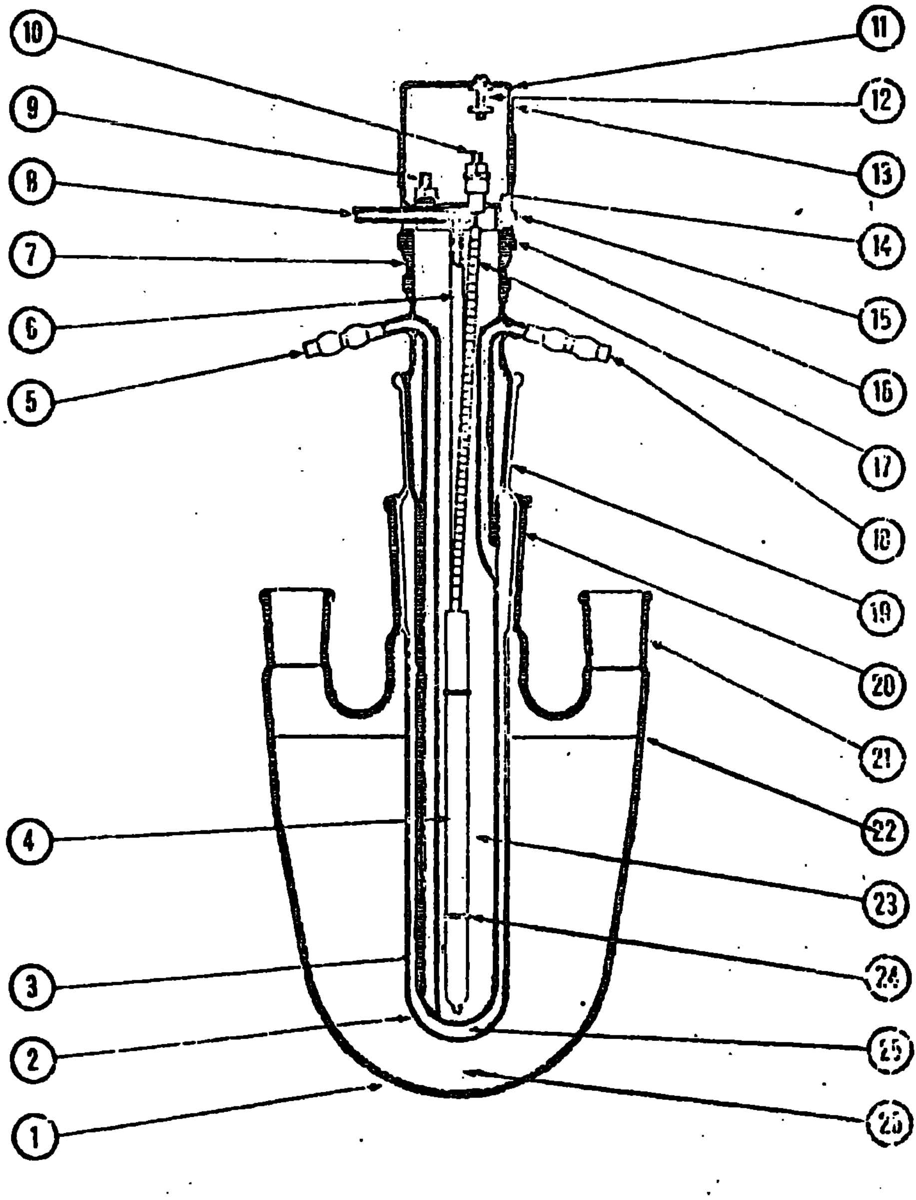
III. Reactions in acetonitrile as solvent

Acetonitrile was found to dissolve all the monomers involved in this work. The acetonitrile used was distilled from P_2O_5 using a fractionating column (80 cms x 2 cms) containing glass helices.

Two solutions (0.066 M and 0.0025 M) of the monomers in freshly distilled acetonitrile were prepared in cylindrical reaction vessels fitted with teflon Rotaflow taps. The solutions were degassed on a vacuum line (10^{-3}m.m. Hg) by three freeze-thaw cycles, after which they were let down to atmospheric pressure under the presence of dry nitrogen. The tubes were irradiated in a Rayonet Reactor

DIAGRAM 3.1

1. Pyrex flask
2. Outer quartz jacket
3. Inner quartz jacket
4. U shaped tube is low pressure
   Straight tube is medium pressure
5. Cooling water or gas flush inlet
6. Arc tube support tube
7. Rubber sleeve
8. Inlet and outlet for gas flush only
9. Earth terminal for arc tube supply cable green core
10. Two ceramic insulated terminals for arc tube power supply red and black cores
11. Terminal cover
12. Cable clamp
13. Inlet for supply cable
14. Terminal block
15. 2 screws to retain terminal cover
16. Rubber sleeve clamps
17. Ceramic insulated leads from terminals to arc tube
18. Cooling water or gas flush outlet
19. B40 cone and socket
20. B45 cone and socket
21. B19 cone and socket
22. Reagent level to permit gas flush above reagent
23. Space for gas flush only
24. Arc tube support clips
25. Space for cooling water or gas flush
26. Space for magnetic stirrer



(3500 A lamps) for 55 hours and the product recovered by evaporation of the solvent. The infrared spectra of the products (Appendix A, 8 and 9 respectively) indicated that again insignificant carbonyl consumption had occurred. This very disappointing result prompted a check on the technique; irradiation of an equimolar solution of benzophenone and benzhydrol in acetonitrile under the same conditions gave benzopinacol quantitatively, the infrared spectrum of the total recovered product is shown in Appendix A; 10.

The disappointing outcome of the attempted polymerizations described above forced the author to examine the optimization of the reductive photopolymerization of meta-dibenzoylbenzene using isopropanol as hydrogen donor.

3.6 Photoreduction of m-dibenzoylbenzene in Benzene : Isopropanol Mixtures

I. Experimental

The investigation of the optimum conditions under which a high molecular weight polybenzopinacol may be formed in the presence of isopropanol as a donor was attempted. Firstly, a preliminary experiment was run after which six tubes were prepared, containing varying benzene isopropanol mixtures and irradiated. The solid products were isolated by evaporation of the solvent and their respective molecular weights were then determined.

a) Experiment 1 m-Dibenzoylbenzene (2.1475 grms.) was dissolved in a mixture of 12.5 mls isopropanol + 62.5 mls benzene in a cylindrical reaction vessel. The solution was nitrogen streamed and then exposed to irradiation at $\lambda = 350$ n.m. for 62.2 hours. The benzene solution was originally colourless but after irradiation it was yellow with a faint white precipitate at the bottom of the tube. The infrared spectra of the precipitated material and the solid obtained on evaporation of the solvent were identical and showed no carbonyl stretching (Appendix A; 11).

b) <u>Experiment 2</u> Six pyrex tubes of approximately 100 mls capacity containing 3 grms (0.01048 moles) m-dibenzoylbenzene dissolved in mixtures of benzene and isopropanol were made up as shown in the table.

Isopropanol mls	Benzene mls	Ratio isopropanol : benzene	No. of moles isopropanol
2	28	1 : 14	0.026
3	27	1 : 9	0.039
5	25	1 : 5	0.065
6	24	1 : 4	0.079
10	20	1 : 2	0.1308
15	15	1 : 1	0.196

The tubes were placed in a Rayonet "Merry-Go-Round" and irradiated at 350 n.m. for one week. There was some precipitation in some of the tubes and all the solutions were yellow. The precipitation was greatest in the tubes containing the higher concentration of isopropanol and there was a gradual reduction in the amount of precipitate as the isopropanol concentration decreased. The tubes having a 1 : 14 and 1 : 9 ratio showing no precipitation. The precipitates were isolated by filtration and the soluble product recovered by evaporation. The i.r. spectra of all products were virtually the same and showed almost complete carbonyl consumption, a typical example is recorded in Appendix A, No. 12.

II. <u>Molecular Weights of the Polybenzopinacols Prepared in Benzene - Isopropanol</u>

a) <u>Apparatus</u>

The apparatus used for these determinations was a Model 115 Molecular Weight Apparatus made by Perkin-Elmer (Hitachi); the essential features of the apparatus are presented schematically in diagram 3.2.

The determination of molecular weight depends on the difference in vapour pressure between a drop of pure solvent and a drop of a solution (of the material under investigation) in the same solvent; such differences are not easily measured directly. In practice two closely matched thermistors each capable of holding a drop of solvent or solution are placed in a thermostated container in which a pool of pure solvent is maintained in equilibrium with its saturated vapour. Each thermistor is part of a Wheatstone Bridge. A drop of pure solvent is placed on one thermistor and a drop of solution on the other, the rate of evaporation and condensation will differ between the two thermistors consequently setting up a temperature differential. The resulting out of balance potential of the bridge can be measured with considerable accuracy and when the system is calibrated with material of known molecular weight the molal concentration of the unknown solution can be obtained and hence the molecular weight of the solution.

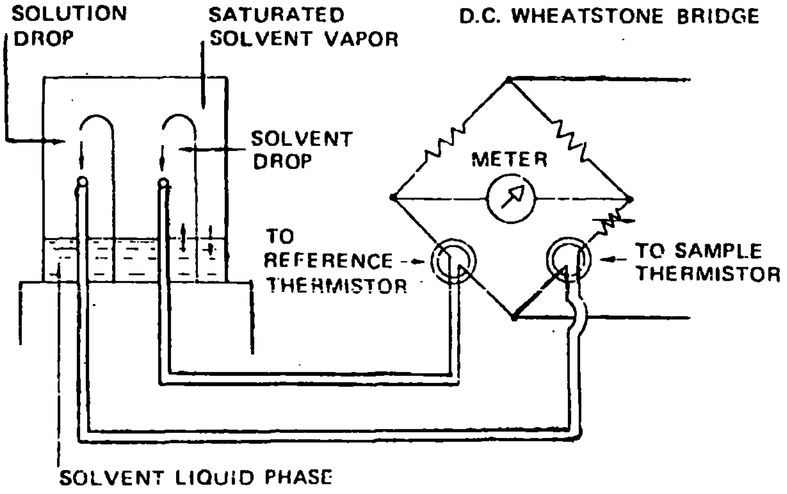


Diagram 3.2

Essential Features of Model 115 Molecular Weight Apparatus

b) The Determinations

The instrument was calibrated using benzil as the standard and chloroform as the solvent. The instrument constant K, which is the slope of the graph representing the out of balance potential (ΔR) measured in arbitrary units plotted against the molal concentration. The constant used in these particular determinations was 51273. The molecular weight of the product from Experiment 1 was obtained by measuring the out of balance potential for several solutions of different concentration and extrapolating to zero concentration using a least squares procedure. $\overline{M}_n$ is then given by the expression

$$\overline{M}_n = \frac{K}{\lim\limits_{C \to 0} \Delta R/C}$$

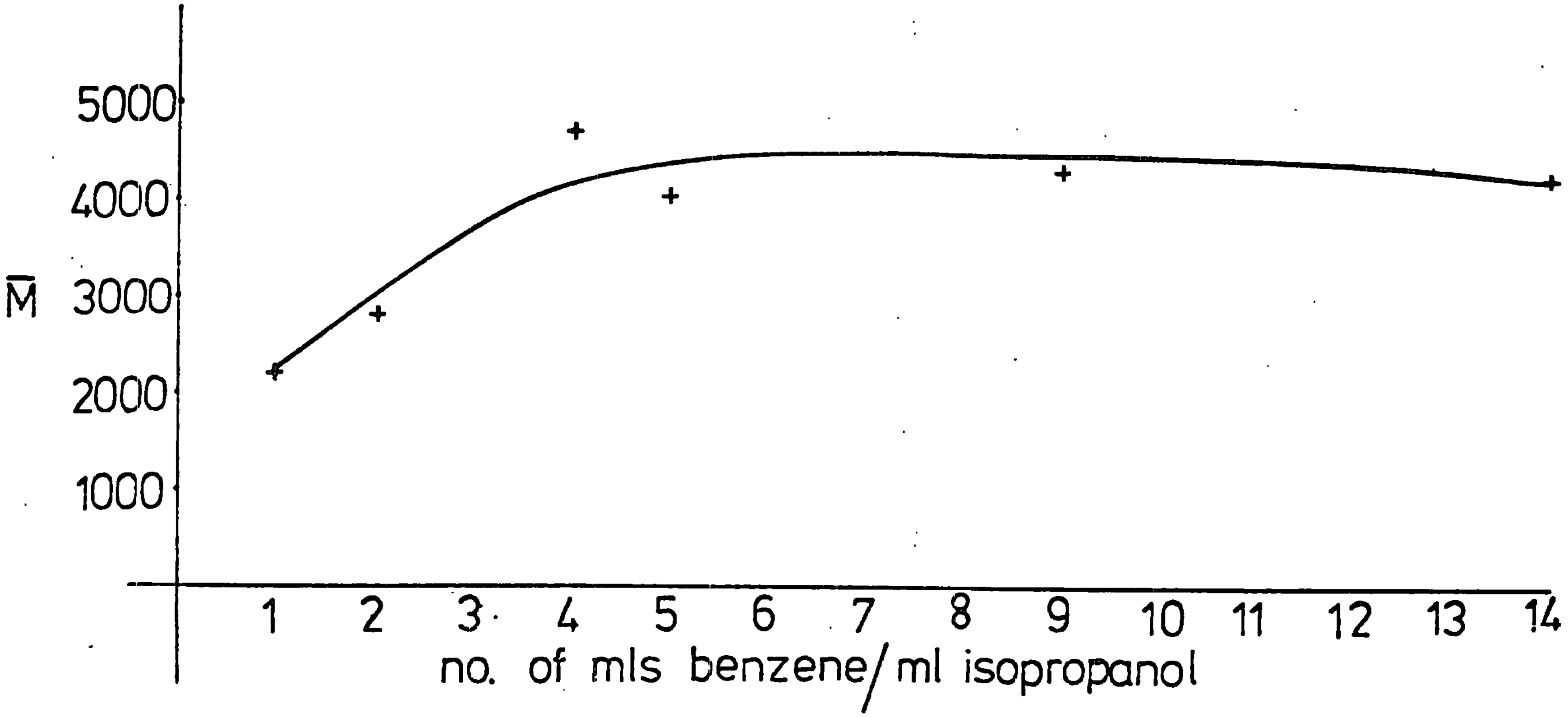
and for this sample was 5080.

Before the values of $\overline{M}_n$ for the products from the six pyrex tubes (Experiment 2) were determined, the instrument was cleaned and re-calibrated giving an instrument constant of 56292. The molecular weights determined for the six products are tabulated below, together with the correlation coefficients for the least squares fit of the extrapolated line.

Isopropanol:Benzene Ratio mls	Correlation Coefficient	$\overline{M}_n$	$\overline{\text{D.P.}}$
1:14	0.700	4280	14.8
1:9	0.878	4310	15
1:5	0.999	4060	14.1
1:4	-	4750	16.5
1:2	0.865	2800	9.7
1:1	0.931	2230	7.7

It is clear from the table that as the concentration of isopropanol decreases the molecular weight of the product initially increases and then reaches a plateau value, this trend is more easily seen in graphical form in Figure 3.3. There are a number of

FIGURE 3.3


$\bar{M}$
5000
4000
3000
2000
1000
1
2
3
4
5
6
7
8
9
10
11
12
13
14
no. of mls benzene/ml isopropanol

factors which may control the molecular weight attained and many of these were discussed in Section 2.4; however, it seems probable that the lower molecular weights of the products which precipitated from the solutions having higher isopropanol concentrations result simply from their being removed from solution before completing reaction, that is a simple solubility effect controls the $\bar{M}_n$ attained. On the other hand, the fact that the polymerization tends to a limiting molecular weight of ca. 4350 (ie a D.P. ~15) may be a result of the ratio of in-cage chain terminating reactions to out-of-cage chain extending reactions; this ratio may be affected by aspects of monomer and solution structure and may well vary from system to system. In the limited time available to the author it was decided not to pursue this matter further but to examine the subsequent steps outlined in Section 2.5.

PART 3. REACTIONS OF POLYBENZOPINACOL IIIa

The three intended steps to polymers XIV and/or XV have already been discussed in Section 2.5 and for the purpose of investigating this proposed sequence of reactions 12.83 grms of polybenzopinacol IIIa was prepared by irradiation of m-dibenzoylbenzene in a 15:1 solution. The infrared spectrum of this starting material is recorded in Appendix A, No.13.

3.7 The Dehydration of Polybenzopinacol (IIIa)

The pinacol-pinacolone rearrangement is a well known reaction; for the model system, benzopinacol to benzopinacolone, the reaction is quantitative. In initial experiments with Polymer IIIa iodine in acetic acid and dimethyl sulphoxide were tried as catalysts since they were known to be effective for the model compound reaction.

Experiment 1 Polybenzopinacol (IIIa - 1 grm) was refluxed in a mixture of benzene (24 mls), glacial acetic acid (25 mls) and an iodine crystal. Only after 20 hours refluxing did the reaction go to completion as judged by infrared spectroscopy (Appendix A; No.15). A molecular weight determination on the product isolated from this reaction showed that degradation had taken place ($\overline{M}_n$ = 706, $\overline{D.P.}$ = 2.4) T.l.c. indicated the presence of one component only.

Experiment 2 Polybenzopinacol (IIIa - 1 grm) was refluxed in a 1:1 (v/v) mixture of D.M.S.O. and benzene for several hours after which no reaction had taken place as judged by infrared spectroscopy (Appendix A; No. 14). The spectrum shows the presence of occluded D.M.S.O. which was very difficult to remove despite prolonged pumping on the vacuum line.

Higgins and coworkers worked on the polybenzopinacols resulting from photocondensation of p,p'-dibenzoyldiphenyl ether, p,p'-dibenzoyldiphenylmethane and p,p'-dibenzoyl-1,2-diphenylethane and achieved the desired dehydration using sulphuric acid-dioxane solutions. Their analysis suggested that the rearrangement expected did not take place (i.e. migration of a phenyl group) but instead chain migration took place, thus their analysis predicts structure XI rather than X (see 2.5 Stage 2).

Experiment 3 Polybenzopinacol (IIIa - 5 grms) was added to a stirred solution (at room temperature) of conc. H_2SO_4 (25 mls) and 1,4 dioxan (150 mls), which was left stirring for 16 hours. The resulting dark-brown solution was then added to iced water, stirred for several minutes, and then filtered. The solid was redissolved in T.H.F. and slowly added to a large volume of water (ca. 2 litres). The product did not precipitate, as expected by analogy with Higgins' work, but formed an emulsion. This emulsion could only be broken by adding large quantities of dilute HCl after which a precipitate formed. The precipitate was recovered by filtration, washed with Na_2CO_3 solution, then water, and eventually dried on the vacuum line. The infrared spectrum of this product (Appendix A; No.16) indicated complete consumption of OH function and formation of an intense carbonyl at 1675 cm^{-1}, consistent with the formation of either X or XI. At this stage in the work the molecular weight apparatus was not functioning and so it was not possible to determine if the dehydration had been accompanied by degradation as in Experiment 1; however, the avoidance of high temperatures in this last procedure gives cause for optimism that it occurred without degradation.

3.8 Reduction of Polymer X and/or XI

The attempted reduction with sodium borohydride of a toluene solution of the product Experiment 3, Section 3.7 was totally unsuccessful as judged by the infrared spectrum of the isolated product (Appendix A; No.17). Repetition of the reaction using dioxane as solvent resulted in a product in which the carbonyl function at 1675 cm^{-1} in the infrared spectrum (Appendix A; No. 18) was almost completely consumed and replaced by a broad band at 3220 cm^{-1} assigned to hydroxyl; this result being consistent with the formation of polymers XII and/or XIII (see Section 2.5).

3.9 Dehydration of Polymers XII and/or XIII

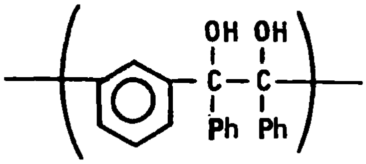
In order to try and complete the sequence of proposed reactions the product obtained as described in the previous section was refluxed in a mixture of acetic acid, benzene and iodine. After the usual isolation and drying procedure a product was obtained, the infrared spectrum of which is shown in Appendix A; No.19. If everything had gone according to plan this product should have been either XIV and/or XV.

This result poses important questions; namely is it just the last stage of the sequence which has failed to go according to plan, or was the starting material for the last stage not as originally assumed. It is possible that the carbonyl absorbtions observed in spectrum 19 results from the product of esterification of the hydroxyls present in the starting material; acetate carbonyl would be consistent with the bandat 1750 cm^{-1}. The strong band at 1675 cm^{-1} might be ascribed to an acetylation product of the aromatic rings, acetophenone carbonyl absorbs at ca 1685 cm^{-1}, although this explanation seems somewhat unlikely.

Clearly this final result raises questions which can only be answered by further experiment, unfortunately the author's restricted time did not allow these experiments to be carried out.

PART 4. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The investigation of the photoreductive polymerization of m-dibenzoylbenzene demonstrates some of the difficulties which can be encountered in syntheses of this type. Although it may be possible to improve on the molecular weights obtained for polymer IIIa in this work by manipulation of reaction conditions the results reported here suggest that such improvements are likely to be small.



IIIa

The factors limiting the attainable molecular weight are not completely clear but are probably complex; on the one hand simple solubility of monomers has been demonstrated to be important and on the other it may be factors such as steric hindrance of the growing chain and the way in which it is coiled and/or solvated.

A preliminary examination of the proposed sequence of reactions using polymer IIIa as starting material was all that could be carried out in the time available to the author. However, on the basis of these results the first two steps appear to proceed as expected although the single attempt at the third stage was unsuccessful.

If this project is investigated further it would seem appropriate to examine the synthetic scheme proposed in Section 2.5 in more detail before spending further time on attempting to obtain higher molecular weight samples of the starting material, polymer IIIa.

In the initial stages of any continuation, investigation by means of conventional techniques such as molecular weight measurements and ^{1}H n.m.r. spectroscopy would seem to be the obvious first step; unfortunately in the latter stages of the present author's work these techniques were not available.

If the programme was brought to a satisfacory synthetic conclusion, the problem of distinguishing between isomeric structures of the possible products remains. Here again, however, simple techniques may well be able to provide definitive answers; for example on ozonolysis polymer XIV should theoretically be degraded completely to m-dibenzoylbenzene, whereas the isomeric polymer XV should yield benzophenone and a polymeric ketone.

APPENDIX A

APPARATUS AND INSTRUMENTS

Vacuum System

Volatile compounds were handled in a conventional vacuum system incorporating a mercury diffusion pump and rotary oil pump.

Infrared Spectra were recorded with both a Perkin-Elmer 457 and 557 Grating Infrared Spectrophotometer.

Ultraviolet Spectra were recorded with a Unicam SP800 spectrophotometer.

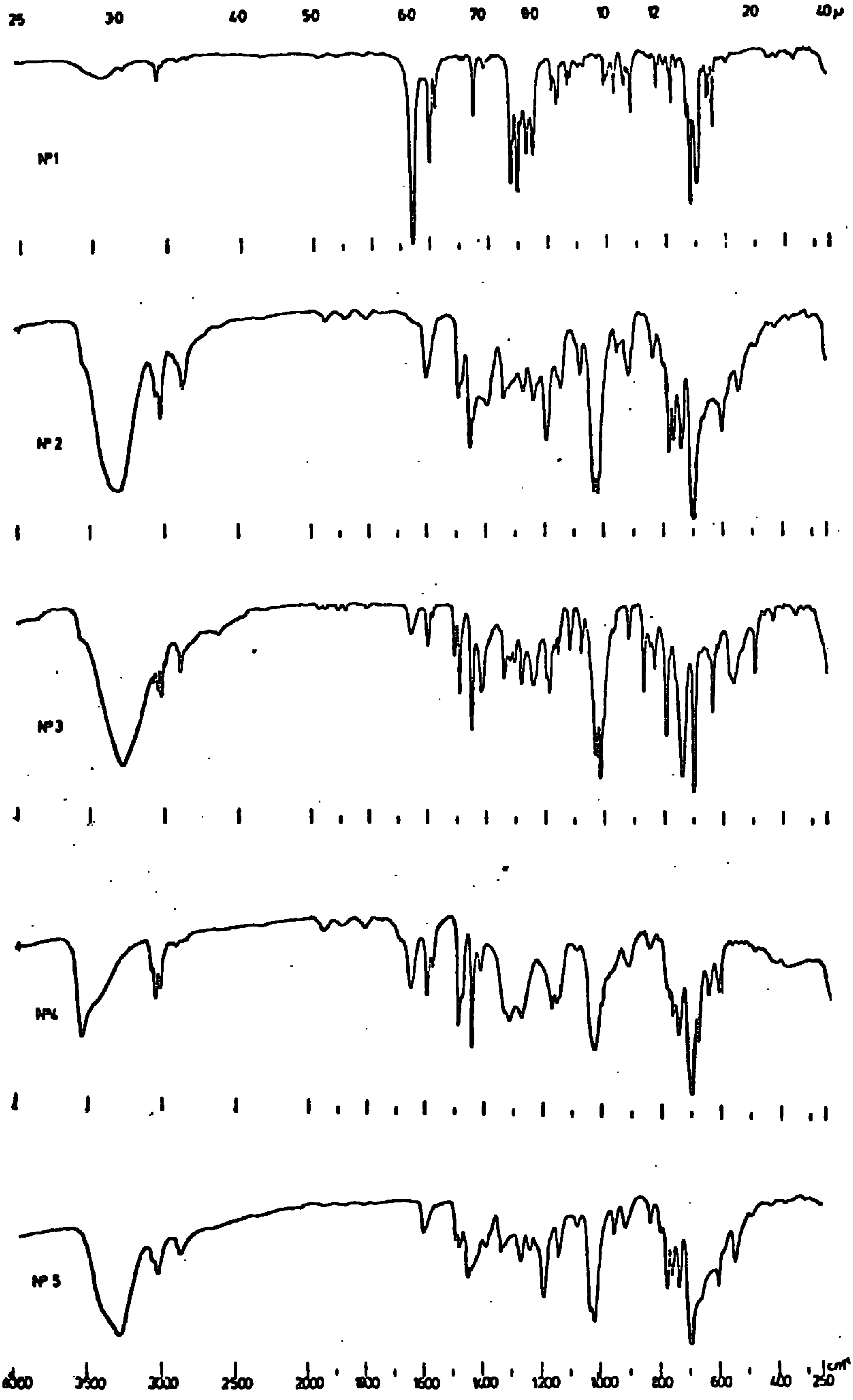
Carbon and Hydrogen Analysis were carried out with a Perkin-Elmer 240 CHN Analyser.

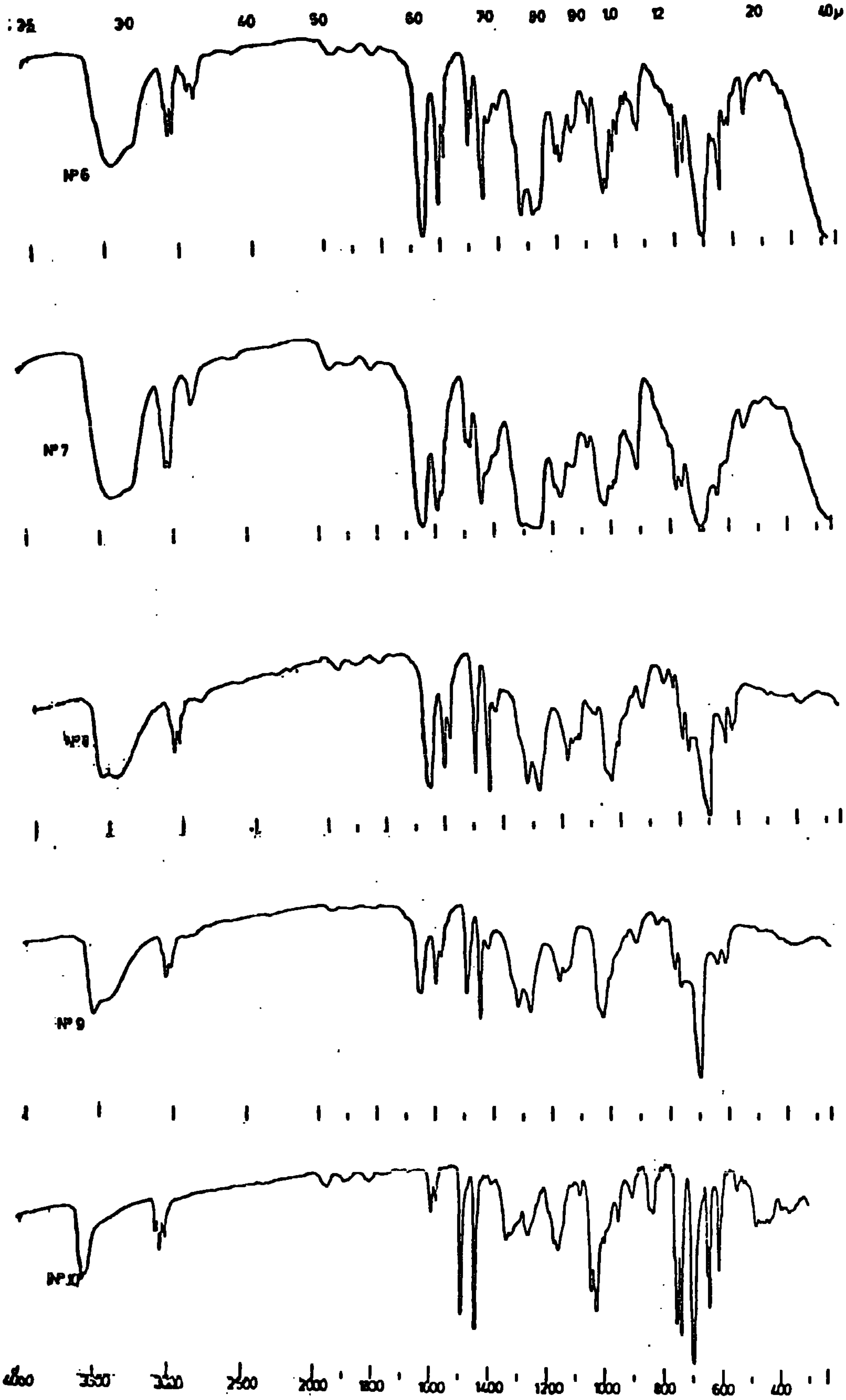
APPENDIX B

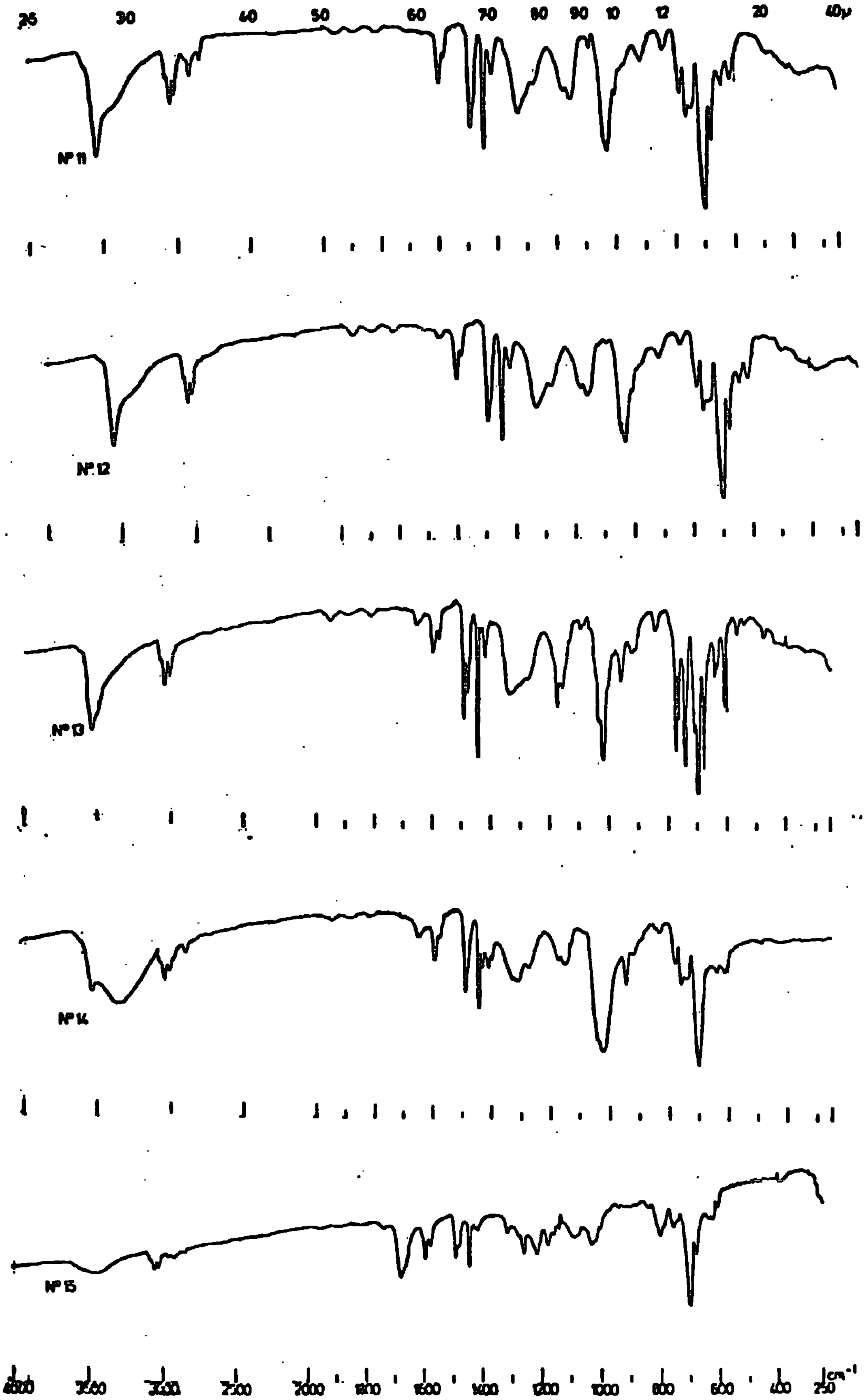
INFRARED SPECTRA

INDEX TO INFRARED SPECTRA

Spectrum No.	Compound (where known)	Reference to Diagram or Script
1	m-dibenzoylbenzene	(a) - Diagram
2	m-bisbenzhydrol	-
3	p-bisbenzhydrol	-
4	-	3.5 i)
5	-	3.5 ii) a)
6	-	3.5 ii) a)
7	-	3.5 ii) b)
8	-	3.5 iii)
9	-	3.5 iii)
10	-	3.5 iii)
11	polybenzopinacol	3.6 i) Experiment 1
12	" (derived from merry-go-round reactions)	3.6 i) Experiment 2
13	-	Part 3 Introduction
14	-	3.7 Experiment 2
15	-	3.7 Experiment 1
16	X and/or XI	3.7 Experiment 2
17	XII and/or XIII	3.8
18	XII and/or XIII	3.8
19	XIV and/or XV	3.9


2.5
3.0
4.0
5.0
6.0
7.0
8.0
10
12
20
40μ
N°1
N°2
N°3
N°4
N°5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
cm⁻¹


2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
20
40μ
N°6
N°7
N°8
N°9
N°10
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


25
30
40
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80
90
10
12
20
40μ
Nº 11
Nº 12
Nº 13
Nº 14
Nº 15
4000
3500
3000
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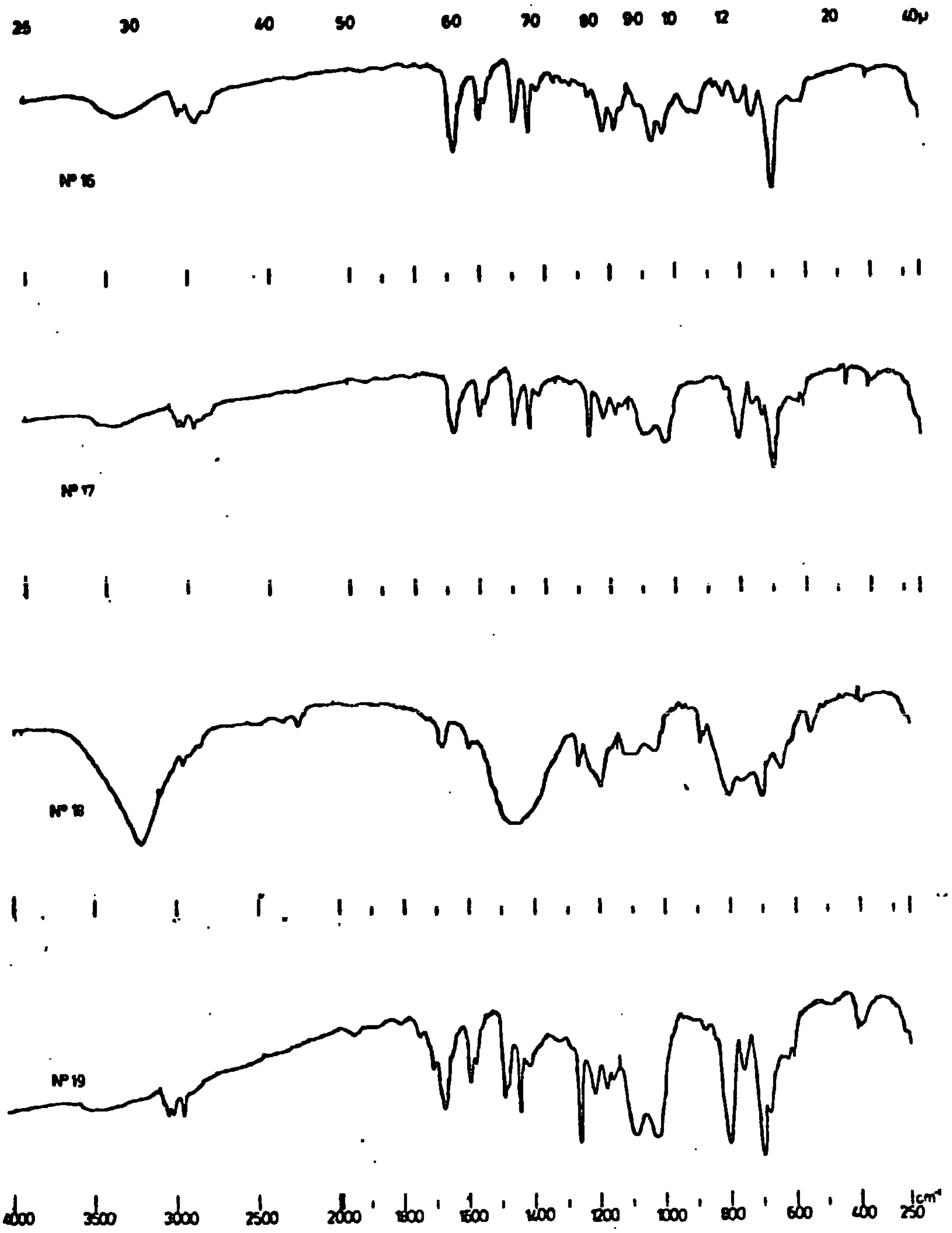
2000
1800
1600
1400
1200
1000
800
600
400
250
cm⁻¹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N° 16
N° 17
N° 18
N° 19
4000
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3000
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1600
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1200
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600
400
250
cm⁻¹

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