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Ahmed, Abdullah Mosed (1991) *The synthesis of new main-chain liquid crystalline polymers as materials for non-linear optics*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/5990/

THE SYNTHESIS OF NEW MAIN- CHAIN LIQUID CRYSTALLINE POLYMERS AS MATERIALS FOR NON-LINEAR OPTICS

A thesis submitted for the Degree of Master of Science

by

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1991

This work is dedicated with gratitude to my family.

ACKNOWLEDGEMENTS

First of all I would like to express my deep gratitude to my Supervisor Prof. W.J. Feast for his unfailing supervision, guidance, invaluable advice and encouragement during the course of this work. I would also like to acknowledge my sincere thanks to Dr. J. Tsibouklis for many helpful discussions, continuous encouragement, practical advice, assistance and patience during the past year. I am indebted to Dr. L. Shahada of Qatar University for her guidance and would like to express my appreciation for her help, encouragement and supervision during the time I spent at that institution. I am also grateful to Dr. P. Bayliff, Dr. M. AbdelKader and Dr. E. Khosravi for many helpful discussions. Thanks are also due to the members of the academic and technical staff at the University of Durham and in particular to Dr. A. Kenwright and Mrs. J. Say for recording the NMR spectra and Mr. G. Forrest for carrying out the G.P.C. and D.S.C. experiments. I also thank my Durham colleagues in the IRC for many helpful discussions. Finally I would like to express my appreciation to my family and friends the continuous spiritual support and encouragement.

MEMORANDUM

The work reported in this thesis was carried out in the Laboratories of the Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, between October 1990 and September 1991. This work has not been submitted for any other degree and is the original work of author, except where acknowledged by reference.

ABSTRACT

The work described in this thesis is concerned with the synthesis of new main-chain liquid crystalline polymers. A new series of liquid crystalline monomers based on an unsymmetrically disubstituted stilbene containing alcohol and carboxylic acid, groups has been synthesised and characterised. The monomers could be polymerised in the presence of N-N'-dicyclohexyl carbodiimide and 4-pyrolidinopyridine to give a novel class of main-chain liquid crystalline polymers which may have potential applications in the field of non-linear optics. The effect of the length of the flexible spacer units on the liquid crystalline phase transitions is also discussed. The thesis is divided into four chapters. In the first chapter the introduction and background of (i) liquid crystals and liquid crystalline polymers, (ii) non-linear optical materials, (iii) polyesters and step-growth polymerization as it relates to this work, is discussed. The second chapter describes the experimental details for the synthesis, characterization and polymerization of the monomers. In the third chapter the chemistry and physical characterization of the main-chain liquid crystalline polymers are described and discussed. The conclusions reached are summarised in chapter four and a few suggestions for extending the work described in this thesis are put forward.

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CHAPTER 1: INTRODUCTION AND BACKGROUND

1. LIQUID CRYSTALS AND LIQUID CRYSTALLINE POLYMERS

Liquid Crystalline materials can be subdivided into lyotropic and thermotropic as shown in figure 1.[1]

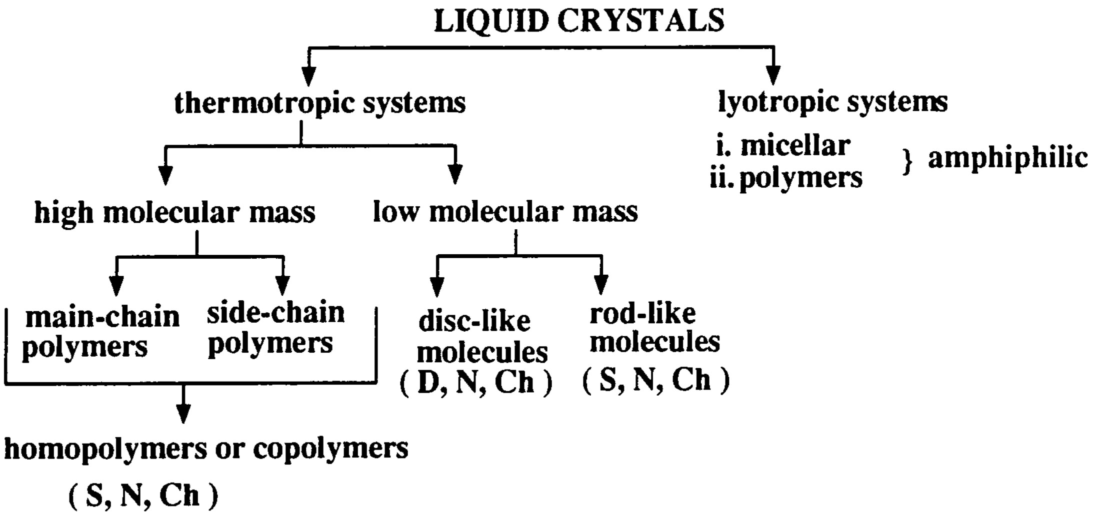


FIGURE 1. SUB-DIVISIONS OF LIQUID CRYSTAL SYSTEMS
Key : S. Smectic; N. Nematic; Ch. Cholesteric; D. Discotic.

1.1. Lyotropic liquid crystals

Lyotropic liquid crystals are made up of two or more components.[2] Generally, one of the components is an amphiphile and the other is water or another solvent. A familiar example of such a system is sodium dodececyl sulphate in water. The types of molecular packing in these mesophases are represented schematically in figure 2 and figure 3.[3] In the lamellar, or neat phase, water is sandwiched between the polar heads of adjacent layers, while the hydrocarbon tails, which are disordered (i.e. in a liquid-like configuration), are in a non-polar environment, see figure 2. In the cubic or viscous isotropic phase the layers are bent to form spherical units, the polar heads lying on the surface of the sphere and the hydrocarbons filling up the inside. The spherical units form a body-centred cubic lattice arrangement,[4] water taking up the space between the units. In the hexagonal or middle phase, the layers are rolled up into cylinders. The cylindrical units of indefinite length are arranged parallel to one another in a hexagonal array (figure 3). A nematic type of ordering has also been observed in some soap systems.[5] It is believed that there exists a cylindrical superstructure similar to the hexagonal phase, but this has not been proved conclusively.[6] Two mesophases may coexist over small ranges of composition and temperature (scheme 1). Phase diagrams have been constructed for a large number of binary systems. Transitions may be brought about from any one of the mesophases directly to the isotropic solution (scheme 1)[1] at appropriate temperatures.

SCHEME : 1. LYOTROPIC LIQUID CRYSTALS[1].

Phase changes effected by changes in concentration or temperature or both.

$$\textbf{Crystalline solid} \underset{\text{evaporation}}{\overset{\text{solvent}}{\rightleftharpoons}} \textbf{one or more lyotropic L.C.phase} \underset{\text{evaporation}}{\overset{\text{solvent}}{\rightleftharpoons}} \textbf{isotropic solution}$$

Ternary and higher component systems exhibit essentially the same types of structures, the phase diagrams being of course much more complicated. Lyotropic liquid crystals occur abundantly in nature, particularly in living systems. [7] Their structures are quite complex and are only just beginning to be elucidated.

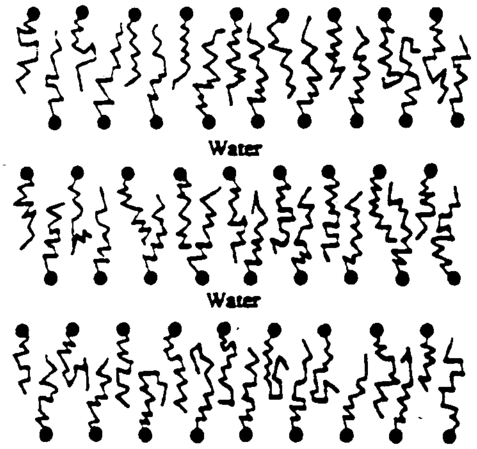


Figure 2. The lamellar or neat phase of soaps

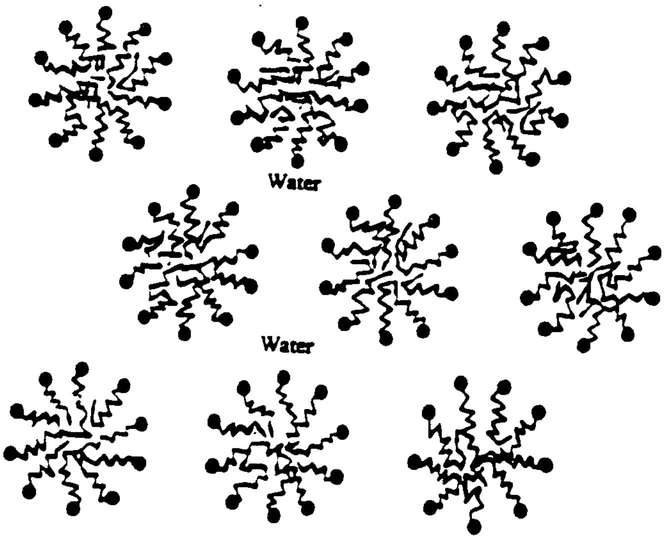


Figure 3. The hexagonal or middle phase of soaps

1.2. Thermotropic liquid crystals

In thermotropic liquid crystals changes in temperature effects phase transitions, see scheme 2 [1].

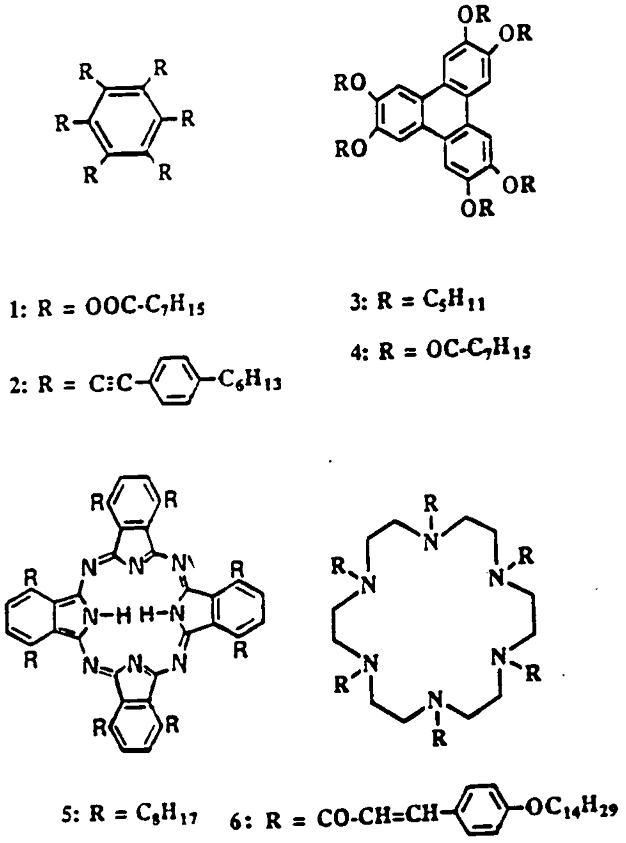
SCHEME : 2. THERMOTROPIC LIQUID CRYSTALS.

$$\text{Crystalline solid} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{one or more thermotropic L.C.phase} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \text{amorphous isotropic liquid}$$

Thermotropic liquid crystals, can be subdivided into two main types: namely low molecular mass and polymeric materials. Both these categories can be subdivided into discotic and calamitic.

1.3. Discotic liquid crystals.

Discotic liquid crystals[8] were discovered in 1977. They are formed by disk-shaped molecules, i.e. typically by large planar aromatic, or by rather inflexible macrocyclic moieties. surrounded by a number of flexible so-called "wing groups". A selection of discotic liquid crystals is shown in Figure 4.[9] Discotic liquid crystals exhibit columnar mesophases which distinguish them from the well-known calamitic (rod-shaped) LCs. These cores, pack in various ways.[8]



1: R = $OOC\text{-}C_7H_{15}$

2: R = $C{\equiv}C\text{-}C_6H_4\text{-}C_6H_{13}$

3: R = C_5H_{11}

4: R = $OC\text{-}C_7H_{15}$

5: R = C_8H_{17}

6: R = $CO\text{-}CH{=}CH\text{-}C_6H_4\text{-}OC_{14}H_{29}$

Figure 4. A selection of discotic liquid crystals.

1.4. Calamitic liquid-crystals

In 1922 Friedel[10] proposed a classification system, dividing calamitic liquid crystals into three classes:

i.Smectic.

The name is derived from the Greek word for soap. In smectic substances, the rod-like molecules are parallel or approximately so, with their centres in planes, forming layers [figure 5][3] in which the molecules may have their long axes orthogonal or tilted with respect to the planes. The molecular centres may be randomly distributed in each layer plane or arranged hexagonally or orthorhombically. A smectic liquid crystalline substance behaves optically like a three dimensional crystal such as quartz. The velocity of light transmitted perpendicularly to the layers is less than that transmitted parallel to the layers and therefore smectic liquid crystalline compounds are often birefringent. In practice it has been found that there are many variants in the detailed arrangement within this general scheme and so far variants from S_A to S_K have been classified.

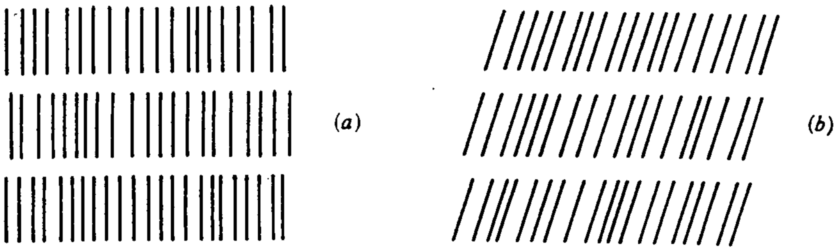


Figure 5. Normal(a) and tilted(b) smectic structures.

ii. Nematic.

The name is derived from the Greek word for thread. This name was selected by Friedel because these substances contain microscopic threadlike structures, either floating free or attached to the surface of the container. Nematic liquid crystals are not as highly ordered as smectic substances [figure 6].[3] Although the molecules in the nematic phase are arranged with their long axes parallel, they are not separated into layers.

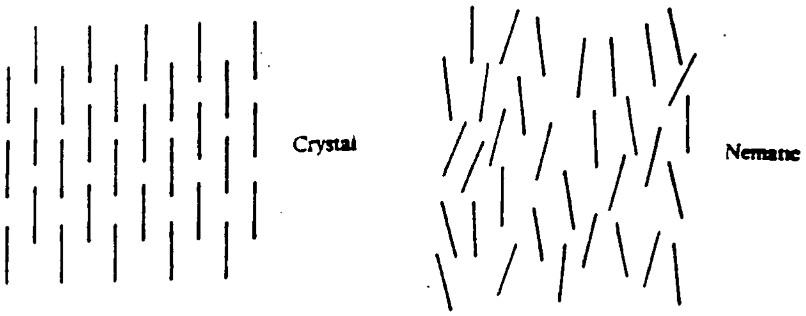


Figure 6. Schematic representation of molecular order in the crystalline and nematic phase.

Like smectic liquid crystals, nematic liquid crystals are optically anisotropic. The preferred orientation of the molecular long axes is referred to as the director; this may vary from point to point in the nematic medium.

iii. Cholesteric.

This class of materials were so named by Friedel because their structure is characteristic of a large number of compounds that contain the cholesteryl group. Cholesteric liquid crystals are regarded simply as spontaneously twisted nematics since the cholesteric phase replaces the nematic if the molecules are chiral and there is an excess of one optical enantiomer. The structure of the phase may be represented as a stack of nematic sheets with a superimposed helical twist about an axis orthogonal to the nematic director in each uniformly aligned sheet [figure 7].[3]

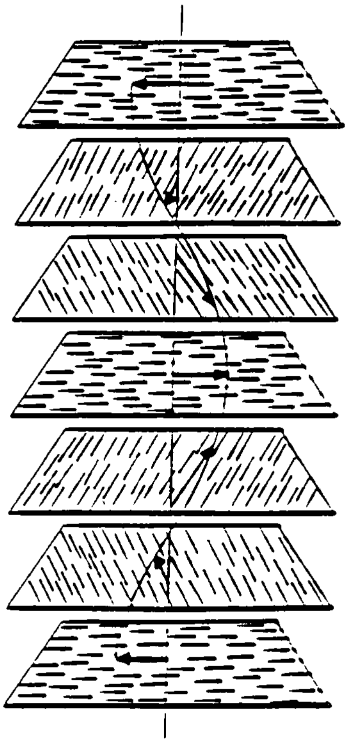


Figure 7. Molecular organisation in the cholesteric phase.

1.5. Side-chain liquid crystalline polymers

Side-chain, comb-like polymers are formed by chemically linking low molecular mass liquid crystals as pendant side groups to a flexible or semi-flexible polymer backbone. Side chain polymer liquid crystals can combine the viscoelastic properties of conventional polymers with the electro-optic properties of liquid crystals. Recent studies have shown that nematic or smectic side chain polymer liquid crystals can exhibit electro-optic effects similar to those observed in low molar mass liquid crystals. The kinds of structure involved are illustrated in diagrammatic form in figure 8.[11] The high viscosities of the polymers appear to limit the applicability of such materials in display devices, but there are potential applications in the areas of optical information storage and laser writing.

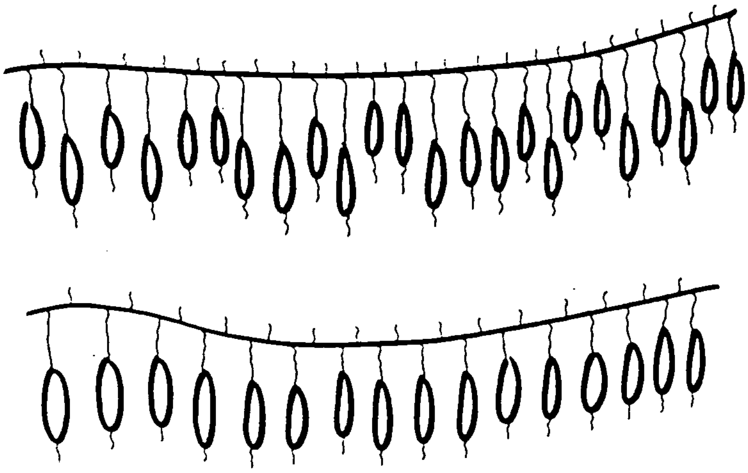


Fig. 8 . Schematic of side chain polymers; Nematic (top) and Smectic (bottom).

1.6. Main-chain liquid crystalline polymers

Main-chain polymer liquid crystals are formed by the chemical linkage of low molecular mass liquid crystals to form a thin and long mesomorphic polymer chain (figure 9a and 9b).[11] Polyesters appear to have been the most commonly synthesised L.C. polymers.[12] A number of L.C. polyethers have also been synthesised and are reported to possess lower melting temperatures and a broader mesophase stability range than analogous polyesters.[13] The rigid unit does not have to exhibit liquid crystallinity in itself in order to act as a mesogen in main chain L.C. polymers.[14] The critical requirements for the mesogen are those of rigidity and asymmetry in shape.[15] The most commonly used rigid unit consists of a number of aromatic rings connected in the para position by short stiff links in order to maintain the linear arrangement. Examples of links that satisfy the conditions for the development of liquid crystallinity in polymers include carbonyls,[12] direct bonds,[16,17] aze groups[18] and substituted stilbenes.[19,20] Technological interest in main-chain systems is due to their potential use in the production of ultra-high modulus fibers and their utilisation as active elements in non-linear optical devices.

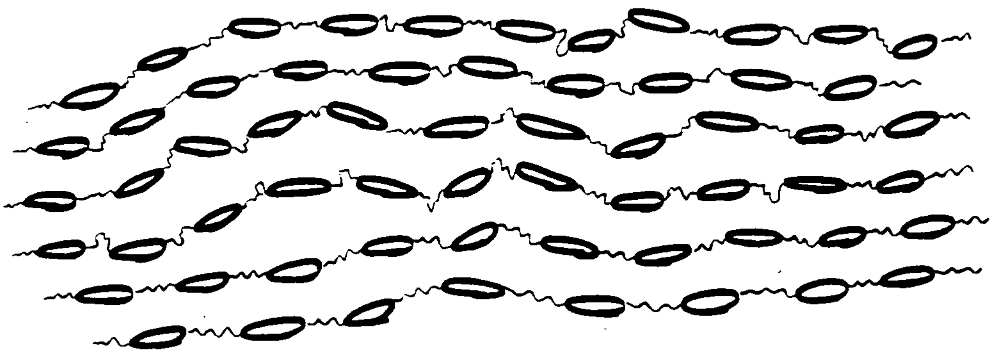


Fig. 9 a. Nematic Organization in Main Chain Polymer.

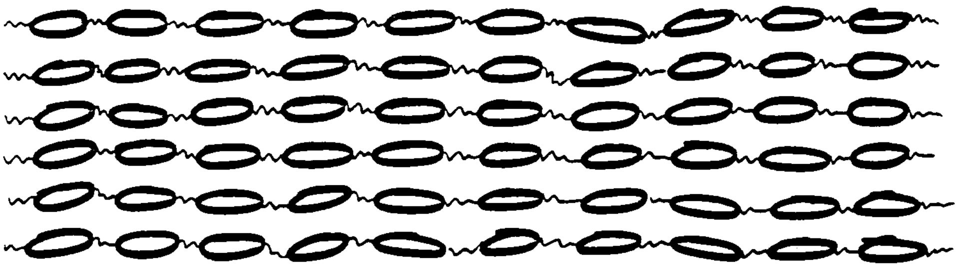


Fig. 9 b. Smectic Organization in Main Chain Polymer.

2. NON-LINEAR OPTICAL MATERIALS

Compounds whose optical properties depend upon the intensity of incident light are described as non-linear optical (NLO) materials. In non-linear optical materials the relationship between the induced polarisation and the electric field strength is non-linear. At present, a large number of practical applications of non-linear optical processes are waiting the development of suitable materials in a usable form. Potential applications of such materials include image processing, multiplexing, efficient switching and use in bistable optical devices.

During the past two decades, it has been recognized[21] that organic compounds with a delocalized π-electron system may exhibit extremely large non-linear optical responses, which theoretically, are several orders of magnitude large than those of inorganic NLO materials. Furthermore, since this non-linear optical response in organic compounds is electronic in nature, an extremely fast response rate can be expected which is beyond the theoretical limit of inorganic materials. This theoretical prediction together with the fact that some organic compounds have been claimed to be more resistant to laser irradiation than inorganic NLO materials has stimulated investigations into the development of new organic materials.

The optical properties of such materials are a function of the degree of polarization induced by light. For a small volume of material the dependence of the total polarization [P(E)] on the electric field strength is expressed as :

$$\mathbf{P(E) = P(0) + \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + ...}$$

where P(0) = intrinsic polarization when E = 0 and $\chi^{(n)}$= Linear and Non-Linear susceptibility.

The susceptibilities, $\chi^{(n)}$, are tensorial quantities which provide a measure of binding of the electrons to the nuclear framework. The larger the compliance the further away from the equilibrium position the polarisable electrons are driven and the larger is the polarization.

The macroscopic polarization, P, of organic compounds is related to the optically induced dipole moment of the molecule, $\Delta\mu$. Similarly in an intense electric field, the induced dipole moment is :

$$\Delta\mu = \mu (\mathbf{E}) - \mu (\mathbf{0}) = \alpha \mathbf{E} + \beta \mathbf{EE} + \gamma \mathbf{EEE} + \dots\dots\dots$$

where α = linear polarizability tensor of the molecule and β,γ = non-linear polarizability tensors.

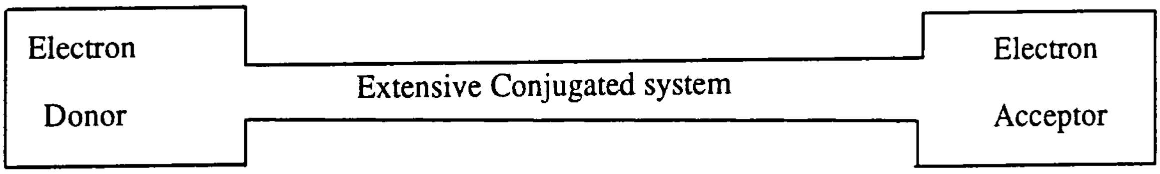
It has been found[22] that only non-centrosymmetric crystalline lattices are capable of producing second order, $\chi^{(2)}$, responses. Furthermore, it is now recognised[22,23] that organic compounds with large β values must possess a charge transfer electronic transition with the following characteristics:

(a) the transition probability must be large;

(b) the transition dipole moment must be large; and

(c) the absorption frequency must be close to twice the excitation frequency.

To satisfy conditions (a) and (b), the molecule should have extensive and uninterrupted electronic delocalization with electron donating and electron withdrawing groups present in the system. Condition (c) determines the choice of excitation frequency with the limitation that the molecule must not reabsorb the harmonic that it produces. An organic molecule with large β would therefore, be expected to have a basic structure such as :



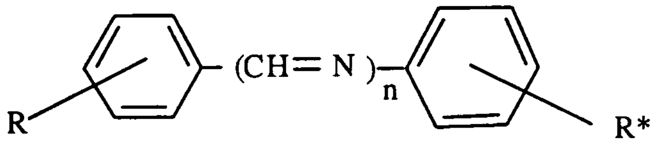
The design of organic molecules with large β would hence require;

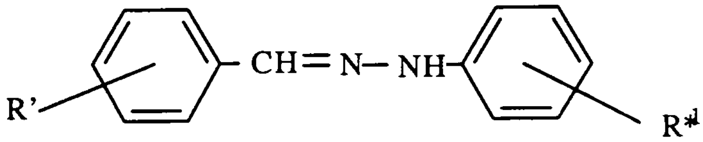
(i) the identification of strong electron acceptor and donor groups;

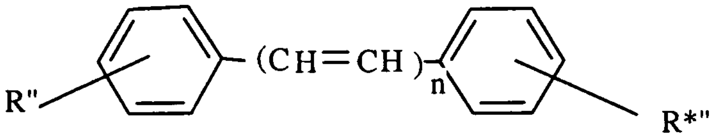
(ii) the identification of effective conjugated systems; and

(iii) the optimisation of the length of the conjugated system.

A study of the substituent effect[24] in a series of disubstituted compounds of the type illustrated below showed that para-NO_2 and para-CN substituents exhibit the strongest electron withdrawing capability and therefore had the largest effect on β . The same study concluded that para-NMe_2 groups were excellent electron donors.







In many instances, interactions between push-pull molecules of this type result in the formation of more energetically favourable centrosymmetric crystal structures in which the dipoles align in an antiparallel fashion. As a result considerable research efforts have been directed towards the development of materials capable of arranging themselves in a noncentrosymmetric manner.

Many approaches have been tried in attempts to control the molecular packing in NLO materials; the options that are open are:

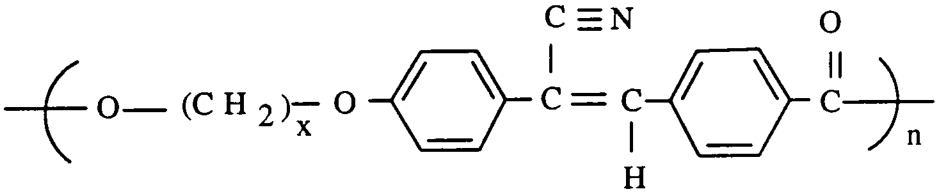
1. introduce a chiral centre in the molecule;

2. design a molecule that can form Langmuir-Blodgett films;
3. design a liquid-crystalline NLO material; and/or
4. incorporate the NLO molecule into an ordered polymer matrix.

Main-chain liquid crystalline polymers containing noncentrosymmetric arrangements of electric dipole moments can exhibit second order NLO effects.[25] Warner[26] has predicted a large enhancement of the non-linear dielectric response of polymeric and mesogenic systems by using polymer liquid crystals. It was proposed that the gain would depend on the molecules being stereo-regular, having a dipolar coherence induced by a combination of nematic fields and molecular stiffness and on having defect mediated dynamics.[27]

3. OBJECTIVES OF THIS WORK

This work is concerned with the synthesis of a new class of main-chain liquid crystalline polymers of structure (I) which might be of potential use as second order NLO materials and will serve as a test of Warner's[27] predictions.



(I)

x=3,6,7,8,9,10,11,12.

The conjugated mesogen which is substituted with electron donating and electron withdrawing groups should satisfy the requirements for second order non-linear optical behaviour by lending itself to noncentrosymmetric molecular alignment on the application of an external electric field.[28]

4. POLYESTERS

An ester is a compound whose structure may be derived by the replacement of the hydrogen of an acid by alkyl, aryl, alicyclic or hetero cyclic group. The most important esters are those derived from carboxylic acids. The structural formula of these esters is:

R-COO-R'

R,R'= alkyl, aryl, alicyclic or heterocyclic group.

Most polyesters can be made by direct esterification. Esterification reactions have been studied since the last century.[29] The first polyesters were synthesised directly from diacids and diols, or by ester exchange. The exchange reaction between carboxyl and ester groups is commonly called acidolysis:

$$\mathbf{nR''CO_2RO_2CR'' + nHO_2CR'CO_2H \rightleftharpoons RCO_2(RO_2CR'CO_2)_nH + (n\text{-}1)R''CO_2H}$$

Another type of ester-exchange reaction can occur between two ester groups:

$$\mathbf{RCO_2R'' + R'CO_2R^* \rightleftharpoons R'CO_2R'' + RCO_2R^*}$$

This reaction is called interchange, double ester exchange or esterolysis.

A third type of esterification reaction can take place between an ester and an alcohol.

$$\mathbf{R''\text{-}OH + R\text{-}COOR' \rightleftharpoons R\text{-}COOR'' + R'\text{-}OH}$$

R= -H, methyl, ethyl.

This reaction is often carried out in the presence of titanium (IV) isopropoxide in order to avoid basic or acidic conditions. The reaction is promoted by the removal of the water or alcohol which can be accomplished by a variety of methods. Application of vacuum, utilisation of a stream of inert gas and azeotropic distillation have all been applied successfully.

It was only in the late 1920s that Carothers[30] applied esterification reactions to diesters, or diacids with diols or mixed alcohol-acid compounds to synthesise polyesters.

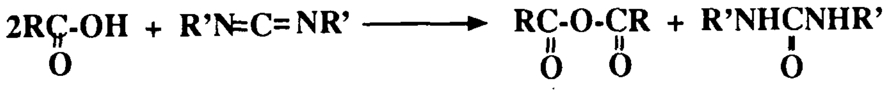
$$\mathrm{HO\text{-}R\text{-}OH + R''\text{-}OO\text{-}C\text{-}R'\text{-}COO\text{-}R''} \rightleftharpoons \left(\mathrm{O\text{-}R\text{-}OO\text{-}C\text{-}R'\text{-}CO} \right)_n + \mathrm{2R''\text{-}OH}$$

$$\mathrm{nHO\text{-}R\text{-}COOR''} \rightleftharpoons \left(\mathrm{O\text{-}R\text{-}CO} \right)_n + \mathrm{nR''\text{-}OH}$$

R"= H, methyl, ethyl.

Since then the reaction has been applied to the synthesis of a wide variety of polyesters. In reality, in order to drive the reaction to completion and to get high molecular weight polymers, drastic conditions , such as high temperature (180°C-230°C), efficient stirring and vacuum application, are needed. Although polyesterification reactions usually proceed smoothly with aliphatic diols bearing primary and secondary hydroxyl groups, they are not generally suitable for diols having aromatic and tertiary hyroxy groups because of their poor nucleophilicity and competing elimination reactions.

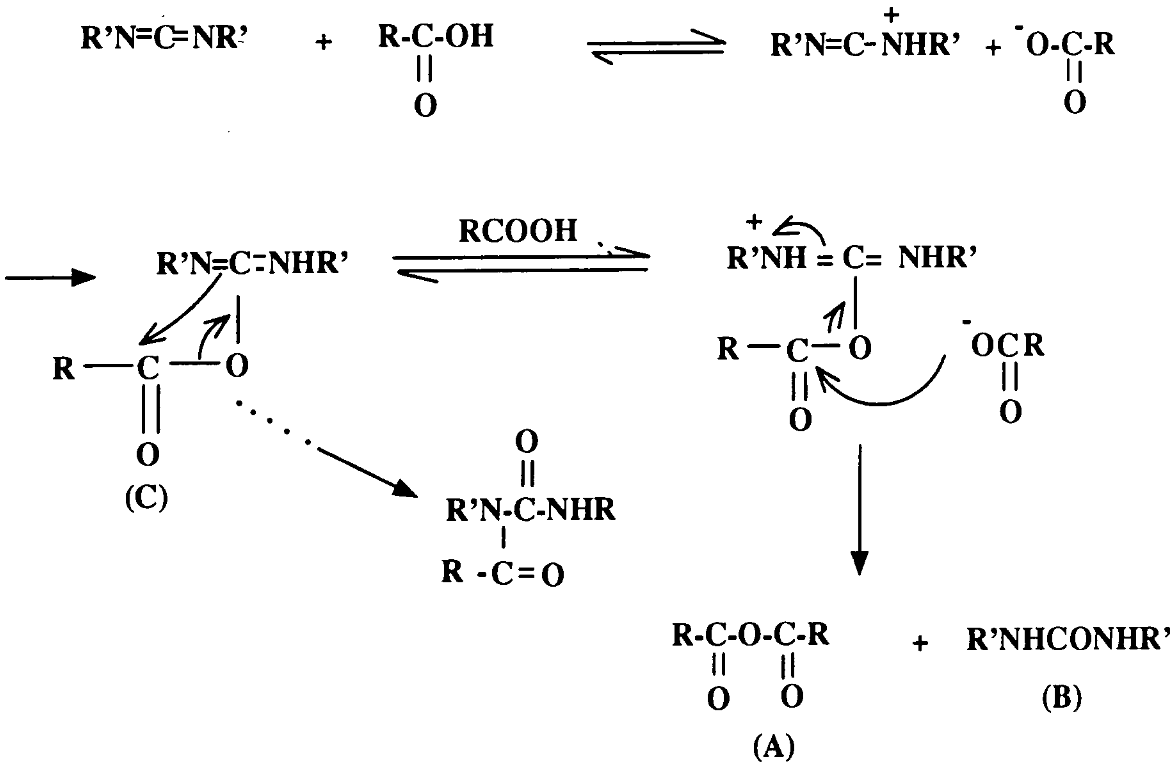
In current practice, esterification reactions between acids and alcohols are often accomplished under mild conditions using highly reactive derivatives of acids. In certain cases reagents such as **DCC** (N,N'-Dicyclocarbodiimide) can be employed to convert the acid to the more reactive anhydride (A). The by-product of this reaction is the appropriate N,N'-disubstituted urea (B).



$$\mathrm{2R}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{\text{-}OH + R'N{=}C{=}NR'} \longrightarrow \mathrm{R}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{\text{-}O\text{-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{R + R'NH}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{NHR'}$$

(A) (B)

The above picture of this reaction is idealized and over-simplified, in practice there are two possible pathways which can lead to complications. The reaction has been studied in detail by Khorana[31,32,33] who has put forward the following mechanism to explain its bidirectional course:



In the first step carbodiimides are protonated and then the acid anion attacks the C atom of the cation formed leading to the formatiom of the very active O-acylisourea(C) which can react further in two ways. On the one hand, intramolecular migration of the acyl group from the O atom to N yields an undesired N-acylurea; on the other hand, after initial protonation of O-acylisourea (C) by an acid molecule the anion of that acid may then attack the carbonyl carbon of the protonated C to give the acid anhydride (A) and urea (B). The rate of the reaction of carbodiimides with carboxylic acids and the ratio of products obtained are affected by a whole range of factors. Among them the most important are:

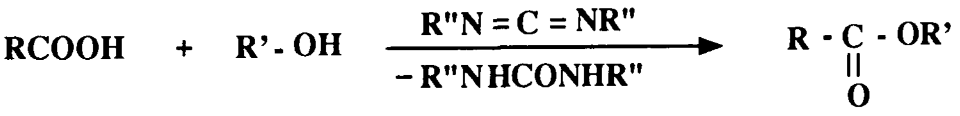
(i) type of carbodiimide used;

(ii) strength of the acid and the nucleophilicity of its anion;

(iii) kind of solvent; and,

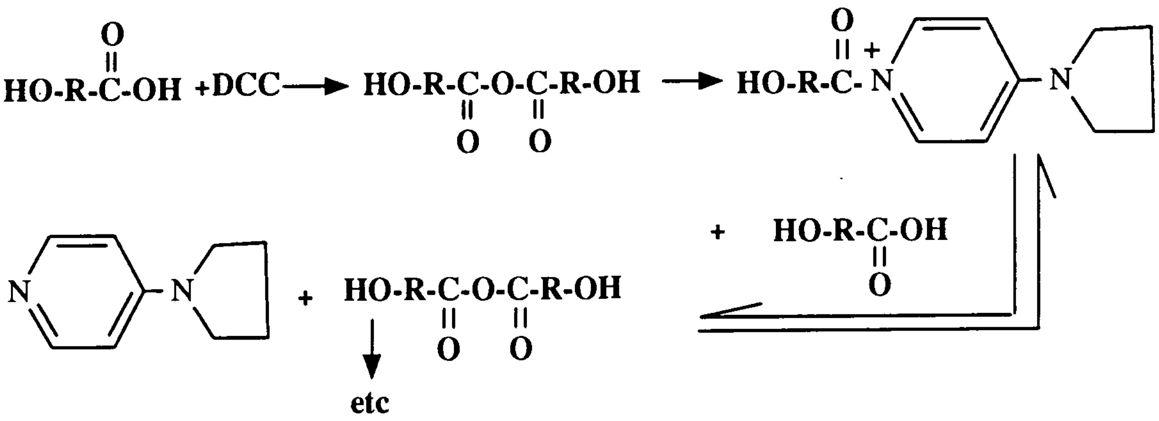
(iv) presence in the reaction medium of other active compounds.

Equimolar mixtures of acids and alcohols undergo condensations in the presence of carbodiimides giving esters in high yields.[34]



$$\mathrm{RCOOH} + \mathrm{R'\text{-}OH} \xrightarrow[-\,\mathrm{R''NHCONHR''}]{\mathrm{R''N=C=NR''}} \mathrm{R\text{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{\text{-}OR'}$$

This reaction has been widely utilised for the synthesis of polyesters. It is generally accepted that the mechanism for the formation of esters in the presence of **DCC** is analogous to that established for the synthesis of anhydrides. It is found that addition of a strongly nucleophilic base, such as 4-pyrrolidinopyridine, increases the yield of the reaction. The carboxylic anhydride which is initially formed by the reaction of the acid with **DCC** acts as an acylating agent for the pyridyl nitrogen which then reacts with an alcohol function to generate the ester bond, as shown below.



This route has been used for the synthesis of all the polyesters described in this thesis.

5.STEP GROWTH POLYMERIZATION

Polymerization reactions can be subdivided into two classes,namely:

(i) chain growth polymerization, in which polymers are formed by chain reactions, and
(ii) step growth polymerization, in which the polymers are formed by the stepwise addition of monomers.

In step growth polymerization reactions the polymer formation is often accompanied by the elimination of a small molecule, such as water, at each step. The small molecule is normally removed as it forms in order to avoid the establishment of an equilibrium. The first step in the reaction is the formation of a bifunctional dimer. As the reaction proceeds, longer chain trimers, tetramers, and so on, form through reactions which are essentially identical in rate and mechanism until ultimately the reaction yields a mixture of polymer chains. Depending on the nature of the monomer involved two main types of step growth polymerisation reactions can be identified.

In the first type, two polyfunctional monomers, each possessing only one distinct functional group, take part in the reaction:

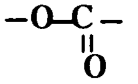
$$\mathbf{A\text{-}A + B\text{-}B \longrightarrow -\!\!\left(A\text{-}A\text{-}B\text{-}B \right)\!\!-}$$

The second type is characterised by the reaction of monomers containing more than one functional groups:

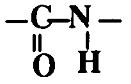
$$\mathbf{nA\text{-}B \xrightarrow{\qquad\qquad} -\!\!\left(A\text{-}B\text{-}A\text{-}B \right)\!\!-}$$

Step growth polymers normally have a basic structure which can be represented as:

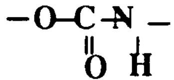
Where R can be $-(CH_2)_x-$ or  and the link —□— is usually an ester, an amide or urethane group.


$-O-\underset{\overset{\|}{O}}{C}-$

ester

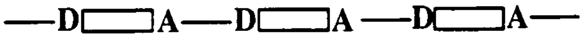

$-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{H}}{N}-$

amide


$-O-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{H}}{N}-$

urethane

The step growth polymerisation reactions described in this work were carried out by the reaction of difunctional stilbenes to give a polymer of the general structure:



Where **D** is an ether group (electron donating) and **A** an ester (electron withdrawing) group linked together by means of a conjugated stilbene system.

CHAPTER 2: EXPERIMENTAL

1. EXPERIMENTAL

2.1 MATERIALS

All reagents and starting materials were bought from the Aldrich Chemical Company.

2.2 INSTRUMENTAL

Infrared spectra were recorded as KBr discs using a Perkin Elmer 1600 FTIR spectrophotometer. Solution ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a VARIAN VXR 400 S spectrometer operating at 399.952MHz and 100.577MHz respectively using $CDCl_3$ or acetone-d_6 as solvent. Studies of thermal properties were carried out using Perkin Elmer a DSC7 differential scanning calorimeter and a Stanton Redcroft TG-760 thermal analyser. Optical microscopy experiments were performed with an Olympus BH-2 polarising microscope equipped with a Linkam THM 600 hot stage. Mass spectra were recorded on a 7070E VG analytical spectrometer. Elemental (CHN) analyses were carried out using a Carlo Erba 1106 elemental analyser. The purity of compound (II) was checked by HPLC using a Perkin Elmer 601 liquid chromatograph equipped with a Perkin Elmer LC55 spectrophotometric detector operating at 254nm. Experiments were performed at room temperature on an ODS column with tetrahydrofuran (THF) as solvent using a flow rate of $1cm^{3}min^{-1}$. Molecular weight distribution studies on the polymer (I) were performed by GPC in THF solution using a VISCOTEK instrument equipped with two mixed columns of PL-gel (pore size: 10^{4}nm; Polymer laboratories Ltd.). Measurements were carried out at room temperature using a flow rate of $1cm^{3}min^{-1}$. A GPC calibration graph was obtained using a series of polystyrene standards.

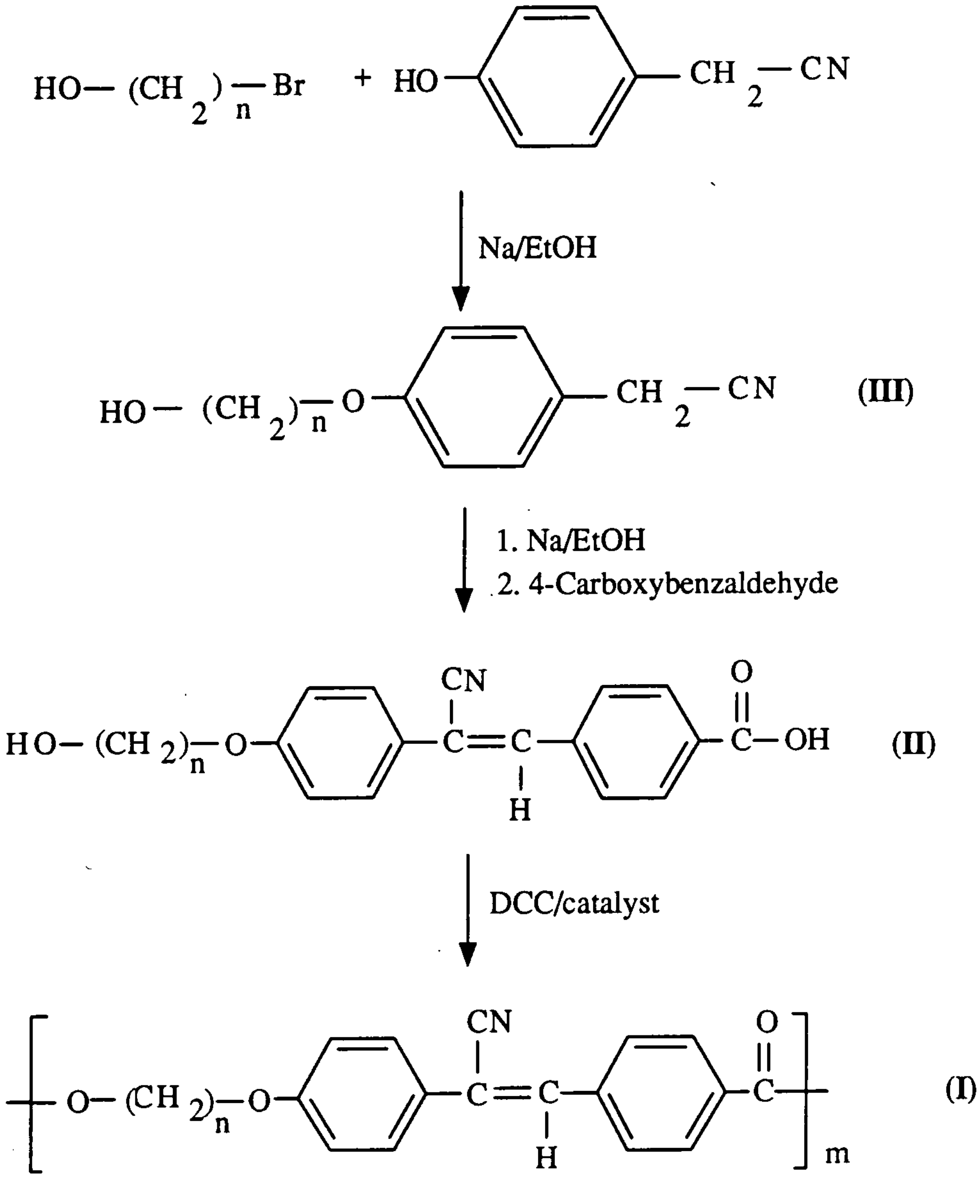
SYNTHESIS

Scheme 3 outlining the Synthetic routes from the starting ω-bromoalkanols and

4-hydroxybenzyl cyanides, via intermediates (III) and (II) to the Polymers (I), which were the primary objectives of this work.

2.3 Synthetic Scheme

Scheme 3. Starting materials, monomer and polymer synthesis



$n = 3, 6, 7, 8, 9, 10, 11, 12$

2.4 GENERAL METHOD FOR THE SYNTHESIS OF (III)

Sodium metal (0.23g, 0.01mol) and dry ethanol (5 cm^3) mixed in a dry, flask ($25cm^3$) equipped with double surface reflux condenser. After the sodium had completely dissolved a solution of 4-hydroxybenzyl cyanides (1.33g, 0.01mol) in absolute ethanol ($5cm^3$) was added with stirring followed by the appropriate ω-bromoalkanol (0.015mol). Once the addition was complete the reaction mixture was refluxed for 6 hrs. Ethanol was removed by rotary evaporation, ether ($50cm^3$) was added to the residue and the resulting solution was washed with 10% aqueous sodium hydroxide solution ($3x5cm^3$), aqueous sulphuric acid solution (1M, $3x5cm^3$) and water ($3x10cm^3$). Evaporation of the dried (magnesium sulphate) ether solution gave the crude product which was purified by chromatography on silica (6 cm x 2 cm^2) using ether/ethyl acetate (7:3) as the eluent to give (IIII) as a white crystalline solid.The yields and some spectroscopic parameters for compound (III) are given in table 1 on the following page.

2.5 TABLE 1. SPECTROSCOPY, MELTING POINT AND YIELD FOR STARTING MATERIALS(III).

n	ν(CN) /cm^{-1}	ν(OH) /cm^{-1}	^{1}H-NMR/ppm	M$^+$mass spec	m.p./^{o}C	Yield/%
3	2246	3419	7.2(d,2H);6,9(d,2H); 4.1(t,2H);3.9(t,2H); 3.7(s,2H);2.1(b,2H).	191	55-56	27%
6	2246	3297	7.2(d,2H);7(d,2H); 3.9(t,2H);3.6(s,2H); 3.5(t,2H);1.7(b,8H);	233	49.5	35%
7	2249	3383	7.2(d,2H);6.9(d,2H); 4(t,2H);3.6(s,2H); 3.5(t,2H);1.5(b,10).	247	62	90%
8	2245	3295	7.3(d,2H);7.2(d,2H); 3.9(t,2H); 3.8(s,2H); 3.7(t,2H);1.7(b,12).	261	65	89%
9	2245	3328	7.2(d,2H);6.8(d,2H); 3.9(t,2H); 3.6(s,2H); 3.5(t,2H);1.7(b,14).	275	74	60%
10	2245	3302	7.2(d,2H);6.9(d,2H); 4(t,2H); 3.7(s,2H); 3,6(t,2H);1.3(b,16H).	289	75	86%
11	2245	3317	7.2(d,2H);6.8(d,2H); 3.9(t,2H); 3.6(s,2H); 3.5(t,2H);1.7(b,18H).	303	80	67%
12	2245	3285	7.3(d,2H);6.9(d,2H); 4(t,2H); 3.6(s,2H); 3.5(t,2H);1.3(b,20).	317	85	59%

2.6 GENERAL METHOD FOR THE SYNTHESIS OF (II)

4-Carboxybenzaldehyde (2g, 0.013mol) was added to a solution of sodium (0.6g, 0.026mol) in absolute ethanol (25cm^3). Compound (III) (0.013mol) was added and the resulting mixture was stirred (magnetic follower) under a nitrogen atmosphere for 3 days. The mixture was poured into aqueous hydrochloric acid solution (0.1M, 200cm^3) and the solid which precipitated was recovered by filtration, washed with acetone (5x50cm^3) and dried in *vaccuo* (20C/10^{-2}mbar) to give cyanostilbene hydroxy acids (II). Some spectroscopic characterisation data and elemental analysis results for the monomers made are given in table 2. The purity of these compounds was checked by HPLC; a single narrow peak was displayed in all cases.

2.7 TABLE 2. SPECTROSCOPY AND ELEMENTAL ANALYSIS FOR MONOMERS(II)

n	ν(CN) /cm^{-1}	ν(C=O) /cm^{-1}	^{1}H-NMR/ppm	M^+ (mass spec)	λ_{max} /nm	FOUND(CALCULATED)		
						C %	H %	N %
3	2218	1682	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,2H).	323	332	**71.07** 71.31	**5.29** 5.52	**4.33** 4.17
6	2221	1694	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,8H).	365	331	**72.35** 72.13	**6.03** 5.87	**3.63** 3.44
7	2218	1706	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);7.0(d,2H);4.0(t,2H); 3.7(t,2H);1.4(10H).	379	332	**72.52** 72.80	**6.46** 6.65	**3.31** 3.69
8	2220	1693	8.2(d,2H);7.9(d,2H);7.6(d,2H); 7.5(s,1H);7.0(d,2H);4.0(t,2H); 3.7(t,2H);1.3(b,12H).	393	332	**73.18** 73.25	**7.02** 6.91	**3.44** 3.56
9	2221	1692	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);7.0(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,14H).	407	333	**73.99** 73.68	**7.39** 7.17	**3.38** 3.43
10	2215	1705	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,16H).	421	331	**74.40** 74.08	**7.60** 7.41	**3.23** 3.32
11	2221	1690	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,18H).	435	332	**74.48** 74.48	**7.76** 7.78	**2.95** 3.20
12	2219	1693	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.0(t,2H); 3.6(t,2H);1.3(b,20H).	449	331	**74.00** 73.97	**7.64** 7.46	**3.21** 3.47

2.8 GENERAL METHOD FOR THE SYNTHESIS OF (I)

A solution of (II)(0.010mol), N,N'-dicyclohexylcarbodiimide (2.06g, 0.010mol) and 4-pyrrolidinopyridine (0.015g, 0.0001mol) in dried dichloromethane (20cm^3) was stirred under reflux for 24hrs under a dry nitrogen atmosphere. The mixture wasfiltered,washed with methanol (3x50cm^3), ethyl acetate(3x50cm^3)and dried under vacuum (20C/10^{-2}mbar) to give (I) as a pale yellow solid. The yields, some spectroscopic parameters and the molecular weight distributions for the polymers synthesised are given in table 3.

2.9 TABLE 3. CHARACTERIZATION DATA FOR POLYMERS(I).

n	ν(CN) /cm^{-1}	ν(C=O) /cm^{-1}	^{1}H-NMR/ppm	FOUND (CALCULATED)			λ_{max} /nm	YIELD %	M_n
				C %	H %	N %			
3	2216	1717	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.6(t,2H); 4.0(t,2H);1.3(b,2H).	——	——	——	——	62	——
6	2217	1717	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,8H).	**76.56** 76.05	**5.78** 6.09	**3.44** 4.03	——	63	——
7	2216	1716	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);7.0(d,2H);4.3(t,2H); 4.0(t,2H);1.4(10H).	**76.28** 76.45	**6.63** 6.41	**4.28** 3.88	337	56	6,500
8	2218	1718	8.2(d,2H);7.9(d,2H);7.6(d,2H); 7.5(s,1H);7.0(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,12H).	**76.18** 76.80	**7.00** 6.72	**3.44** 3.73	336	62	11,000
9	2215	1717	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);7.0(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,14H).	**77.74** 77.12	**7.08** 6.99	**4.18** 3.60	335	55	3418
10	2215	1716	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,16H).	**77.88** 77.38	**7.35** 7.24	**3.80** 3.47	338	91	5,600
11	2216	1715	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,18H).	**77.22** 77.66	**7.46** 7.40	**3.30** 3.35	337	54	9,650
12	2216	1715	8.1(d,2H);7.9(d,2H);7.6(d,2H); 7.4(s,1H);6.9(d,2H);4.3(t,2H); 4.0(t,2H);1.3(b,20H).	**77.35** 77.92	**7.54** 7.70	**3.16** 3.24	336	78	4,500

CHAPTER 3: RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

3.1. Synthesis of compounds (III), 4-(ω-hydroxyalkoxy)-benzylcyanides.

The general method for the synthesis of compounds (III) is recorded in detail in the experimental section. These compounds were obtained by the S_N2 reaction of the phenolate ion with the appropriate 1-bromosubstituted alcohol (see scheme 3, page 21). The highest yield was obtained with 7-bromo-1-heptanol (n=7), 8-bromo-1-octanol (n=8) and 10-bromo-1-decanol (n=10). The lower molecular weight analogues (n=3 and n=6) were the least reactive. This, unexpected behaviour, can probably be explained in terms of the formation of cyclic ether by-products which may be favoured for the shorter chain analogues.

The products were characterised by ^{13}C-nmr, ^{1}H-nmr, ir, mass spectroscopy and elemental analysis. The spectroscopic data for one such material are to be found in Appendix 3; the data for other materials were similar.

According to the ir results (table 1, page 23), the ν(OH) stretching vibration occurs at lower wavenumbers in compounds containing an even number of aliphatic ($-CH_2-$) moieties (n=6,8,10,12) than in their odd membered analogues. The bands are broad and typical for hydrogen-bonded -OH groups bands. The shifts appear to indicate stronger hydrogen bonding interactions in the even series of compounds, possibly a reflection of differences is packing in the solid state.

As regards the melting points of these materials an increasing trend is observed from n=3 to n=12 with one exception, n=6, for which an anomalously low melting point is observed (see table 1).

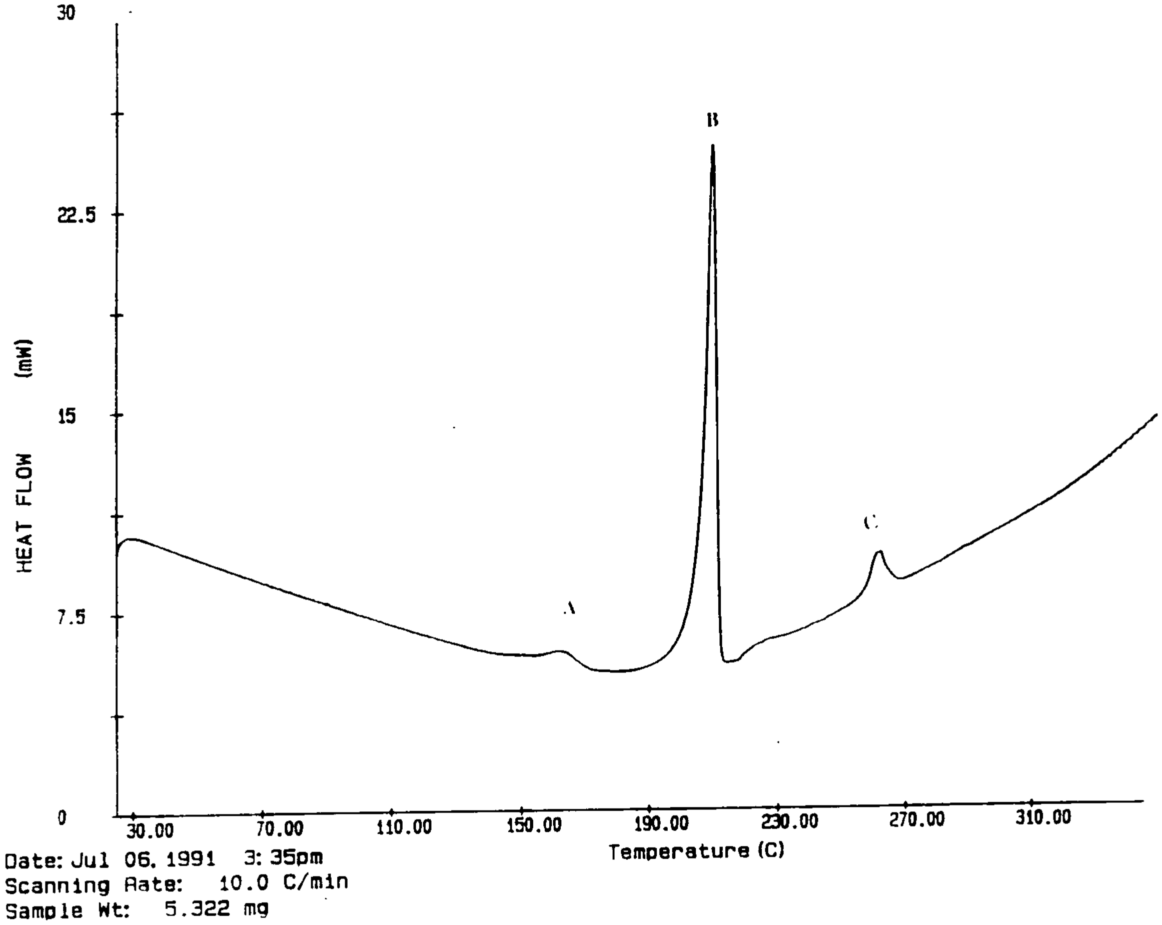


Figure 10. DSC thermogram for monomer, n=3; first heating (heating rate 10 °Cmin^{-1}).

3.2. Synthesis of monomers (II), cyano-stilbenes.

The monomers (II) were synthesised by the reaction of compound (III) with 4-carboxybenzaldehyde as shown in scheme 3, page 21. The products were characterised by ^{1}H-mnr, ir, uv/vis, mass spectroscopy, elemental analysis, dsc, TGA and optical microscopy.

The absorption maximum (λ_{max}) in the UV/vis spectra of the monomers (II), given in table 2, page 24, are characterised by the presence of a strong band at about 332 nm which is attributed to the π-π^* absorption of the conjugated, unsymmetrically disubstituted cyano-stilbene. The length of the aliphatic chain does not seem to affect the position of the absorption maximum.

The ^{1}H-NMR data are tabulated in Table 2. No evidence for the presence of more than one isomers could be identified on the basis of these spectra. It is believed that the monomers exist in the more thermodynamically stable *trans*-form.

Liquid crystalline transitions of monomers

All monomers exhibited liquid crystallinity. A combination of DSC and TG data as well as optical microscopy investigations have demonstrated that the monomer crystals undergo liquid-crystal phase transitions to nematic phases. A typical DSC thermogram is shown in figure 10. The area and position of endotherm A depends on the heating conditions suggesting a crystal-crystal transition. The enthalpy change associated with peak B is of the order of 40 kJmol^{-1} and marks the crystal to liquid crystal phase transition. The liquid crystal to isotropic phase transition, computed from the area of endotherm C is characterised by an enthalpy change of c.a. 4.5 kJmol^{-1}. These values are typical of all the monomers investigated. Evidence for the formation of a nematic phase was obtained by the observation under the polarising microscope of disinclination textures containing both two and four brushes (figures 11a, 11b,and 11c).

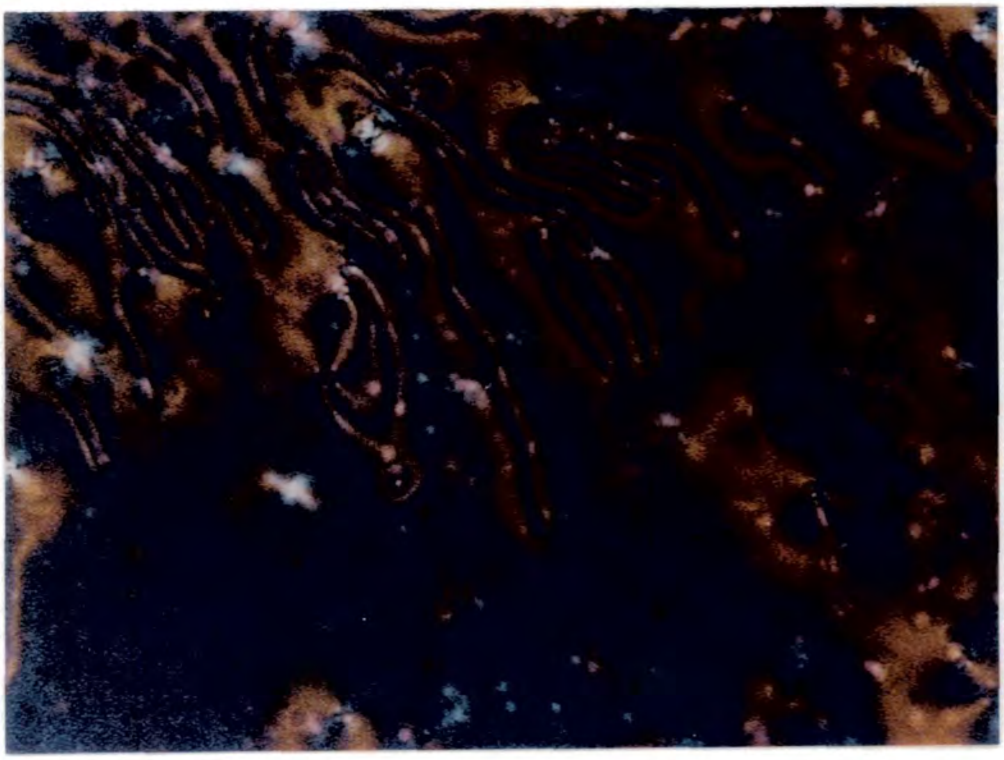


Figure 11a. Photomicrograph (x100) of monomer (n=3) at 254 °C showing the existence of a nematic mesophase

Figure 11b. Photomicrograph (x100) of monomer (n=8) at 205 °C showing the existence of a nematic mesophase

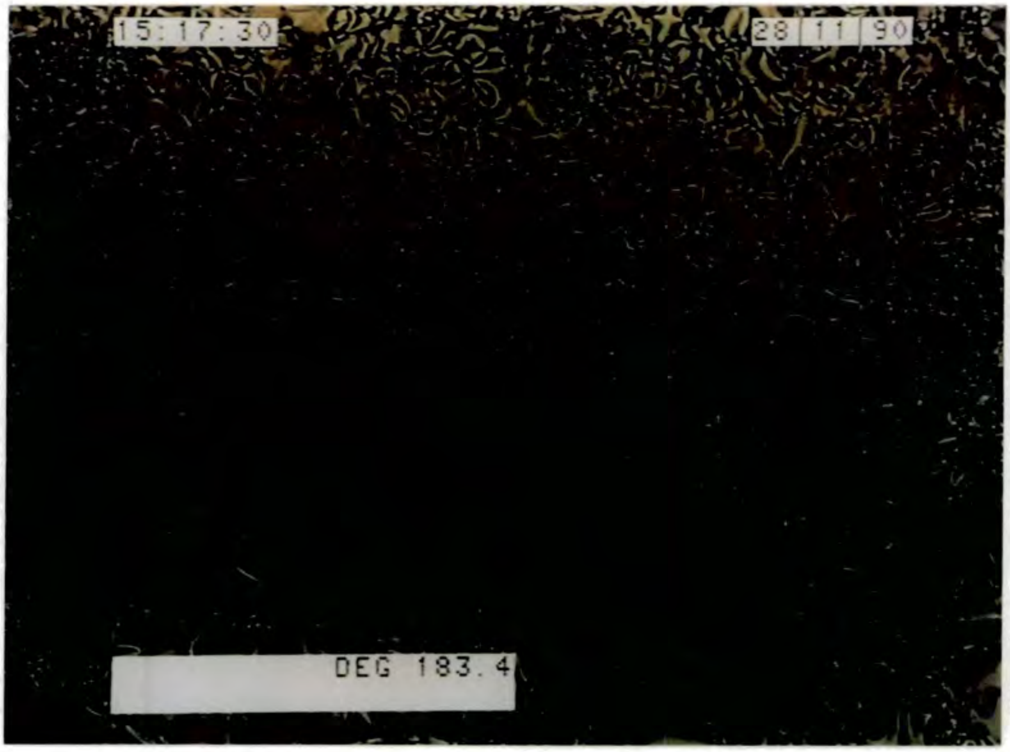


Figure 11c. Photomicrograph (x100) of monomer (n=11) at 183 °C showing the existence of a nematic mesophase

As expected, the crystalline to liquid crystalline transitions of the monomers decreased in a regular manner with increasing length of the aliphatic chain. In parallel with the decrease in the crystal to liquid crystal transition temperatures, a similar decrease in the liquid crystal to isotropic liquid transition temperatures was observed (table 4). This relationship, is depicted in figure 12 .

3.3. Synthesis of polymers (I)

The polymers (I) were obtained via the solution polymerisation of (II) in yields ranging from 55% to 91%. The polymer syntheses are recorded in detail in the experimental procedures.

Infrared spectroscopy revealed that the carbonyl band of the acid monomers at about 1690 cm^{-1} disappears on polymerisation giving place to a new absorption at approximately 1715 cm^{-1} due to the ester carbonyl. In figures 13a and 13b a typical monomer spectrum is compared with that of the corresponding polymer.

The major difference between the ^{1}H-nmr spectra of the monomers as compared to those of the polymers (figure 14) is the disappearance of the $C\underline{H}_2$-OH resonance at 3.5 ppm and the appearance of a new triplet due to -CO_2-$C\underline{H}_2$- at 4.3 ppm. Other differences between the monomer and polymer spectra include a 0.3 ppm downfield shift in the position of the Ph-O-$C\underline{H}_2$- resonance and a 0.3 to 0.4 ppm shift in the -CO_2-CH_2-$C\underline{H}_2$- resonance. All the other spectral features remain unaffected on polymerisation. The ^{1}H-nmr data are reproduced in Table 3.

Comparison of the uv/vis spectra of the polymers with those of the monomers (tables 2 and 3) reveals a slight shift in the position of the absorption maximum which reflects the difference in electron accepting power between the acid and ester groups. The electronic absorption spectra for a typical monomer and the corresponding polymer are shown in figure 15.

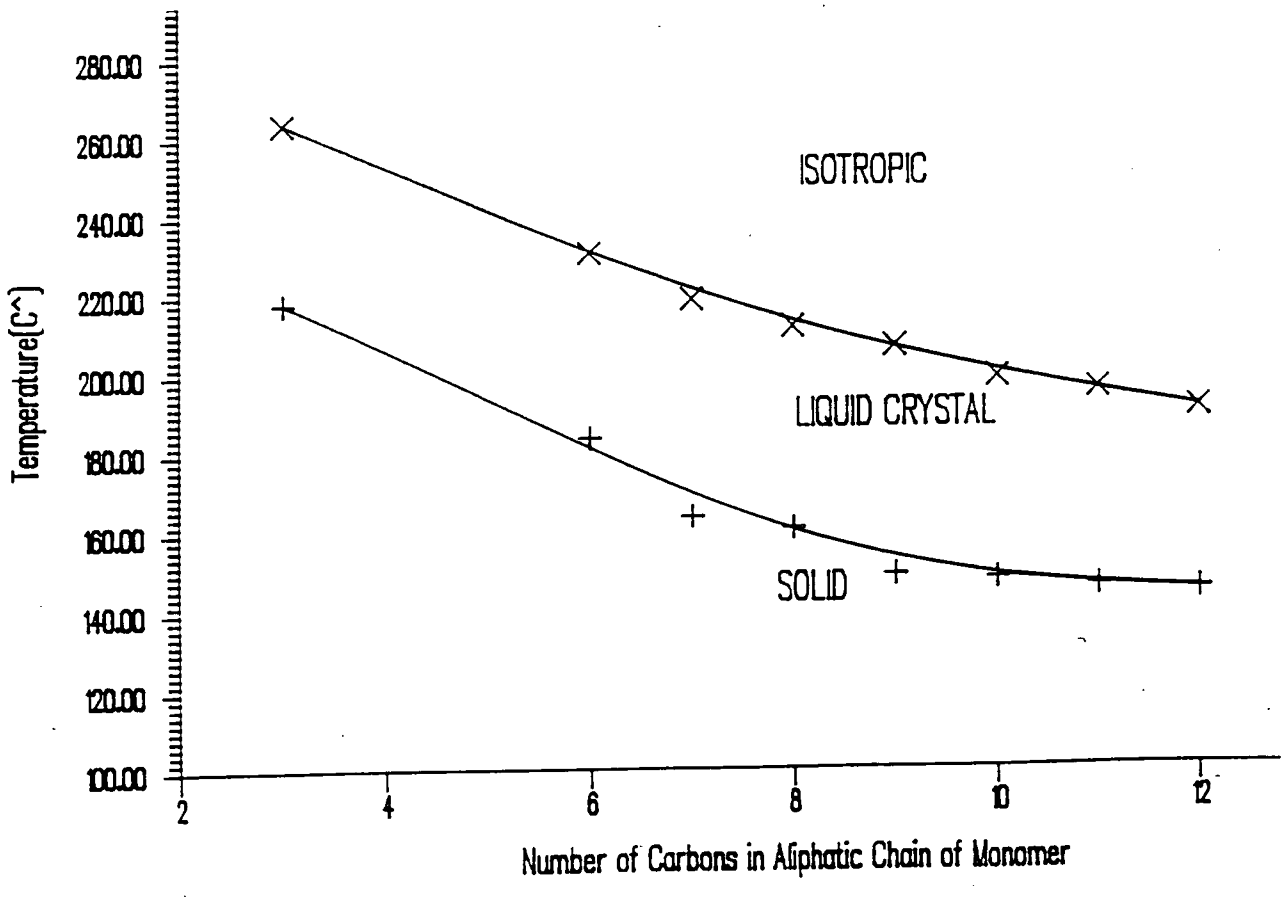


Figure 12. Transition temperatures for the liquid crystalline monomers as a function of the number of carbon atoms in the aliphatic chain.

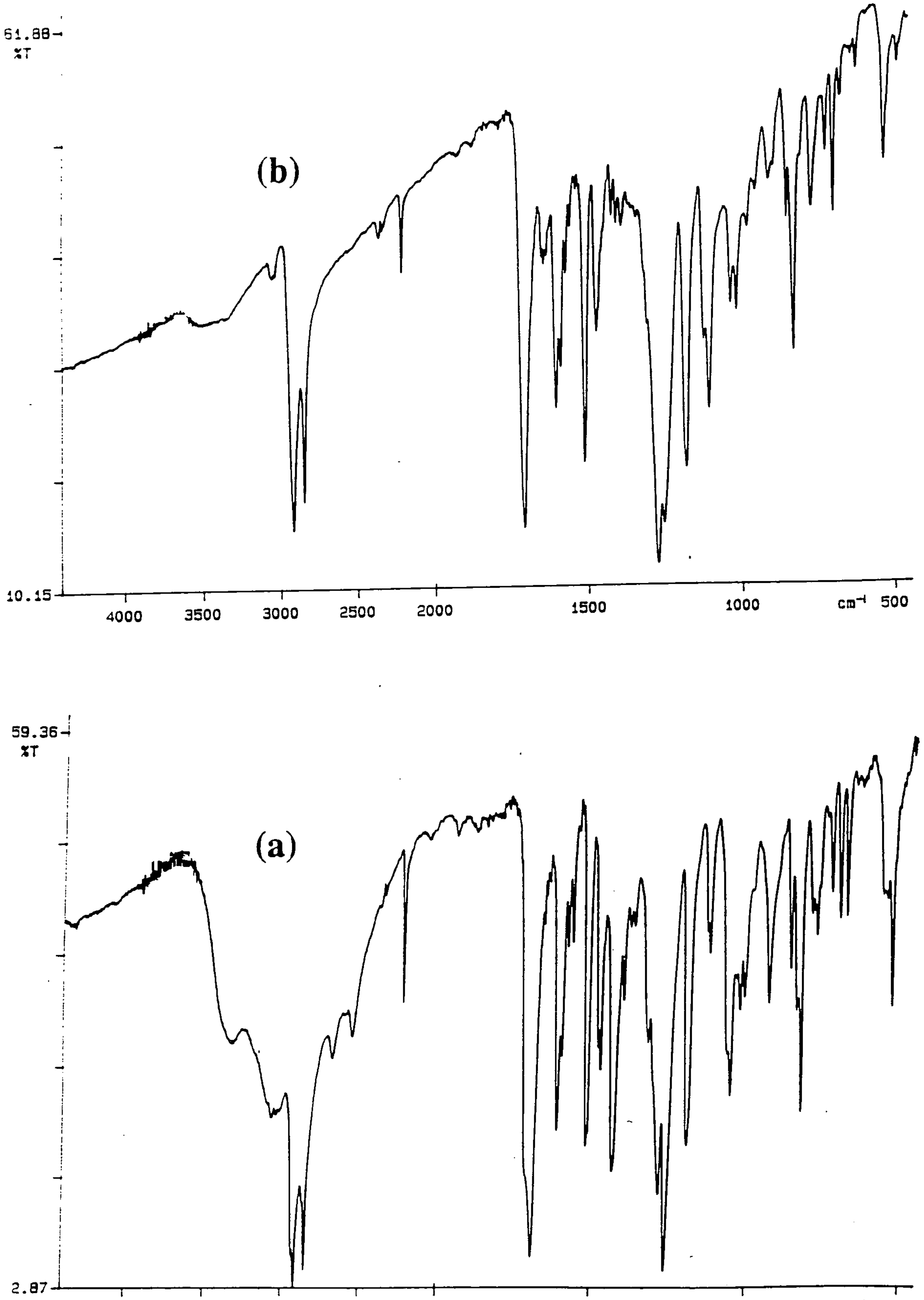


Figure 13. Infrared spectra of (a) monomer (n=11); and (b) polymer (n=11)

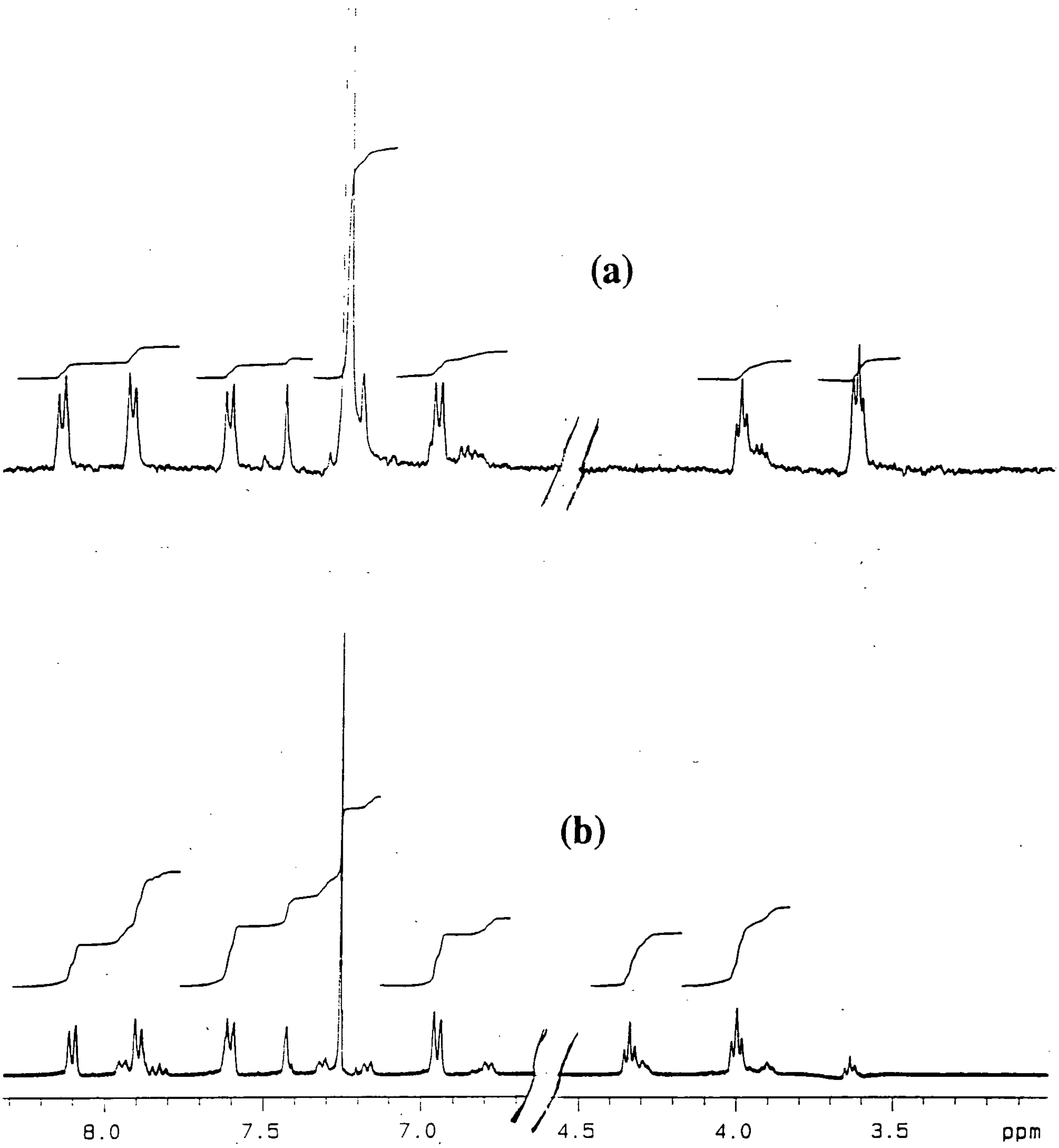


Figure 14. ^{1}H-NMR spectra of (a) monomer (n=11); and (b) polymer (n=11)

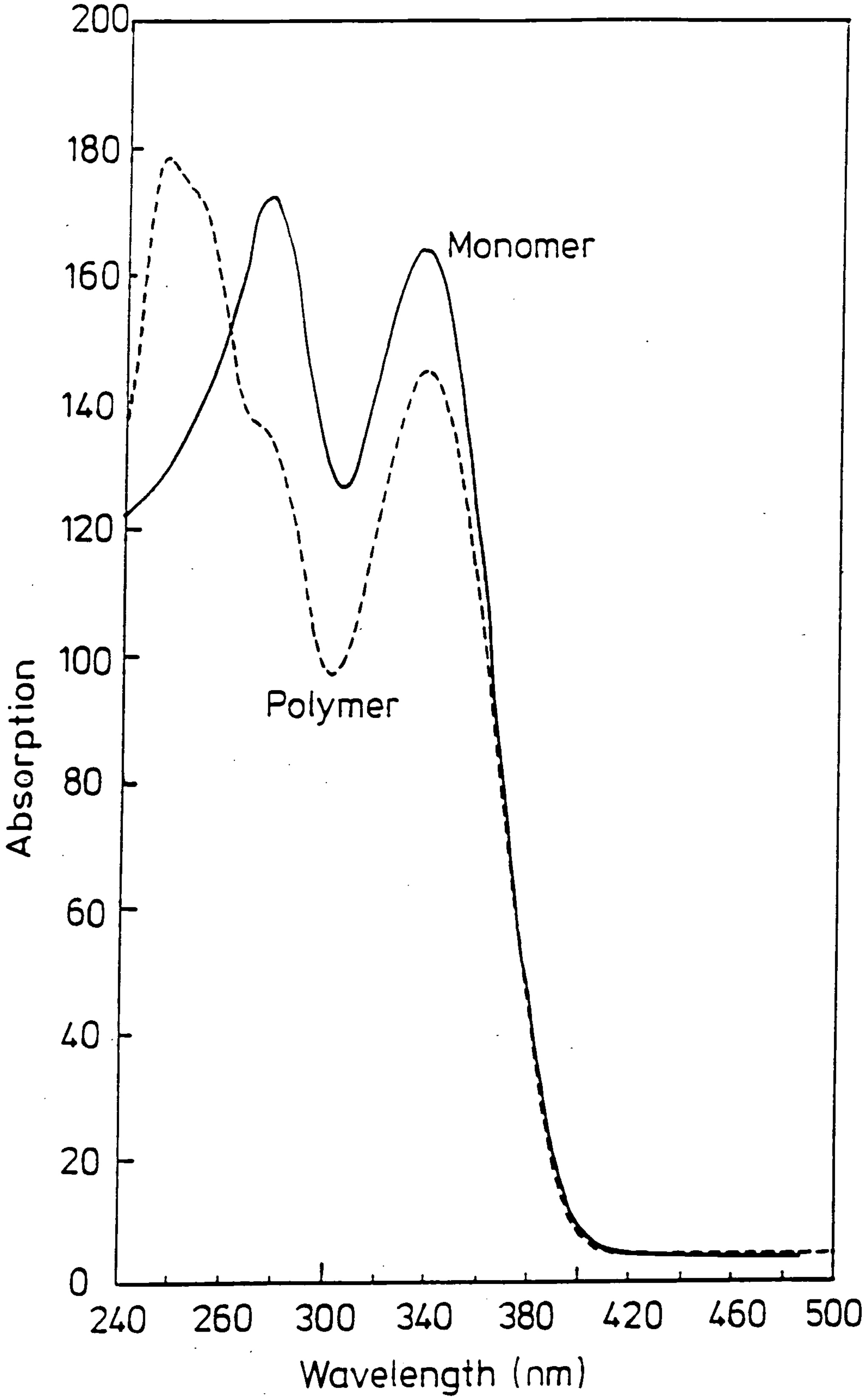


Figure 15. UV/Vis spectra of (a) monomer(n=8); and (b) polymer (n=8)

The number average molecular weights of the polymers, as determined by GPC using a VISCOTEC instrument, are given in Table 3. A typical GPC chromatogram is shown in figure 16.

Liquid crystalline transitions of polymers

The thermal behaviour of most of the polymers as determined by polarised optical microscopy and differential scanning calorimetry is illustrated in the scheme below.

$$\textbf{Solid Polymer} \xrightarrow{\textbf{HEAT}} \textbf{Nematic Polymer} \underset{\textbf{COOL}}{\overset{\textbf{HEAT}}{\rightleftarrows}} \textbf{Isotropic Polymer}$$

Figure 17 shows the mesophase stability range for all the polymers. The transition temperatures of the polymers are given in Table 4. In accord with observations on the monomer samples, the crystal to liquid crystal transitions of the polymers were found to decrease with increasing length of the (-CH_2-) spacer unit. By polarised optical microscopy most polymers, when quenched from the melt state, showed coarse, thread-like nematic textures at room temperature. Above the crystal to liquid crystal transition temperature, the majority of polymers exhibited an apparent homeotropic texture which was retained until the true clearing transition was reached. When a light pressure or shear was applied to the polymer sample opalescence could be observed; a typical photomicrograph is shown in figure 18. The exception to this behaviour was that of C_7-polymer which exhibited a highly birefringent texture (figure 19), throughout the mesophase stability range.

Table 4. Thermal transitions of the liquid crystalline polymers
and the corresponding monomers

n	**monomer**		**polymer**	
	T_1	T_2	T_1^*	T_2^*
3	218(nematic)	264(isotropic)	——	——
6	184(nematic)	231(isotropic)	169(nematic)	228(isotropic)
7	164 (nematic)	219(isotropic)	127(nematic)	222(isotropic)
8	161(nematic)	212(isotropic)	116(nematic)	214(isotropic)
9	149(nematic)	207(isotropic)	131(nematic)	172(isotropic)
10	148(nematic)	199(isotropic)	95(nematic)	126(isotropic)
11	146(nematic)	196(isotropic)	——	——
12	145(nematic)	191(isotropic)	69(nematic)	181(isotropic)

T_1 = Crystalline to liquid crystalline transition (monomer)

T_2 = Liquid crystalline to isotropic phase transition (monomer)

T_1^*= Crystalline to liquid crystalline transition (polymer)

T_2^*= Liquid crystalline to isotropic phase transition (polymer)

The clearing temperatures for the polymers showed a tendency to decrease with increasing length of the flexible spacer up to C_{10}. In polymers with longer spacers the

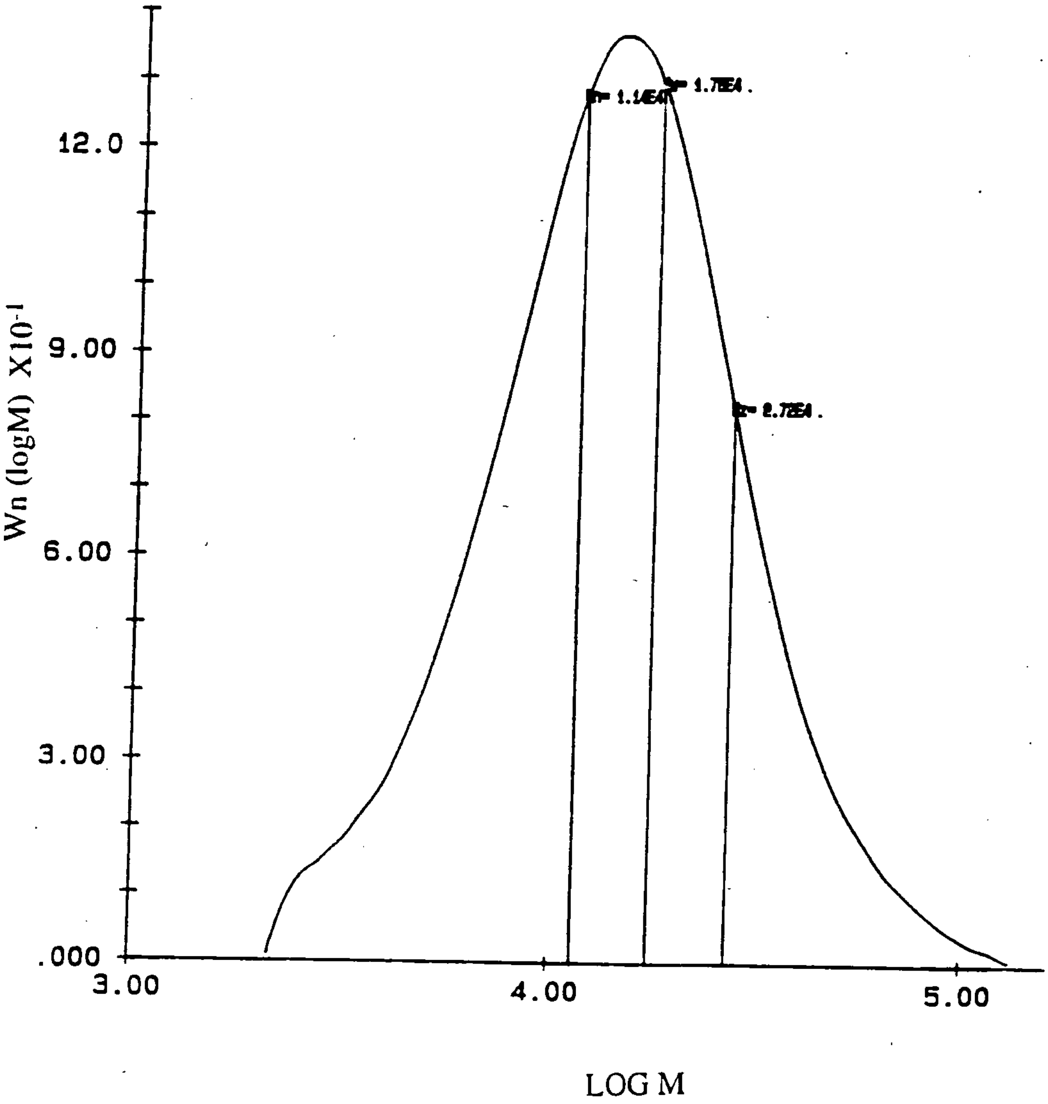


Figure 16. Molecular weight distribution (GPC) for polymer (n=8)

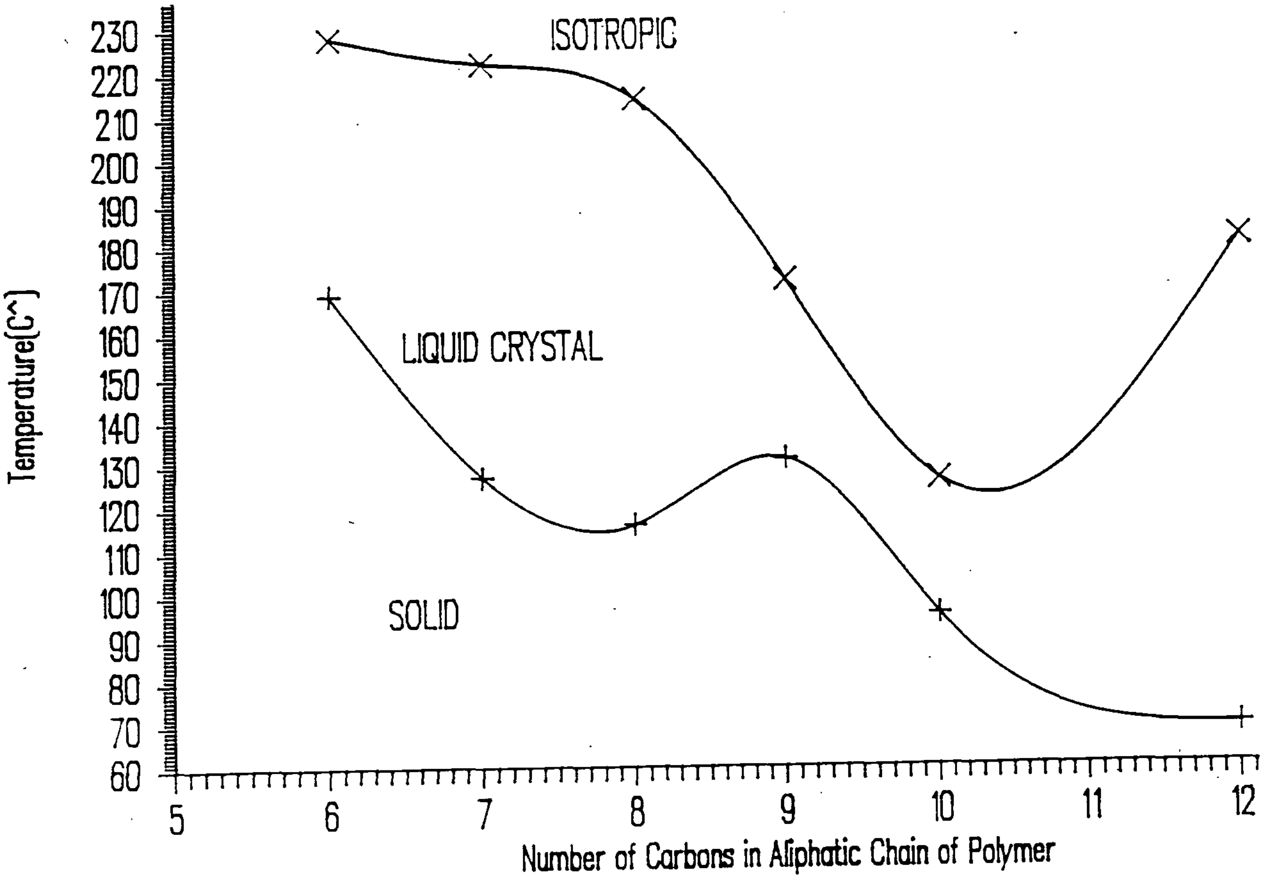


Figure 17. Transition temperatures for the liquid crystalline polymers as a function of the number of carbon atoms in the aliphatic chain.

Figure 18. Photomicrograph (x100) of polymer (n=8) at 138 °C in the heating cycle showing the existence of a nematic mesophase.

Figure 19. Photomicrograph (x100) of polymer (n=7) at 167 °C in the heating cycle showing the existence of a nematic mesophase.

liquid crystal to isotropic transition temperature exhibited an anomalous behaviour in that the C_{12}-polymer showed a much higher clearing temperature than the C_{10} analogue and that a sample of the C_{11}-polymer (prepared under the same reaction conditions) failed to exhibit liquid crystalline properties. It is clear from the results summarised in table 4 that the thermal behaviour of the polymers depends on both the length of the flexible spacers and the overall length of the polymer chains. Nevertheless, these unsymmetrically disubstituted stilbene polymers follow the well documented general trends observed with other main-chain liquid crystalline polymers.[35-38]

In order to investigate the effect of the polymer chain length on the liquid crystal transition temperatures a series of C_{11}-polymers of different molecular weight were synthesised by varying the reaction time or temperature. The results, which are summarised in table 5, demonstrate that the ability of this polymer to develop a liquid crystalline mesophase depends on the length of the polymer chain.

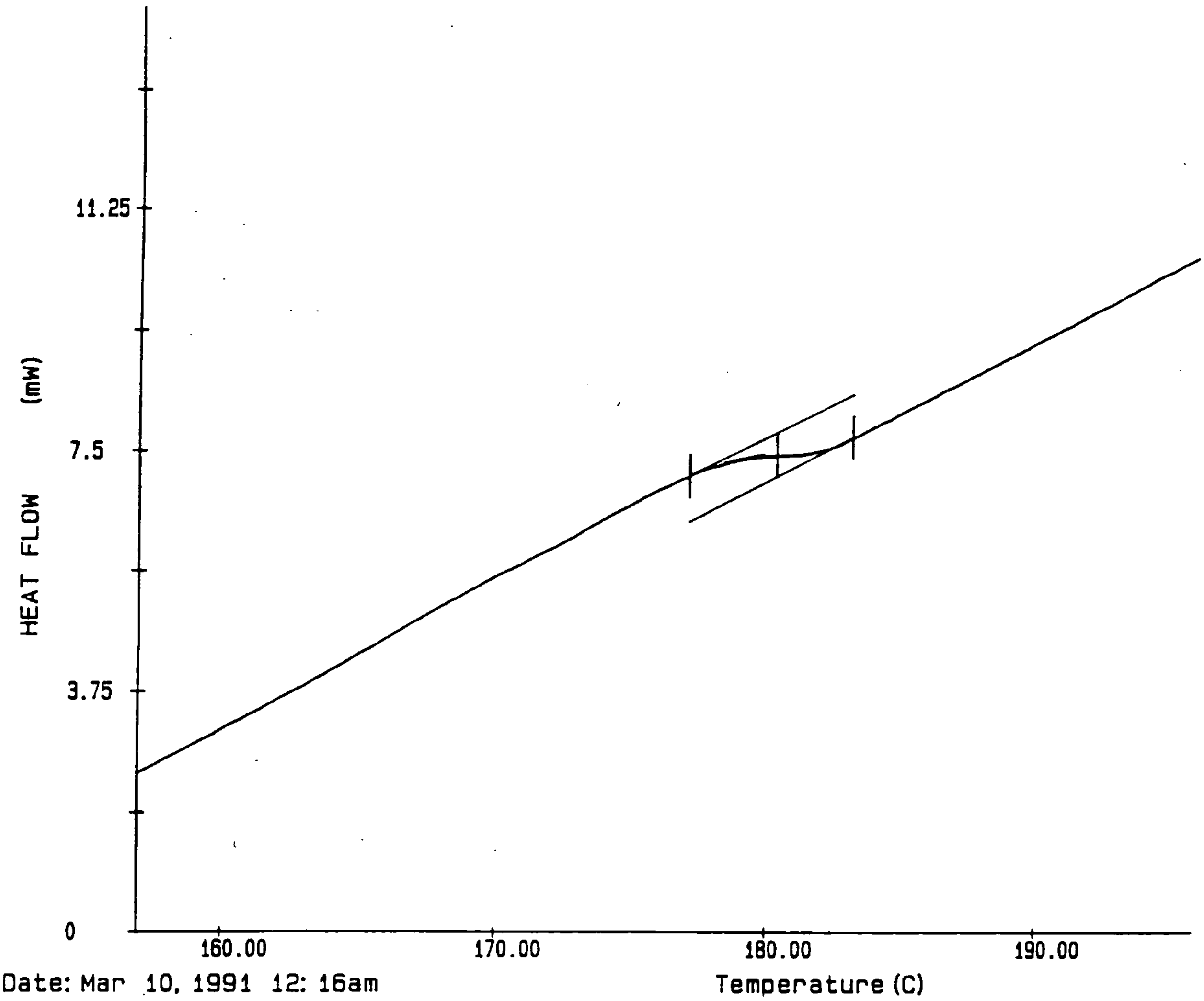
Table 5. The effect of C_{11}-polymer chain length on the liquid crystalline transtition temperatures

Reaction conditions		**M_n(avg)**	**Transition temperatures /C**	
Reaction time /hrs	**Reaction temperature /C**		T_1	T_2
24	48	5,212	no observable liquid crystallinity	
24	50	6,954		
24	54	26,000		
6	reflux	9,600	186	397

T_1 = Crystalline to liquid crystalline transition (polymer)

T_2 = Liquid crystalline to isotropic phase transition (polymer)

The DSC thermogram (figure 20) obtained from a C_{11}-polymer sample (number average molecular weight: 9,600) clearly demonstrates the presence of a glass transition at about 186 C above which temperature the polymer develops the nematic mesophase (figure 21a and 21b) which persists to 397 C. On cooling the isotropic liquid the nematic phase is recovered (figure 22). The results, which are summarised in Table 5 suggest that there is an optimum molecular weight range in which polymeric LC behaviour is observed for this polymer in the absence of extensive thermal treatment. We do not know if this is a general phenomenon. Thermogravimetric experiments (see figure 23) have demonstrated that in all cases compounds I and II decompose at about the same temperature (c.a. 440C).



Date: Mar 10, 1991 12: 16am
Scanning Rate: 10.0 C/min
Sample Wt: 3.000 mg

Figure 20. DSC thermogram showing the glass transition temperature for polymer (n=11; M_n= 9,600).

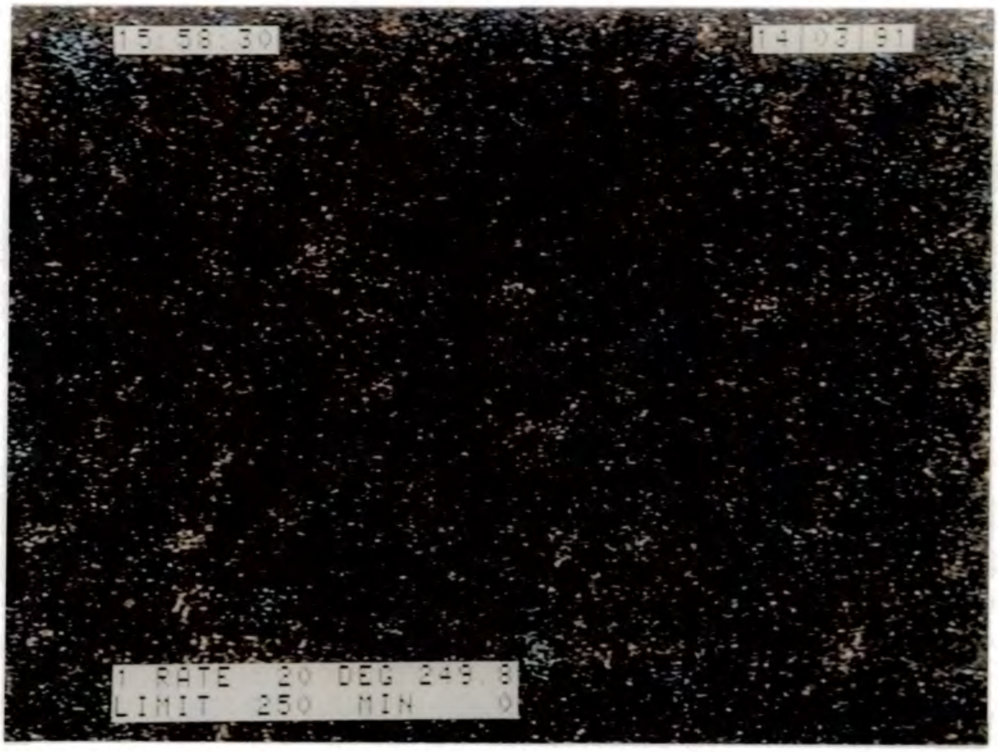


Figure 21a. Photomicrograph (x100) of polymer (n=11; M_n= 9,600) at 250 °C in the heating cycle showing the existence of a nematic mesophase.

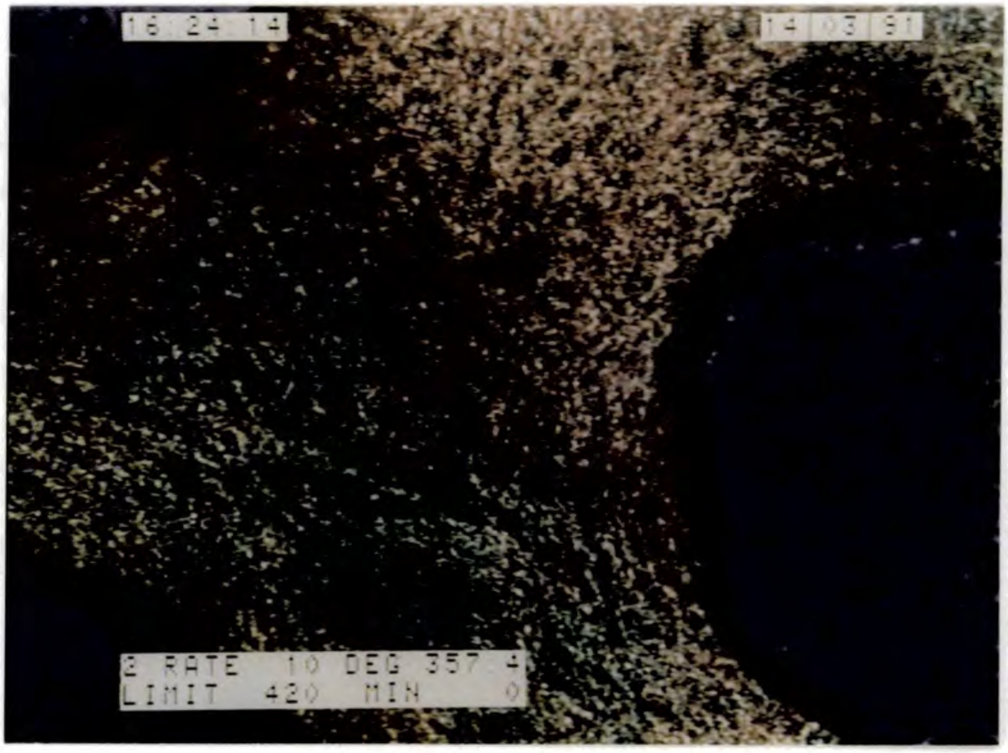


Figure 21b. Photomicrograph (x100) of polymer (n=11; M_n= 9,600) at 357 °C in the heating cycle showing the existence of a nematic mesophase.

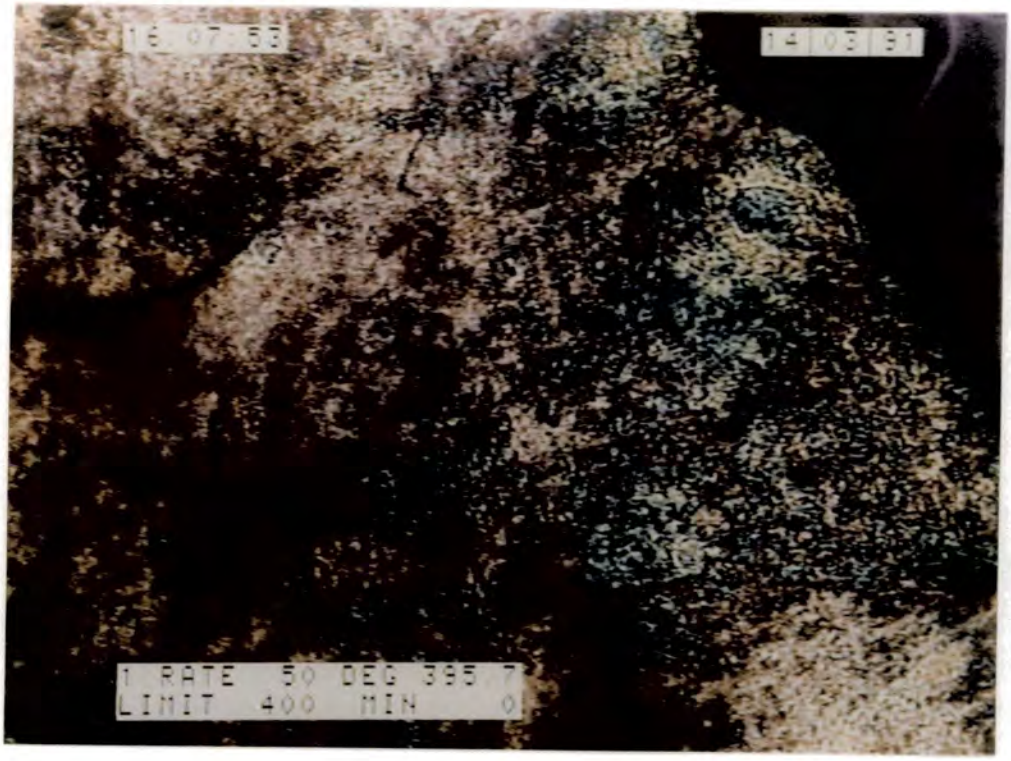


Figure 22. Photomicrograph (x100) of polymer (n=11; M_n= 9,600) at 396 °C in the cooling cycle showing the development of a nematic mesophase from the isotropic liquid.

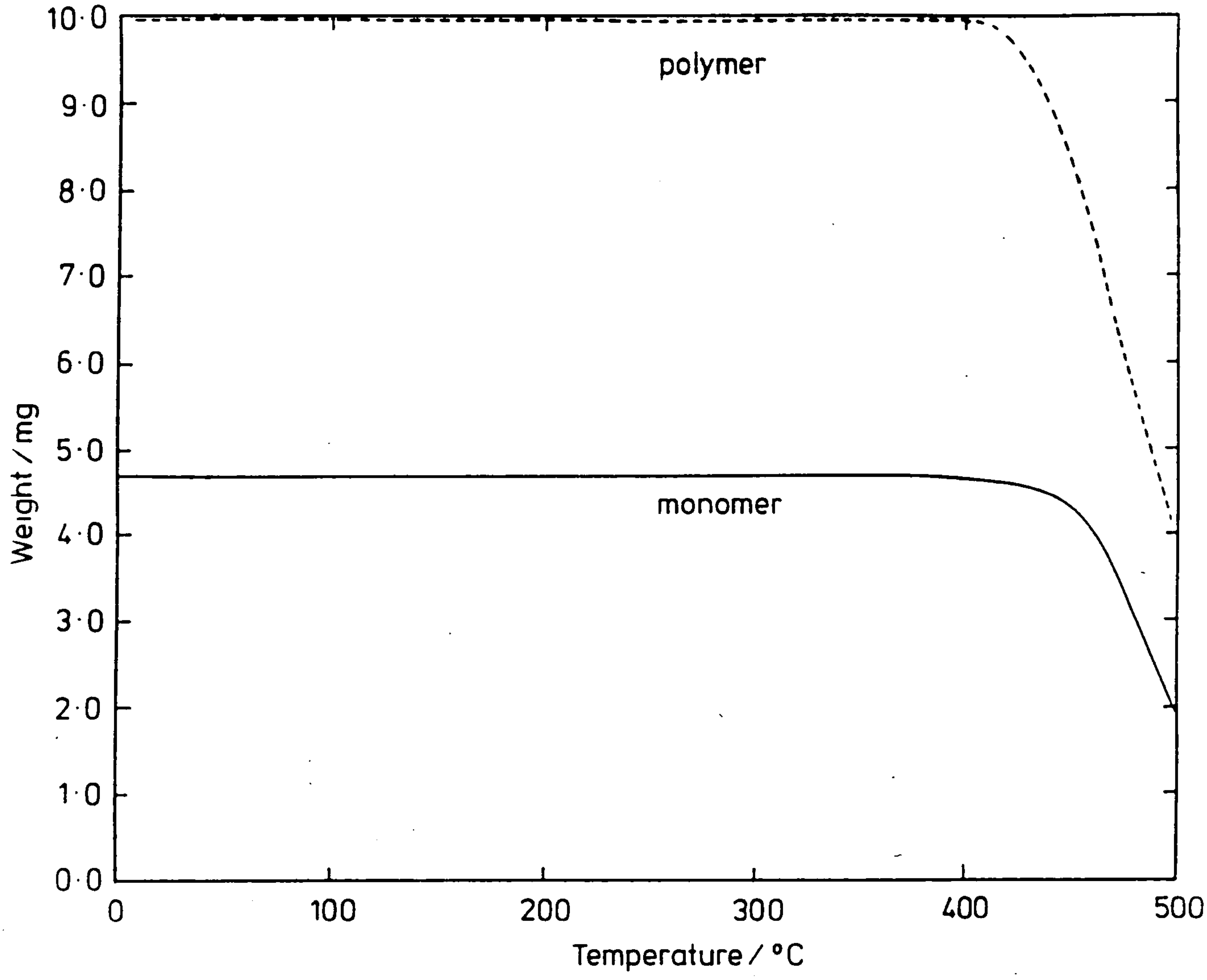


Figure 23. Weight loss (TGA) as a function of temperature for (a) monomer and (b) polymer (heating rate 10 °Cmin^{-1}).

CHAPTER 4: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

4.1. CONCLUSIONS

A number of liquid crystalline monomers based on an unsymmetrically disubstituted cyano-stilbene containing hydroxy- and carboxylic acid moieties have been synthesised and characterised. These were polymerised in the presence of N,N-dicyclohexyl carbodiimide and 4-pyrolidinopyridine to give a new class of main-chain liquid crystalline polymers consisting of a π-conjugated repeat unit which is separated by aliphatic spacers of different lengths. In these polymers the conjugated chromophore is part of the backbone and the dipole moments associated with it point in the same (head to tail) direction along the length of the polymer chain. These dipoles may be capable of non-centrosymmetric alignment in the presence of electric and/or magnetic fields thus making the polymers suitable candidates for utilisation as active elements in nonlinear optical devices. The second-order nonlinear optical properties of the polymers are currently under investigation.

The effect of the length of the aliphatic spacer unit on the mesophase stability range was also investigated as was the relationship between the number average molecular weight and the ability of one of the polymers to exhibit liquid crystalline behaviour.

4.2. SUGGESTIONS FOR FURTHER WORK

The following suggestions are proposed for further work:

1. Synthesis of other stilbene derivatives in which the cyano- group is replaced by a range of electron donating or electron withdrawing groups.
2. Synthesis of a new class of polymers in which the aliphatic spacer is replaced by ether linkages of various lengths.
3. Evaluation of the second order nonlinear optical properties of both monomers and polymers. (This aspect of this work is to be carried out by workers at Cambridge University).

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APPENDIX 1: RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

The Board of studies in chemistry requires that postgraduate research thesis contains an appendix listing all research colloquia, seminars and lectures by external speakers held in the department as well as all conferences attended by the author during the period of research.

1. Lectures attended (October 1990 and July 1991)

11th October 1990
Macdonald, Dr. W. A. (ICI Wilton), Materials for the space age.

24th October 1990
Bochmann, Dr. M. (University of East Anglia), Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyl

26th October 1990
Soulen, Prof. R. (South Western University, Texas), Preparation and Reactions of Bicycloalkenes.

31st October 1990
Jackson, Dr. R. (Newcastle University), New Synthetic Methods: α-Amino Acids and Small Rings.

1st November 1990
Logan, Dr. N. (Nottingham University), Rocket Propellants.

6th November 1990
Kocovsky, Dr. P. (Uppsala University), Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metal.

7th November 1990
Gerrard, Dr. D. (British Petroleum), Raman Spectroscopy for Industrial Analysis.

8th November 1990
Scott, Dr. S. K. (Leeds University), Clocks Oscillations and Chaos.

14th November 1990
Bell, Prof. T. (Suny, Stoney Brook, U.S.A.), Functional Molecular Architecture and Molecular Recognition.

21st November 1990
Prichard, Prof. J. (Queen Mary & Westfield College, London University), Copper Surfaces and Catalysts.

28th November 1990
Whitaker, Dr. B. J. (Leeds University), Two-Dimensional Velocity Imaging of State-Selected Reaction Products.

29th November 1990
Crout, Prof. D. (Warwick University), Enzymes in Organic Synthesis.

5th December 1990
Pringle, Dr. P. G. (Bristol University), Matel Complexes With Functionalised Phosphines

13th December 1990
Coley, Prof. A. H. (University of Texas), New Organometallic Routes to Electronic Materials.

15th January 1991
Alder, Dr. B. J. (Lawrence Livermorw Labs. California), Hydrogen in all its Glory.

17th January 1991
Sarre, Dr. P. (Nottingham University), Comet Chemistry.

24th January 1991
Sadler, Dr. P. J. (Birkbeck College London), Design of Inorganic Drugs: Precious, Hypertension + HIV.

30th January 1991
Sinn, Prof. E. (Hull University), Coupling of Little Electrons in Big Molecules. Implications for the Active Sites of (Metalloproteins and other) Macromolecules.

31st January 1991
Lacey, Dr. D. (Hull University), Liquid Crystals.

6th February 1991
Bushby, Dr. R. (Leeds University), Biradicals and Organic Magnets.

14th February 1991
Petty, Dr. M. C. (Durham University), Molecular Electronics.

20th February 1991
Shaw, Prof. B. L. (Leeds University), Syntheses with Coordinated, Unsaturated Phosphine Ligands.

28th February 1991
Brown, Dr. J. (Oxford University), Can Chemistry Provide Catalysts Superior to Enzymes?

6th March 1991
Dobson, Dr. C. M. (Oxford University), NMR Studies of Dynamic in Molecular Crystals.

7th March 1991
Markam, Dr. J. (ICI Pharmaceuticals), DNA Fingerprinting.

24th April 1991
Schrock, Prof. R. R. (Massachusetts Institute of Technology), Metal-Ligand Multiple Bonds and Metathesis Initiators.

25th April 1991
Hudlicky, Prof. T. (Virginia Polytechnic Institute), Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.

20th June 1991
Brookhart, Prof. M. S. (University of N Carolina), Olelfin Polymerizations, Oligomerization and Dimerizations Using Electrophilic Late Transition Metal Catalysts.

29th July 1991
Brimble, Dr. M. A. (Massey University, New Zealand), Synthetic Studies Towards the Antibiotic Griseusin-A.

2. THE BASICS OF POLYMER SCIENCE AND TECHNOLOGY, AN INTRODUCTORY COURSE IN THE PHYSICS, CHEMISTRY AND ENGINEERING OF POLYMERS. HELD AT HUGH RILEY HALL, RIPON, THREE LECTURES AND TWO RESEARCH COLLOQUIA ON EACH OF THE FOLLOWING DATES:

19th October 1990
2nd November 1990
16th November 1990
30th November 1990
14th December 1990
25th January 1991
8th February 1991
22nd February 1991
8th March 1991
22nd March 1991

3. RESEARCH CONFERENCES:

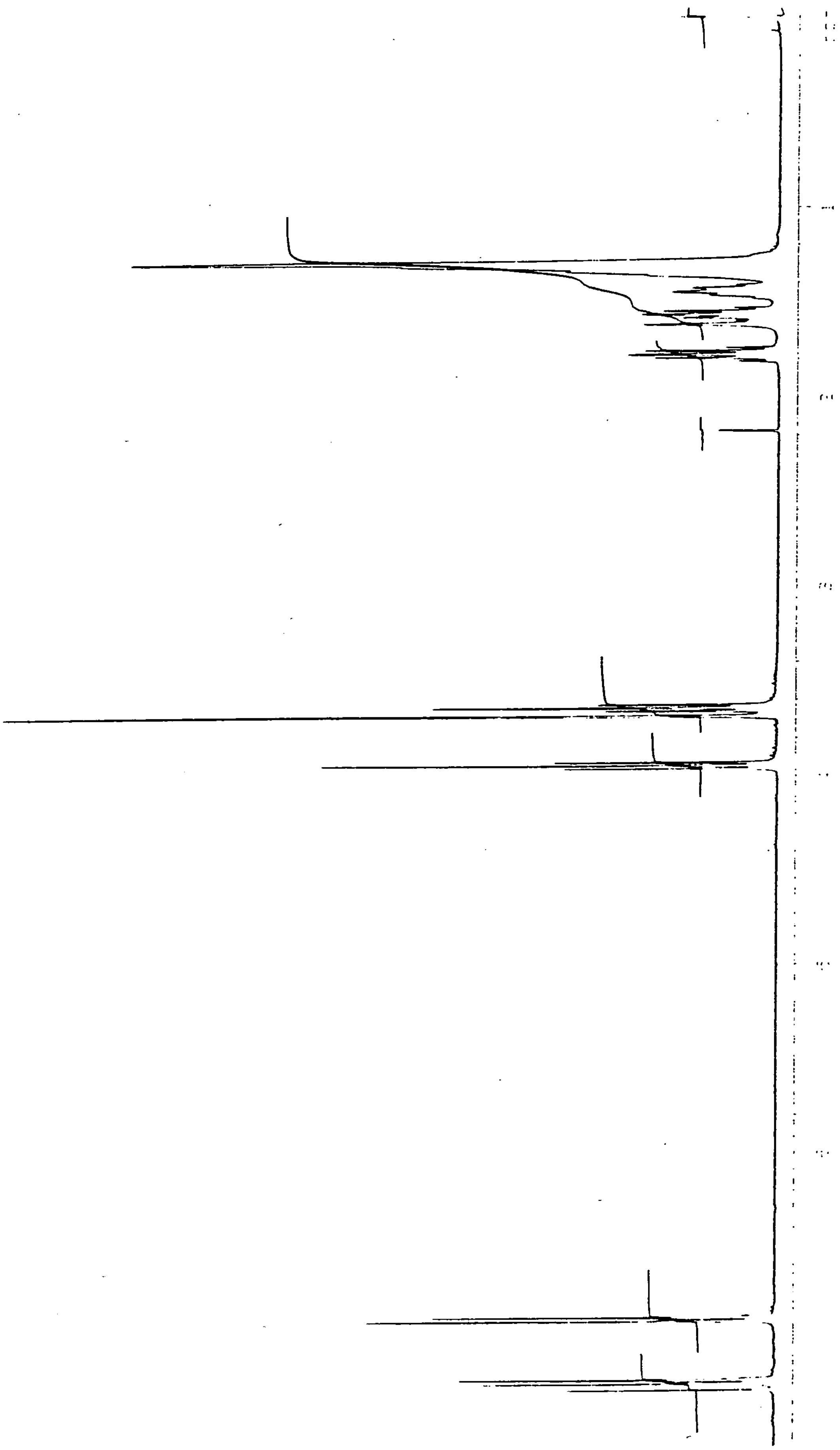
(a). Macro Group Polymer Meeting,(Lancaster University,26th-28th March 1991)

(b). Polymer Surfaces and Interfaces II an International Symposium,(Durham University, 22th-26th July 1991).
(c).Graduate Symposium at Newcastle University, 15th May 1991.

4. Polymer Chemistry Graduate Lectures:

(a). Polymer Synthesis (6 Lectures, **Feast**, Prof. W. J.)
(b). Polymer Physical Chemistry (6 Lectures ,**Richards**, R. W.)

APPENDIX 2: EXPERIMENTAL DATA



Figurte 24. ¹H-NMR spectrum for 4-(hydroxy alkoxy)-benzylcyanide, n=11

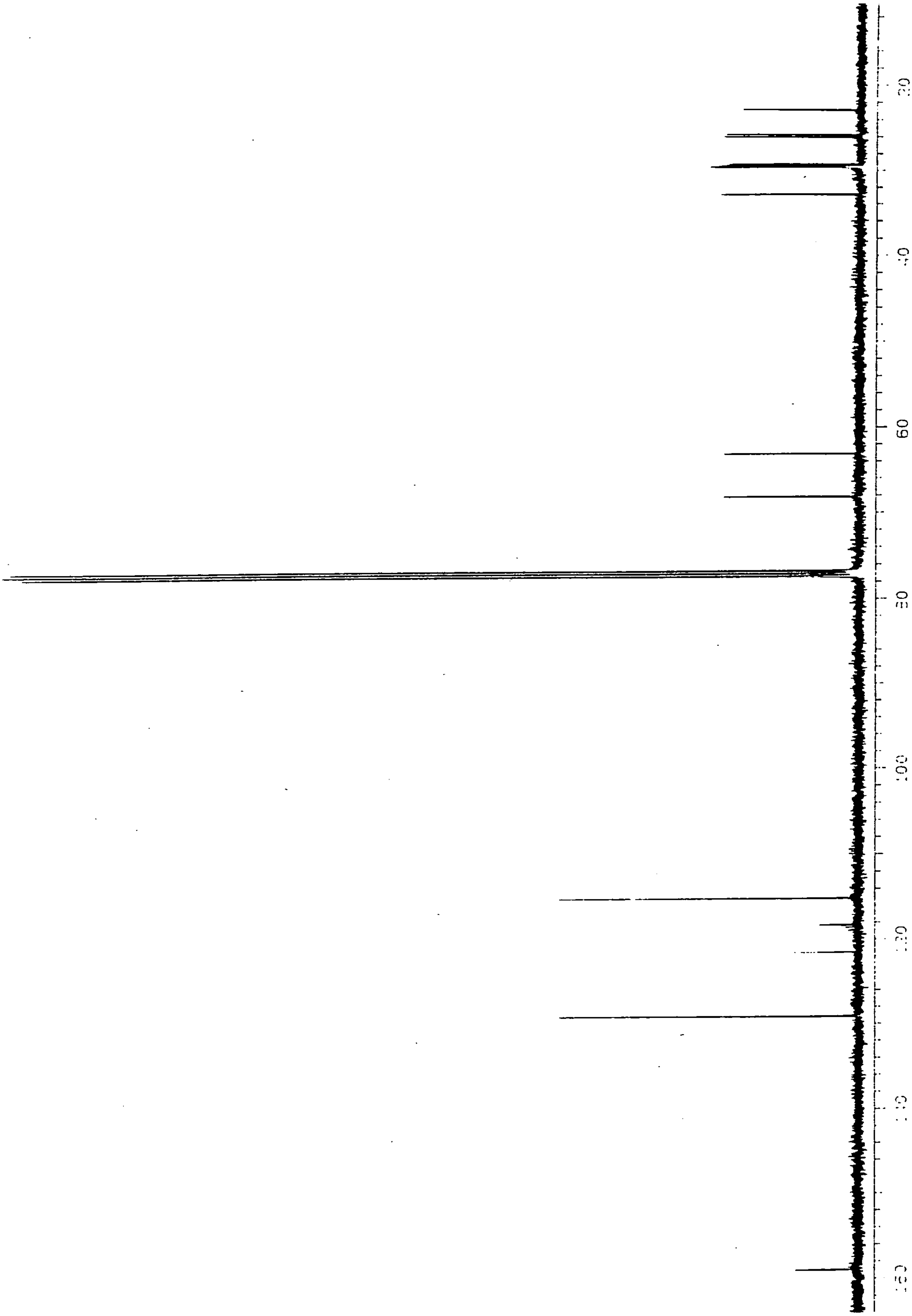
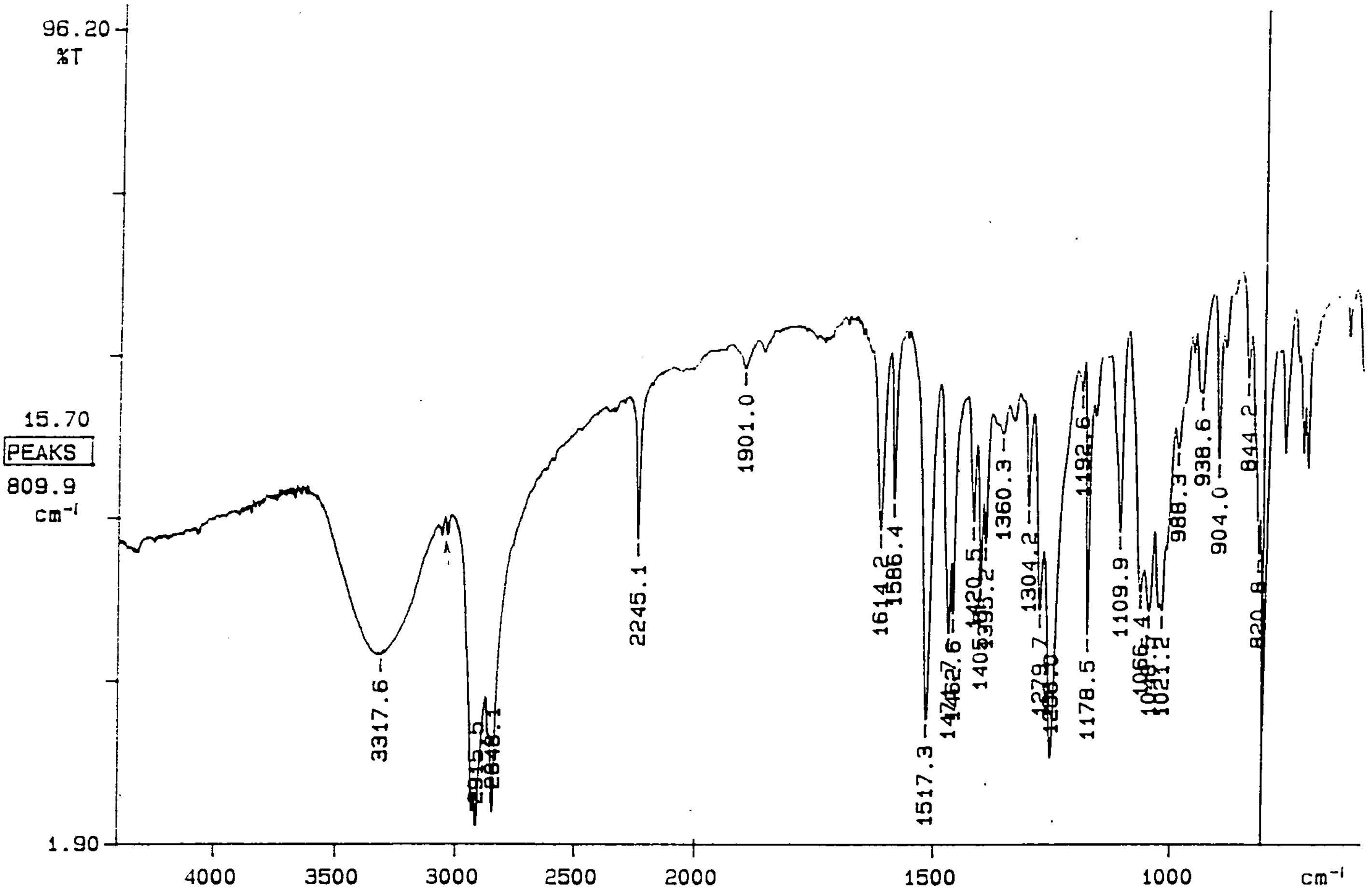


Figure 25. ^{13}C-NMR spectrum for 4-(ω-hydroxy alkoxy)-benzylcyanide, n=11.



90/11/06 17:26
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Figure 26. Infrared spectrum for 4-(ω-hydroxy alkoxy)-benzylcyanide, n=11.

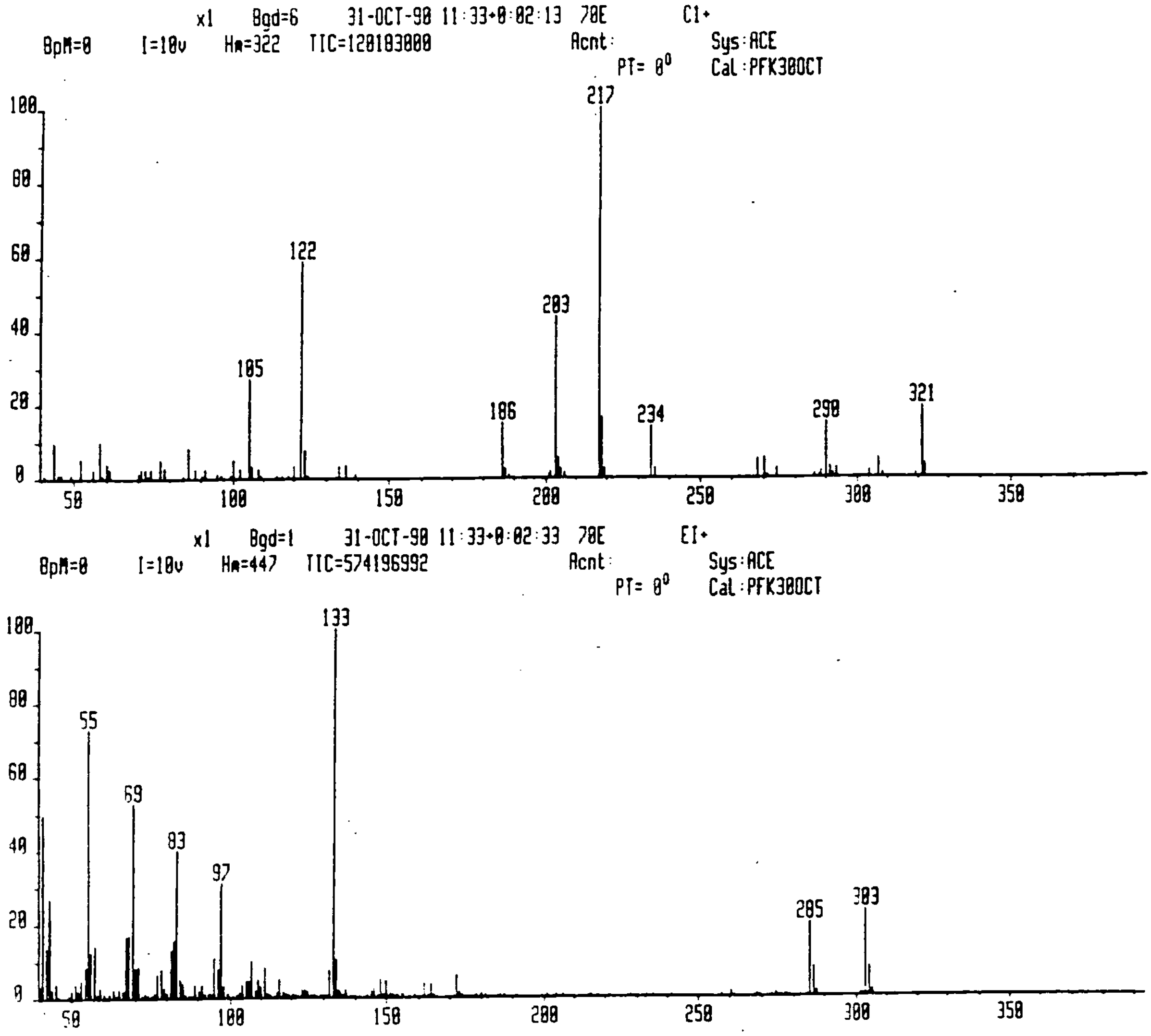

Figure 27. Mass spectrum for 4-(ω-hydroxy alkoxy)-benzylcyanide, for n=11.

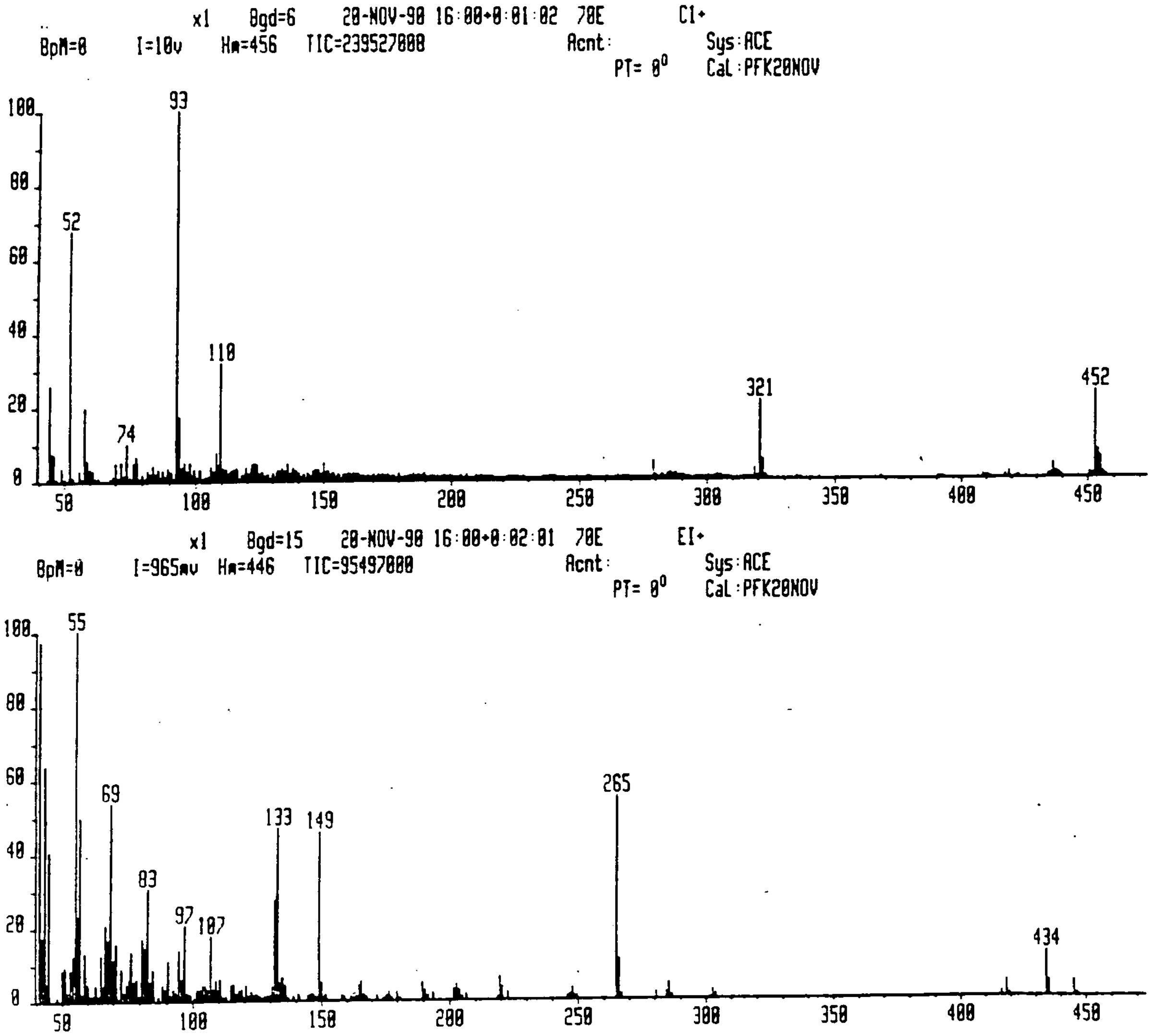

Figure 28. Mass spectrum for monomer, n=11.

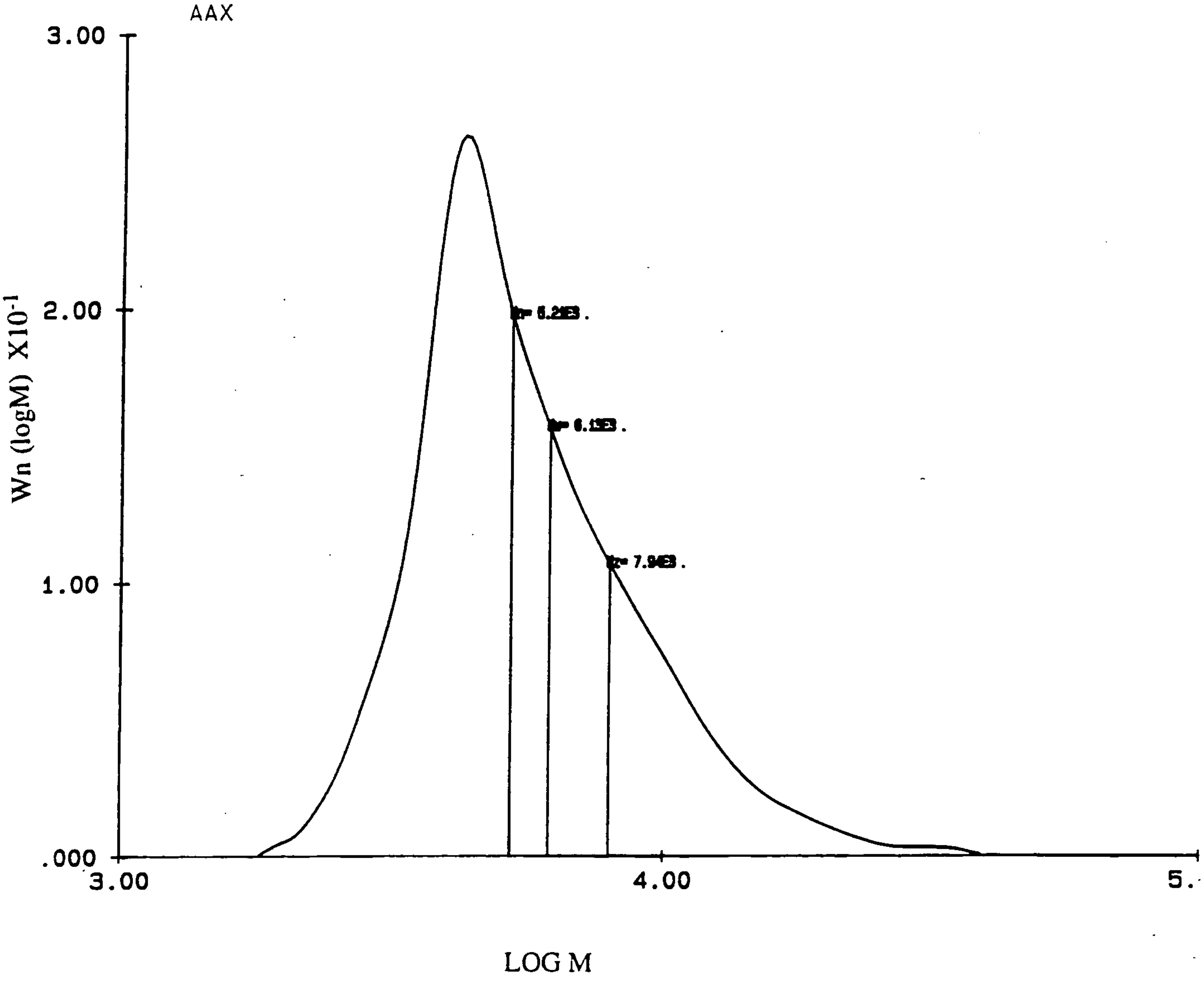

Figure 29. Molecular weight distribution (GPC) for polymer (n=11; M_n=5,212).

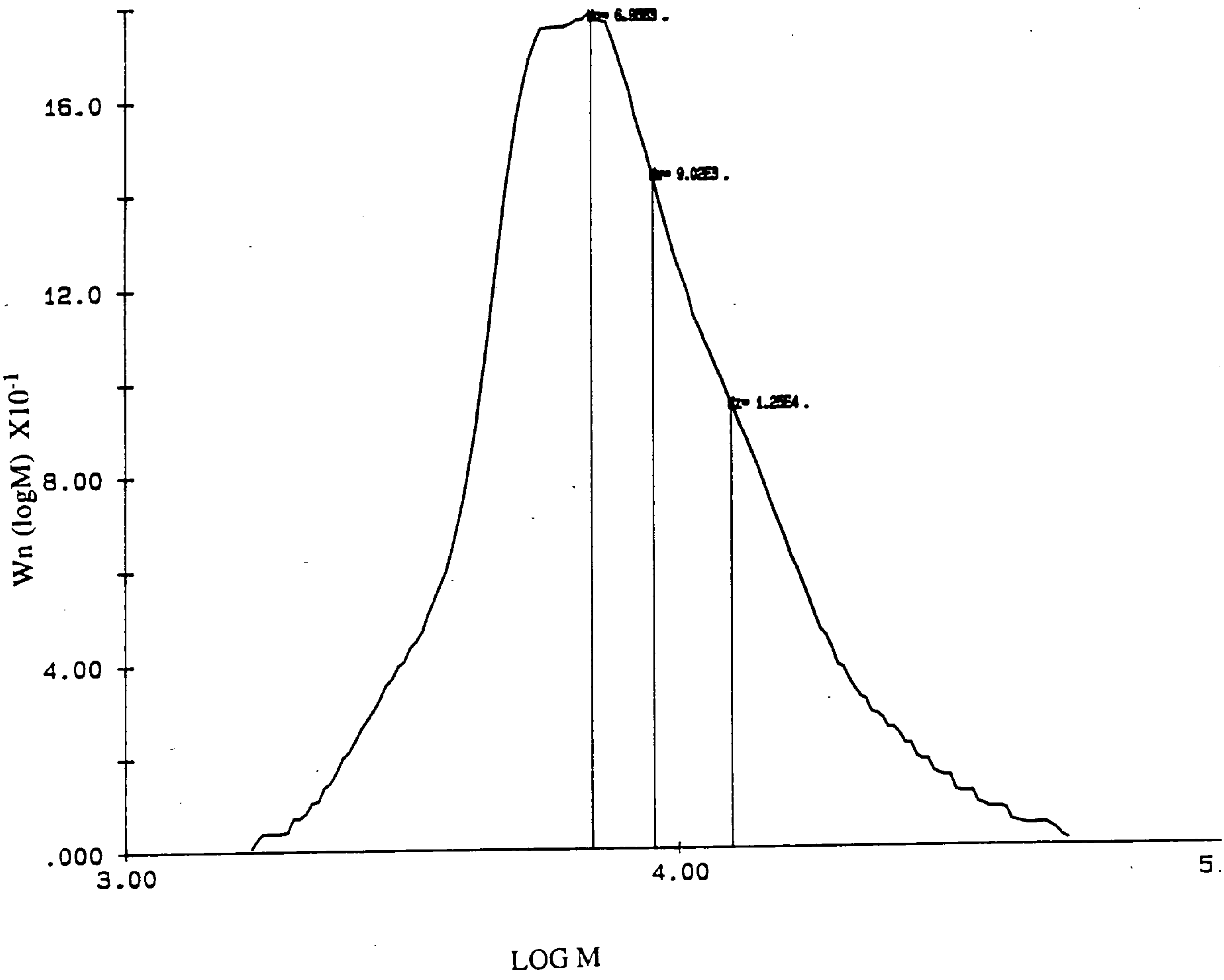

Figure 30. Molecular weight distribution (GPC) for polymer (n=11; M_n=6,954).

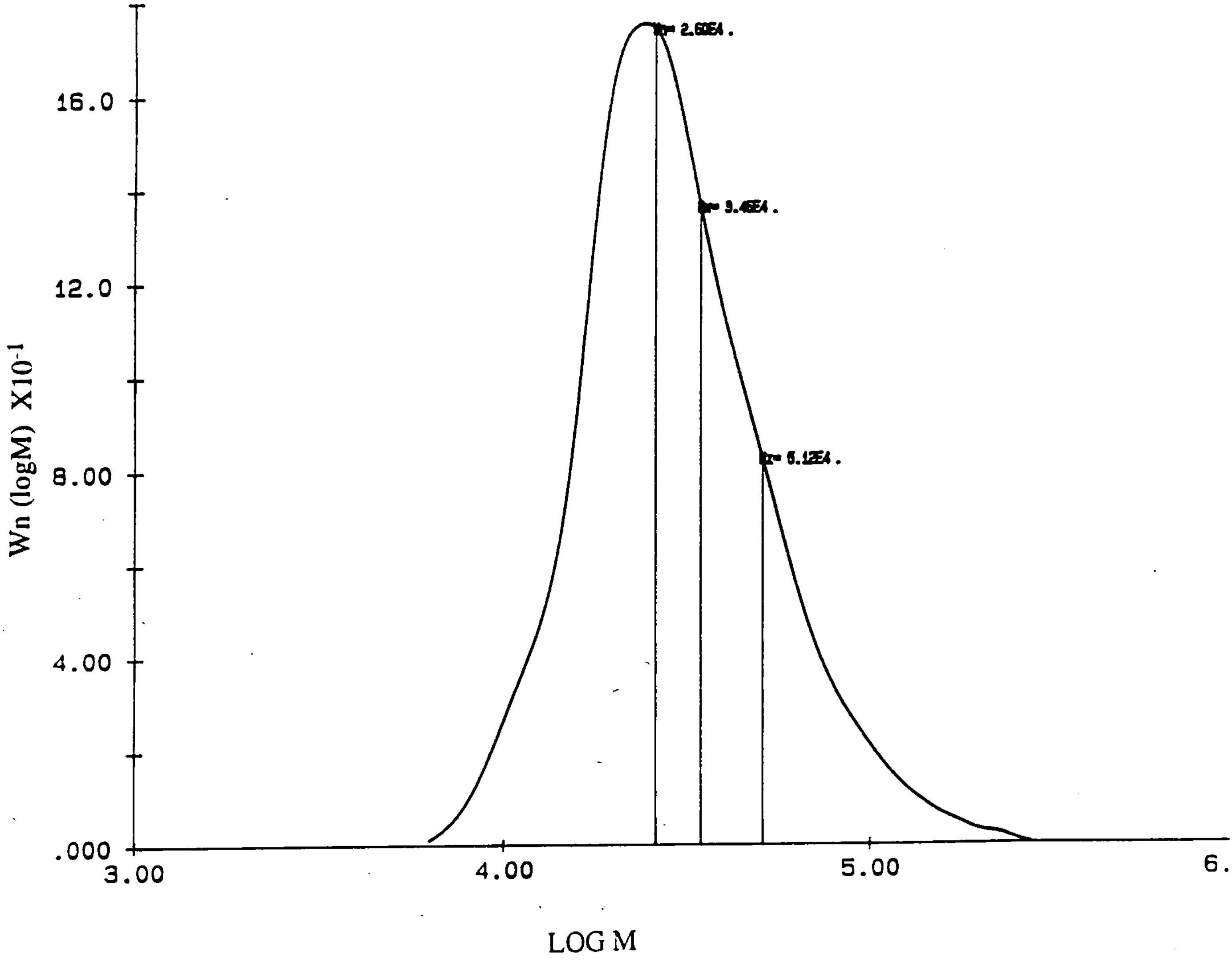

Figure 31. Molecular weight distribution (GPC) for polymer (n=11; M_n=26,000).

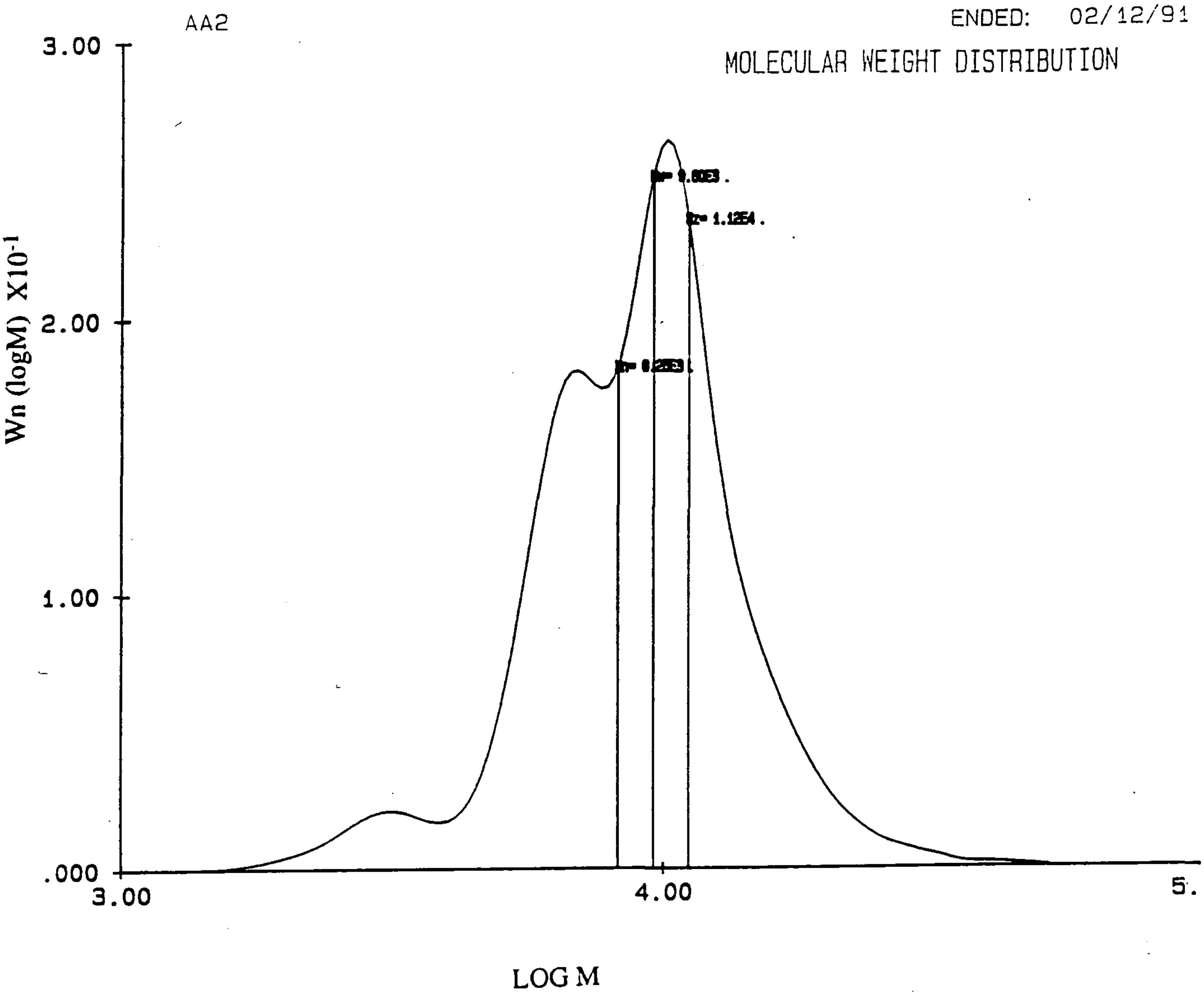

Figure 32. Molecular weight distribution (GPC) for polymer (n=11; M_n=9,600).