SYNTHESIS AND CHARACTERIZATION OF NOVEL LIQUID CRYSTAL POLYMERS CONTAINING AZOBENZENE MESOGEN

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BY

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Dedicated To

MY PARENTS

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CERTIFICATE

This is to cetify that the thesis entitled "**Synthesis and Characterization of Novel Liquid Crystal Polymers Containing Azobenzene Mesogen**" is an authentic record of the research work carried out by **Mr. M.Saminathan**, M.Sc., under our supervision in partial fulfilment of the requirements for the degree of **Doctor of Philosophy** of the University of Kerala and further that no part thereof has been presented before for any other degree.

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DECLARATION

I, M.Saminathan, do hereby declare that this thesis entitled "**Synthesis and Characterization of Novel Liquid Crystal Polymers Containing Azobenzene Mesogen**" is a bonafide record of research work done by me and that no part of this thesis has been submitted earlier for the award of any other Degree, Diploma, Title or Recognition.

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PREFACE

The emergence of liquid crystal polymers (LCP) which exhibit the coupled properties of low molar mass liquid crystals and that of polymers unfolded many more avenues for technological applications in diverse fields like ultra high strength fibers, nonlinear optical (NLO) and information storage systems etc. Despite the availability of a large number of well known LCPs with a wide range of structures and properties, there is still a strong demand for high performance LCPs. Recent developments in polymer science and technology have made available information necessary for tailormaking polymers with any desired property for any application. Among the functional groups used for the synthesis of LCPs, azobenzene is of great interest due to its exciting colour, structural rigidity and photoisomerization. The recent developments in azobenzene polymers show that azobenzene polymers exhibit LC property and this class of polymers would be useful for the development of LC displays, NLO and information storage devices etc. This has given rise to a resurgence of research and development activities all over the world to develop speciality polymers containing mesogenic azobenzene group.

The present investigation is mainly concerned with the synthesis and characterization of novel main chain and side chain LCPs containing azobenzene mesogen. The first chapter provide a review on LCPs. The next three chapters deals with the synthesis and characterization of azobenzene monomers, polymers and a study on their LC behaviour, thermal stability etc. The last three chapters deals with the synthesis and characterization of azobenzene acrylate monomers, polymers and a study on their LC behaviour. An attempt has been made to highlight the possibility of NLO activity in monomers and polymers used for this study.

This study forms a part of a large programme being conducted at the Regional Research Laboratory (CSIR), Trivandrum, to explore the potential of cardanol as a raw material for the development of high performance polymers. So, significant structural modifications to bring out property improvement in cardanol based polymers were developed.

The results of the present investigation have been published / patented or are under publication as described below.

1. "Synthesis and Characterization of Main-Chain Liquid Crystalline polymers Containing a p-Phenyleneazo Group", Macromolecules (1993) 26, p.7103.

2. "Synthesis and Characterization of Poly(1,3-Phenyl Octanoate): A Heat Resistant Polyester", J.Polym.Sci., Polym.Chem.Ed.(Accepted) 1994.

3. "Novel Thermotropic Liquid Crystalline Polymers Containing Azo Mesogenic Group" in Polymer Science: Recent Advances, I.S.Bharadwaj (Ed), Allied Publishers, New Delhi, Vol.I, pp.424-430 (1994).

4. "Synthesis and Characterization of Poly(1,3-Phenyl Octanoate): A Moderately Heat-Resistant Homopolyester" in Polymer Science: Recent Advances, I.S.Bharadwaj (Ed), Allied Publishers, New Delhi, Vol.I, pp.239-244(1994).

5. Synthesis and Characterization of Azobenzene Main Chain Liquid Crystal Polymers (manuscript under preparation)

6. Synthesis and Characterization of Azobenzene Side Chain Liquid Crystal Polymers (manuscript under preparation)

7. Main Chain and Side Chain Liquid Crystal Polymers from Azobenzene Functionalized Cardanol (manuscript under preparation)

Patents Filed:

1. "A process for the preparation of 4-[(4-hydroxy-2-pentadecylphenyl)azo] benzoic acid: A bifunctional monomer" ; Patent Application No.1280/ DEL/92, dt. 31.12.1992.

2. A process for the preparation of poly[4-[(4-hydroxy-2-pentadecylphenyl) azo]benzoic acid] : A processable liquid crystalline homopolyester ; Patent Application No.1279/DEL/92, dt.31.12.1992

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CHAPTER - I

INTRODUCTION

The serendipitic discovery by Friedrich Reinitzer[1] in 1888 of the peculiar thermal behaviour of cholesteryl benzoate followed by Otto Lehmann's[2] (who coined the term "liquid crystal" in 1889) identification of the 'partially ordered fluid phase' laid the foundation for liquid crystal research. In the following years, Gattermann[3] and Vorlander et al[4] had synthesised several aromatic compounds with azoxy linking group and discovered 'nematic' and 'smectic' phases respectively. Vorlander, after studying the structure-property relationship[5] of the LC properties shown by these compounds, proposed a general rule that 'the LC state is obtained for the most linear shape of the molecules'. It was further shown by Chandrasekhar et al[6]. that 'disc shaped molcules can also form LC phase', namely discotic phase. In addition to the thermally induced LC phase formation viz. thermotropic LCs, Bawden and Pirie[7] in 1937, discovered LC order in a solution of tobacco mosaic virus viz. lyotropic LCs. For the following twenty years natural and synthetic lyotropic biopolymer systems such as viruses, collagen and poly (γ-benzyl-L-glutamate)[8-10] were studied.

About the same time Paul J Flory[11] in 1956 proposed 'Rigid Rod-Anisotropic solutions' theory, which in essence showed, that "a solution of a rod-like synthetic polymer of suitable rigidity at the appropriate concentration would be a lyotropic system'. This theoritical prediction was well demonstrated in the case of aramid polymers. The potency of LC phase on material properties was demonstrated by the introduction of aramid fiber 'Kevlar'[12], the first commercially successful synthetic LC polymer from Du Pont in 1965 with outstanding tensile properties. A similar phenomenon was proved in polymer melts too through the commercialization of a copolyester, Ekkcel I-2000[13], by Carborundum company in 1972. These breakthroughs stimulated academic and industrial research worldwide towards the newer materials with extraordinary properties.

1.1. DESCRIPTION OF MESOPHASES

The liquid crystal state also called the fourth state of matter, represents a number of different states whose degree of order lies between that of perfect crystals and isotropic liquids[14]. Order and mobility are the two basic principles of nature, which governs the structure of the condensed phase. Crystalline, amorphous and liquid are the three conventional limiting states of the condensed phase. Crystals have long range orientational and positional order, where as the amorphous solids have only a short range order. Going from the crystal to liquid, one loses order and gains molecular or conformational mobility at the melting point. The amorphous solids or glasses do not undergo melting instead they exhibit glass transition.

In a normal melting process, the degree of freedom of the molecules increases in three dimensions. Thus those molecules, which were ordered in the solid state, tumbles freely in the amorphous liquid. However, in the melting process mediated by mesophase behaviour, there is a stepwise breakdown of the order and a concomitant selective increase in the number and the type of degree of freedom. Each step in the break down of the order coincides with the formation of a thermodynamically stable mesophase[15]. Based on the simplified description of melting and glass transition, it is possible to propose three major types of mesophases, namely liquid crystals, plastic crystals, condis crystals and their glasses.

1.1.1 Liquid Crystals(LCs)

The molecules with sufficient rigidity and linearity forms LC phase. The asymmetry in molecular shape allows the thermodynamically stable orientational order in the prefered direction of molecular long axis. These "orientationally ordered" liquids or "positionally disordered" solids are widely known as liquid crystals[16]. The name liquid crystal was given because of the obvious liquid like flow of these materials. The liquid crystal glasses(LCG) are obtained by quenching the LC phases. This is obtainable only when the glass transition is lower than the decomposition temperature. In LCGs, the LC phase exist as "frozen-in" state. Larger mesogens produced by rigid linear macromolecules such as all aromatic para linked polyamides and polyesters are the best exambles.

1.1.2 Classification of Liquid Crystals

Liquid crystalline state appears in the phase diagram between the crystal and liquid phases. In general, it exhibits long range molecular orientation, but long range positional order is absent and it combines the properties of both crystalline and liquid phases. They can be classified into two major classes based on their formation. The LC formation may be induced purely by thermal effect, namely, thermotropic systems or by the influence of solvents, namely, lyotropic systems. A relatively new class of LC phase was observed by the elevation of pressure i.e. barotropic systems[17]. The LCs may further be divided into two categories: Low Molar Mass LCs or Monomeric LCs (LMMLCs) and Polymeric LCs (PLCs).

1.1.3 Lyotropic Liquid Crystals(LLCs)

Lyotropic LCs which arise from the action of a solvent are multi component mixtures where none of the components in LLC phase is individually mesomorphic[18]. LLCs are formed when a certain classes of organic compounds and polymers are dissolved in a suitable solvent[19-21]. There are three important variables to be optimised. They are solvent strength, concentration of the solution and temperature[22,23]. In the case of polymers the molecular weight should be above certain critical value. The solvents widely used are water, sulfuric acid, trifloroacetic acid, anhydrous HF etc[18-21]. Polar aprotic solvents like dimethyl formamide, dimethylacetamide with small percentage of lithium chloride or calcium chloride salts are also used in certain cases[24]. The simple LLCs are amphiphilic compounds like soaps,lipids etc., which shows most of the known LC phases whereas LLC polymers show nematic phase predominantly. Examples of LLC polymers are poly(γ-benzyl-l-glutamate), poly(p-phenylene terephthalamide) etc.

1.1.4 Thermotropic Liquid Crystals(TLCs)

In thermotropic liquid crystals, the phase transitions are brought about by the influence of temperature. These phases are strongly anisotropic, though the phases themselves may be as mobile as water. The first order transition points are used to distinguish these TLCs from the crystal and the normal liquid. Based on the macroscopic structure formed by the mesogens, four distinct structural classes of LCs have been identified, namely, Smectic, Nematic, Cholesteric or Chiral Nematic[25] and Discotic[26] mesophases. The structures are related to the dimensionality and packing aspects of the residual molecular order.

1.1.5 Smectic Liquid Crystals(SLCs)

The structure of SLCs may be described as an orientationally ordered fluid on which is superimposed a one dimensional density wave[28]. The layers in SLCs are liquid-like with the molecules upright on the average and negligible in-plane and inter layer positional correlations (Figure 1). In essence, SLCs are one dimensional crystals and two dimensional fluids[27]. This make the SLCs to have a soapy feel and hence the name smectic (Greek; smectic = soap-like). Indeed soaps and detergents in water show lyotropic smectic mesophase. SLCs show polymorphism in which the layer structure is the common feature. Due to the layered structure the large scale movement in any direction other than tangential to the layer surface is, however, difficult. Therefore, smectic phases are quite viscous and solid-like[29]. SLCs have been classified based on the intra layer molecular arrangements[30]. Among SLCs smectic A and C phases are the most important phases.

Fig. 1: Smectic phase

SLCs can be recognised microscopically from their characteristic textures which arises due to the stable defects from the layer fluctuations[31,32]. The arrangement of molecules could give the appearance of a uniaxial birefringent crystal. Based on the misibility studies, X-ray diffraction and microscopic textures[27-30], SLCs are classified into a minimum of twenty six types.

Lyotropic Smectic Phases: Without LCs there would be no life. Even the simplest single-celled creature has an outer skin whose fabric is LC. Such is the importance of lyotropic LCs and in most of the cases, the dominant phase is smectic phase. This was recognised as early as 1855 by a German optholmologist called C.Mettenheimer who while studying myelin under a polarizing microscope, noted that, although it flowed like a liquid, it was brightly coloured, or "birefringent" like a crystal when viewed between cross polarizers[33]. It was not, however, until much later that myelin was identified as a LC material. Apart from biological systems, soaps and detergents also show smectic phase in water. The amphiphilic soap molecules[16,34-36] arrange themselves in a bilayer in water solution making cubic and hexagonal arrangements. Smectic arrangements of lyotropic mesophase are observed in some phospholipids.

1.1.6 Nematic Liquid Crystals(NLCs)

Nematic LCs are three dimensional fluids with a high degree of long range orientational order of the molecules approximately parellel to the long molecular axis[37-39](Figure 2). Among all known LC phases NLCs are the least ordered mesophase. Thus, specific heat, volume expansion and compressability in NLCs are similar to those of normal liquid. The term nematic (Greek; nemato = thread like) was introduced by Freidle on account of the linear discontinuities, twisted like threads, which are the optical features characteristic of this type of LCs. The main features of molecular organization are as follows:

1. The spontaneous alignments along the long molecular axis generates highly birefringent, optically uniaxial and positive materials with dissimilar refractive indices for polarized light along and perpendicular to the optical path. 2. The axis of preferred molecular orientation defines the director,n, both directions of which, +n and -n are equivalent and varies from point to point in the medium. 3. Application of a magnetic or electric field will result in a uniform alignment and give a optically uniaxial monodomain.

Fig. 2: Nematic phase

1.1.7 Cholesteric or Chiral Nematic Liquid Crystals(CLCs)

The unique optical properties of the cholesteric phase were recognised by both Reinitzer and Lehmann at the time of early investigations which culminated in the discovery of the liquid crystalline state. The name cholesteric is obviously due to the observation of CLCs in cholesterol derivatives at early times[25].CLCs can be obtained even in non-steroidal, rigid-rod, optically active compounds or by doping nematic phase with miscible optically active compounds[40]. Locally, Cholesteric is very similar to a nematic material with a spontaneous twist about an axis perpendicular to the molecular long axis or the director,n. The molecular layer is very thin and the long axes of the molecule are aligned parellel to the plane of the layer[41,42]. The director n is not constant in space, so that in each layer the director,n, is displaced to a constant angle with the "precession" of the director,n, about the helical axis (Figure 3). Hence the structure is helicoidal with the pitch of the helix much larger than the molecular dimensions.

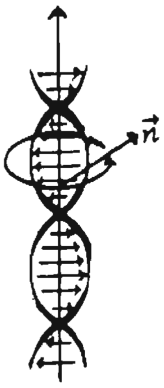


Fig. 3: Cholesteric phase

1.1.8 Discotic Liquid Crystals(DLCs)

Breaking the barrier of the belief of about nine decade, of the concept of the rod-like molecules, S.Chandrasekar et al. in 1976 proved that the 'disc-like' molecules can also form stable LC phases, namely, discotic mesophases[43]. The molecules of disc shaped or nearly so with the flexibilizers of atleast five carbon atoms and four or more lateral substituents, normally alkoxy and ester groups, are found to form DLCs. The structures are based on the tendency of the discs to align with their short axis (which is normal to the average molecular plane) parallel[44,45](Figure 4). There are two fundamental types: nematic and columnar. The basic types of LC formation is determined by the particular shape of the disk-like molecule.

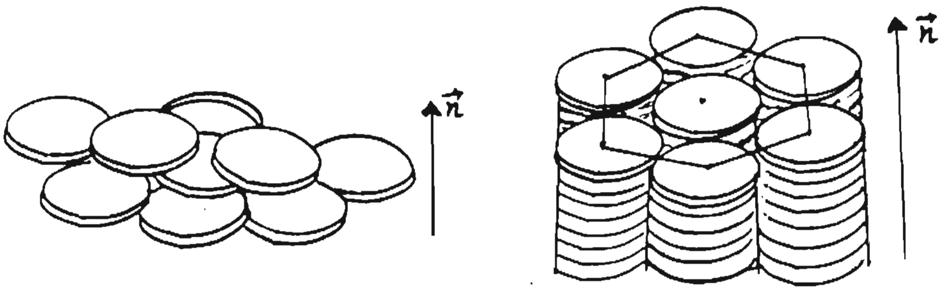


Fig 4: Discotic phase

1.2 LIQUID CRYSTAL POLYMERS(LCPs)

The liquid crystalline property in organic compounds have been recognised and widely studied for more than a century. As far as the polymers are concerned, the first reported natural polymer was a solution of tobacco mosaic virus, reported in 1937 by Bawden and Pirie and the occurrence of LC phases have long been reported only for various natural polymers. Elliott and Ambrose were the first to synthesise a polypeptide, namely, poly(γ-benzyl L-glutamate)(PBLG) and later Robinson showed that it forms lyotropic LC phase in non-protic solvents like dioxan and methylene chloride. A major impetus was given to work, both academic and industrial, in the field of lyotropic systems by the developement, by DuPont, of commercial fibers having exceptionally high tensile strength and modulus through the use of nematic anisotropic solutions of relatively rigid-chain aromatic polyamides.

The first reported observation of thermotropic liquid crystalline behaviour in polymers was made by Roviello and Sirugu[46] that describes a polyester containing regularly alternating rigid and flexible segments where the rigid segment is derived from a nematic compound of low molecular weight and a range of highly aromatic polyesters with a substatial proportion of extended-chain conformation. The production by Jackson and kuhfuss of thermotropic random copolyesters of poly(ethylene terephthalate) with p-hydroxybenzoic acid paved the way for a series of commercial LC polymers[47]. It was also shown in 1975 that incorporation of rigid-rod and mesogenic units into the side chain of acrylate or methacrylate polymers could lead to thermotropic products[48].

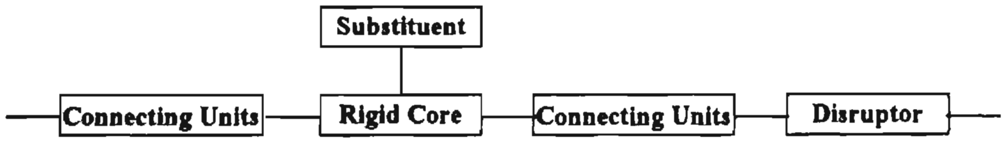
1.2.1 Thermotropic Liquid Crystal Polymers

Thermotropic polymers form a liquid crystalline phase within a defined temperature range. There has been an increased research activity focused on the main chain LC polymers (MCLCPs). After the reports of Raviello and Sirigu and Jackson and Kuhfuss, acadamic interest focused largely on characterizing these systems and understanding their structure-property relationships[49-57]. Commercial interest has concentrated on thermotropic MCLCPs and there is a large increase in the commercialization of MCLCPs since 1984.

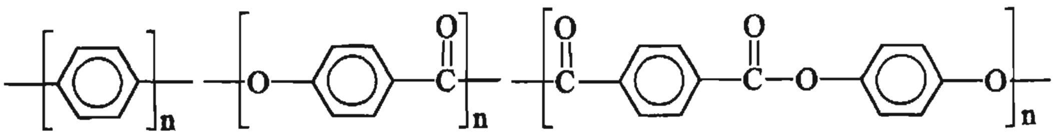
Apart from the advantages mentioned above LCPs have a lot of flexibilities to tailor make the desired properties and the monomers used for polymerization need not always be LCs. According to the Flory's lattice theory[49,60], an axial ratio of only 6.42 is required for a polymer to be stiff enough to form LC phase. This is achievable by non-mesogenic rigid rod and/or semiflexble monomers on polymerization either as main chain and/or as the side chain polymers.

1.2.2 Main Chain Liquid Crystal Polymers(MCLCPs)

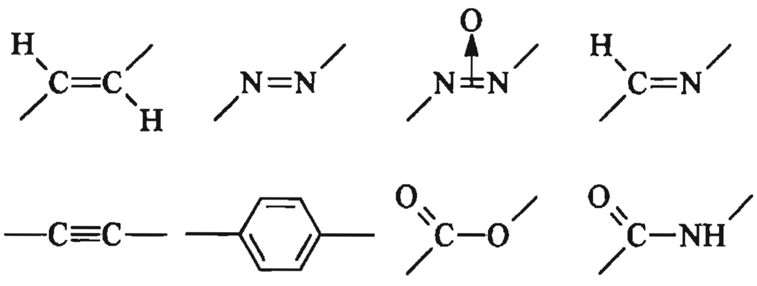
The majority of synthetic LCPs consists of a succession of rigid unit that are individually characterised by possessing chain-continuing bonds that are either collinear or parallel and oppositely directed. The example are the p-phenylene and 1,5-naphthalene units respectively. Scheme 1 give an idea on the design of an LCP. Examples of the rigid cores used are given in scheme 2a and the connecting units are usually of the structures given in scheme 2b.



Scheme 1: Schematic form of MCLCP structure



Scheme 2a: Basic structures involved in MCLCP



Scheme 2b: Sturctures of connecting units

A wide range of p-substituted aromatic rings have found their use in LCP synthesis. The rigid structural cyclic units involved need not be aromatic in character and trans 1,4-substituted cyclohexane units are of this class. These ring structures are conformationally rigid, and are main-chain components of nearly all the LC synthetic polymers of this type known. The trans conformations required to meet the criterion are maintained either by the presence of double bonds or, as in the case of the amide and ester groups, by a substantial energetic preference for that conformation. A deviation of atleast 9° from parallelism in units containing two main chain atoms is tolerable[61].

The basic structures in general in MCLCPs are benzene rings interlinked at para positions. However, such rodlike molecules tend to be infusible, largely intractable crystalline solids. LC properties are observed for oligomers of poly(p-phenylene) with n=5-7 but when n>7 decomposition occurs below the melting temperature[62]. Melting points of 610 and 600°C were measured by DSC (scan rate of 80°C/min to minimize degradation) for poly(p-hydroxy benzoic acid) and poly(p-phenylene terephthalate), respectively[63]. Hence the problem of thermotropic MCLCP design is to lower the melting point to a melt processable range without destroying LC formation. There are three possible ways of accomplishing this by disrupting the perfect regularity of simple but intractable para linked aromatic polymers[49,56,57,63-65]. (1) introduction of disruptors(flexible spacers or rigid kinks) into the straight polymer chains; (2) substitution of the aromatic rings; and (3) copolymerization. It should be noted that usually it is necessary to use a combination of atleast two of these approaches to lower the melting point sufficiently for melt processability and to achieve high mechanical properties.

1.2.3 Synthesis of Liquid Crystal Main chain polymers

Thermotropic LC polyesters have been widely synthesised[50]by Scotton-Baumann reaction, Ogata method[68-70], mixed anhydride method[71,72], ester exchange reaction[66]and acidolysis[67]. Among these reactions, ester exchange and acidolysis reactions are the indusrially important reactions. A representative reaction is given in the scheme 3. All the above discussed methods are found to work equally well with the aryl hydroxy carboxylic acid monomers.

$$\mathrm{CH_3O\overset{\overset{O}{\|}}{C}Ar\overset{\overset{O}{\|}}{C}OCH_3 + HOAr'OH \longrightarrow -\!\!\left[\overset{\overset{O}{\|}}{C}Ar\overset{\overset{O}{\|}}{C}OAr'O\right]_n\!\!- + CH_3COOH}$$

Scheme 3: Synthesis of MCLCPs

1.2.4 Characterization of Liquid Crystal Polymers[52]

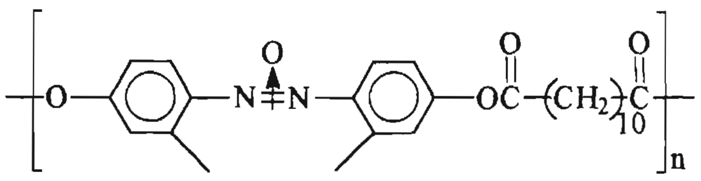
Liquid crystals are characterized using differential scanning calorimetry (DSC), hot stage polarized light microscopy (PLM), X-ray diffraction and miscibility studies. In liquid crystals, there is a breakdown or onset of molecular order during the formation of the phases and hence the energy change. The change in energy can be measured quantitatively as a measure of change in heat capacity (Δcp) using DSC. The heat capacities are different for different phases and are characteristic of each phase. Normally LC phases are birefringent under cross polarized light and the stable defects arises due to the molecular alignment form textures characteristic of each phase. Combination of DSC and PLM is commonly used for LC characterization and classification. The transition temperatures in DSC thermogram should match with the PLM observations within the experimental error for confirmation.

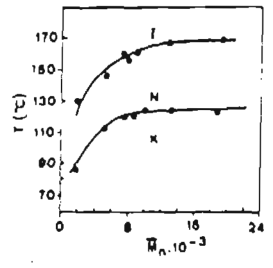
X-ray diffraction (XRD) depends on the order present in a material. The LCs, being ordered fluids, can be characterized by XRD in which diffractions characteristic of crystalline order are observed at small angle (typically ~ 1-5°) and a hollow at wide angle (~20°) characteristic of isotropic materials. Exceptions are the discotic columnar phase and some of the smectic isomorphs such as SB, SD etc., which are perfect crystals or nearly so. XRD is useful when DSC and PLM fail to diagonize the phase or the isomorphs. Miscibility studies are most commonly used in low molecular mass LCs. This is done by melting a known and an unknown LC having similar transition temperature range and allowing them to mix at interface. If both are forming same phase the interphase will show uniform texture under PLM, otherwise the immiscible phase boundaries will be seen.

1.2.5 The Structure - Property Relationship

The physical and chemical properties of polymers are the direct reflection of their basic structural units. In an analogues polymer series introduction of additional units would bring about the changes in their transition temperatures, chemical reactivity, crystallinity etc. The knowledge acquired from such studies would be useful for engineering polymers for specific applications. In liquid crystal polymers DSC, PLM and XRD are used to study the structure - property relationship. The DSC curves of thermotropic polyesters show a glass transition (Tg), a melting peak and mesophase/mesophase and/or mesophase/ isotropic liquid transitions. Quenched samples may show cold-crystallization when heated above the Tg[73,74]. This may be an indication of polymorphism in the solid state, but more often it is caused by fundamental differences in crystal morphologies or by interconvertable forms of polymer, which differ only in degree of crystal size and perfection. It is worth noting that usually on cooling of the isotropic liquid, the mesophase-isotropic liquid and mesophase-mesophase transitions are almost reversible while marked supercooling is observed for the solid-mesophase and solid-solid transitions[46,75,76,77].

Thermotropic melts are generally nematic. The randomness of the units in the copolymers and the molecular weights of the polymers have a marked influence on the phase behaviour of polymers. Usually, transition temperatures reach a plateau at average chain lengths of approximately 10-15 repeating units[78-80](Figure 5). An illustrative example is the case of poly (4,4'-dioxy-2,2'-dimethyl azoxy benzene dodecanedioyl) (Scheme 4). The entropy change[81] and order parameters[82] at the N/I transition follow a similar trend.



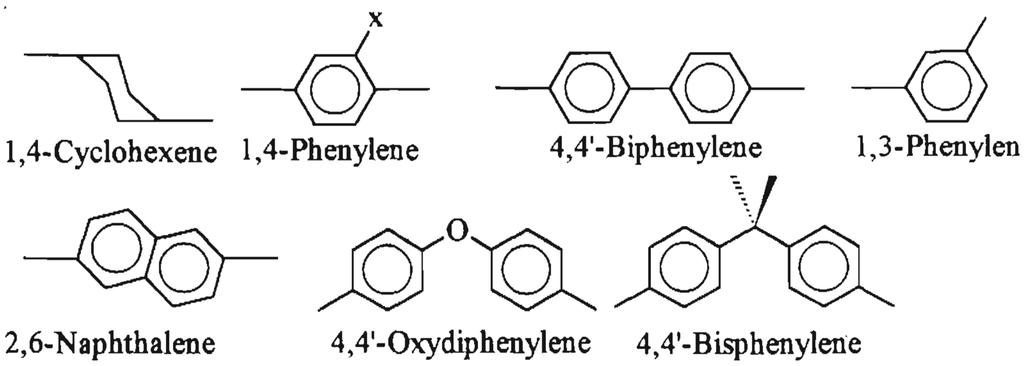


Scheme 4: Structure of MCLCP with varying Mn ; Fig 5: Plot of Mn Vs Trans. Temp.

Thermotropic LC extrusions show a 'skin-core' morphology[83], as observed in poly(*p*-phenylene terephthalamide) fibers in which the structure of the melt is frozen into the crystalline solid on extrusion[84]. The oriented fiber or extrudate consists of a hierarchy of structures from microfibrils to macrofibrils in a highly oriented skin. The orientation of the microfibrils depends on the thickness of the extrudate.

1.2.6 The Effect of Disruptors on Mesophases

Copolymerization: Copolymerisation is one of the best methods known to alter the transition temperatures of MCLCPs and widely studied. The homo polymers are structurally homogeneous and tend to give perfectly oriented conformation. The copolymerisation introduces inhomogenity in the parallel chain orientation[49,56,57,63-65]. The following structural units are found to introduce disruption to the chain packing (Scheme 5).

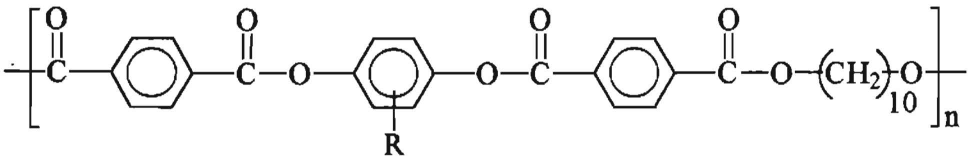


Scheme 5: Structure of disruptor units

Copolymers that contain only rigid rod segments are of particular interest because highly oriented samples are expected to exhibit higher moduli than those derived from copolymers that contain flexible or angular segments [63,85,86].

Inflexible and relatively rigid and angular unit of 4,4'-disubstituted diphenyl ether groups introduce an angle of approximately 120° into the rigid chain, and such units appear to be particularly effective in reducing or suppressing the tendency to crystallize[87].

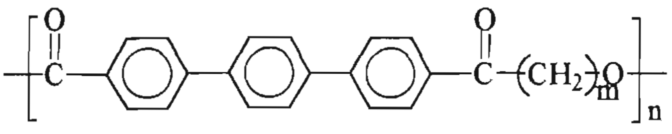
Substituents: Introduction of a substituent into the aromatic ring of the mesogen destroys the plane of symmetry and leads to the random occurrence of head-to-head and head-to-tail isomerism disrupt the ability of the chain segments to pack into crystallites[88,89]. The substituents used were H, Cl, Br, CN, NO_2, CH_3, OCH_3, alkyl and ethyleneoxy groups (Scheme 6). The presence of substituents results in a decrease of both mesophasic(Tm) and isotropization (Ti) transition temperatures.



where R= $-(CH_2)_m-H$ (with m = 0,1,2,...6,8,10),
$-CH_2O(CH_2CH_2O)_mCH_3$ (with m=0,1,2,3.)
OCH_3, Cl, Br, CN, NO_2.

Scheme 6: Structure of MCLCPs with varying substituents

Flexible Spacers: Long chain alkyl and oxyalkyl groups are the most commonly used lateral substituents with the chain length upto about ten carbon atoms as demonstrated in the following structure[77,52,91-93] (Scheme 7). The transition temperatures decreases and the melting and clearing temperatures alternate typically (Figure 6). This is known as odd-even effect [76,90,94]. The tendency for predominantly nematic behaviour gives way to purely smectic behaviour in the higher homologues[78,95,96]. Yet another spacer often used is oligosiloxane spacer units in which the uniform distribution results in smectic phase formation whereas random distribution give nematic phase[97,98].



Scheme 7: Structure of MCLCP with varying spacer length

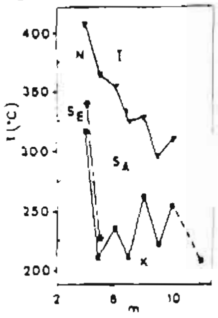


Fig. 6: Plot of m Vs trans. temp

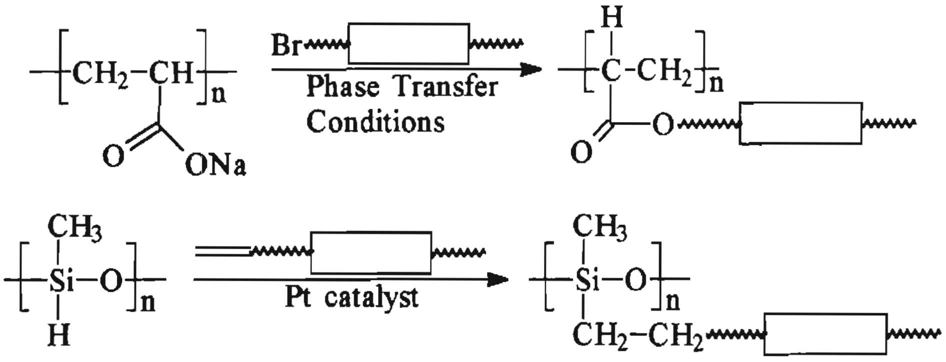
1.2.7 Side Chain Liquid Crystal Polymers (SCLCPs)

It is well known that low molar mass liquid crystals(MLCs) can be ordered unidirectionally in an electric field or in a magnetic field. LCPs can also be ordered similarly. This concept has received considerable attention in recent years and the side chain LCPs(SCLCPs) have been found to be particularly interesting in this aspect. Side chain LCPs emerged as an area of practical importance is due to their outstanding optical properties which are useful in electro-optical device applications. In SCLCPs the mesogenic groups are linked via suitable reactive substituents, to an existing polymer backbone. Polymers with mesogenic side chains are usually thermotropic and the mesogenic group maintain a degree of orientational freedom depending on the coupling strength to the backbone. The alignment of mesogens may be altered by the application of electric field[55] and the alignment takes place on a time scale order of magnitude faster for SCLCPs than for MCLCPs. This allows the optical properties of SCLCPs to be altered readily by the use of an external electric field.

Although the LC properties of the polymers parallel those of the low molecular weight analogues, the differences are mainly due to (a) the high melt viscosity which restricts the structural rearrangements influenced by the external fields and (b) the interaction of polymer backbone chain which try to assume a random coil conformation and the mesogenic group which try to organize in the LC phase. The backbone-mesogen interaction may be decoupled to some extent by introducing spacer groups between the backbone and the mesogenic groups[55].

1.2.8 Synthesis

The SCLCPs are synthesised by polymerising monomers containing active vinyl groups attached to mesogens directly or through spacer groups[48,100-103](Scheme 8). The most commonly used monomers are acrylates and methacrylates. The another method of SCLCPs synthesis involve the addition of vinyl monomers to oligosilanes (Scheme 8). Typical spacer groups consist of between 3 and 12 methylene units. However, oligooxy ethylene[104-115] or oligosiloxane[105] units may be used to enhance the degree of decoupling through a more flexible spacer. The polymerisation of acrylic monomers were carried out using free radical initiators[108-111], anionic[112,113], group transfer[114,115] and cationic[107,116,117] polymerisation techniques. The siloxane groups are normally introduced by hydrosilylation reaction using platinum compounds as catalyst[118].



Scheme 8: Synthesis of SCLCP

1.2.9 Properties

The direct attachment of mesogens to the polymer backbone mostly yielded an amorphous polymers with high Tg[48,119]. Decoupling of the side groups by using a flexible spacer allows the main chain motion to occur without disturbance of the anisotropic arrangement of the side chains[55].

Since the polymerization of mesogenic monomer stabilizes the LC state, nematogenic monomers often yield higher order smectic polymers and mesogenic but isotropic monomers yield nematic polymers. Therefore it is not surprising that efforts to make cholesteric polymers from a cholesterol derivative invariably resulted in smectic polymers. Cholesteric polymers however, can be obtained by copolymerisation of a binary mixture of chiral monomers or of a nematogenic monomer with a chiral comonomer. The addition of a chiral monomer converts the nematic guest phase into a cholesteric phase[55].

The increase of spacer length results in reduction of Tg. This behaviour is quite general for the polyacrylate and polymethacrylate series and reflects the increased plasticizing action of the flexible spacer[55,99,120-122]. Moreover, purely nematic behaviour tends to give way to predominently or purely smectic behaviour in the higher homologues. The odd-even effect is observed in SCLCPs also. The even numbered spacers favour smectic phase formation and the odd numbered favour nematic phases[123-125].

1.3 AZOBENZENE POLYMERS

1.3.1 Introduction

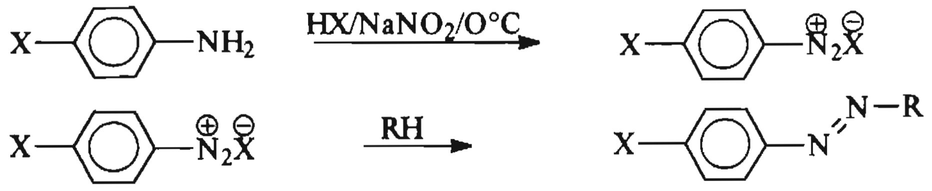
It can be noted from the preceding discussion that azobenzene group is one among the rigid units used in the design of LCPs. This is because it offers the required structural rigidity imparted by the coplanarity of all atoms adjacent to a double bond as well as of the double bonded nitrogen atom themselves. Colour, which is the attractive feature of the azobenzene compounds, is responsible for one's stirrings of interest in chemistry, and it is this visual aspect of the science that makes for much of its appeal to the embryo scientist. The contribution of azobenzene compounds to dyes and pigments industries as well as to the colour chemistry, eversince the discovery of azobenzene dyes by Peter Greiss in 1858, is innumerable. The versatility of this class stem largely from the ease of with which azo compounds can be made, and almost any diazotized aromatic amine can be coupled with any stable nucleophilic unsaturated system to give a coloured azo product[135]. The driving force for the formation of azobenzene compounds may be due to the extension of conjugation between aromatic or unsaturated systems through azo linking group. By extending the conjugation this way, or by incorporating large ring systems, or different electron donor groups, a full spectral range of colours can be obtained, with almost any desired chemical or physical properties[136-138].

Azobenzene derivatives are more often synthesised by diazo coupling reaction but for the polymers, oxidative coupling was the reaction applied widely. Polymers containing azobenzene group are known as early as 1955 where the oxidative coupling of aromatic primary amines using Cu^+/pyridine/O_2 system has been reported[138]. In 1961 a patent by Blake and Hill of Du Pont company describes the synthesis of azobenzene polymer by polycondensation of azobenzene derivatives[139].

Synthesis of azopolymer by diazo coupling of bisdiazonium salts with phenols was reported in 1964[140-143]. Apart from the above discussed reactions azo polyamides and polyesters can be synthesised via interfacial or solution polymerization of azobenzene monomers[144-147]. Highly conjugated polymers have been obtained by the condensation of 4,4'-diamino azobenzene with terephthalaldehyde and a polymer of 4,4'-azo dibenzaldehyde with a bifunctional wittig salt[148].

1.3.2 Synthesis of Azobenzene Derivatives

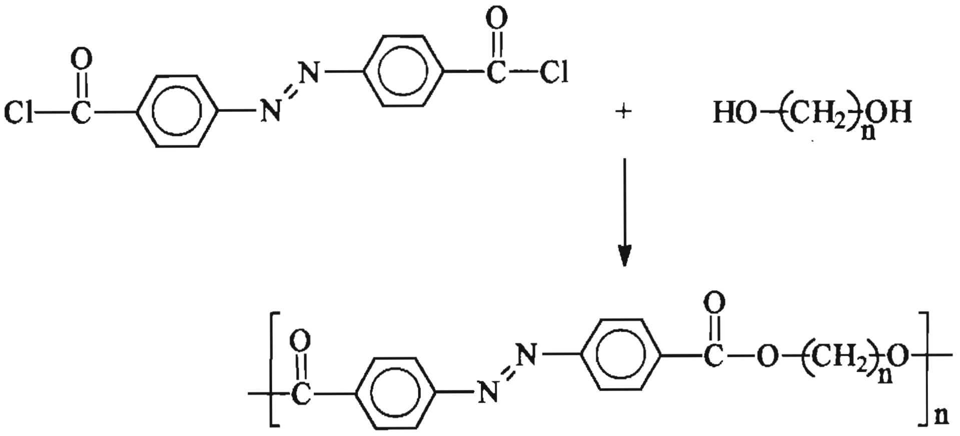
Synthesis of azobenzene derivatives can be accomplished by many different methods, of which the most representative methods are condensation[149], reductive coupling[150], oxidative coupling[151] and diazo coupling reactions. Among these reactions diazo coupling is the long known and the single most synthetic route to azo dyes[135,137]. All coupling components used to prepare azo dyes possess one common feature i.e. an active hydrogen atom bound to a carbon atom like phenols, naphthols, aromatic amines, compounds that possess enolizable carbon containing an acidic proton etc. The reaction (scheme 9) is as follows.



Scheme 9: Synthesis of azobenzene compounds

1.3.3 Synthesis of Azobenzene Polymers

Polymers containing azo groups can be synthesised through the polymerization of azobenzene derivatives or through azo group formation during polymerization. The polymers are synthesized polycondensation[145], polyoxidative coupling[138], polydiazotization[140] etc. LC polymers are synthesized only by polycondensation of azobenzene derivatives. A representative reaction is given in the scheme 10 below.



Scheme 10: Synthesis of Azobenzene main chain polymer

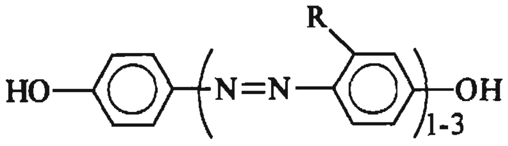
1.3.4 Liquid Crystal Polymers with Azobenzene Mesogen

The presence of a double bond generally has profound consequences on stereo chemistry; it gives the molecule more rigidity and restrict the number of possible forms. The main feature is the coplanarity of all atoms adjacent to a double bond as well as of the double bonded nitrogen atoms themselves[152]. Moreover azo group is a good electronic bridge between the two aromatic groups on either side. These molecular characteristics have led to the interest in using azo aromatic compounds in liquid crystalline and conducting polymer applications. Although the *p*-phenylene azo link is reported to favour LC behaviour in small molecules, it has only recently been reported to cause LC polymer formation[153].

1.3.5 Mesogenic Main Chain Azobenzene Polymers

Polyesters have been the most popular type of thermotropic LC polymers. The mesogenic polymers are synthesised from the azo benzene derivatives either as backbone and/or as side chain polymers by solution or interfacial polycondensation. Hall et al.[154] have synthesized a number of aromatic and aliphatic LC polyesters from bisphenols containing one to three p-phenylene azo groups (Scheme 11). Aromatic polyformals based on multiazo bisphenols have also been reported and an important factor in these studies was the tractability of the resulting polymers. Relatively soft diacid units and isophthaloyl units were used to avoid the problem of intractability. Solubility of the polymer was improved by the substitution of 5-t-butyl group in isophthalic acid and the methoxy group into the azobenzene monomer. The occurrence of LC behaviour depended strongly on the bisphenol monomer and on the diacid and showed nematic textures.

The results agree with the notion that extended rod-like character is required for LC behaviour. From these studies it is clear that the flexibility needed to offset the rigidity if the azo aromatic polymers is about eight methlene groups i.e. sebacate group. But in polyformals and isophthalates the disruption is introduced by the kink structure of the isophthalate residue and methylene formal units.

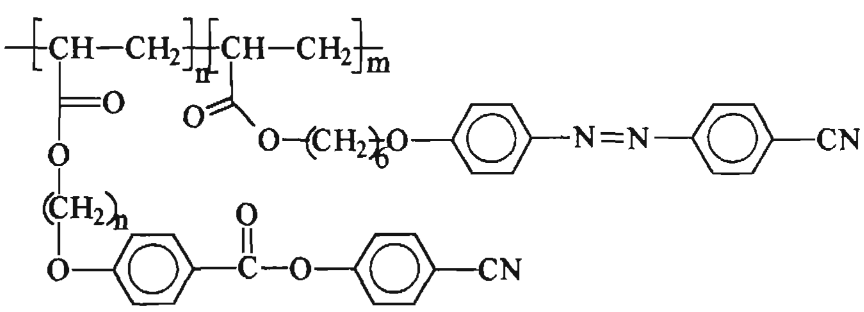


Scheme 11: Structure of monomers used for azobenzene LCP synthesis

1.3.6 Mesogenic Side Chain Azobenzene Polymers

Liquid crystal side chain polymers combine well-known properties of low molar mass LCs with those of polymers. For LC side chain polymers all relevant types of mesophases such as nematic, cholesteric and smectic have been realized. A large number of polymers such as polyacrylates, polymethacrylates and polysiloxanes containing mesogenic pendant groups have been reported[155-158]. Thermotropic LC polymers were prepared by introducing flexible spacers which decouples the motions of the mesogenic groups from the polymer main chain.

Polyacrylates homo- and copolymers containing pentant substituted phenyl azo groups show LC nematic phases (Scheme 12). New enantiotropic LC compounds based on 4-(*p*-substituted phenylazo)phenol and *m*-cresol esters containing an acryloxy group were synthesised by Naikwadi et al[159]. The polyacrylates have broader nematic ranges and higher nematic to isotropic transition temperatures compared to corresponding monomers. The nematic range is dependent on both the lateral substituents and terminal substituents. The laterally substituted polyacrylates gave a narrower nematic range than unsubstituted compounds. Increase in carbon number in the terminal alkyl group led to a broader nematic range.

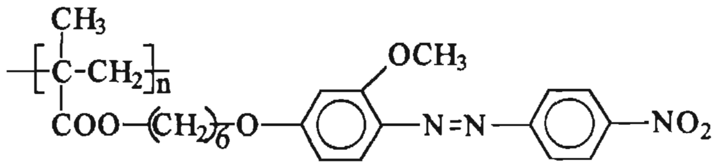


Scheme 12: Structure of azobenzene SCLCP

Ringsdorf et al.[160] have reported coloured LC polymers with an azo dye content upto 40%. The polymer showed and nematic mesophase and electro-optic effects under applied field. The macromolecularly oriented nematic structure could be frozen-in below the Tg resulting in a polymer film with dichroic properties.

1.3.7 Azobenzene Polymers with Non-Linear Optical Effect

Polymers that possess high non-linear optical activities have seen a recent growth in interest. Hall et al.[161] have recently synthesized polyesters containing multiple *p*-phenylene azo groups, which have strongly delocalised electrons. The introduction of donor and acceptor substituents in a *push-pull* arrangement to these polymers through the diphenyl azo group is expected to make them highly attractive as polymeric non-linear optical substrates. Methacrylate or acrylate polymers containing dipolar *p*-phenylene azo groups in the side chain have been reported to exhibit a large third order or second order optical effect (Scheme 13). In these cases, the azo linkage acts more like a conduit than an acceptor.



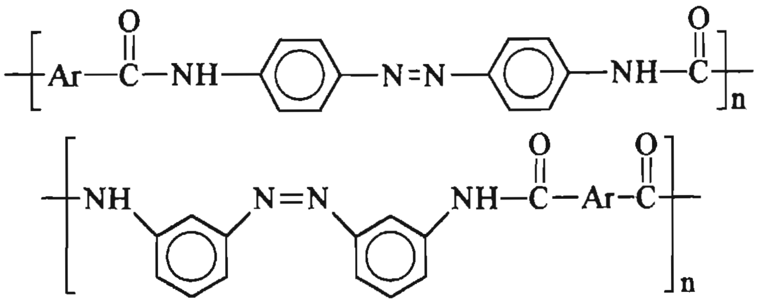
Scheme 13: Structure of azobenzene NLO SCLCP

To retain NLO property in a polymer it is important to prevent the dipole reversal or relaxation. This is achieved by introducing crosslinks during alignment or synthesising polymers with high Tg. Yu et al.[185] have studied crosslinkable NLO polymers and observed that the poled, crosslinked film remained NLO active for more than 1000 hr at room temperature and for 500 hr at 90°C. The polymers having high Tg was reported by Hall et al.[161] and the "lock-in" dipole alignment was retained due to the restricted molecular mobility.

1.3.8 Thermally Stable Azobenzene Polymers

The largest and the most important group of linear acyclic nitrogen polymers is polyamides[162]. As far as bond rotation is concerned, the structural considerations that apply to the amide group apply also to the azo group. Aromatic azo compounds exhibit *cis-trans* isomerism and the *trans* form is known to be considerably more stable than the *cis* form, which is directly related to the almost coplanar structure of the former compounds. Thus polyamides with *p*-phenylene azo units have attracted a great deal of attention.

Fonton et al.[163] and Nanjan et al.[146,164-167]have prepared polyamides from aromatic diacid chlorides and 3,3'-diamino azobenzene and 4,4'-diamino azobenzene (Scheme 14). They have also reported other azo polymer types in order to study the influence which other different groups exert on the heat resistance and solubility to verify the action of the azo group on these polymeric structures.



Scheme 14: Structure of thermally stable azobenzene polymers

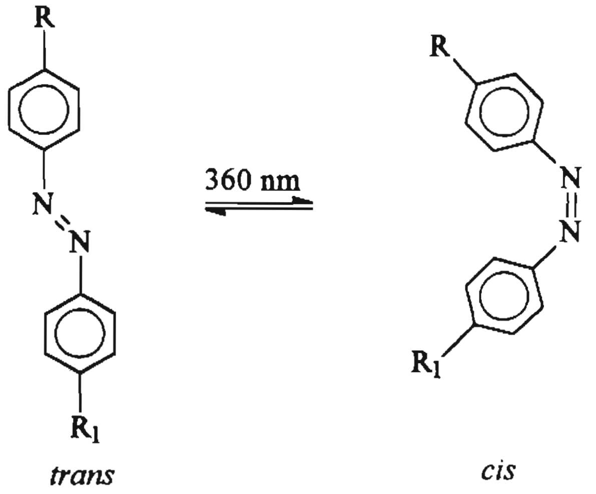
Normally for azo polymers the TGA curve in air and nitrogen are comparable, indicating that the mechanism of decomposition is nearly the same in both the conditions. New silicone-containing azopolyamides[169] have been prepared from 4,4'-diamino azobenzene and few structurally related organosilicon acid chlorides. The study on the effect of structures on the thermal stability of the polyamides, the thermooxidative degradation was studied by TG, DTA and DTG curves for all the polymers, which showed more or less similar patterns. The highest stability in air than in nitrogen is explained by a weight gain arising from oxidation, thus compensating for some of the weight loss caused by expulsion of N_2. These polymers were stable to more than 300°C, but decomposed with a catastropic weight loss (>10%) in the range of 360-400°C. Rapid thermal degradation was always accompained by a strong exotherm. This exotherm combined with the narrow range (360-400°C) of its occurrence irrespective of polymer structure indicates that the first step in the degradation is the elimination of the azo group as molecular N_2. Fully aromatic azopolymers described showed no melting or softening upto the temperature of thermal degradation.

Aromatic azo polymers also show a high degree of crystallinity without annealing as evidenced by X-ray diffraction patterns[168]. The high degree of crystallinity of poly(azo phenylene oxide) is surprising in view of the fact that other polymers such as PPO and polysulfone which have a predominance of aromatic linkages in the backbone show little or no crystallinity unless they are annealed for several days in a suitable solvent.

1.3.9 Photochemistry of Azobenzene Polymers

In 1911, Ciamician had described in his historical address, "...... Photochromic substances, which often assume intense colours in the light, and afterwards return in the darkness to the primitive colour might be used very effectively. .... The dress of a lady so prepared would change its colour according to the intensity of the light....... conforming automatically to the environment, the last word of fasion for the future".[170]

This special feature of azobenzene compounds arises from their *cis-trans* photoisomerization under the influence of light (Scheme 15). The possibility thus arises that conformations of azobenzene containing polymers can be controlled by photo induced configurational changes of azobenzene so that they may provide desired chemical functions.



Scheme 15: *cis-trans* isomerization of azobenzene compounds

The photoisomerization of polymeric trans azo compounds were initially studied by Morawetz and coworkers[171-173] who first demonstrated that the irradiation of the *trans* polymer produced photo stationary states comprised of mixture of polymers differing only in *trans-cis* linkages. Conformational change in a polymer either in the main chain or in the side chain will result in the change of physical properties. In azobenzene polymers, the *cis-trans* isomerization is useful in studying and understanding the nature of hindered rotation in polymers, the volume distribution in glassy state and the flexibility of polymers[186].

Moreover, azobenzene compounds can be used as photo lables in polymers, crosslinked networks and in polymer chain ends as photochromic "probes"[187]. The same physical phenomenon is used in modern technologies for information storage, optical windows etc. Furthermore, photoisomerization in polymers is found to alter the viscosity of the polymer solutions[174-177], conformational changes in polypeptides[178,179], permiability of polymer membranes[180-182] etc. Copolymers containing side chain azo group have been studied by Komogawa et al.[183] who studied photoisomerization of several azobenzene polymers. Thermo recording have been successfully done on an azobenzene side chain polymer[184] and it was surprising that the information stored does not vanish due to a thermal *cis-trans* isomerization, which was found to occur in polymers with azobenzene moieties in the polymer main chain or side chain even at temperatures below Tg[284].

1.4. APPLICATION OF THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

The versatility of the LCPs are such that it can be engineered to any desired application where the performance is the only criterion. LCPs can be suited to any structural and functional performances by suitable modifications in basic structure of the backbone functional groups. Application of LCPs fall mainly under the following areas.

Fibers: A closely packed ensembles of parallel extended polymer chains should exhibit the highest achievable specific strength. These unique characteristics of uniaxially oriented polymers are the basis for the technology of ultrahigh-strength organic polymer fibers. Polyaramides and rigid aromatic polyesters are the best examples.

Films: The inherent properties of rigid rod LCPs such as like good solvent resistance, low flammability and excellent solder resistance permit its use in a wide range of electronic applications, information industry and as a coating for optical fibers. The low water absorption and excellent barrier properties offers potential use in film packaging[126,127]. LC polyesters are finding their opening in such areas.

Plastic and Resins: Thermotropic polymer melts have negligible die swellability[128], very low mould shrinkage, high heat distortion temperature and high continous use temperature and these properties permits their use in moulding of high performance structural parts and coatings. The low creep, low linear coefficient of thermal expansion and very low viscosity of the anisotropic melt allow the fabrication of intricate structures as thin as 0.4mm possible. Wholly aromatic polyesters are used for these purposes.

Non-Linear Optics: Optically nonlinear materials are substances exhibiting nonlinear polarizations when subjected to electric, magnetic or electromagnetic (optical) fields. Polymers containing dipolar groups in a *push-pull* electronic arrangement are found to exhibit NLO behaviour. SCLCPs[59,130,131] with donor and acceptor built-in to bring about the dipole oscillation, could be a valuble substitute for the currently used inorganic NLO single crystals such as Lithium Niobate, KH_2PO_4 etc.

Information Storage Devices: The spontaneous alignment of the mesogens in a highly ordered manner and the homeotropic alignment under applied external fields prompted the LCPs as an attractive information storage medium[59,130]. This behaviour can be exploited to record information on an aligned liquid crystal using laser that can heat line spots and melt spots on the clear film. When they cool down they form spots rich in defects, which when viewed between crossed polarizers the spot stand out in high contrast as bright against a black background.

Holography: Polymers containing photosensitive group are the candidates for this application where the three dimensional virtual image is stored by shining light on interference pattern that encode the image in a photosensitive film as a refractive index grating[59,130]. SCLCPs containing stilbene units, azobenzene units etc. show *cis-trans* isomerism. Shining light on the material converts the *trans* form into *cis* form. This alter the refractive index of the material in such a way as to produce an interference pattern and the information can be read without further treatment.

Chromatography: The single as yet very well developed application of SCLCPs is in Gas-Liquid Chromatography(GLC)[80]. Mesomorphic stationary phases have only recently been introduced and have proved to be useful for GLC separations. The unique flexibility of the polysiloxane backbone as well as its low surface tension ensure quite good column efficiency. The remarkable GC selectivity of these mesomorphic stationary phases was demonstrated for polycyclic aromatic hydrocarbons, polychlorinated biphenyls, fatty acid methyl esters etc. SCLCPs are also used recently in control of permeation of gases and simple drugs.

Miscellaneous: Important uses for cholesteric SCLCPs might arise from their helical structure which results in a number of unique optical properties such as selective reflection of light (λ_R can be adjusted within 300nm< λ_R < l), high sensitivity of selective light reflection to temperature and an extreemly high optical activity[58,59]. These properties enable their use as selective wavelength, notch and bandpass filters, Fresnel zone plates[59,133,134], highlty sensitive thermoindicators, IR and super high frequency radiation visualizers and thermographic materials for medical diagnoses and non-perturbing quality control of electronic devices. Important uses for Sc* SCLCPs[58,59] might arise from the possibility of unwinding the helix to obtain a monodomain having a non-vanishing spontaneous polarization. Applications fall into four classes: display devices, transducers, pyroelectric detectors and non-linear optics.

1.5. THE FUTURE OF LIQUID CRYSTAL POLYMERS

Liquid crystal polymers offer vast scope for both functional and high performance polymers. The tensile strength and modulus of the LC fibers and films are substantially higher than the conventional materials such as steel. The well known application of LC rigid main chain polymers are in the aerospace and military departments as high performance fibers, films, coatings and intricate machine parts[129]. LCPs are used in electronic industry as base for high density integrated circuits. The chemical and thermal stability of LCPs are exploited in chemical industries such as corrosive chemicals storage tanks, distillation towers etc[129]. The main applications of side chain polymers, in particular silicone polymers, is in gas liquid chromatography(GLC)[59]. There are promising developments in ferro-electric side chain LC polymers to be used in display devices where the switching time is critical. Other potential applications for LCPs are in the area of telecommunication as wave guides, NLO devices, Optical windows, Optical gratings etc. A lot of efforts have been put on development of LCP materials worldwide.

Though LCPs can find wide applications, the raw materials availability and cost are limitations for the mass production. The multistep synthesis, non-availability of the state-of-the-art technologies for the manufacture and the difficulties involved in processing are important impediments to be overcome. Hence, in future, the state-of-the-art technologies have to be developed for the production of speciality chemicals to feed the industries to develop advanced LCP materials. The ferroelectric LC polymers and NLO active polymers[59] are envisaged to be futuristic advanced materials. The problems to be overcome in these polymers are their switching time and dipole relaxation[132] respectively. There are several methods deviced to solve these problems. The future of LCPs are certainly bright owing to their unmatched performance.

1.6. SCOPE AND OBJECTIVE OF THE PRESENT WORK

The importance of liquid crystal azobenzene polymers in view of rapidly developing demand for speciality polymers have been focused in the preceding discussion. Azobenzene compounds contributed to the dye industries and colour chemistry, innumerably, eversince their discovery. The versatility of this class stemslargely from the ease with which azo compounds can be made, and almost any diazotized aromatic amine can be coupled with any stable nucleophilic unsaturated system to give a coloured azo product. A full spectral range of azobenzene products can be made, by varying coupling components, with almost any desired chemical and/or physical properties. Azobenzene liquid crystals are known for more than a century and this property arises due to their molecular rigidity and coplanarity. The special structural features, such as *cis-trans* photoisomerizable azobenzene group, of this class of compounds allow them to find use in LC displays, NLO and information storage devices, optical windows etc. Only recently, liquid crystal polymers containing azobenzene group have been reported.

While going through literature on azobenzene group containing liquid crystal polymers, it was observed that there is a lacuna in information on the effect of substituents on both main chain and side chain polymers particularly relating to long chain substituents. It is noted that there are some natural phenolic monomers such as cardanol which has long chain substituent and which can be easily converted to azobenzene group containing hydroxy carboxylic acid.

It is well known that p-hydroxybenzoic acid is found to exhibit LC behaviour on polymerization, but the LC polymers are intractable and insoluble. The introduction of the azobenzene group is expected to reduce the transition temperature so as to make them melt processable. The structural features of the azobenzene monomers and polymers might exhibit non-linear optical property and so such studies might generate useful information for the development of NLO devices.

Hence, it would be interesting to study the synthesis and characterization of novel LCPs containing azobenzene mesogen in the main chain and side chain. In the present study, p-hydroxyphenylazobenzoic acid and its derivatives containing methyl and -C_{15} alkyl chain have been used. The monomer containing *cis* olefinic -C_{15} substituent is derived from cardanol, which is a long chain hydrocarbon phenol containing non-conjugated double bonds.

Therefore, the objectives of the present study are:

1. Synthesis and characterization of azobenzene monomers, containing hydroxy and carboxylic acid group, prepared through diazo coupling of 4-aminobenzoic acid with respective phenols.
2. Polymerization of azobenzene monomers by self polycondensation to obtain main chain polymers.
3. Synthesis and characterization of acrylate derivatives of azobenzene monomers and their polymerization to yield side chain polymers.
4. Studying and comparing the LC behaviour of main chain and side chain polymers.
5. A study on thermal stability of LC main chain polymers.
6. Comparing the effect of substituents on the phase transition temperatures of main chain and side chain polymers and highlighting the possible use of these polymers for nonlinear optical applications.
7. Cationic polymerization of the monomer containing olefinic unsaturation and a study on LC behaviour of the resulting polymer.

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CHAPTER - II

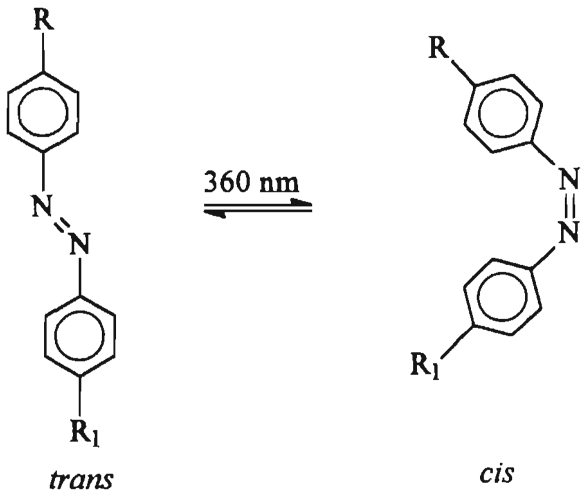
SYNTHESIS AND CHARACTERIZATION OF AZOBENZENE MONOMERS

2.1 INTRODUCTION

It has been shown in Chapter-I that introduction of azobenzene group imparts the rigidity required for the formation of LC phase. Coupled with its admirable colour and their application in areas such as NLO materials, information storage devices etc., it was thought appropriate to study some novel derivatives of compounds containing azobenzene mesogenic group. Moreover, the synthesis of azobenzene compounds can be easily made by a diazo coupling reaction. Diazo coupling reaction is the first reported reaction for the synthesis of azobenzene compounds by Peter Greiss in 1858 and it is the single most reaction used for the synthesis of azo dyes in industries till date. This electrophilic substitution reaction leads to regioselectivity and usually to higher yield of the product. The reaction involves coupling between an aromatic diazo compound and a coupling components such as phenols, naphthols, aromatic amines and active methylene compounds.

In the present investigation the *p*-hydroxyphenylazobenzoic acid derivatives, for which the chemical structures are shown in scheme 16, form the main constituent of the polymers synthesised.

The regioselectivity of the diazo coupling reaction leads to the formation of *p*-isomers only, in activated aromatic compounds, if the position is available for coupling[1]. There are two geometric isomers are known for azobenzene derivatives, namely, *cis* and *trans*. Among these two isomers *trans* form is the stable one and the *cis* isomer can be made photochemically from the *trans* isomer. The *trans* isomer, as a whole, possesses rod like structure as required for the anisotropy of the shape necessary for the mesogenic behaviour.



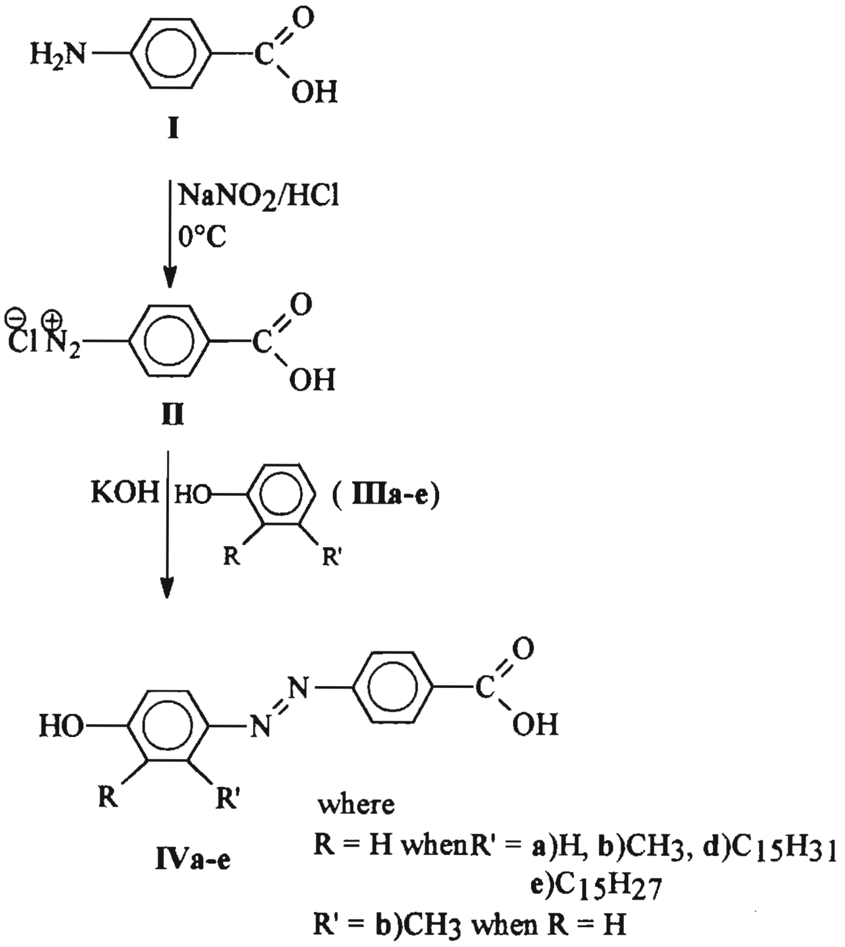
Scheme 16: Geometric isomers of azobenzene compounds.

This section deals with the discussion on the synthesis and characterization of *p*-hydroxyphenylazobenzoic acid derivatives containing hydrocarbon substituents. The reaction route is illustrated in scheme 17.

2.2 EXPERIMENTAL

The reaction used to synthesize azobenzene monomers in this study is diazo coupling reaction between *p*-aminobenzoic acid and phenolic derivatives with varying hydrocarbon substituents.

The monomers obtained were characterized using elemental analysis and spectral methods. Melting points of the monomers were observed under hot stage polarized light microscope (PLM) using Leitz 1350 heating stage coupled with PLM. IR spectra were recorded using Perkin-Elmer 882 infrared spectrometer and ^1H & ^{13}C NMR from Jeol JNM-EX 90 FT NMR system. UV-Vis spectra were obtained in DMF using Shimatzu UV-160A spectrophotometer and Mass spectra from 5890 Series II GC connected to 5970 Mass Detector.



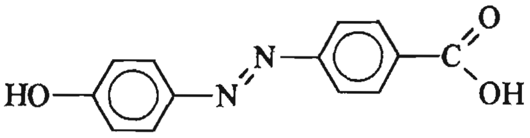
where
R = H whenR' = a)H, b)CH_3, d)$C_{15}H_{31}$
e)$C_{15}H_{27}$
R' = b)CH_3 when R = H

Scheme 17: Synthesis of azobenzene monomers

The typical procedure for the synthesis of monomers is given below.

1. *Synthesis of 4-[(4-hydroxyphenyl)azo]benzoic acid* (**IVa**): *p*-Aminobenzoic acid (**I**, 13.71g, 0.1mol) was dissolved in dilute HCl (20 mL of concentrated HCl in

200mL of water) and diazotized with a sodium nitrite (6.90g, 0.1mol in 20 mL of water) solution at 0°C with stirring in an ice bath. The solution was diluted with chilled methanol(400 mL). Phenol (**IIIa**, 9.41g, 0.1mol) was dissolved in a chilled solution of potassium hydroxide (10.77g, 0.19mol) in methanol (100 mL) and added dropwise to the diazonium salt solution. The red dye formed was stirred for a further 2 h and poured into a dilute HCl solution with stirring. The red solid separated was filtered, washed thoroughly with water, and dried. The dye was then purified by column chromatography on silica gel (60-120 mesh) using chloroform as eluent. Solvent was removed and recrystallized from a methanol-water mixture: yield 17.5g (76%); red crystals; m.p. 274-275°C. Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.17; N, 11.56. Found: C, 61.40; H, 4.56; N, 10.81.



(IVa)

i) M.Wt. : 242.2

ii) m.pt. : 274-275°C

iii) UV-Vis (λ_{max}) : 363nm (ε_{max} = 12 651 M^{-1} cm^{-1})

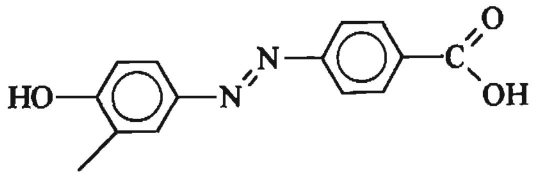
iv) IR (KBr; cm^{-1}) : 3550, 3460 (Ar-OH), 1680 (Ar-COOH), 1600, 1550 (Ar: C=C), 1145 (-N=N-).

v) ^{1}H NMR (DMSO-d_6) : δ 6.8 - 8.4 (8H, m, Ar)

vi) ^{13}C NMR (DMSO-d_6) : 116.4, 122.4, 125.6, 130.8, 132.0, 145.7, 154.9, 161.8, 167.2 ppm.

All the monomers were prepared following the procedure mentioned above. In the case of monomer from cardanol, the double bond equivalence of cardanol unsaturations is two as reported by Tyman et al.[2] Hence, the monomer containing unsaturated side chain is treated as diene through out this investigation.

2. *4-[(4-hydroxy-3-methylphenyl)azo]benzoic acid* (**IVb**): A total of 20.75g (81%) of the product was obtained from *p*-aminobenzoic acid (**I**, 13.71g; 0.1 mol), sodium nitrite (6.9g; 0.1 mol), and *o*-cresol (**IIIb**, 10.81g; 0.1 mol): red orange crystals; mp 245-246°C (dec.). Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 64.91; H, 5.05; N, 9.98.



(IVb)

i) M.Wt. : 256.2

ii) m.p. : 245-246°C (dec.)

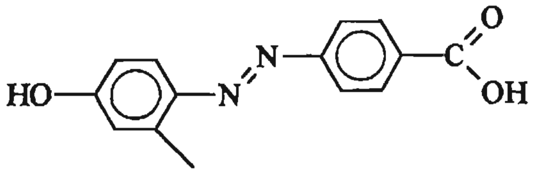
iii) UV-Vis (λ_{max}) : 368 nm (ε_{max} = 14 205 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 3520, 3430 (Ar-OH); 1685 (Ar-COOH); 1600, 1550 (Ar,C=C); 2940, 1460, 1360 (-CH3), 1145 (-N=N-).

v) ^{1}H NMR (DMSO-d_6) : δ 6.8-8.3 (7H, m, Ar); 2.1-2.4 (3H, s, -CH3);

vi) ^{13}C NMR (DMSO-d_6) : 16.1, 115.3, 124.0, 125.5, 125.1, 130.8, 131.9, 145.0, 154.9, 160.0, 167.1 ppm.

3. *4-[(4-hydroxy-2-methylphenyl)azo]benzoic acid* (**IVc**): A total of 21.26g (83%) of the product was obtained from *p*-aminobenzoic acid (**I**, 13.71g; 0.10 mol), sodium nitrite (6.9g; 0.10 mol), and *m*-cresol (**IIIc**, 10.81g; 0.10 mol): red orange; mp 240-241°C (dec.). Anal. Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.10; H, 3.98; N, 11.20.



(IVc)

i) M.Wt. : 256.2

ii) m.p. : 240-241°C (dec.)

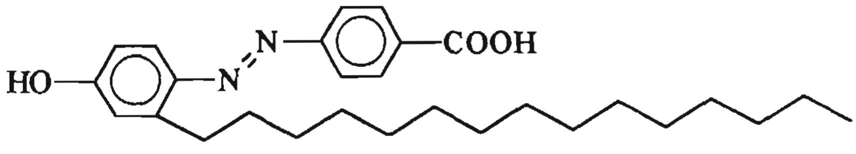
iii) UV-Vis (λ_{max}) : 372 nm (ε_{max} = 19 509 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 3300 (Ar-OH), 1685 (Ar-COOH), 1600, 1580, 1560, 1540 (Ar,C=C), 2920, 1480, 1380 (-CH3), 1150 (-N=N-).

v) ^1H NMR (DMSO-d_6) : δ 6.6-8.3 (7H, m, Ar); 2.6-2.8 (3H, s, -CH3).

vi) ^{13}C NMR (DMSO-d_6) : 15.8, 113.0, 116.1, 121.1, 129.6, 130.5, 141.0, 143.2, 154.7, 160.5, 165.7 ppm.

4. *4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid* (**IVd**): A total of 36.61g (81%) of the product was obtained from *p*-aminobenzoic acid (**I**, 13.71g; 0.10 mol), sodium nitrite (6.9g; 0.10 mol), and 3-*n*-pentadecylphenol (**IIId**, 30.45g; 0.10 mol): red, mp 151-152°C. Anal. Calcd. for $C_{28}H_{40}N_2O_3$: C, 74.30; H, 8.91; N, 6.19. Found: C, 72.80; H, 9.40; N, 5.65.



(IVd)

i) M.Wt. : 452.6

ii) m.p. : 151-152°C

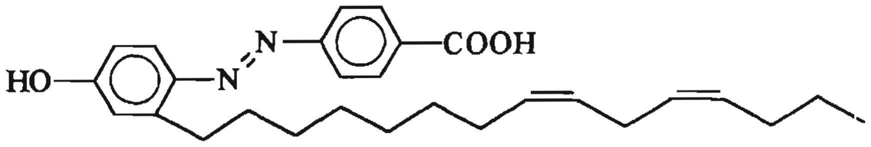
iii) UV-Vis (λ_{max}) : 372 nm (ε_{max} = 12 160 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 3320 (Ar-OH), 2920, 2850 (-CH2-), 1695 (Ar-COOH), 1610 , 1580, 1540 (Ar, C=C), 1150 (-N=N-).

v) ^1H NMR (acetone-d_6) : δ 0.7-3.4 (31H, m, -CH2-), 6.7-8.5 (7H, m, Ar)

vi) ^{13}C NMR (acetone-d_6) :13.9, 22.9, 26.7, 27.6, 28.5, 29.4, 29.6, 29.9, 30.2, 31.1, 31.5, 32.1, 32.5, 114.4, 116.8, 117.4, 122.6, 131.1, 144.2, 147.2, 156.1, 161.8, 166.7 ppm.

5. *4-[(4-hydroxy-2-pentadecadienyl)azo]benzoic acid* (**IVe**): A total of 36.16g (80%) of the product was obtained from *p*-aminobenzoic acid (**I**, 13.71g; 0.1 mol), sodium nitrite (6.9g; 0.1 mol), and cardanol (**IIIe**, 30.05g; 0.1 mol): red; mp 134-135°C. Anal. Calcd. for $C_{28}H_{37}N_2O_3$: C, 74.80; H, 8.29; N, 6.23. Found: C, 76.10; H, 6.95; N, 6.10.



(IVe)

i) M.Wt. : 449.61

ii) m.p. : 134-135°C

iii) UV-Vis (λ_{max}) : 372 nm (ε_{max} = 13 862 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 3320 (Ar-OH), 2920, 2860 (-CH2-), 1690 (Ar-COOH), 1610 , 1580 (Ar, C=C), 3020, 790 (cis -CH=CH-), 1155 (-N=N-).

v) ^{1}H NMR (acetone-d_6) : δ 0.7-3.3 (~27H, m, -CH2-), 5.0-5.6 (m, -CH=CH-), 6.7-8.3 (7H, m, Ar).

vi) ^{13}C NMR (acetone-d_6) :13.2, 22.1, 28.5, 29.0, 29.3, 30.9, 31.4, 31.9, 113.9, 116.2, 116.8, 121.9, 129.4, 130.5, 131.4, 143.5, 146.6, 155.5, 161.5, 166.4 ppm.

2.3 RESULTS AND DISCUSSION

The monomer synthesis was carried out according to the modified procedure of Pansare et al.[3] The solid dyes obtained were purified by column chromatography and recrystallized from a methanol-water mixture. The colour of the monomers are red which is characteristic feature of azobenzene compounds. The purities of the monomers were confirmed by elemental analysis and spectral analysis. The calculated values of the elemental analysis were in good agreement with the experimental values. Molecular weight of the monomers were obtained from the molecular ion peaks (M^+) of the Mass spectra. The melting point of the monomer (**Va**) containing no substituent and the monomers (**Vb** & **Vc**) containing methyl substituent showed fairly high melting points. But the presence of long *n*-alkyl (-C_{15}) side chain in monomer **IVd** and **IVe** reduced the melting points considerably. However, none of the monomers exhibited LC phase.

The IR spectra of monomers (Figure 8) showed characteristic absorption peaks corresponding to the expected group frequencies.[4] The phenolic hydroxyl group stretching appeared in the range of 3550-3300 cm^{-1} and the carbonyl stretching of carboxylic acid dimer at 1680-1690 cm^{-1}. The aromatic C=C vibrations appeared at 1610-1600, 1580-1560 and 1550-1540 cm^{-1}. The methyl substituent of the monomers **IVb** and **IVc** showed characteristic absorptions at 2940-2920 cm^{-1} (-C-H str.) and the bending modes of vibrations at 1480-1460 cm^{-1} and 1380-1360 cm^{-1}. Monomers **IVd** and **IVe** showed strong absorption at 2920 cm^{-1} which is due to the long alkyl chain and monomer **IVe** showed -CH=CH- stretching at 3020 cm^{-1}, bending at 1620 cm^{-1} and a characteristic peak of *cis* alkenes at 790 cm^{-1} which the cardanol side chain possess. It is difficult to diagnize azo linkages by IR spectroscopy, however, *p*-substituted azobenzene derivatives show strong absorptions[5] at 1370 and 1150 cm^{-1}. All the monomers (**IVa-IVe**) showed a strong and characteritic absorption at 1145-1155 cm^{-1}.

^1H NMR spectra supported the assigned structure and hence the formation of azo dyes.[6] Compound **IVa** showed the resonance signals (Figure 9) in the range of 6.8-8.4 δ (8H) corresponding to the aromatic protons. The aromatic protons of the rest of the monomers were also resonated more or less in the same region. The methyl protons of **IVb** (Figure 11) and **IVc** (Figure 13) appeared at 2.3 and 2.7δ respectively. Monomers **IVd** (Figure 15) and **IVe** (Figure 17) differ from **IVa-IVb** by having a -C_{15} alkyl chain protons which resonates in the range of 0.7-3.4δ corresponding to 31 protons and 0.7-3.3δ corresponding to about 27 protons respectively. The olefinic protons of non-conjugated allylic double bonds of monomer **IVe** resonated at 5.0-5.6 δ as multiplet.

The structure of the monomers were further confirmed by ^{13}C NMR spectroscopy and found to be complimentary to the conclusions drawn from ^{1}H NMR studies.[6] The ^{13}C chemical shift value for aromatic carbons of **IVa-IVe** are in the range of 144-164 ppm (**IVa**; Figure 10). The carboxylic carbon resonated at 165.7-167.2 ppm and the phenoxy carbon at 160.1-161.8 ppm. The methyl group carbon of **IVb** (Figure 12) and **IVc** (Figure 14) resonates at 16.1 and 15.8 ppm respectively. The alkyl chain carbons of **IVd** (Figure 16) gave a bunch of peaks between 13.9-32.5 ppm and **IVe** (Figure 18) gave a bunch between 13.2-31.9 ppm for alkyl chain carbons and 129.4 & 130.5 ppm for olefinic carbons. The UV-Vis spectra of all monomers (Figure 7) have one absorption peaks corresponding to 363-372 nm (ε_{max} = 12 160-19 509 $M^{-1}cm^{-1}$) due to π-π^* of azobenzene.[6]

2.4 CONCLUSION

Five 4-[(4-hydroxyphenyl)azo]benzoic acid derivatives were synthesized using diazocoupling reaction of *p*-Aminobenzoic acid with phenol, *o*-cresol, *m*-cresol, *m*-pentadecylphenol and cardanol. The red crystalline compounds were obtained in good yields and showed fairly high melting points except for the monomers containing long alkyl substituent. These units are expected to incorporate liquid crystalline properties to the polymers because of their structural anisotropy. The structure of the monomers were confirmed by spectral methods such as IR, ^{1}H & ^{13}C NMR etc.

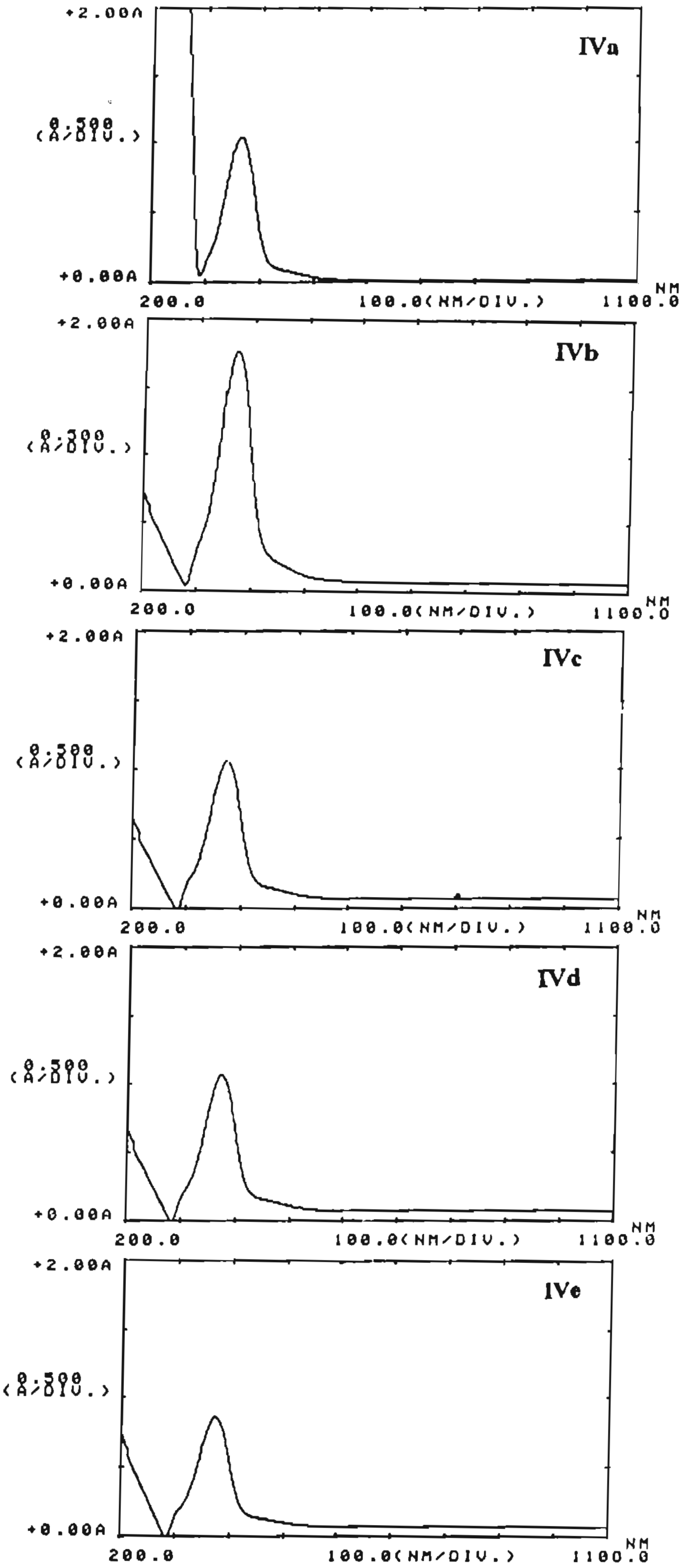


Figure 7: UV-Vis spectra of azobenzene monomers (**IVa-e**)

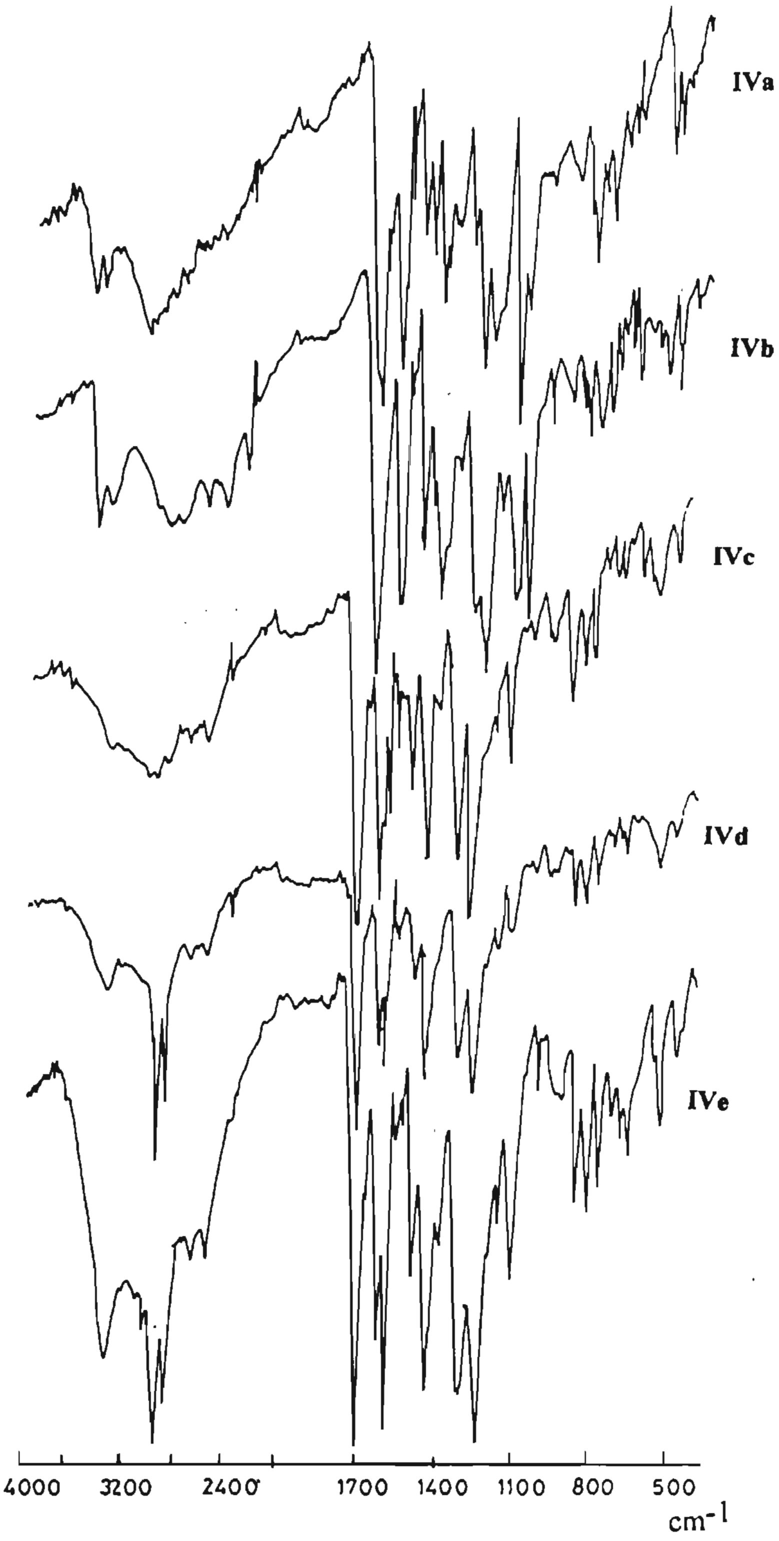


Figure 8: IR spectra of azobenzene monomers (**IVa-e**)

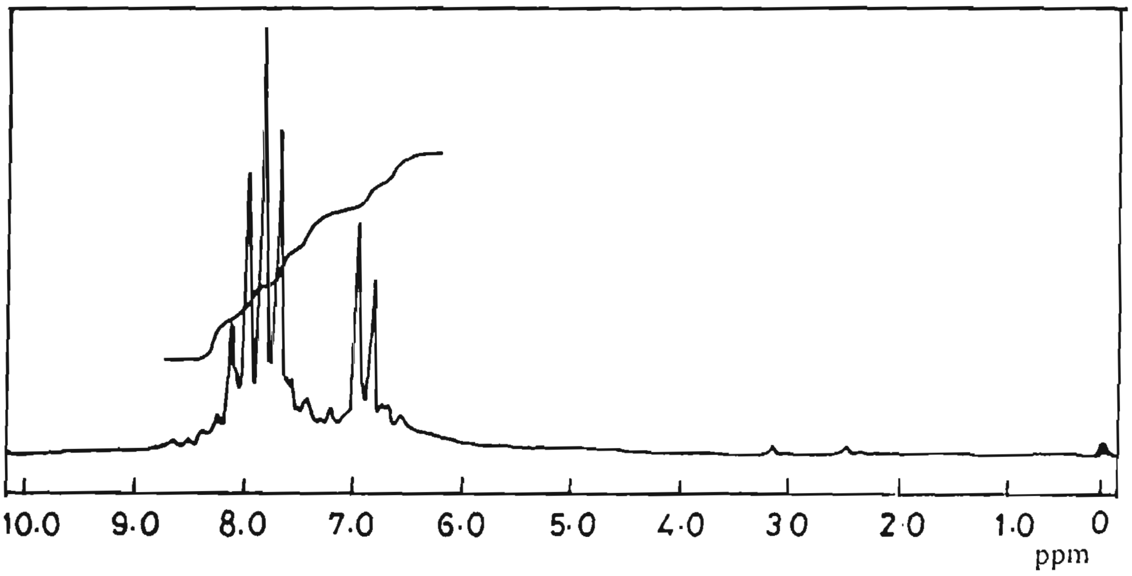
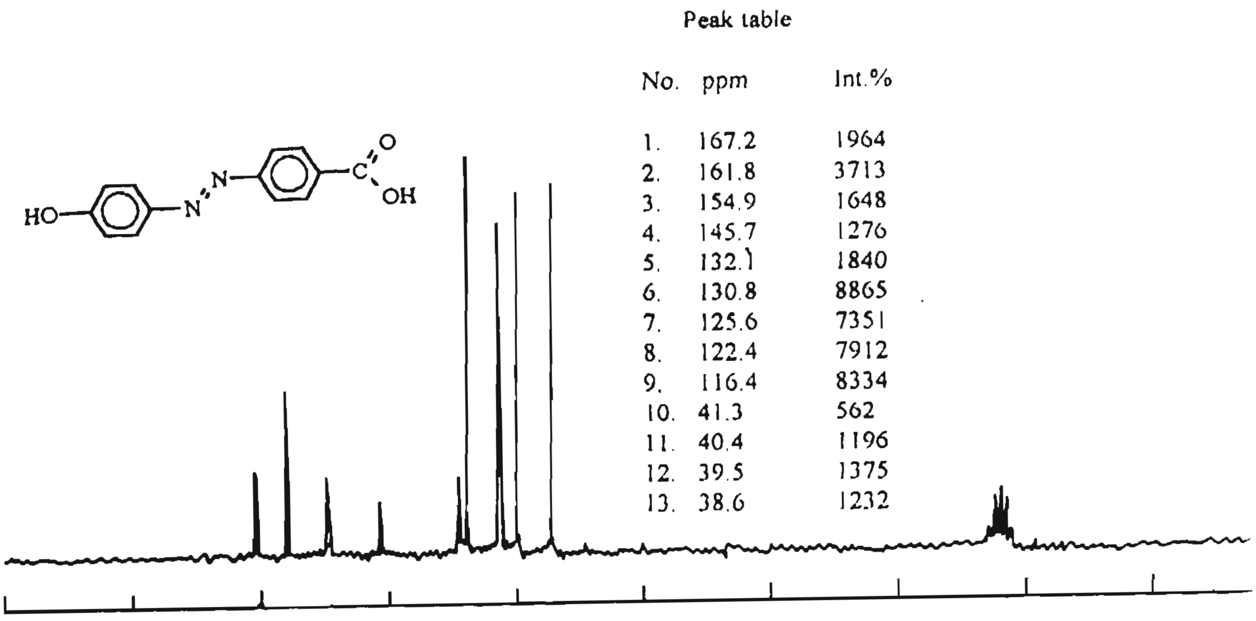


Figure 9: ^{1}H NMR spectrum of monomer **IVa**



No.	ppm	Int.%
1.	167.2	1964
2.	161.8	3713
3.	154.9	1648
4.	145.7	1276
5.	132.1	1840
6.	130.8	8865
7.	125.6	7351
8.	122.4	7912
9.	116.4	8334
10.	41.3	562
11.	40.4	1196
12.	39.5	1375
13.	38.6	1232

Figure 10: ^{13}C NMR spectrum of monomer **IVa**

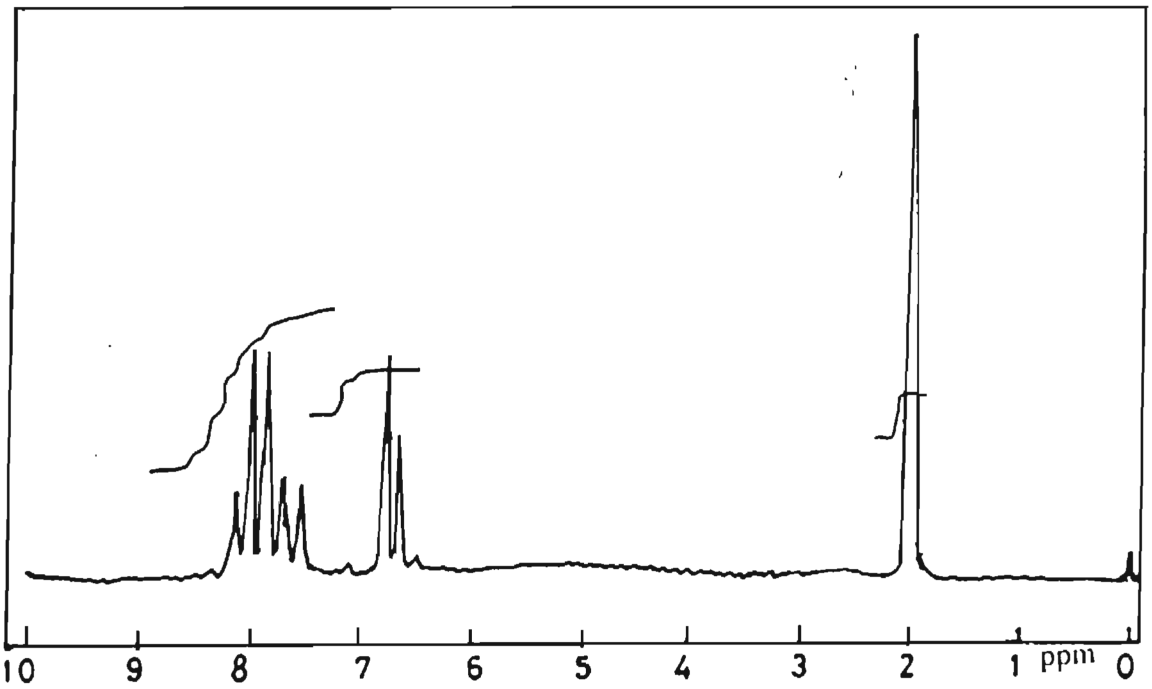
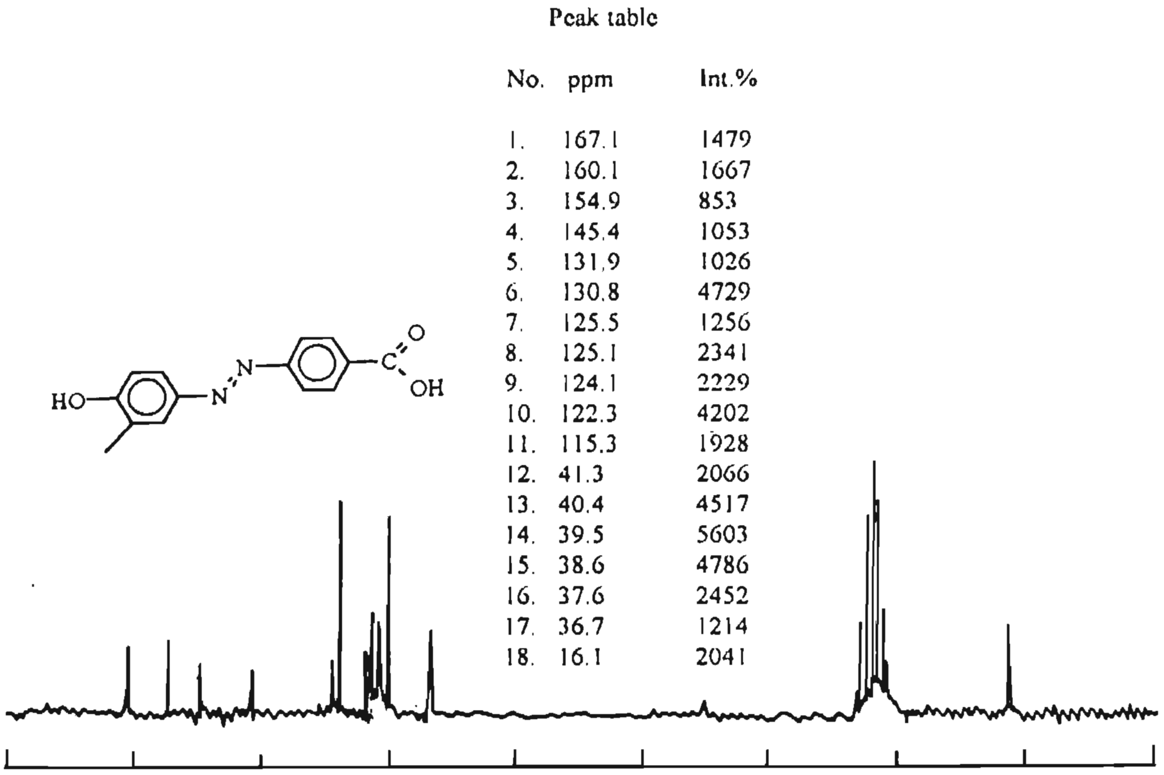


Figure 11: ^{1}H NMR spectrum of monomer **IVb**



Peak table

No.	ppm	Int.%
1.	167.1	1479
2.	160.1	1667
3.	154.9	853
4.	145.4	1053
5.	131.9	1026
6.	130.8	4729
7.	125.5	1256
8.	125.1	2341
9.	124.1	2229
10.	122.3	4202
11.	115.3	1928
12.	41.3	2066
13.	40.4	4517
14.	39.5	5603
15.	38.6	4786
16.	37.6	2452
17.	36.7	1214
18.	16.1	2041

Figure 12: ^{13}C NMR spectrum of monomer **IVb**

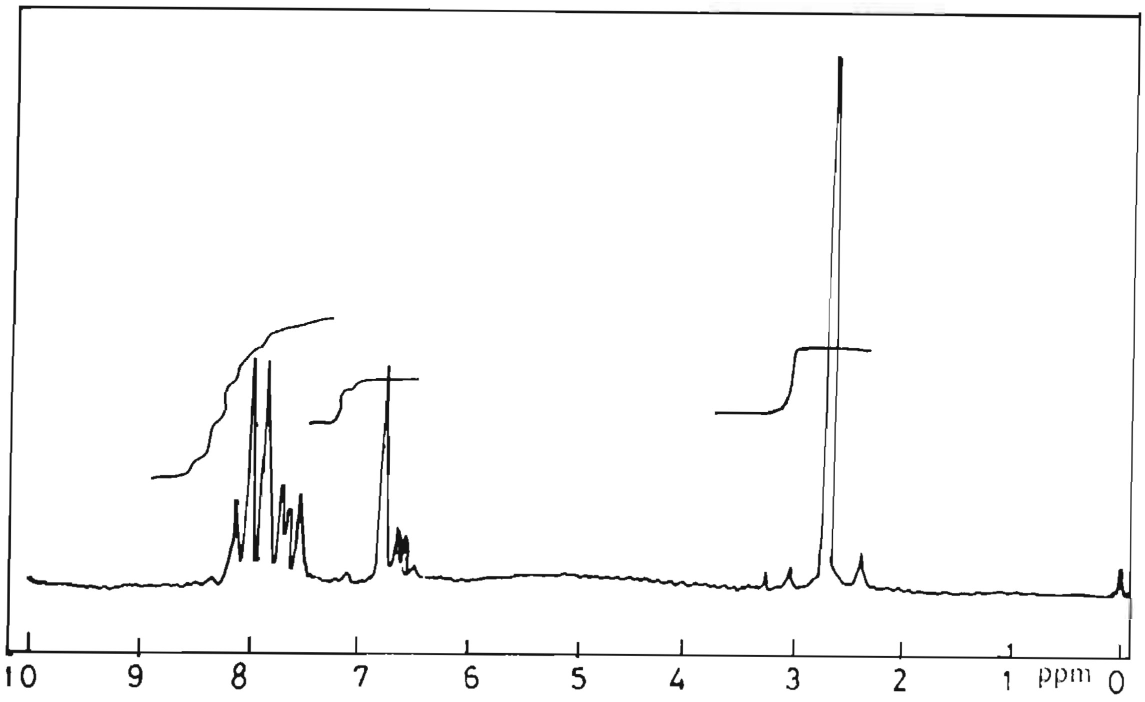


Figure 13: ^{1}H NMR spectrum of monomer **IVc**

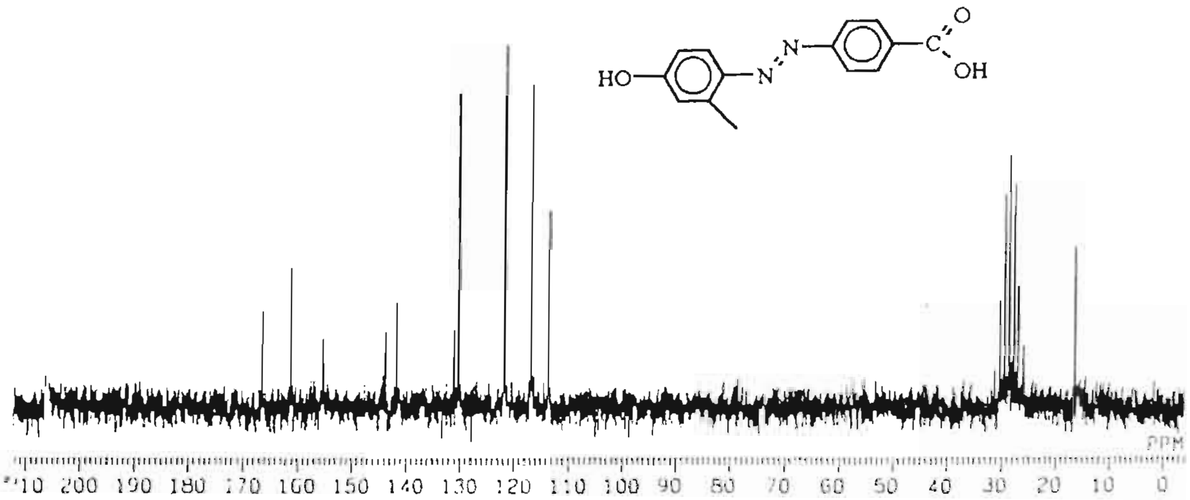


Figure 14: ^{13}C NMR spectrum of monomer **IVc**

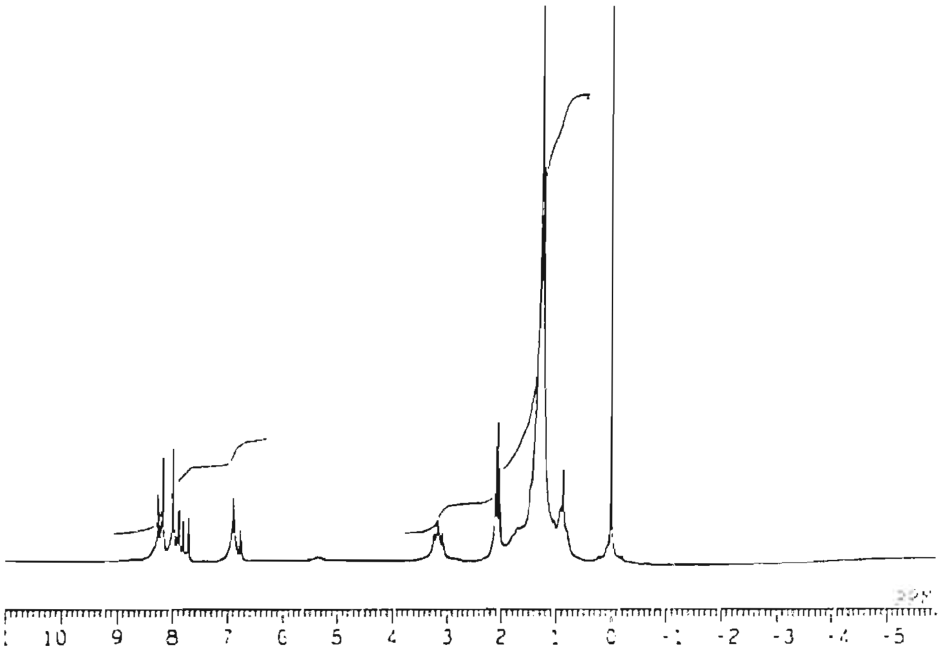


Figure 15: ^{1}H NMR spectrum of monomer **IVd**

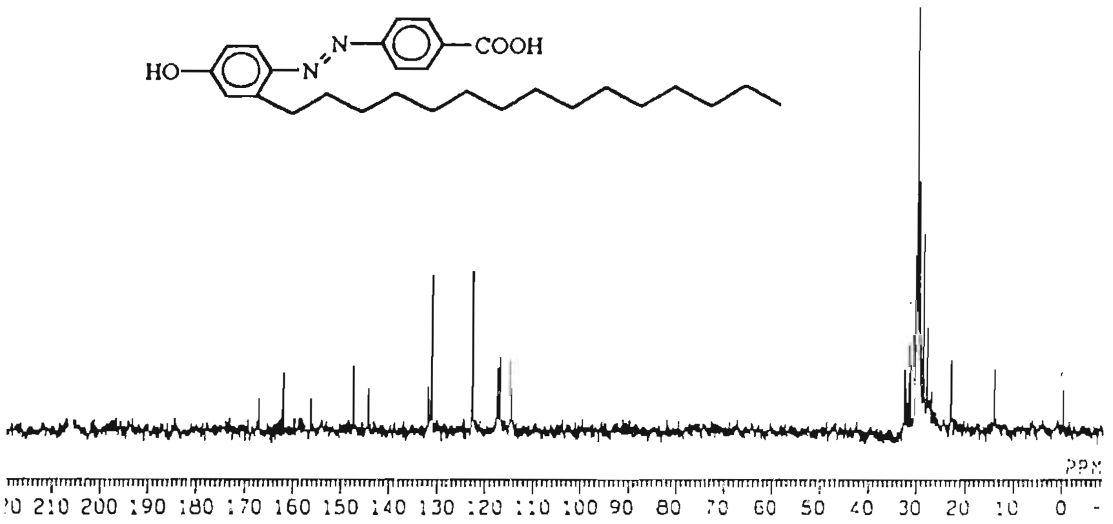


Figure 16: ^{13}C NMR spectrum of monomer **IVd**

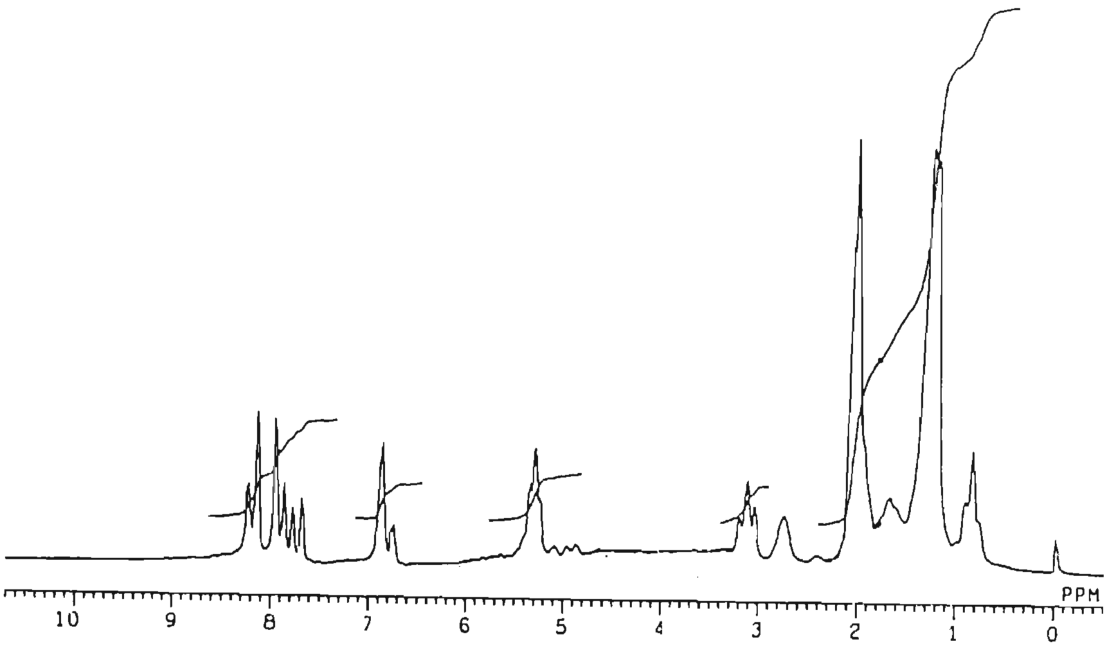


Figure 17: ^1H NMR spectrum of monomer **IVe**

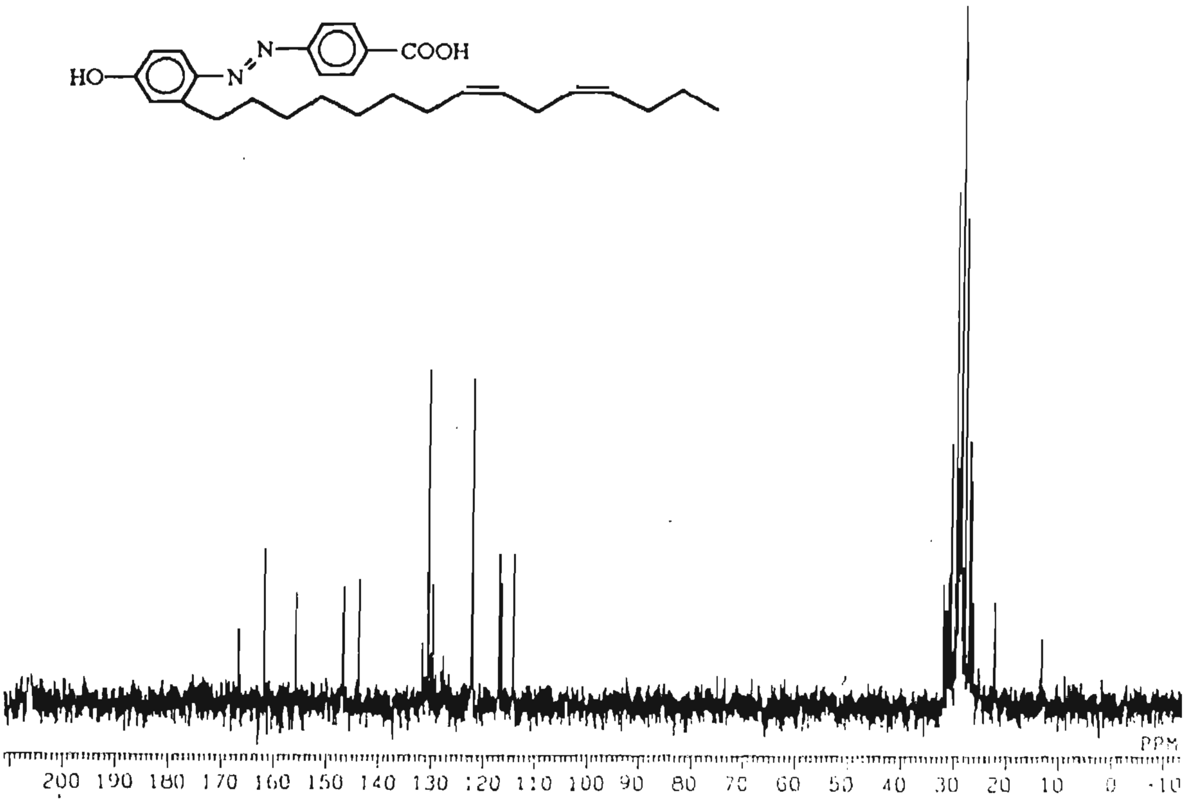


Figure 18: ^{13}C NMR spectrum of monomer **IVe**

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CHAPTER - III

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTAL MAIN CHAIN AZOBENZENE POLYMERS

3.1 INTRODUCTION

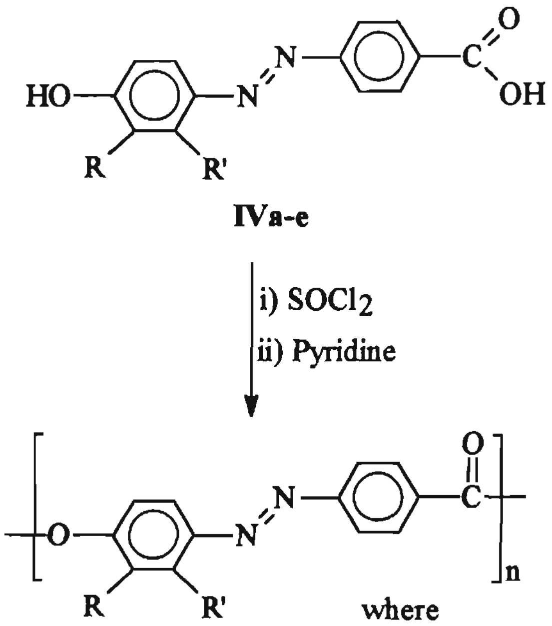
Photoresponsive chromophoric polymers are finding applications in the areas like optical storage devices, data processing, light modulation etc. Azobenzene polymers are suitable for such applications. Azobenzene group is photosensitive and undergo *cis-trans* isomerization in the visible region of the spectrum and this behaviour is useful in opto-electronics. The rigidity and the planarity of azobenzene group gives rise to the anisotropy of shape required to exhibit liquid crystalline (LC) property.[1] The LC property provide an added advantage to the polymers by spontaneous self-organization. But the intractability and insolubility are the main problems associated with the main chain LC polymers. These problems can be overcome by introducing substituents and/or flexible spacers which help in lowering the transition temperatures and improve the polymer solubility in common organic solvents.[2] This is achieved by the disruption of polymer chain packing by the substituents and/or flexible spacers.

3.2 Experimental

Polymerization: Polymerizations were carried out in *o*-dichlorobenzene at 80°C for 12h using thionyl chloride and pyridine. The polymers were precipitated in methanol, washed thoroughly with acetone and dried in vacuo for 12h at 60°C.

The polymers obtained were characterized using elemental analysis, viscosity, spectral and thermal methods. The inherent solution viscosities(η_{inh}) of the polymers were measured using Ubbelode suspended level viscometer at 28°C using conc. sulphuric acid (98%) as solvent. The solution concentration used was 0.5 g/dL. IR spectra were obtained from Perkin-Elmer 882 infrared spectrometer. UV-Vis spectra was obtained in DMF using Shimatzu UV-160A spectrophotometer. The melting points of the polymers were observed under hot stage polarized light microscope (PLM)[3] using Leitz-1350 heating stage coupled with PLM.

The scheme of synthesis of polymer is given below:



IVa-e

i) $SOCl_2$
ii) Pyridine

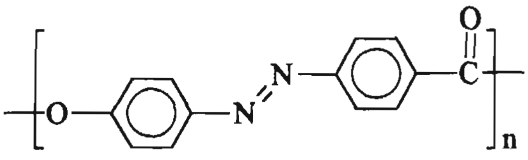
Va-e

where
R = H when R' = a)H, c)CH_3, d)$C_{15}H_3$
e)$C_{15}H_{27}$
R' = b)CH_3 when R'= H

Scheme 18: Synthesis of azobenzene polymers

A typical procedure is as follows: 4-[(4-hydroxyphenyl)azo]benzoic acid (**IVa**, 1.0g; 4.1mmol) was refluxed with an excess of thionyl chloride (1mL) for 1h with stirring. The excess thionyl chloride was distilled off with a nitrogen flush. *o*-Dichlorobenzene was added to dissolve the acid chloride, and then 2 drops of pyridine was added. The polymerization was continued for 12h at 80°C, and the products precipitated.

1. *Poly[4-[(4-hydroxyphenyl)azo]benzoic acid]* (**Va**): yield 0.76 g (82.1%), orange coloured powder. Anal. Calcd. for $C_{13}H_8N_2O_2$: C, 69.63; H, 3.59; N, 12.5. Found: C, 68.1; H, 3.43; N, 12.28.



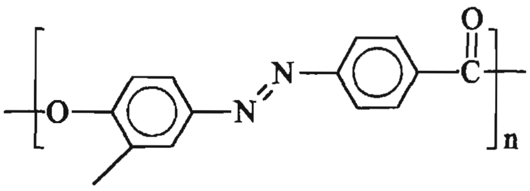
(Va)

i) viscosity : 0.29 dL/g

ii) m.p. (°C) : K 262 N 382 I

iii) IR (KBr; cm^{-1}) : 1735 (ArCOOAr); 1600, 1560 (Ar; C=C); 1150 (-N=N-).

2. *Poly[4-[(4-hydroxy-3-methylphenyl)azo]benzoic acid]* (**Vb**): yield 0.73 g (79%), orange coloured powder. Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 69.10; H, 5.22; N, 10.91.



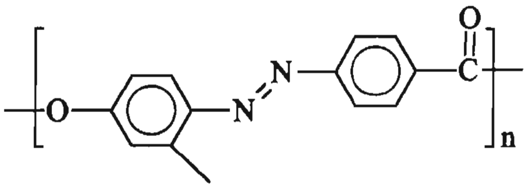
(Vb)

i) viscosity : 0.37 dL/g

ii) m.p.(°C) : K 235 N dec.> 310

iii) IR (KBr; cm^{-1}) : 1740 (ArCOOAr); 1600, 1560 (Ar; C=C); 2931, 1488, 1408 ($-CH_3$); 1145 (-N=N-).

3. *Poly[4-[(4-hydroxy-2-methylphenyl)azo]benzoic acid]* (**Vc**): yield 0.77 g (82.8%), orange coloured powder. Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 68.89; H, 4.10; N, 12.11.



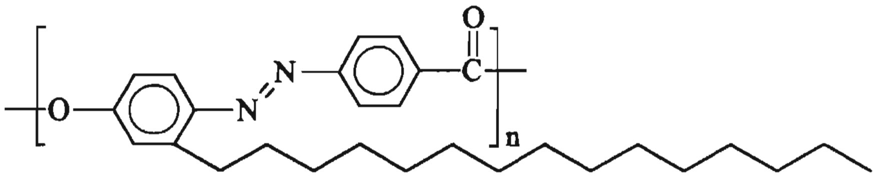
(**Vc**)

i) viscosity : 0.34 dL/g

ii) m.p. (°C) : K 220 N dec.>300

iii) IR (KBr; cm^{-1}) : 1740 (ArCOOAr); 1605, 1560 (Ar; C=C); 2920, 1480, 1405 ($-CH_3$); 1150 (-N=N-).

4. *Poly[4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid]* (**Vd**): yield 0.71g (73.9%), red-orange powder. Anal. Calcd. for $C_{28}H_{38}N_2O_2$: C, 77.37; H, 8.81; N, 6.44. Found: C, 76.19; H, 8.85; N, 5.45.



(**Vd**)

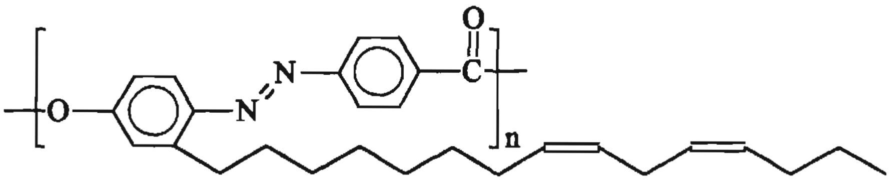
i) viscosity : 0.42 dL/g

ii) m.p. (°C) : K 130 N 262 I

iii) UV-Vis (λ_{max}) : 361 (ε_{max} = 10 000 M^{-1} cm^{-1})

iV) IR (KBr; cm^{-1}) : 1740 (ArCOOAr); 1600, 1580 (Ar; C=C); 2925, 2865, 1480, 1460, 1420($-C_{15}H_{31}$); 1150(-N=N-)

5. *Poly[4-[(4-hydroxy-2-pentadecadienylphenyl)azo]benzoic acid]* (**Ve**): yield 0.85 g (89%), red-orange powder. Anal. Calcd. for $C_{28}H_{34}N_2O_2$: C, 78.1; H, 7.96; N, 6.51. Found: C, 76.89; H, 6.12; N, 5.98.



(**Ve**)

i) viscosity : insoluble

ii) m.p. (°C) : infusible

iii) IR (KBr; cm^{-1}) : 1745 (ArCOOAr); 1620, 1590, 1560 (Ar; C=C); 2925, 2860, 1485, 1465, 1430 (-CH2-); 1150 (-N=N-).

3.3 RESULTS AND DISCUSSION

The polyesters were synthesized by a conventional polycondensation method using thionyl chloride and pyridine. Excess thionyl chloride was used to make acid chlorides. The acid chlorides thus prepared were used without further purification. Polymers **Va-Vc** started precipitating, after the addition of pyridine, in few hours. The polymers were precipitated in methanol and washed thoroughly with acetone to remove unreacted monomers and soluble oligomers. Solubility studies showed that the polymer having hydrocarbon flexible pendant group (polymer **Vd**) in its structure, is, as expected, soluble in common organic solvents such as chloroform, THF, dioxan etc., whereas polymers **Va-Vc** are found to be soluble only in conc. sulphuric acid and methane sulphonic acid. Polymer **Ve** is neither soluble in any solvent nor fusible. This behaviour may be due to the crosslinking of side chain double bonds as reported by George et. al.[4] The inherent viscosities of the polymers **Va-Vd** are in the range of 0.29-0.42 dL/g in conc. sulphuric acid (though it is a dreadful solvent, no notable change in viscosities was observed atleast for about five hours) at 28°C. End group analysis[4] of polymer **Vd** gave a molecular weight of Mn = 14,706. UV-Vis spectroscopy of polymer **Vd** (Figure 20) have one absorption peak at 361 nm (ε_{max} = 10 000 M^{-1} cm^{-1}).[1]

The formation of the polymers was supported by elemental analysis and IR spectroscopy (see experimental section). The IR spectra of polymers **Va-Ve** (Figure 19) gave the characteristic ester carbonyl stretching vibration at 1735-1745 cm^{-1}. Simultaniously, the peaks at 3550-3300 cm^{-1} of the hydroxyl groups and 1700-1670 cm^{-1} of the carbonyl groups of monomers **IVa-e** vanished or largely decreased on polyester formation. The C-H stretching vibrations of aliphatic pendant groups of polyesters **Vb-e** were observed at 2920 and 2860 cm^{-1}. The -N=N- stretching vibration of polyesters were observed at about 1150 cm^{-1}. In addition, polymer **Ve** showed disappearance of 3020 and 790 cm^{-1} peaks characteristic of the side chain olefin of cardanol. The disappearance of the unsaturation in the side chain of cardanol suggest involvement of these carbon atoms in crosslink formation as indicated earlier.[5]

The melting points of the polymers **Va-d** showed the typical melting sequence of LC materials i.e. crystal→LC→Isotropy. Polymers **Vb** and **Vc** decomposed prior to isotropization. This may be due to the higher molecular rigidity of the mesogenic unit containing thermally unstable methyl substituent. Polymer **Vd** isotropized without decomposition. This can be understood from the effect long side chain which reduced the melting point considerably low. Polymer **Ve** underwent decomposition without melting evidencing the crosslinking as observed in the IR spectra.

3.4 CONCLUSION

Five novel polymers based on *p*-substituted azobenzene units have been prepared by self polycondensation of the respective hydroxy carboxylic acids. Polymerization was carried out in *o*-dichlorobenzene at 80°C for12h. The inherent viscosity of the polymer solutions were in the range of 0.29-0.42 dL/g. Polymers are soluble only in conc.sulfuric acid and methane sulphonic acid. Polymer with saturated -C_{15} substituent is soluble in solvents like chloroform, THF, *o*-dichlorobenzene etc., but the polymer with unsaturated -C_{15} substituent is intractable. The melting of the polymers followed the typical crystal→LC→ Isotropy sequence of the LC materials. The polymer formation was further supported by IR spectroscopy.

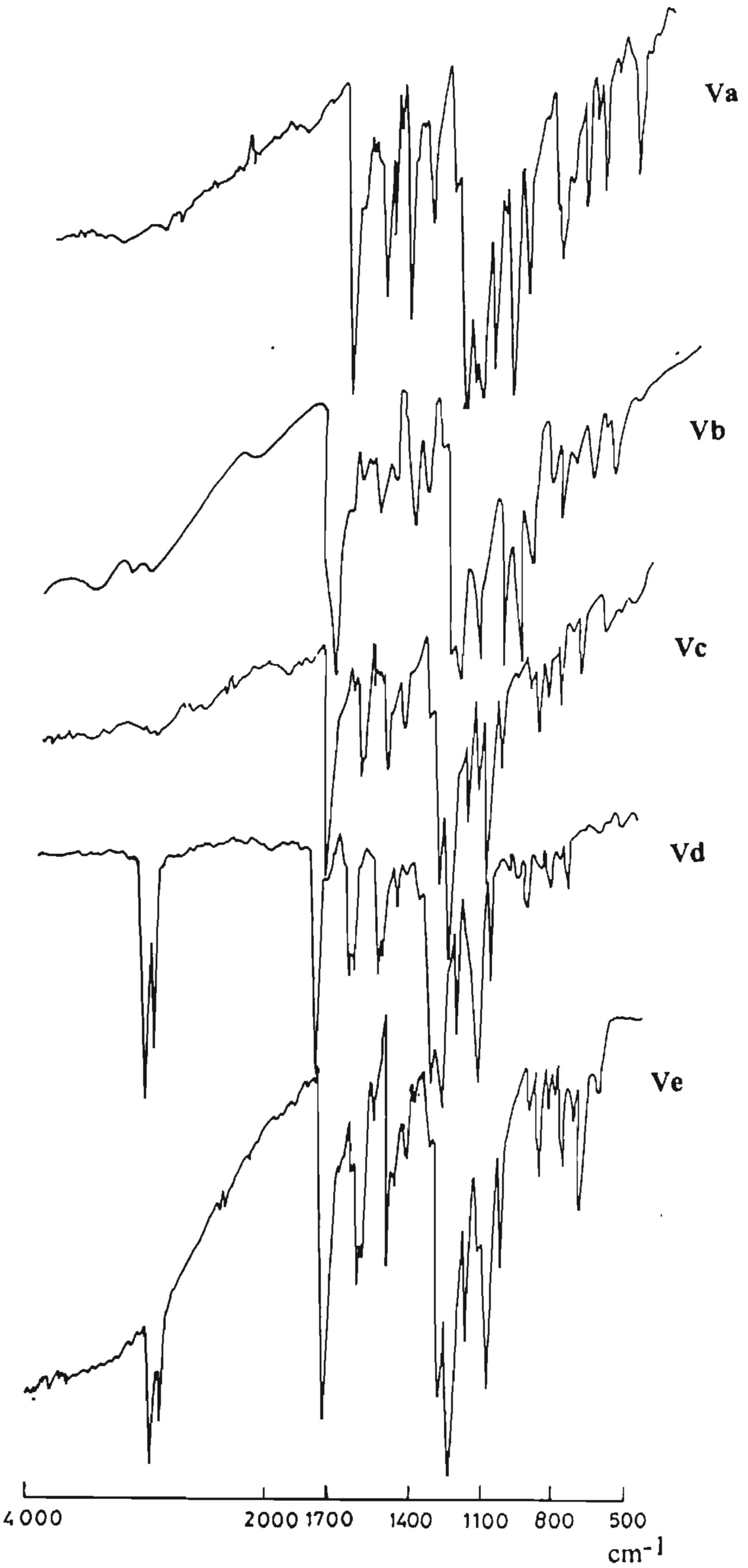


Figure 19: IR spectra of main chain polymers (**Va-e**)

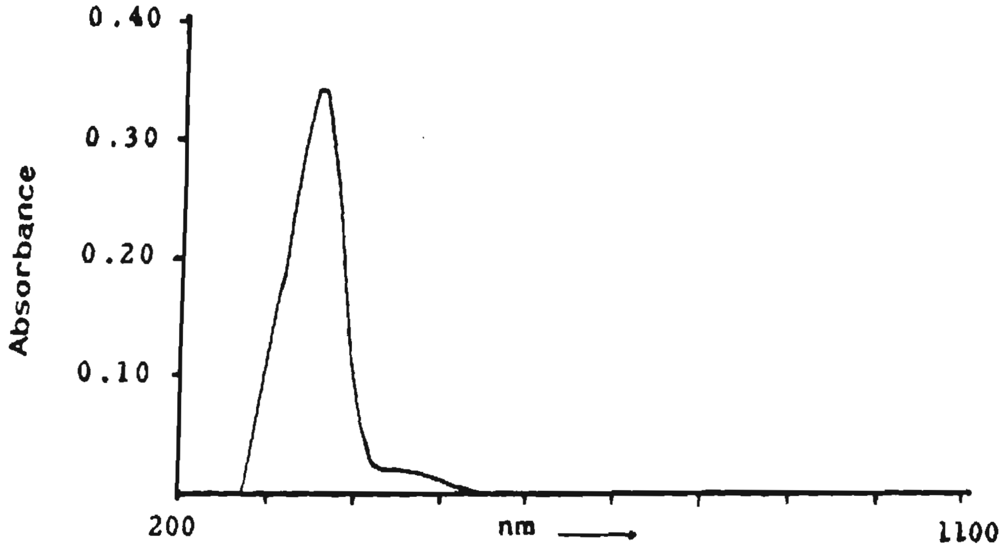


Figure 20: UV-Vis spectrum of polymer **Vd**

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CHAPTER - IV

STUDY OF LIQUID CRYSTALLINE PROPERTY OF MAIN CHAIN POLYMERS.

4.1 INTRODUCTION

The thermal behaviour and crystallinity of the polymers are described in this section. It has already been mentioned that the *p*-substituted azobenzene groups recurring periodically in the polymer backbone are expected to impart liquid crystallinity (LC) to these polymers. Moreover, introduction of dipolar groups is known to impart non-linear optical (NLO) behaviour to the polymer and the very well known *cis-trans* isomerization of azo group which would be useful in optical storage, holography etc. These properties along with LC behaviour enhances the materials performance several fold. Hence, more attention has been paid to the study of LC behaviour in these polymers. The phase transitions are identified using differential scanning calorimetry (DSC), polarized light microscopy (PLM) and thermal stability by thermogravimetric analyzer (TGA). The crystallinity of these polymers were examined using wide angle X-ray diffraction (WAXD).

DSC is used to measure the change in heat capacity of any material quantitatively and it is sensitive to very small changes in heat capacity. In LCPs the breakdown of order involve endothermic transitions. Exothermic transitions are crosslinking, oxidation, decomposition etc. PLM is the technique used to characterize the LC phases visually where the stable defects formed by the fluctuations in spontaneously self organized LC materials. A birefringent pattern typical of a particular phase can be observed under cross polarized light between a particular temperature range. TGA is used to characterize the thermal stability of any material in which the weight loss against the temperature change is recorded. The mechanism of decomposition can be worked out when the decomposition steps are well defined.

4.2 EXPERIMENTAL

DSC scans were performed using Du Pont DSC V2.2 A 9900 system under nitrogen, TGA using Du Pont 951 Thermogravimetric Analyzer under air and nitrogen and PLM by Leitz-1350 hot stage coupled cross-polarized light microscope. The heating rate used was 20°C/min in all the cases. X-ray diffractograms were obtained on a Rigaku Miniflex X-ray Diffractometer using nickel filtered Cu K_α radiation.

Endotherms in DSC thermograms are assigned[1] to crystal→mesophase and mesophase→isotropic transitions. In the DSC heating cycle, endotherm at the highest transition temperature corresponds to the transition from LC phase to the isotropic phase. If the transition from crystalline to LC is marked by more than one endotherm (T_1, T_2 & T_3), the highest temperature (T_3) was attributed to the crystal to mesophase transition since the PLM studies did not show any evidence for the fluidity below this temperature. The remaining lower temperature endotherms (T_1 & T_2) represent unidentified crystal to crystal transitions. The peak maximum was taken as the transition temperature. Cooling curves could not be obtained as the polymers decomposes prior to or during isotropization.

In PLM the temperature of appearance of the phase was taken as the crystal→LC transition and the complete disappearance of phase was taken as LC→isotropic transition. Normally, the identification of the transition temperatures[1] is done by coupling the DSC data with the information obtained by the visual examination of the polymer in PLM.

In TGA thermogram, temperature of 5% weight loss was taken as the initial decomposition tempeature (T_i), 50% weight loss as half-decomposition temperature (T_h) and the highest temperature at which the weight loss has ceased was taken as final decomposition temperature (T_f).[2] X-ray diffractograms were recorded for the polymer samples as-prepared and then the samples were heated to the mesophasic temperature, quenched and recorded to observe the characteristic halo at $\theta = 20°$ of isotropic liquids.[1] The small angle sharp diffraction peaks characteristic of crystalline order cannot be obtained in WAXD.

4.3 RESULTS AND DISCUSSION

1. *Poly[4-[(4-hydroxyphenyl)azo]benzoic acid]* (**Va**):

The DSC thermogram for polymer **Va** is given in Figure 21. The polymer shows one low-temperature endotherm at 40°C and three well defined endotherms at 262, 337 and 382°C. Kricheldorf et al.[3] describe the appearance of such a low-temperature endotherm as due to crystalline modification. When observed under PLM on a heating stage, polymer **Va** started melting at 265°C and exhibited the typical threaded nematic texture (Figure 22) which remained up to the isotropization temperature at 382°C. At 338°C a waterlike flow of the polymer was observed without any change in texture. This may be due to the wide molecular weight distribution which can melt in a wide temperature range and hence the clear nematic fluidity was observed at 338°C.

In TGA thermogram, of polymer **Va** under air (Figure 32), T_i was observed at fairly high temperature of about 465°C, T_h at 520°C and T_f at 625°C. The decomposition proceeds in two steps, the first step involving 40% weight loss and the second step 60%. The rapid weight loss in a narrow temperature range may be due to the loss of azo group as nitrogen gas as reported by Jadhav et al.[4] TGA conducted under nitrogen atmosphere (Figure 33) exhibited only a one step decomposition with a sharp weight loss between 460 and 475°C, but the T_i value at 460°C agreed with the former experiment. Based on this observation the second step of decomposition of polymer **Va** under air has to be the decomposition of crosslinked structures formed by the oxidation of polymer **Va**.

X-ray diffractogram (Figure 31) showed that the as-prepared sample is highly crystalline. This sample on melting to phase formation temperature and quenching showed no sharp diffraction peaks but a halo around $\theta = 20°$ was observed. This is characteristic of nematic phase[1] where the isotropicity of the LC phase appears as a halo. The crystallinity is also evident from DSC where there was no Tg characteristic of amorphous materials was observed.

2. *Poly[4-[(4-hydroxy-3-methylphenyl)azo]benzoic acid]* (**Vb**):

The DSC thermogram for polymer **Vb** is given in Figure 32. The polymer shows one low temperature endotherm at 80°C which may be due to the crystal modification[3] and an endotherm at 256°C. When observed under PLM on a heating stage, polymer **Vb** started melting at 258°C and exhibited the characteristic threaded nematic texture (Figure 24) which remained till the polymer started decomposing above 300°C. The waterlike flow was observed at 285°C which did not appear in DSC thermogram. The decomposition was further evident from DSC where the steep raise of base line was observed.

TGA thermograms of polymer **Vb** under air (Figure 32) and nitrogen (Figure 33) supported the decomposition observed under PLM. T_i was observed at 285 and 276°C in air and nitrogen respectively. The polymer showed T_h and T_f under air as 515 and 695°C respectively and the polymer decomposed completely. But under nitrogen the formation of thermally stable structure such as char is evidenced from the increase of T_h to 765°C with 40% residue remained even at 1000°C. The crosslinking leading to the thermally stable structure may be initiated by the pyrolytic elimination of methyl group yielding carbonaceous residue which is stable under high temperatures. Under air, though the formation of thermally stable structures is probable, the crosslinked network can be oxidized to volatile fragments.

X-ray diffractogram (Figure 31) showed that the as-prepared polymer sample is highly crystalline. This sample on melting to the mesophasic temperature and quenching showed a halo around $\theta = 20°$ characteristic of nematic phase. The crystallinity is also evident from DSC which did not show Tg for the polymer.

3. *Poly[4-[(4-hydroxy-2-methyl phenyl)azo]benzoic acid]* (**Vc**):

The DSC thermogram for the polymer **Vc** is given in Figure 25. The polymer showed two endothermic transitions at 180 and 225°C corresponding to the crystal modification and crystal-mesophase transition respectively. When observed under PLM on a heating stage, polymer **Vc** started melting at 228°C and exhibited the characteristic threaded nematic structure (Figure 26) which remained till the polymer started decomposing above 320°C. The waterlike flow, as in the case of polymer **Va**, was observed at 272°C which did not appear in DSC thermogram. In this case too the decomposition is observed as steep raise of base line.

The observation made under PLM is supported by TGA thermograms under air (Figure 32) and nitrogen (Figure 33) T_i was observed at 338 and 310°C in air and nitrogen respectively. The T_h and T_f of polymer **Vc** under air is 588 and 665°C respectively and the polymer decomposed completely. Under nitrogen, as in the case of polymer **Vb**, the formation of thermally stable structure is evidenced from the formation of 55% char which was stable till 1000°C. The increased char yield indicates that the crosslinking proceeds effectively to form more carbonaceous residue and may take place through a mechanism different from that observed for the decomposition of polymer **Vb**. Polymer **Vb** and **Vc** differ in having methyl substituent in different positions. In polymer **Vb** the methyl group is adjacent to the ester whereas in polymer **Vc**, it is adjacent to the azo group. These differences are seen in the thermal stability of the polymers. In comparing the thermal decomposition pattern of these two polymers, it can be noted that polymer **Vb** is more thermally stable than polymer **Vc** in air. This shows that a substituent adjacent to the azo group might possibly favour oxidative decomposition taking place on a higher rate.

The as-prepared sample of polymer **Vc** is found to be highly crystalline as observed from X-ray diffraction (Figure 31). The sample on melting to the mesophasic temperature and quenching showed a halo around $\theta = 20°$ characteristic of nematic phase and DSC also supported this observation where the Tg characteristic of amorphous polymers was not observed.

4. *Poly[4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid]* (**Vd**):

The DSC scan of polymer **Vd** gave two transitions at 130 and 197°C as shown in Figure 27. When observed under PLM, the polymer melted and exhibited a schlieren texture of the nematic phase (Figure 28) at 135°C and isotropized at

262°C which did not appear in the DSC scan. At 202°C, a waterlike flow of the polymer without any texture change was observed as in the case of other polymers.

Though a partial decomposition of the polymer was observed under PLM just above the isotropization temperature i.e. 210°C, TGA showed T_i at 290 and 260°C under air (Figure 32) and nitrogen (Figure 33) respectively. Under air, the T_h and T_f were found to be 510 and 615°C respectively and the polymer decomposed completely. Under nitrogen, though the polymer gave 24% char Ti and Th were less than that of polymer under air. This may be due to the oxidation of the -C_{15} alkyl chain leading to crosslinking increased the T_i to 290°C against 260°C under nitrogen where the pyrolysis is the prominent path. The pyrolysis may lead to crosslinking, as in the case of polymers **Vb** and **Vc**, but the thermal stability of the aliphatic segments are inferior to aromatic groups and the decomposition is extensive leading to char yield of only 24% which was stable upto 1000°C.

X-ray diffractogram (Figure 31) showed that the polymer **Vd** is crystalline and the melted sample showed a halo at $\theta = 20°$ characteristic of nematic phase. The same was supported by DSC as in the case of other polymers.

5. *Poly[4-[(4-hydroxy-2-pentadecadienylphenyl)azo]benzoic acid]* (**Ve**):

The DSC thermogram of polymer **Ve** is given in Figure 29. DSC scan showed an unidentified endotherm at 70°C and an exotherm at 138°C. Above 200°C the polymer started decomposing as indicated by the steep raise of the base line. When observed under PLM, polymer **Ve** did not show melting to form mesophase, instead, it started decomposing above 200°C. This is due to the auto-crosslinking of side chain unsaturations under organized environment as reported by George et. al.[5] During the process of phase formation the spontaneous alignment of mesogenic groups bring the side chains close enough to auto-crosslink which would eventually raise the liquid crystal phase transition temperature to above the decomposition temperature of the polymer. However, the sample prepared by rapid melting and quenching to room temperature within few seconds showed threaded nematic texture (Figure 30) under PLM.

The PLM observation is supported by TGA results where T_i are observed as 209 and 221°C under air (Figure 32) and nitrogen (Figure 33) respectively. The complete decomposition of polymer take place under air with T_h and T_f, 547 and 660°C respectively. The T_i under nitrogen is higher than that of air. This may be due to the crosslinking of the polymer which would require more energy to pyrolyze than oxidation under air. The T_h under nitrogen was 476°C against 547°C under air. This difference in the decomposition temperature may be due to extensive pyrolysis of thermally less stable alifatic fragments whereas under air, oxidation of substituents by air may lead to crosslinking which would decompose at higher temperature. The weight loss under nitrogen ceased at about 500°C with 24% char and the char was stable upto 1000°C.

X-ray diffractogram (Figure 31) showed that the polymer **Ve** is amorphous and this can be explained from the basic structure of the molecule where the presence of cis double bonds and partial crosslinks might have prevented the ordered crystalline arrangement of the polymer. Melting of the polymer is not possible as in the case of other polymers because of the crosslinking.

The results of DSC and PLM are summarized in Table 1. DSC traces of polymers showed that the polymers **Va-c** undergo crystal→crystal modification and the endotherms appear at lower temperature than that of crystal→mesophase transition temperature. Polymer **Vd** did not show any such transition whereas polymer **Ve** showed an unidentified endothermic transition at 70°C which cannot be a crystal→crystal transition because the polymer is amorphous. The transition temperatures are altered by the presence of substituents in the polymer backbone.[6]

Table 1: LC transitions of azobenzene polymers

Polymer	Method	Phase transitions (°C)
Va	DSC	K_1 40 K_2 262 N 382 I
	PLM	K 265 N 382 I
Vb	DSC	K_1 80 K_2 256 N dec.>300
	PLM	K 258 N dec.>300
Vc	DSC	K_1 180 K_2 225 N dec.>320
	PLM	K 228 N dec.>320
Vd	DSC	K 130 N dec.>210
	PLM	K 135 N 262 I
Ve	DSC	X_1 70 X_2 138 (exo.) dec.>200
	PLM	dec.> 200; (N)#

where,
K = crystal
N = nematic phase
I = isotropic
X = unidentified transition
# obtained by rapid melting

Polymer with no substituent started melting at 262°C whereas polymers **Vb** and **Vc** containing methyl substituent started melting at 256 and 225°C respectively. The temperature difference between mesophase transitions of polymers **Va-Vb**, **Va-Vc** and **Vb-Vc** are 6, 37 and 31°C respectively. The difference between polymers **Va-Vb** is mariginal when compared to polymers **Va-Vc**. This may be due to higher molecular weight of the polymer **Vb** as can be seen from the viscosity data given in chapter-III and the reason for the wide temperature difference between **Vb**-**Vc** will be discussed in Chapter - VII. The presence of methyl group not only decrease the crystal-mesophase transitions but also the thermal stability of the polymers. The early decomposition of methyl group hampers the characterization of polymers **Vb** and **Vc** to its full range of mesophase width.

The effect of long alkyl chain on phase transition temperatures is apparent from the lowering of transition temperature of crystal to mesophase by 130°C and its isotropization temperature by 120°C for polymer **Vd** when compared to polymer **Va**. Polymers **Vb** and **Vc** also show a mesophase transition temperature of about 93 and 123°C respectively, which are higher than that of polymer **Vd**. Polymer **Ve** is expected to show LC property at about the same temperature range of polymer **Vd**. This is clear from the exotherm charateristic of crosslinking which appear about the same temperature of polymer **Vd**'s mesophase transition temperature. The crosslinking restricted the observation of mesophase in polymer **Ve**. The absence of reappearance of phases on cooling may be due to the decomposition of the polymers just above or near to their isotropization temperature.

All the polymers (**Va**-**e**), under PLM, showed nematic phase only irrespective of the size of the substituent and the substituent did not show any influence on the type of phase formed as can be expected for the polymers having long pendant side chain. This gives further evidence to the high rigidity of the azobenzene polymers. All the polymers undergo decomposition as observed in DSC and PLM. The transition temperatures observed in PLM were matching well with DSC data.

Although the thermal stability of azo polymers are generally inferior Nanjan et al.[7] have reported that the azobenzene polymers with rigid linking groups are thermally stable. As can be seen from the summarized results of TGA in Table 2, polymer **Va** shows highest thermal stability among all polymers and the least being polymer **Ve**. Polymers containing substituents undergo early decomposition and the increase in aliphatic content reduces the thermal stability considerably. As Jadhav et al.[4] reported, the decomposition of azobenzene polymers may proceed

Table 2 : TGA of LC azobenzene polymers

Polymer	Temp. Atm.	T_i °C	T_h °C	T_f °C	Char yield %
Va	Air	465	520	625	-
	N_2	460	475	475	-
Vb	Air	295	505	650	-
	N_2	280	765	850	40
Vc	Air	338	588	665	-
	N_2	310	-	750	55
Vd	Air	290	510	615	-
	N_2	260	452	615	24
Ve	Air	209	547	660	-
	N_2	221	476	600	24

through elimination of azo group as nitrogen gas within a narrow temperature range. The citable example is polymer **Va** where the decomposition is in narrow temperature range and the absence of char may be due to the evaporation of the by-products formed during degradation. But the polymers having substituents undergo oxidative and pyrolytic decomposition under air and nitrogen respectively. This leads to the formation of thermally stable structures through crosslinking which under air, get oxidized to volatile fragments at high temperatures and under nitrogen, remain as char. The same may be the reason for the increased Ti under air than under nitrogen. All polymers having substituent gave char under nitrogen supporting the formation of thermally stable structures. The Ti of polymers **Vb-e** might be the initiation of decomposition of substituent because the T_i is well below to cause the elimination of azo group, as nitrogen, as was observed for polymer **Va** and the second step may be the elimination of azo group.

4.4 CONCLUSIONS

The liquid crystalline property and the thermal stability of the polymers **Va-e** have been investigated using DSC, hot stage PLM and TGA. All the polymers showed LC property and displayed texture characteristic of nematic phase. The presence of the substituent reduced the transition temperatures and the effect was maximum for the polymer with $-C_{15}$ substituent. Polymer **Va** showed highest thermal stability whereas the presence of alkyl substituents reduced the thermal stability considerably. X-ray diffraction showed that the polymers **Va-d** are crystalline which on melting to LC phase showed a halo at $\theta = 20°$ characteristic of isotropic fluids.

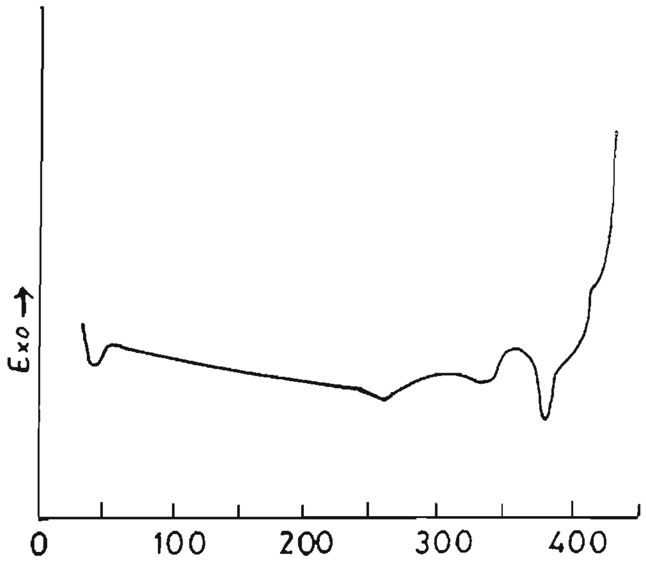

Figure 21: DSC thermogram of polymer **Va**

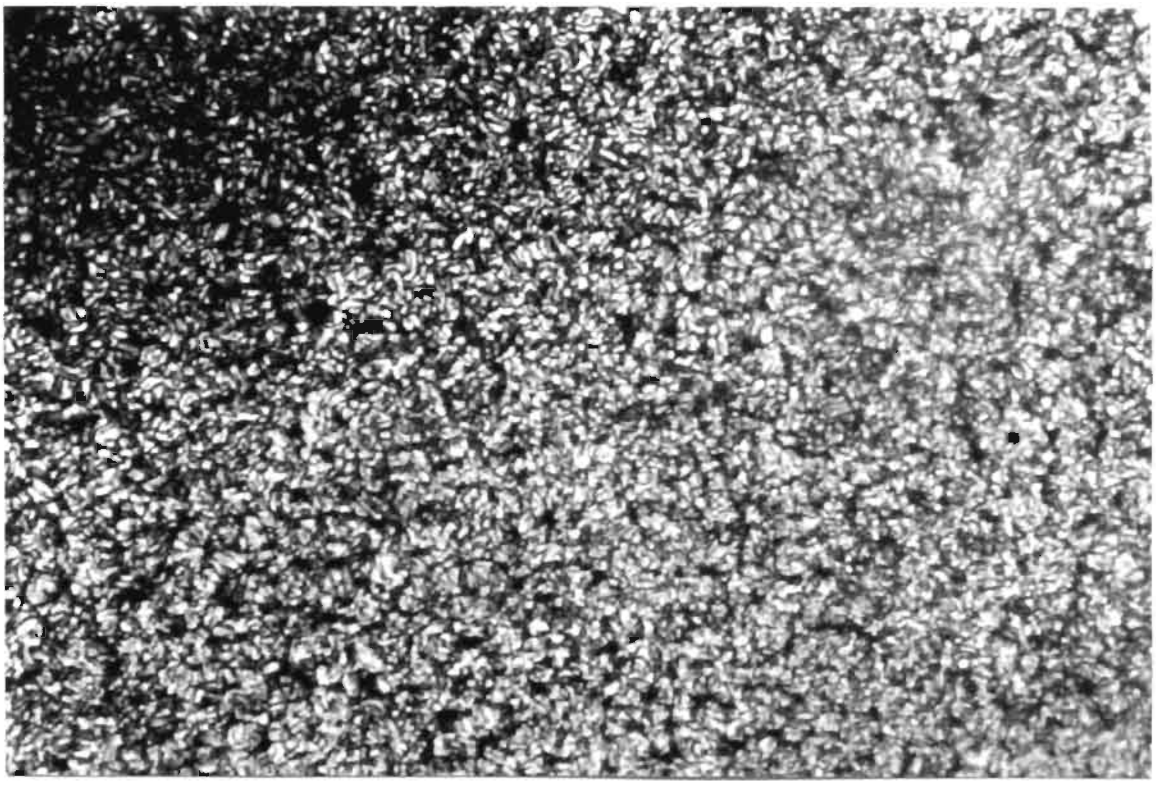

Figure 22: Threaded nematic texture of polymer **Va** at 275°C (X 400)

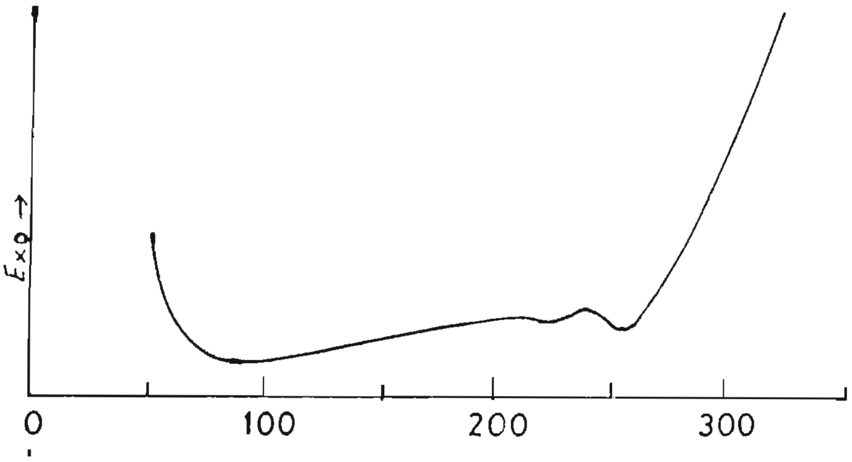

Figure 23: DSC thermogram of polymer **Vb**

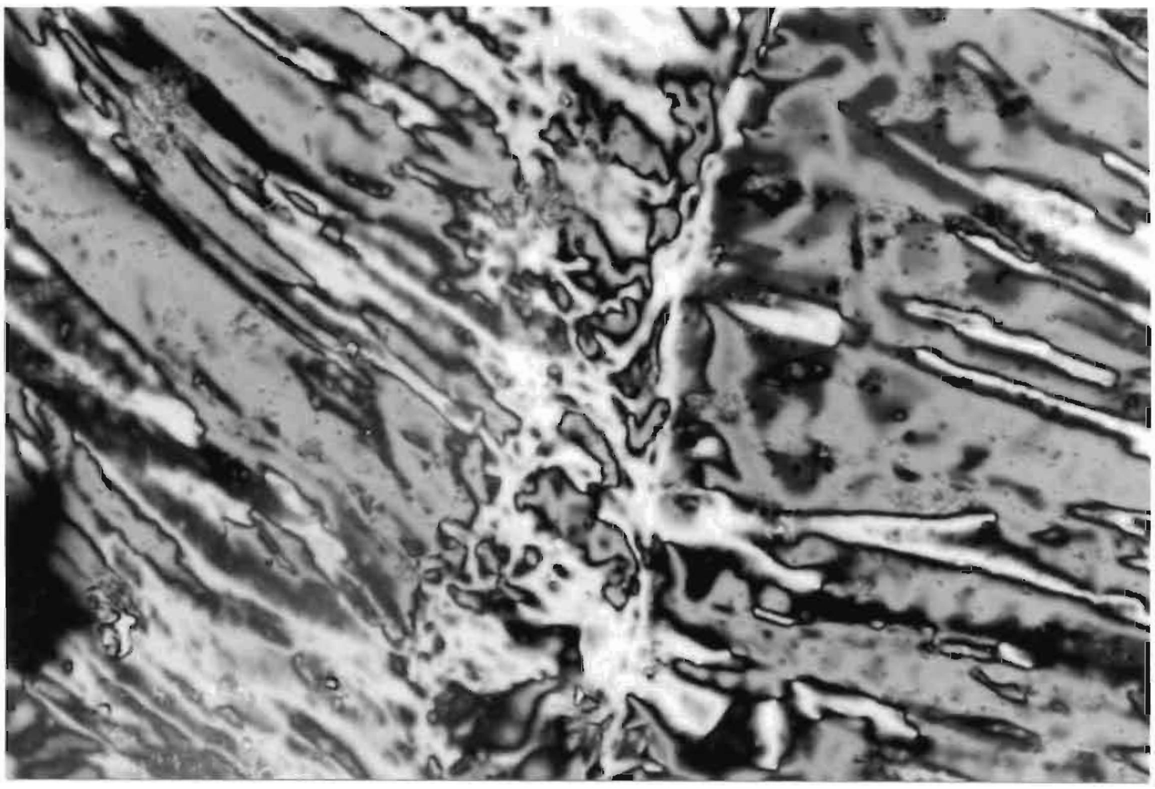

Figure 24: Threaded nematic texture of polymer **Vb** at 263°C (X 200)

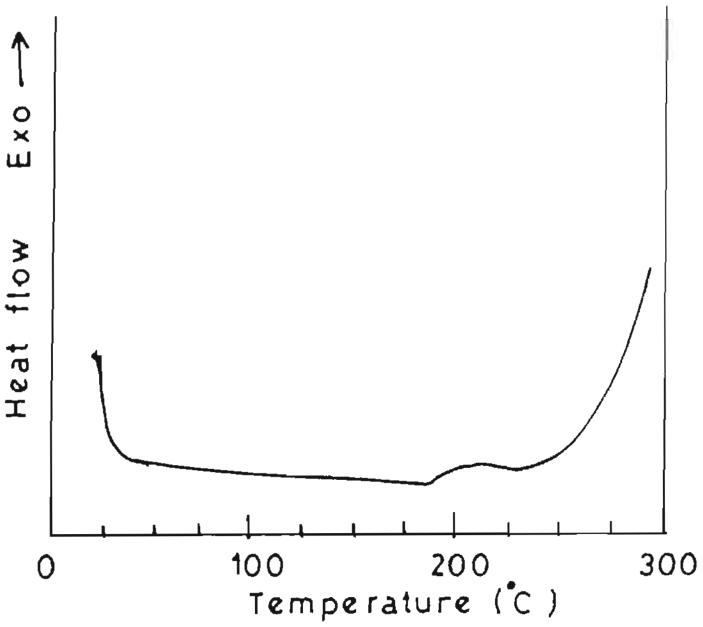

Figure 25: DSC thermogram of polymer **Vc**

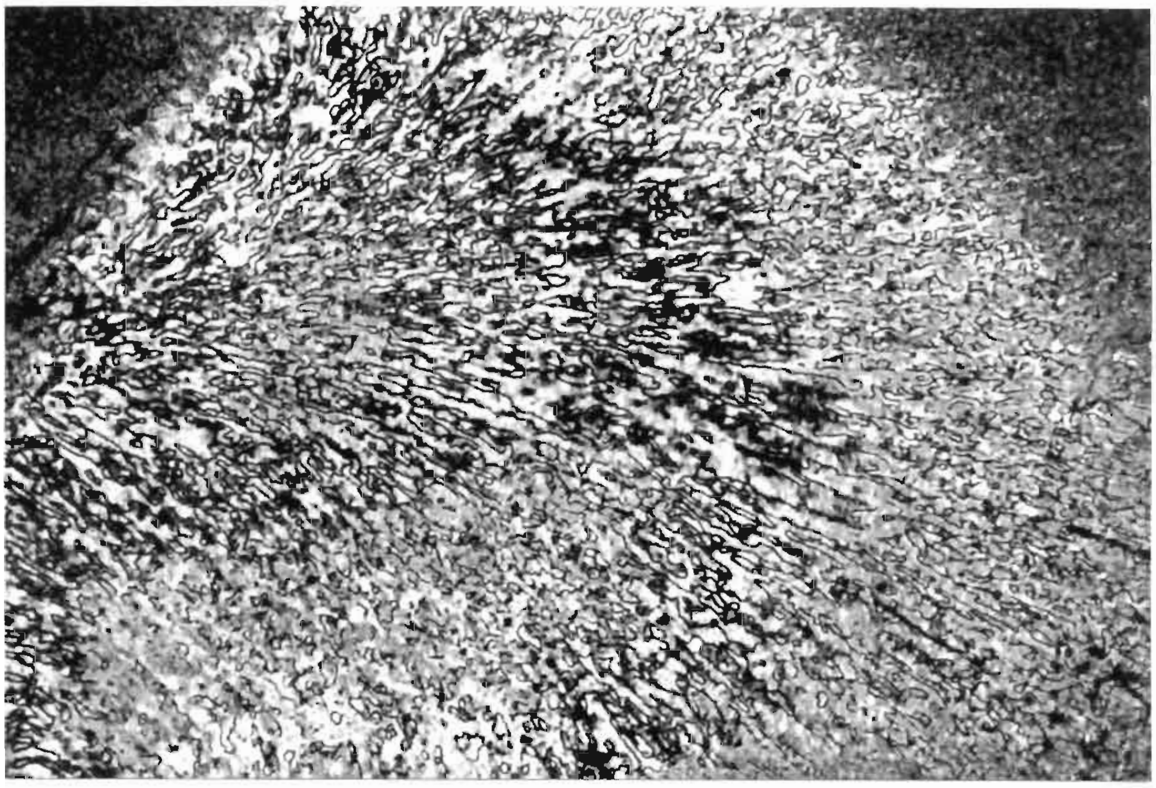

Figure 26: Threaded nematic texture of polymer **Vc** at 232°C (X 200)

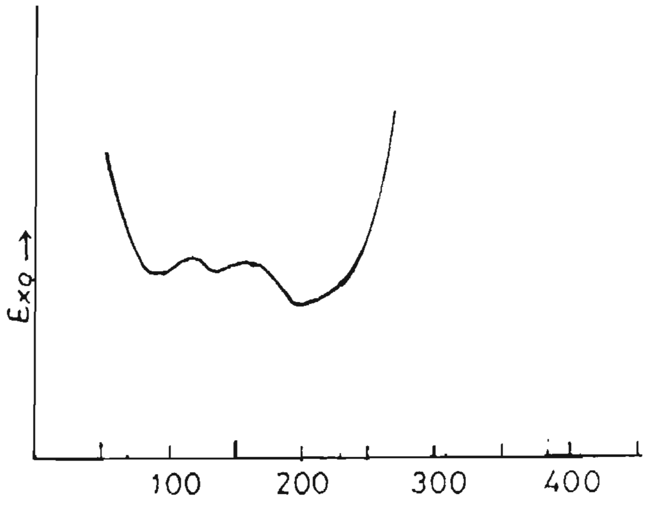

Figure 27: DSC thermogram of polymer **Vd**

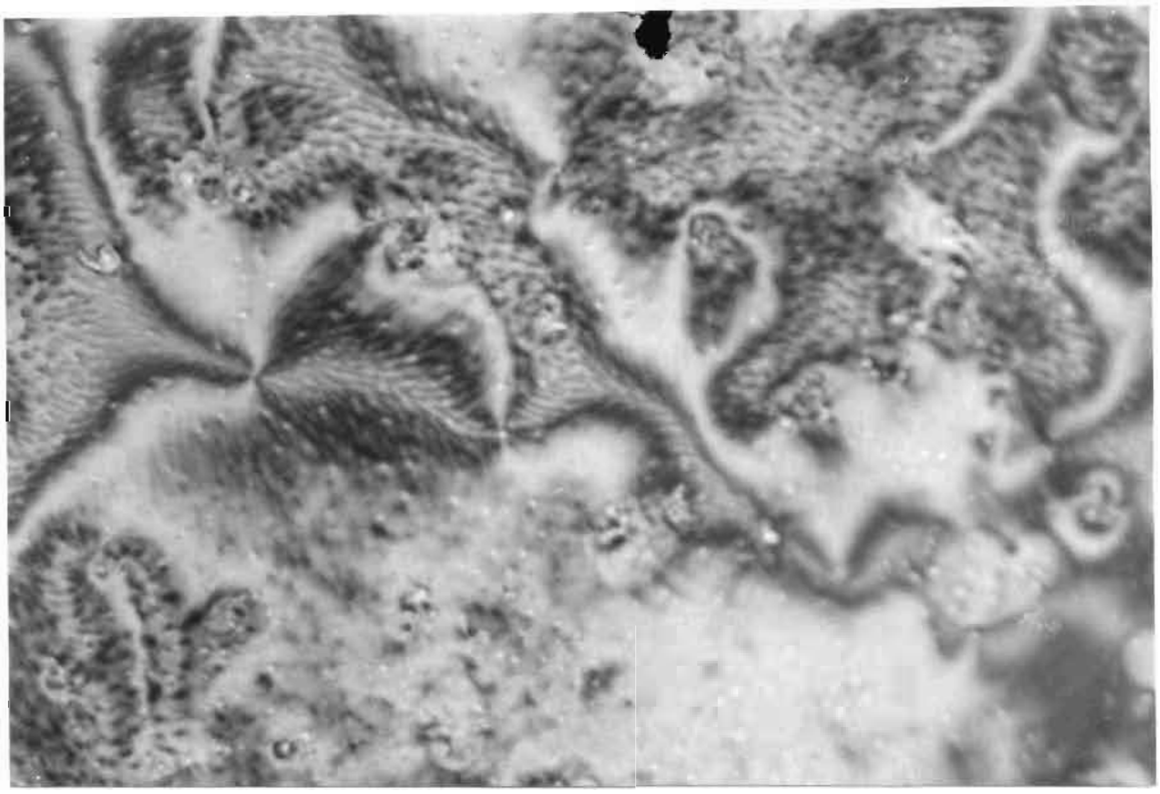

Figure 28: Schlieren nematic texture of polymer **Vd** at 140°C (X 200)

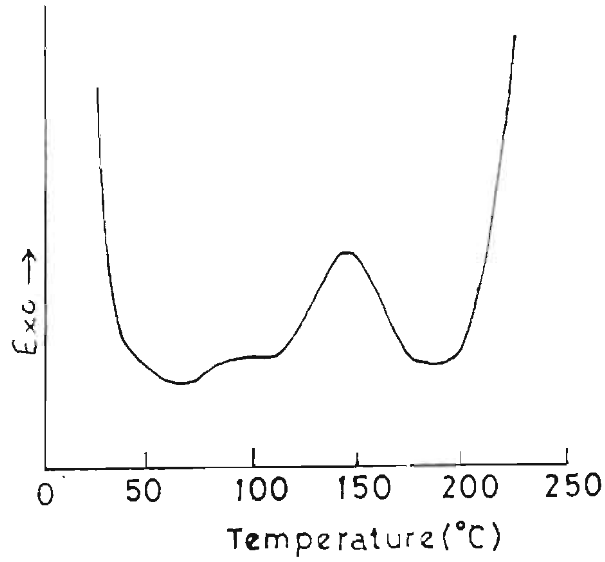

Figure 29: DSC thermogram of polymer **Vc**

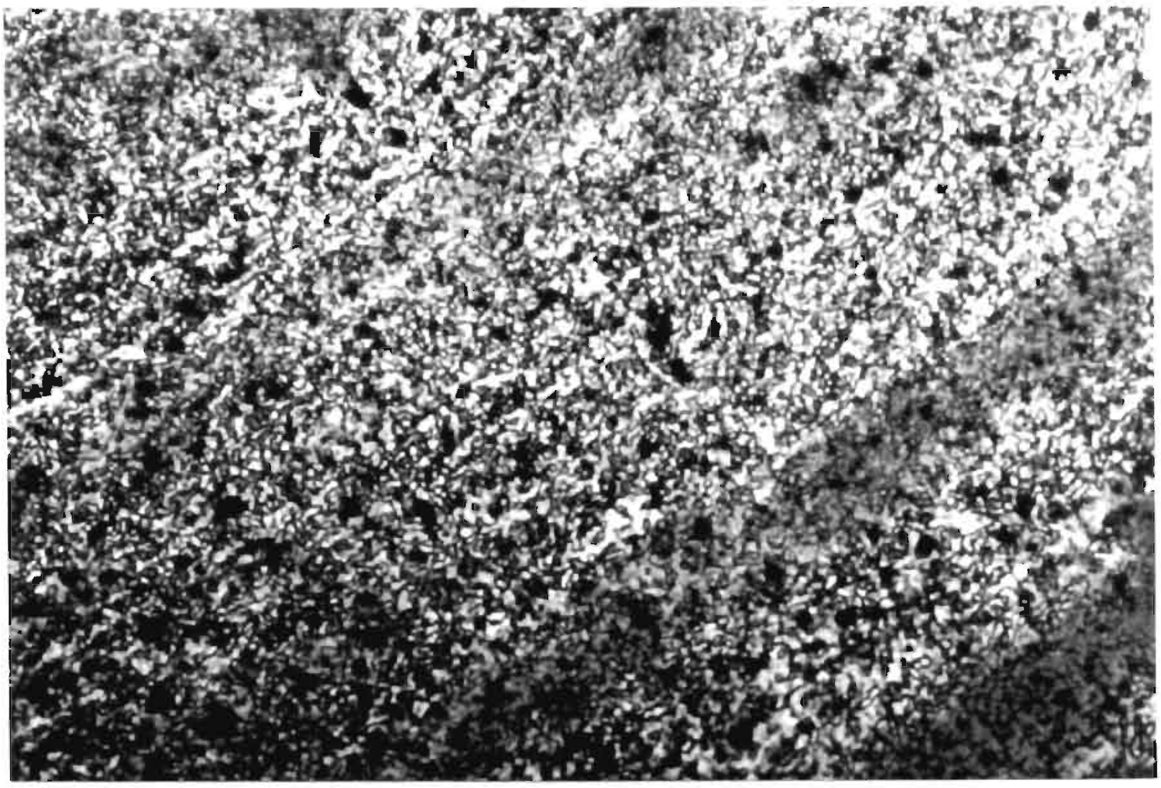

Figure 30: Threaded nematic texture of polymer **Vc** (Rapid melting) (X 400)

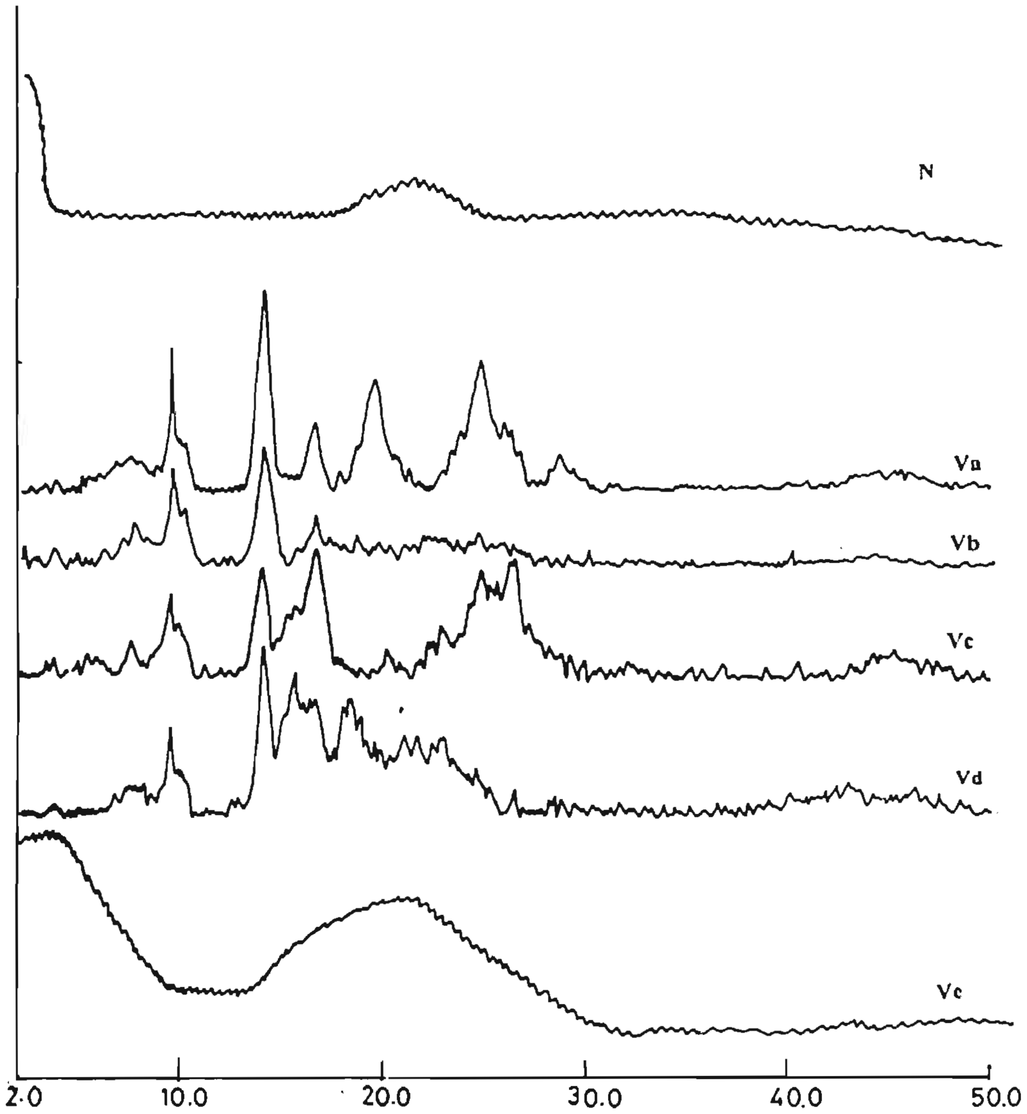

Figure 31: WAXD of polymers (Va-e) and representative WAXD of Va nematic phase (N)

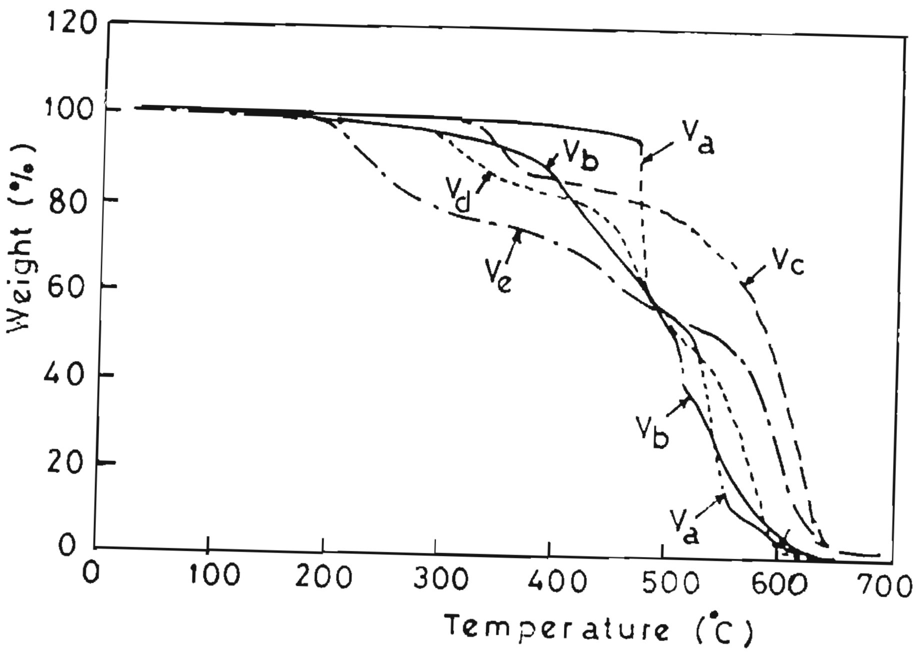

Figure 32: TGA of polymers (**Va-e**) in air

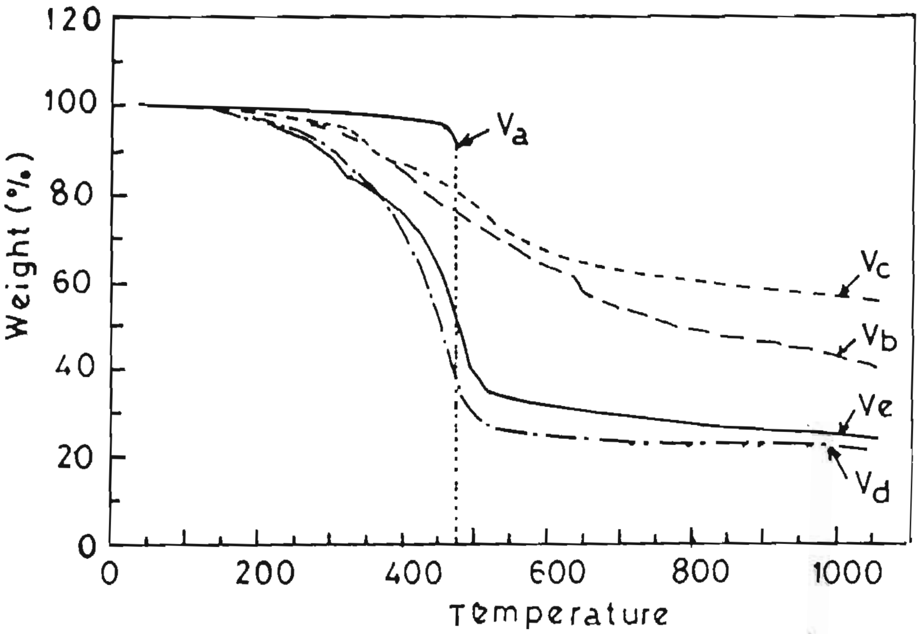

Figure 33: TGA of polymers (**Va-e**) in nitrogen

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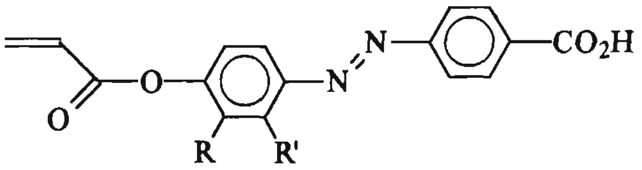
CHAPTER-V

SYNTHESIS AND CHARACTERIZATION OF AZOBENZENE ACRYLATE MONOMERS

5.1 INTRODUCTION

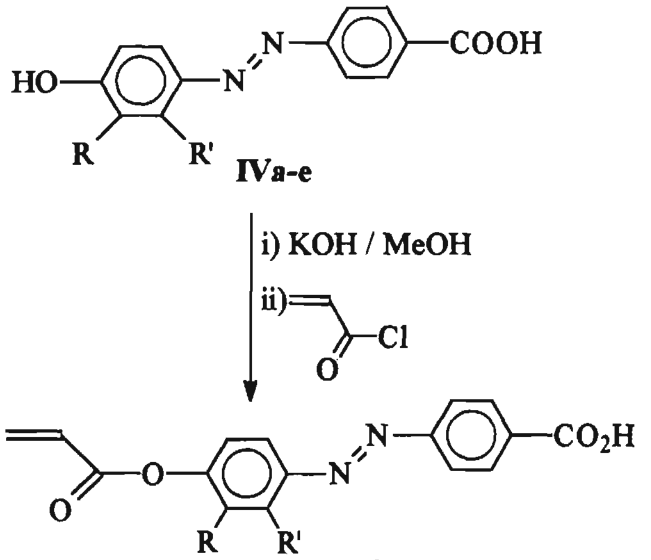
Acrylic polymers are finding wide use in industry and in commodity plastics.[1] Acrylate group is the one having activated vinyl group conjugated to carboxyl group which is used to functionalize the reactive monomers. Polymers of functionalized acrylates are classified as side chain polymers where the functional group is attached to the backbone directly or through spacers[2]. Side chain polyacrylates can be made by synthesis and polymerization of monomers or by grafting the reactive monomers to the polyacrylic acid backbone. The former process is normally prefered. It is widely known that the liquid crystal (LC) mesogens attached directly to the polymer backbone, on polymerization, mostly failed to show LC property[2]. However, in the present case the novel LC acrylate monomers containing the azobenzene mesogen, on polymerization, were found to show LC property.

In the present investigation, the acrylate derivatives of *p*-hydroxy phenylazobenzoic acids, for which the chemical structures are shown in scheme 19, form the main constituent of the polymers synthesized.



Scheme 19: structure of the acrylate monomers

This section deals with the discussion on the synthesis and characterization of acrylate derivatives of *p*-hydroxyphenylazobenzoic acids containing varying hydrocarbon substituents. The reaction route is illustrated in scheme 20.



VIa-e

Where,
R= H when R'= a) H, c) CH_3, d) $C_{15}H_{31}$,
e) $C_{15}H_{27}$
R= b) CH_3 when R'= H

Scheme 20: Synthesis of azobenzene acrylate monomers

5.2 EXPERIMENTAL

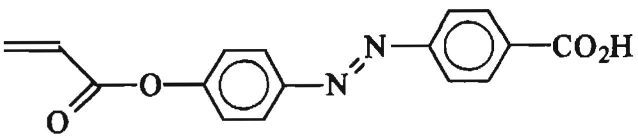
Azobenzene acrylate monomers were synthesized by reacting acryloyl chloride with potassium salt of monomers (**IVa-e**), with varying hydrocarbon substituents, in dimethyl acetamide (DMAc) and subsequent work up gave acrylates in good yields.

The monomers obtained were characterized using elemental analysis and spectral methods. IR spectra were recorded using Perkin-Elmer 882 infrared spectrometer and ^1H & ^{13}C NMR from Jeol JNM-EX 90 FT NMR system.

UV-Vis spectra were obtained in DMF using Shimatzu UV-160A spectrophotometer and the molecular weights were obtained from vapour pressure osmometer.

The typical procedure for the synthesis of azobenzene acrylate monomers is as follows.

1. *Synthesis of 4-[(4-acryloyloxyphenyl)azo]benzoic acid* (**VIa**): Compound **IVa** (1g; 4.1mmol) was dissolved in methanolic solution of KOH (0.38g; 6.7 mmol in 10mL MeOH). The solution was evaporated to dryness and dissolved in DMAc (5mL) with cooling in an ice bath. Acryloyl chloride (0.61g; 6.7mmol) was added in drops to the cold DMAc solution with stirring. The stirring was continued for an hour and the solution was poured into ice water (500mL). The precipitated product was filtered and washed thoroughly with cold water. The precipitate was dissolved in ether, dried using anhydrous sodium sulphate and filtered. Solvent was removed under reduced pressure and the product was chromatographed on silica gel (100-200 mesh) using chloroform as eluent. Solvent was removed under reduced pressure. Yield 0.93 g (76%); yellow-orange solid; m.p. 225-227°C. Anal. Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.85; H, 4.08; N, 9.46. Found: C, 63.21; H, 5.13; N, 8.94.



(VIa)

i) M.Wt. : 296.3

ii) mp : 225-227°C

iii) UV-Vis (λ_{max}) : 335 nm (ε_{max} = 17 549 M^{-1} cm^{-1})

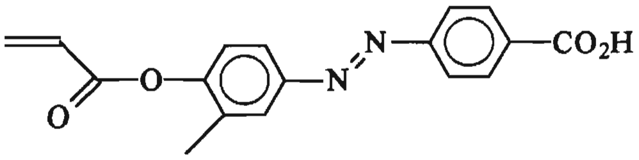
iv) IR (KBr; cm^{-1}) : 2931, 2859 (CH_2:CH-); 1741 (CH_2:CH-COOAr); 1683 (ArCOOH); 1659 (CH2:CH-) 1591 (Ar; C=C); 1147 (-N=N-).

v) ^{1}H NMR (DMSO-d_6) : δ 7.5-8.6 (8H, m, Ar); 6.4-7.0 (3H, m, CH_2:CH-).

vi) ^{13}C NMR (DMSO-d_6) : 166.7, 163.9, 154.2, 152.9, 149.6, 132.9, 130.6, 130.3, 129.3, 127.4, 124.1, 122.8, 122.5, 122.1.

All monomers were prepared following the procedure mentioned above.

2. *4-[(4-acryloyloxy-3-methylphenyl)azo]benzoic acid* (**VIb**): A total of 0.96 g (79%) of the product was obtained from **IVb** (1 g; 3.9 mmol), KOH (0.44 g; 7.8 mmol), and acryloyl chloride (0.71 g; 7.9 mmol): yellow solid; mp 210-212°C. Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.79; H, 4.55; N, 9.03. Found: C, 64.23; H, 5.10; N, 8.35.



(VIb)

i) M.Wt. : 310.3

ii) mp : 210-212°C

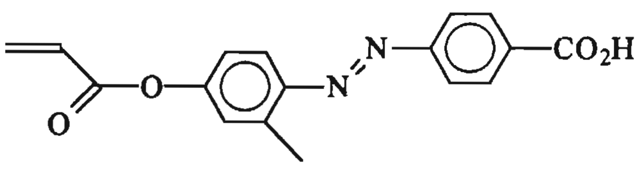
iii) UV-Vis (λ_{max}) : 346 nm (ε_{max} = 21 175 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2931, 2861 (-CH_3), 1730 (CH_2:CH-COOAr); 1695 (ArCOOH); 1656 (CH2:CH-); 1602 (Ar; C=C), 1453, 1369 (-CH_3), 1146 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 7.3-8.5 (7H, m, Ar); 6.1-7.0 (3H, m, CH_2:CH-); 2.3 (3H, s, -CH_3)

vi) ^{13}C NMR (DMSO-d_6) : 166.7, 163.5, 154.2, 151.6, 149.7, 132.8, 131.4, 130.6, 129.3, 128.5, 127.1, 125.2, 123.1, 122.5, 121.7, 15.7.

3. *4-[(4-acryloyloxy-2-methylphenyl)azo]benzoic acid* (**VIc**): A total of 0.87 g (72%) of the product was obtained from **IVc** (1 g; 3.9 mmol), KOH (0.44 g; 7.8 mmol), and acryloyl chloride (0.71 g; 7.9 mmol): yellow solid; mp 193-195°C. Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.79; H, 4.55; N, 9.03. Found: C, 64.98; H, 4.11; N, 9.87.



(VIc)

i) M.Wt. : 310.3

ii) mp : 193-195°C

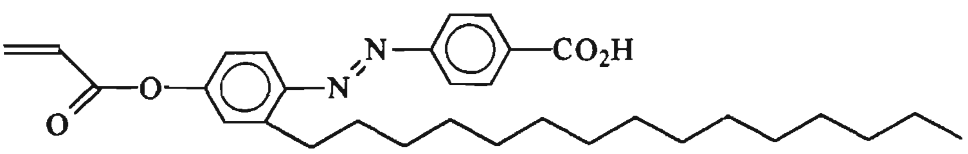
iii) UV-Vis (λ_{max}) : 346 nm (ε_{max} = 24 603 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2985, 2893 (-CH_3); 1748 (CH_2:CH-COOAr); 1690 (ArCOOH); 1657 (CH_2:CH-); 1606, 1586, 1547 (Ar; C=C); 1488, 1360 (-CH_3); 1157 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 6.9-8.1 (7H, m, Ar); 5.9-6.4 (3H, m, CH_2:CH-); 2.5 (3H, s, -CH_3)

vi) ^{13}C NMR (DMSO-d_6) : 166.7, 163.7, 154.6, 152.9, 147.6, 140.2, 133.8, 132.7, 130.5, 129.6, 128.2, 127.4, 124.1, 122.5, 120.1, 116.4, 17.0.

4. *4-[(4-acryloyloxy-2-pentadecylphenyl)azo]benzoic acid* (**VId**): A total of 0.92 g (83%) of the product was obtained from **IVd** (1 g; 2.2 mmol), KOH (0.25 g; 4.5 mmol), and acryloyl chloride (0.41 g; 4.5 mmol): red solid; mp 122-125°C. Anal. Calcd. for $C_{31}H_{42}N_2O_4$: C, 73.49; H, 8.35; N, 5.53. Found: C, 72.50; H, 9.23, N, 5.30.



(VId)

i) M.Wt. : 506.7

ii) mp : 122-125°C

iii) UV-Vis (λ_{max}) : 348 nm (ε_{max} = 17 088 M^{-1} cm^{-1})

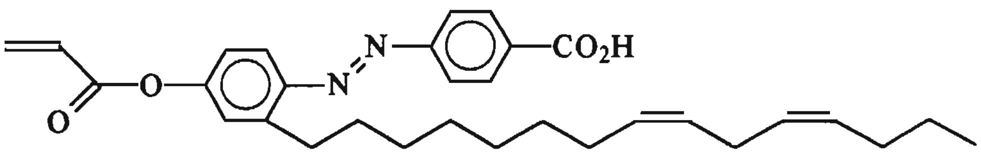
iv) IR (KBr; cm^{-1}) : 2940, 2830 ($-CH_2-$); 1745 (CH_2:CH-COOAr); 1700 (ArCOOH); 1660 (CH_2:CH-); 1605, 1580, 1540 (Ar; C=C); 1150 (-N=N-)

v) ^1H NMR (DMSO-d_6) : δ 7.1-8.2 (7H, m, Ar); 6.1-6.6 (3H, m, CH_2:CH-); 0.8-2.1 (31H, m, $-CH_2-$)

vi) ^{13}C NMR (DMSO-d_6) : 166.6, 163.6, 154.6, 153.0, 147.2, 144.7, 132.8, 130.5, 129.3, 128.1,127.4, 122.9, 122.4, 120.2, 116.4, 31.3, 29.0, 28.7, 22.1, 13.8

5. *4-[(4-acryloyloxy-2-pentadecadienylphenyl)azo]benzoic acid* (**VIe**): A total of 0.89 g of the product was obtained from **IVe** (1 g; 2.2 mmol), KOH (0.25 g; 4.5 mmol) and acryloyl chloride (o.41 g; 4.5 mmol): red solid; mp 118-120°C. Anal.

Calcd for $C_{31}H_{38}N_2O_4$: C, 74.08; H, 7.62; N, 5.57. Found: C, 73.11; H, 6.94; N, 6.12.



(VIe)

i) M.Wt. : 502.6

ii) mp : 118-120°C

iii) UV-Vis (λ_{max}) : 347 nm (ε_{max} = 19 319 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2932, 2860 (-CH_2-); 1742 (CH_2:CH-COOAr); 1694 (ArCOOH); 1662 (acrylic CH_2:CH-); 1609, 1585 (Ar; C=C); 3016, 780 (olefinic -CH:CH-); 1151 (-N=N-)

v) ^1H NMR (DMSO-d_6) : 7.7-8.3 (7H, m, Ar); 6.1-6.6 (3H, m, CH_2:CH); 0.7-2.9 (~27H, m, -CH_2-)

vi) ^{13}C NMR (DMSO-d_6) : 166.6, 163.5, 154.5, 153.0, 147.2, 144.7, 132.8, 130.5, 129.4, 127.8, 127.4, 123.1, 122.4, 120.1, 116.3, 31.4, 31.1, 30.9, 30.4, 29.0, 28.6, 28.2, 26.5, 25.1, 22.0, 13.7, 13.4

5.3 RESULTS AND DISCUSSION

The monomers were synthesized by reacting acryloyl chloride with potassium salt of azobenzene monomers **IVa-e** in DMAc. The solid dye derivatives obtained were purified by column chromatography. The purities of the monomers were confirmed by elemental analysis and spectral methods. The calculated values of the elemental analysis were in good agreement with the experimental values. Molecular weight of the monomers were obtained using vapour pressure osmometer. The characteristic colour of the monomers are red, orange and yellow. The melting point of **VIa-c** are fairly high may be due to the carboxylic acid dimer but the presence of long n-alkyl substituent in **VId** and **VIe** reduced the melting points considerably.

The IR spectra of monomers (Figure 35) showed characteristic absorption peaks corresponding to the expected group frequencies.[3] The alkyl group -C-H stretching of acrylates **VIb-e** appeared in the range of 2985-2931 and 2893-2830 cm^{-1}. The acrylate ester carbonyl and carboxyl carbonyl peaks appeared at 1748-1730 and 1700-1683 cm^{-1} respectively along with the characteristic $H_2C{=}CH$- double bond stretching of acrylate group at 1662-1656 cm^{-1}. This evidences the formation of acrylates **VIa-e**. The methyl group -C-H bending vibrations of **VIb** and **VIc** appeared in the region of 1453, 1369 cm^{-1} and 1488, 1360 cm^{-1} respectively. Monomer **VId** and **VIe** showed very strong absorptions at 2940-2932 and 2860-2830 cm^{-1} due to the long alkyl chain and **VIe** showed -CH=CH- strecting at 3016 cm^{-1}, bending at 1620 cm^{-1} and a characteristic peak of *cis* alkenes at 780 cm^{-1} which the cardanol side chain possesses. The aromatic C=C stretching modes were obseved in the region of 1609-1591 cm^{-1} and the characteristic *p*-substituted azobenzene absorption peak at 1157-1147 cm^{-1}.

^1H NMR spectra supported the assigned structure and hence the formation of acrylates.[4] The aromatic protons of **VIa-e** resonated at 6.9-8.6 δ and the acrylic protons at 5.9-7.0 δ as typical acrylic multiplet (**VIa**; Figure 36). The alkyl groups of **VIb** (Figure 38) and **VIc** (Figure 40) appeared at 2.3 and 2.5 δ respectively. The long chain alkyl protons of **VId** (Figure 42) and **VIe** (Figure 44) appeared in the region of 0.7-2.9 δ. The olefinic protons of non-conjugated allylic double bonds of monomer **VIe** resonated at 4.9-5.4 δ as multiplet.

The structure of the monomers were further confirmed by ^{13}C NMR spectroscopy and found to be complementary to the conclusions drawn from ^{1}H NMR studies. The ^{13}C chemical shift values[5] of carboxylic acid carbon and acrylic ester carbon of **VIa-e** were in the range of 166.6-166.7 and 163.5-163.9 ppm respectively (**VIa**; Figure 37). The acrylic CH_2= and =CH- carbons resonated at 129.3-130.5 and 128.1-129.3 ppm respectively. The phenoxy carbon shifted from 160.1-161.8 ppm to 154.3-154.6 ppm due to esterification. The methyl group of **VIb** (Figure 39) and **VIc** (Figure 41) resonates at 15.7 and 17.0 ppm respectively. The alkyl chain carbons of **VId** (Figure 43) and **VIe** (Figure 45) gave a bunch of peaks between 31.4-13.8 ppm and the number of peaks for **VIe** are more than **VId** is due to the presence of olefinic and allylic carbons. The UV-Vis spectra of all monomers (Figure 34) have one absorption peak at 332-345 nm (ε_{max} = 17 088 - 24 603 M^{-1} cm^{-1}) due to azobenzene group.[4]

5.4 CONCLUSION

Five novel acrylate derivatives of **IVa-e** were made by reacting potassium salt of respective monomers with acryloyl chloride. The red to yellow coloured solids were obtained in good yields. The melting points of the acrylates **VIa-c** are high may be due to the dimerized carboxylic acid group, however, the melting points of **VId** and **VIe** are brought down by long n-alkyl substituent. The azobenzene units in the side chain is expected to impart LC property to the polymers because of their structural anisotropy. The structure of the monomers were confirmed by spectral methods such as IR, ^{1}H & ^{13}C NMR etc.

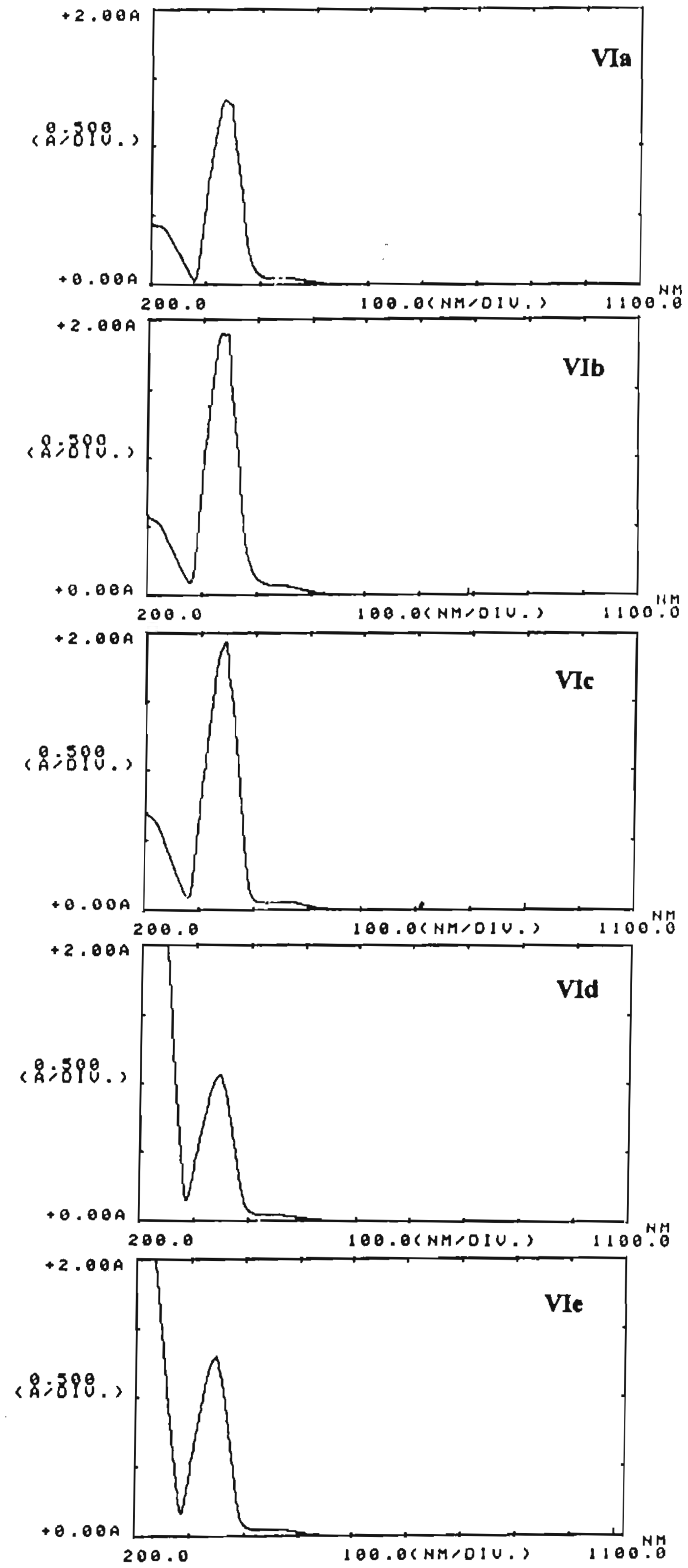


Figure 34: UV-Vis spectra of azobenzene acrylates (**VIa-e**)

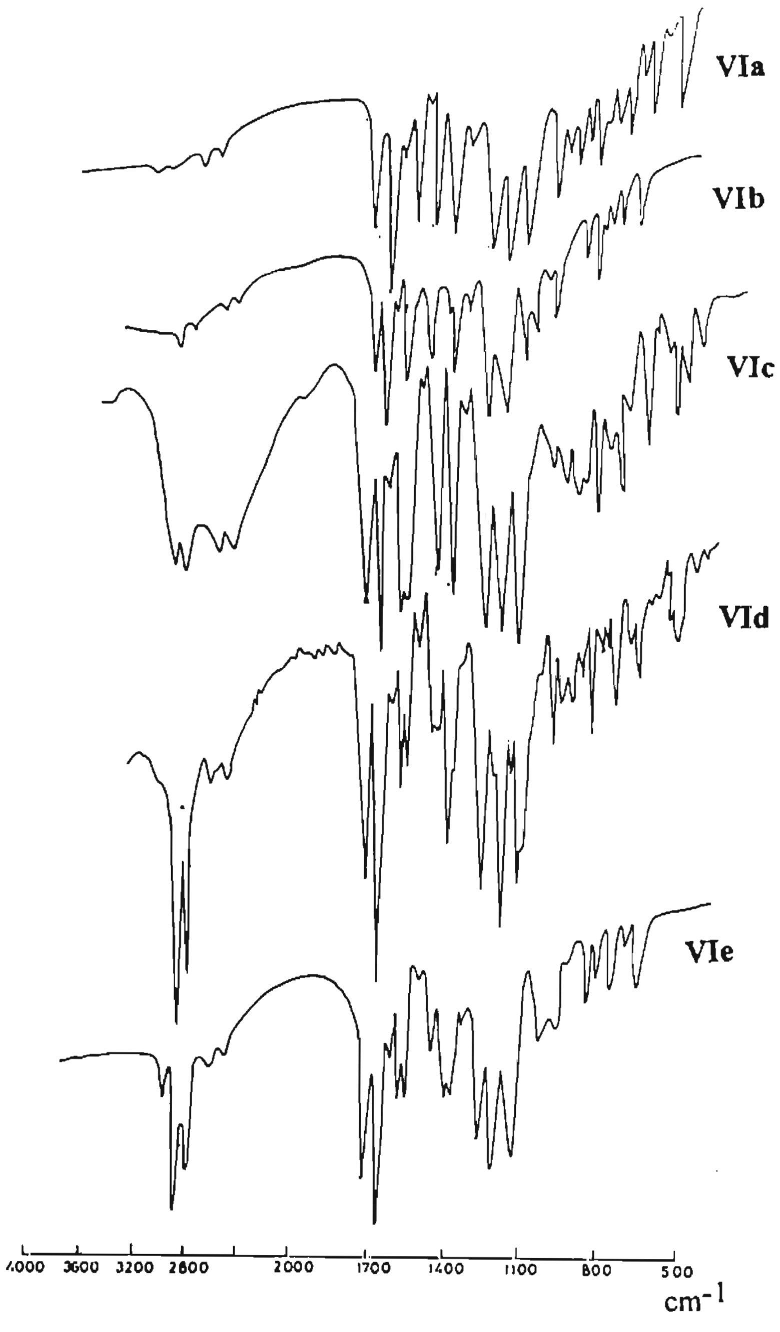


Figure 35: IR spectra of azobenzene acrylates (**VIa-e**)

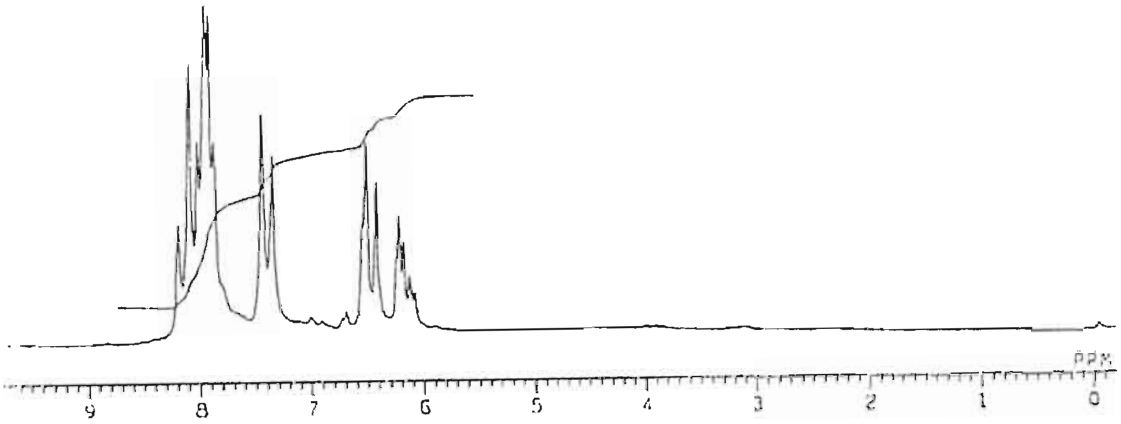


Figure 36: ^{1}H NMR spectrum of acrylate monomer **VIa**

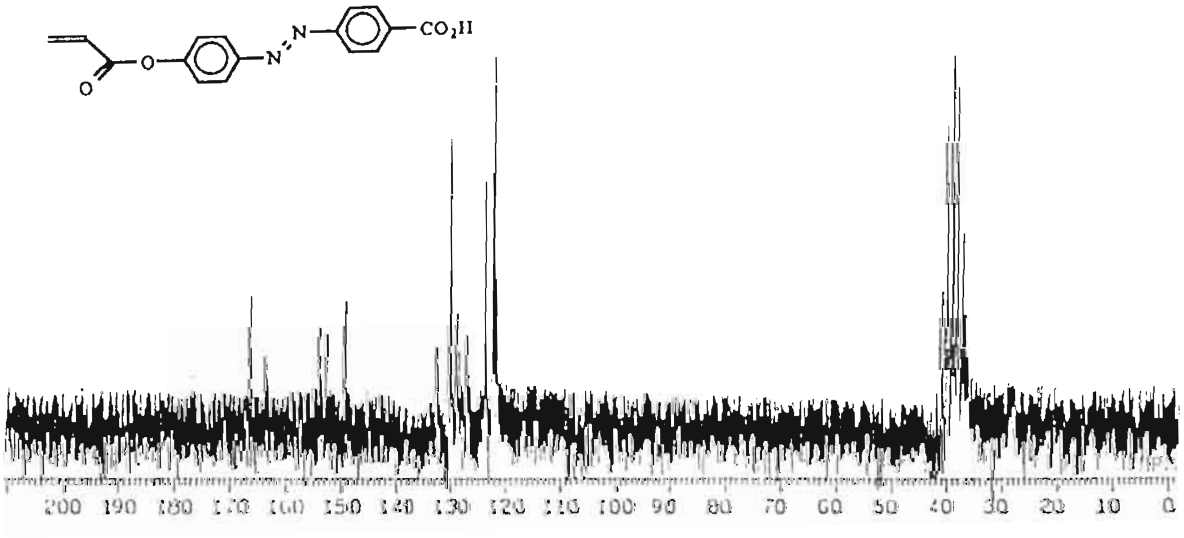


Figure 37: ^{13}C NMR spectrum of acrylate monomer **VIa**

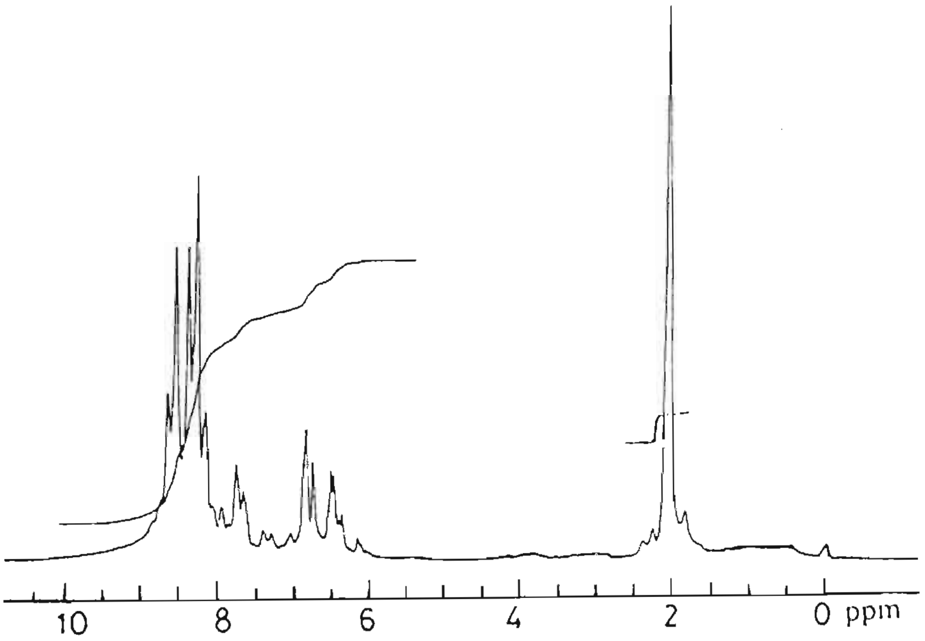


Figure 38: ^{1}H NMR spectrum of acrylate monomer **VIb**

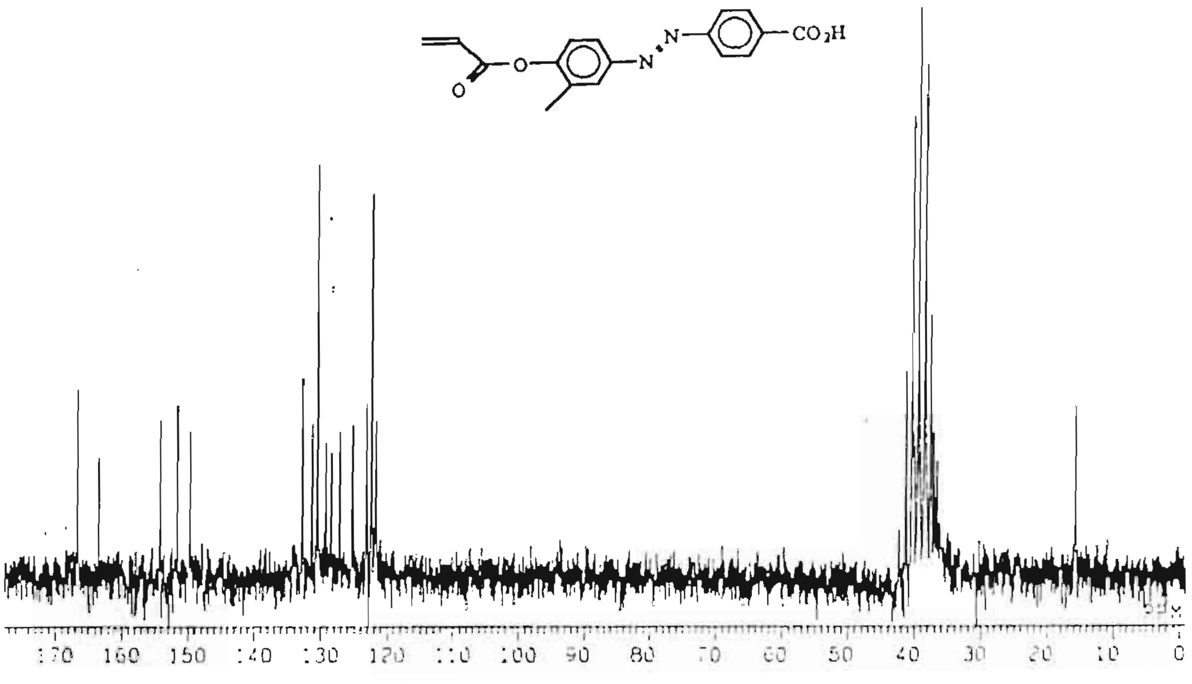


Figure 39: ^{13}C NMR spectrum of acrylate monomer **VIb**

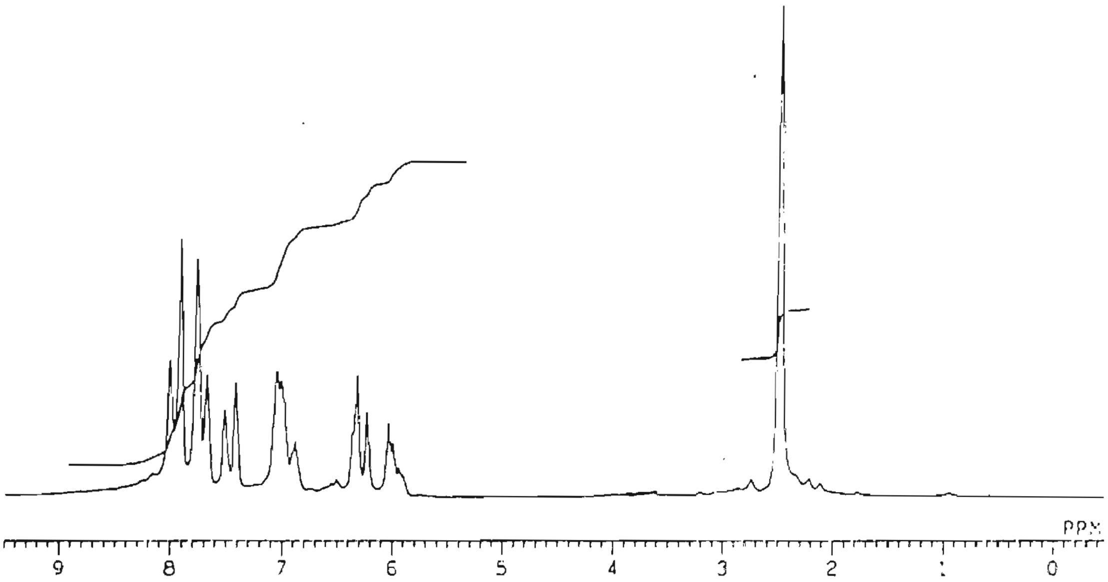


Figure 40: ^{1}H NMR spectrum of acrylate monomer **VIc**

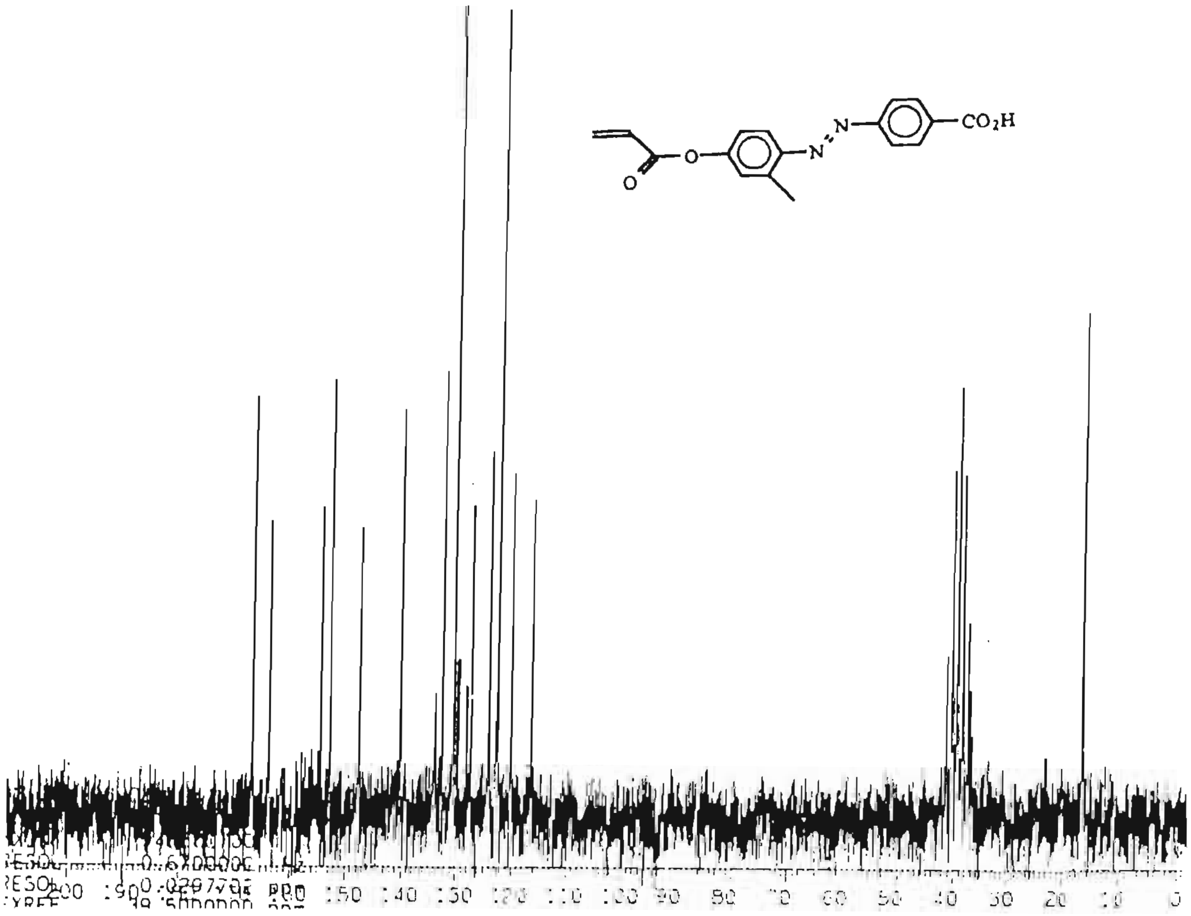


Figure 41: ^{13}C NMR spectrum of acrylate monomer **VIc**

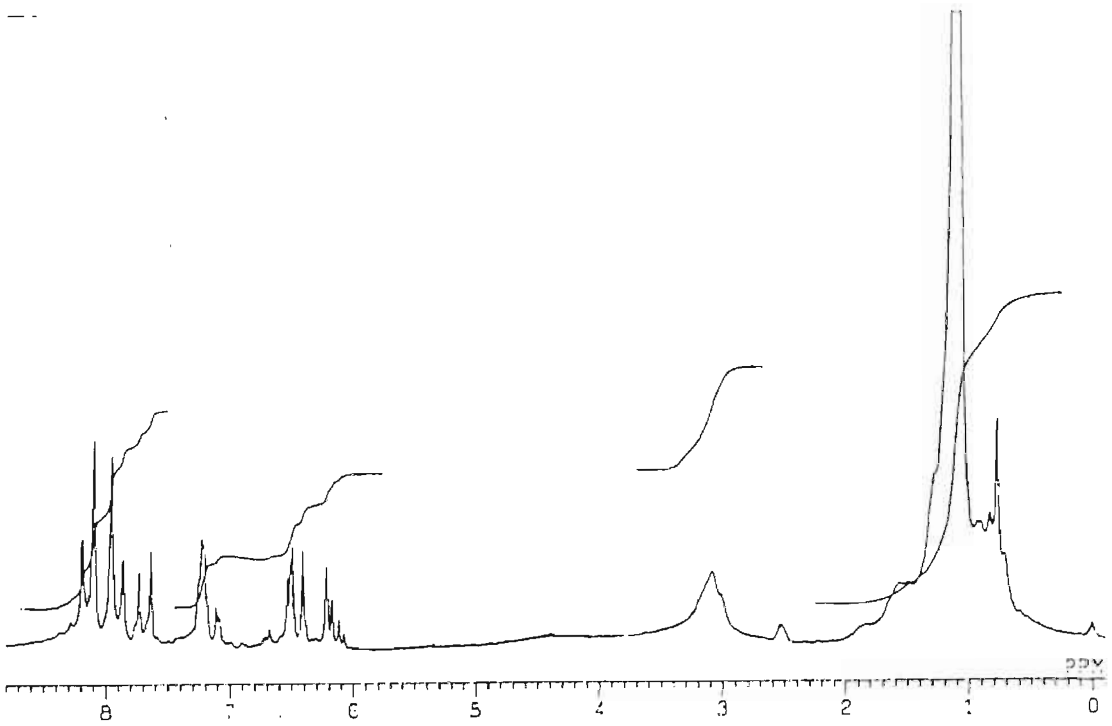


Figure 42: ^{1}H NMR spectrum of acrylate monomer **VId**

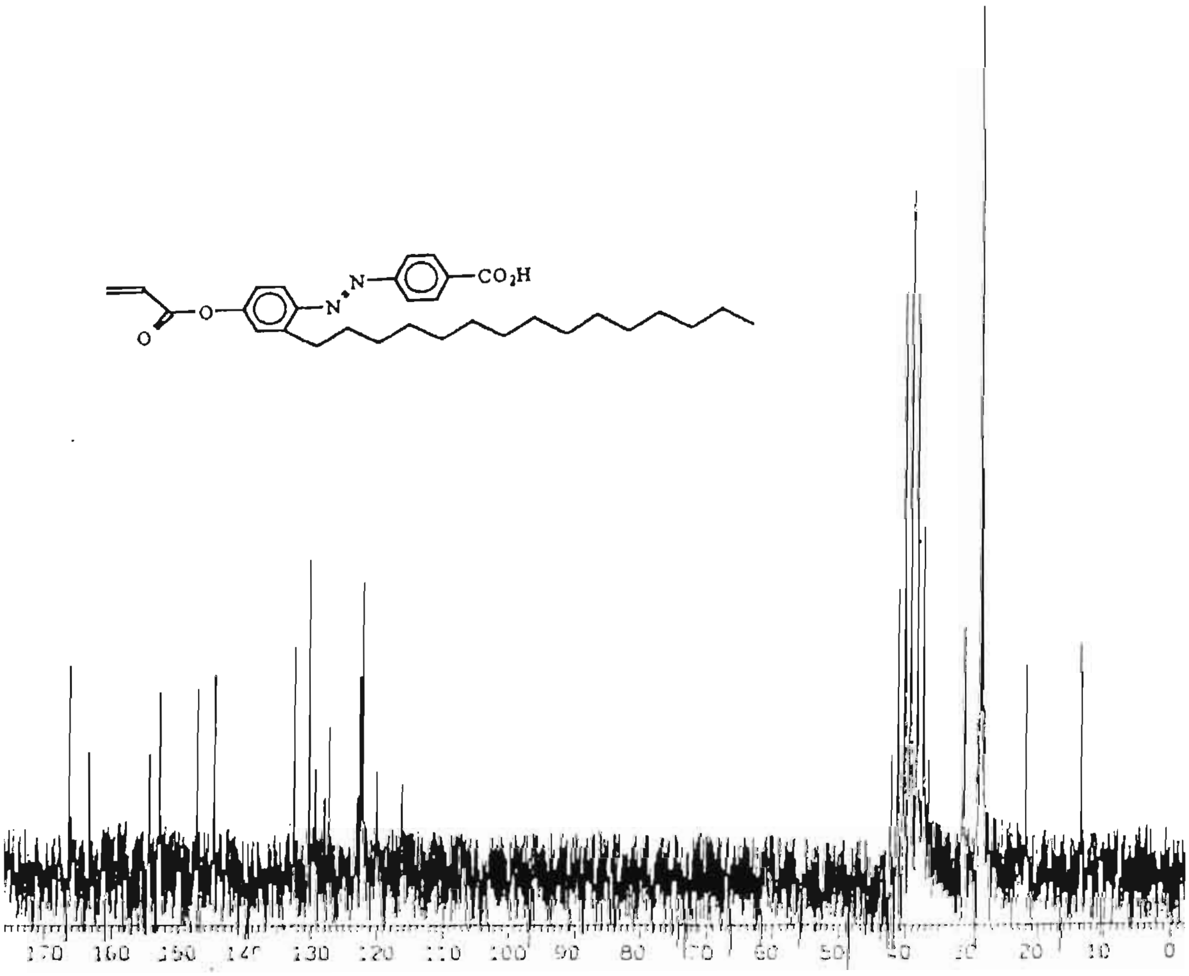


Figure 43: ^{13}C NMR spectrum of acrylate monomer **VId**

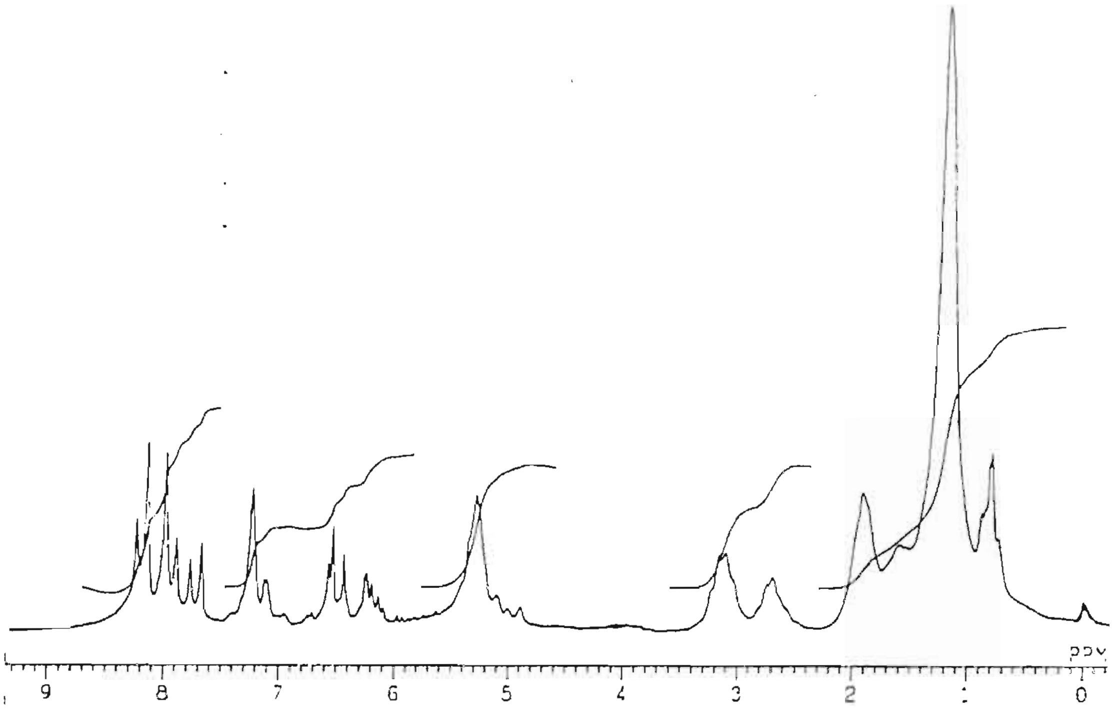


Figure 44: ^{1}H NMR spectrum of acrylate monomer **VIc**

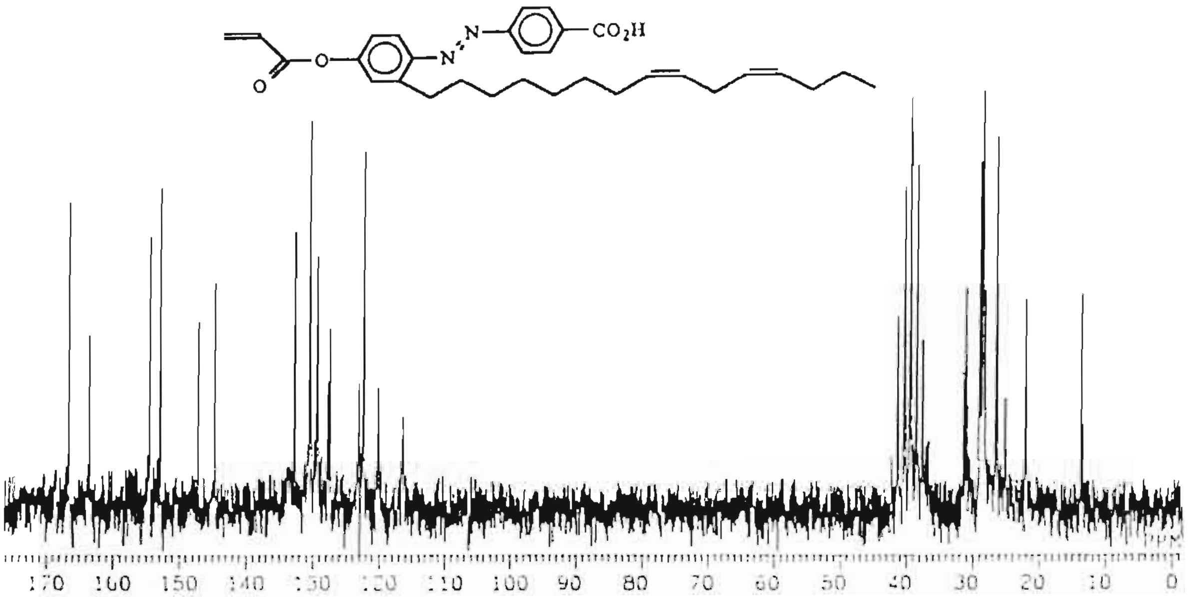


Figure 45: ^{13}C NMR spectrum of acrylate monomer **VIc**

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CHAPTER - VI

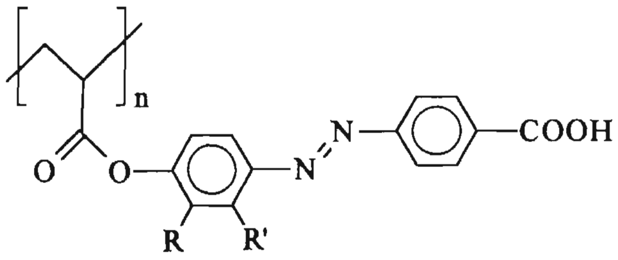
SYNTHESIS AND CHARACTERIZATION OF SIDE CHAIN LIQUID CRYSTAL AZOBENZENE POLYMERS

6.1 INTRODUCTION

The field of side chain liquid crystal polymers (SCLCPs) have attracted considerable interest in both industrial and academic reseach not only due to their combined properties of low molecular mass liquid crystals (MLC) and that of macromolecules, but also because of the superior properties they possess over the main chain liquid crystal polymers (MCLCPs)[1,2]. The SCLCPs have several choices for structural modifications compared to MCLCPs. Besides the choice of selection of different mesogenic units, in SCLCPs one can have different polymer backbones[1] like polysiloxanes, polyacrylates or methacrylates, polyphosphazenes, etc. to which mesogens are chemically connected. Substituents and/or spacers can be introduced and varied for their different chemical structure and length. The tailing end of the mesogen can also be varied[2]. These alterations in the structure bring about interesting change in the LC properties of the polymers. What is important here is the role of substituents and/or spacer in the realization of the LC state which results in the formation of a rich variety of LC phases such as nematic, smectic A, smectic C, etc., and makes this class of polymers more fascinating[1].

The melt viscosity of the SCLCPs are lower than that of MCLCPs and hence mesogens show small response time to the external magnetic or electric fields compared to MCLCPs, which is one of the main requirement for the LCPs to find use in the development of LC displays, NLO materials and information storage devices. Besides having low melt viscosity, SCLCPs generally have low transition temperatures and good solubility in common organic solvents. These factors are helpful in the easy processability of the polymers. The direct attachment of a mesogenic group into the backbone (without spacer) does not always lead to LCPs due to steric hinderances imposed by the main chain on the packing of the main groups[1]. However, in the present case the mesogens are attached directly to the acrylate backbone and were found to show LC property.

The syntheses of SCLCPs involve the "chemical binding" of the molecules of low molar mass LCs or rigid rod compounds as pendant to the polymer backbone. In the present chapter, a new class of side chain liquid crystal polymers have been reported which contain substituted azobenzene units as pendant to the polyacrylate backbone. The polymer have the following general structure given in scheme 21.

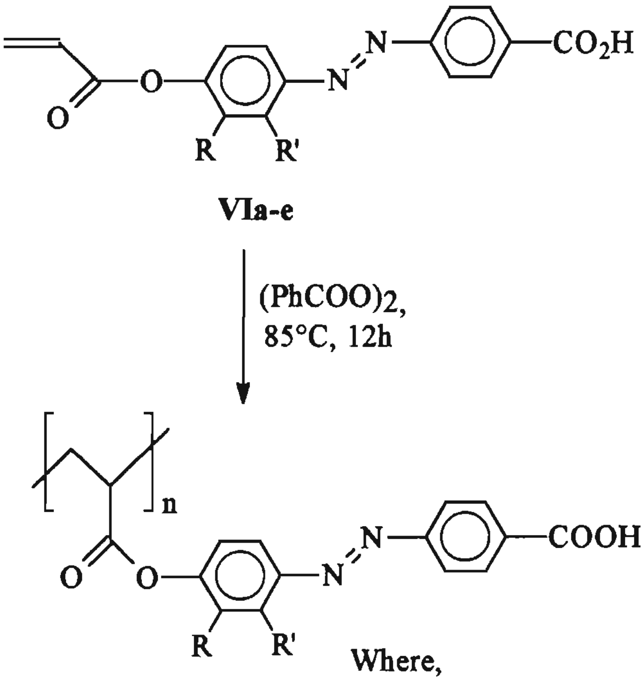


Scheme 21: structure of the side chain polyacrylates

The syntheses, structural characterization and studies on LC properties of these polymers are presented in this chapter.

6.2 EXPERIMENTAL

Polymerization : Polymerization of acrylate monomers were carried out in o-dichlorobenzene using benzoyl peroxide initiator at 85°C for 12h. The polymers were precipitated in methanol, washed thoroughly with methanol or acetone and dried in vacuo for 12h at 80°C. The scheme of synthesis of polymers is illustrated in Scheme 22.



VIa-e

VIIa-e

Where,
R= H when R'= a) H, c) CH_3, d) $C_{15}H_{31}$,
e) $C_{15}H_{27}$
R= b) CH_3 when R'= H

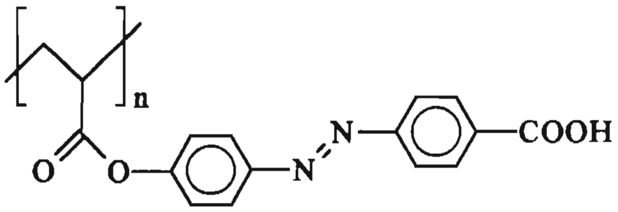
Scheme 22: Synthesis of azobenzene polyacrylate polymers

The polymers obtained were characterized by elemental analysis and spectral methods. IR spectra were recorded using Perkin-Elmer 882 infrared spectrometer and ^1H and ^{13}C NMR from Jeol JNM-EX 90 FT NMR system. UV-Vis spectra were obtained in DMF using Shimatzu UV-160A spectrophotometer and the inherent solution viscosities(η_{inh}) of the polymers were measured using Ubbelode suspended level viscometer at 28°C using DMSO as solvent. The solution concentration used was 0.5 g/dL. The melting points of the polymers were observed under hot stage polarized light microscope (PLM) using Leitz-1350 heating stage coupled with PLM.

The studies on LC properties of side chain polymers were performed using DSC and hot stage polarized light microscope (PLM). The DSC used was Du Pont DSC V2.2 A 9900 system under nitrogen and PLM by Leitz 1350 hot stage coupled cross- polarized light microscope. The heating rate used was 20°C/min in all the cases. X-ray diffractogram was obtained on a Rigaku Miniflex X-ray Diffractometer using nickel filtered Cu K_α radiation.

The typical procedure for the synthesis of azobenzene acrylate polymers is as follows.

1. *Synthesis of poly[4-[(4-acryloyloxyphenyl)azo]benzoic acid]* (**VIIa**) : 1g of 4-[(4-acryloyloxyphenyl)azo]benzoic acid (**VIa**) was dissolved in 10mL *o*-dichloro benzene and 10mg (1wt%) of benzoyl peroxide was added and dissolved with stirring. The reaction flask was corked with rubber septum and purged with pure, dry nitrogen gas for 15 minutes. The reaction mixture was heated to 85°C on an oil bath with stirring. The polymerization was continued for 12h and the polymer formed was precipitated, filtered and dried. Yield 0.64 g (64%); yellow powder. Anal.Calcd. for $C_{16}H_{12}N_2O_4$: C, 64.85; H, 4.08; N, 9.46. Found: C, 62.97; H, 5.10; N, 10.10.



(VIIa)

i) Viscosity : 0.35 dL/g

ii) m.p. (°C) : K 277 N 329 dec.

iii) UV-Vis (λ_{max}) : 337 nm (ε_{max} = 20 111 M^{-1} cm^{-1})

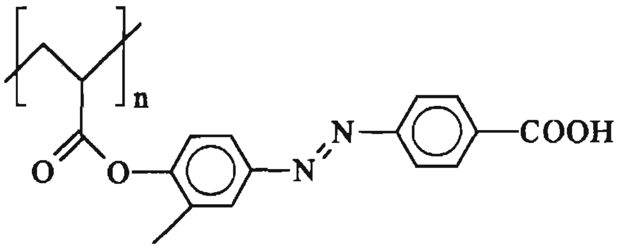
iv) IR (KBr; cm^{-1}) : 2920, 2870 (-CH_2-); 1750 (>CHCOOAr); 1690 (ArCOOH); 1590, 1510 (Ar;C=C); 1430 (-CH_2-); 1150 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 1.2-1.5 (-CH_2-); 2.1-2.4 (>CHCOO-); 7.0-8.6 (Ar)

vi) ^{13}C NMR (DMSO-d_6) : 166.6, 163.7, 154.1, 152.8, 149.5, 133.8, 132.8, 130.5, 127.3, 124.1, 122.7, 122.4, 46.3, 36.6 ppm

All polymers were prepared following the procedure mentioned above.

2. *Poly[4-[(4-acryloyoxy-3-methylphenyl)azo]benzoic acid]* (**VIIb**): yield 0.72 g (72%); orange powder. Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.79; H, 4.55; N, 9.03. Found: C, 64.95; H, 4.10; N, 10.21.



(VIIb)

i) viscosity : 0.33 dL/g

ii) m.p. (°C) : K 242 N 299 I

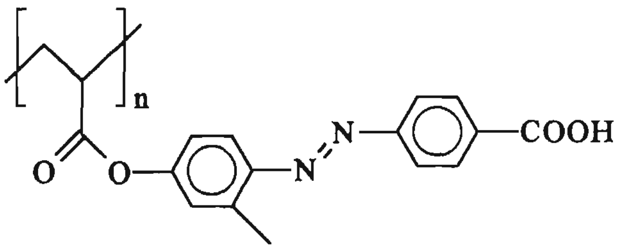
iii) UV-Vis (λ_{max}) : 344 nm (ε_{max} = 22 275 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2960, 2885 (-CH_2- & -CH_3); 1750 (>CHCOOAr); 1700 (ArCOOH); 1620, 1590 (Ar;C=C); 1435 (-CH_2-); 1155 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 1.2-1.7 (-CH_2- & -CH_3); 2.1-2.4 (>CHCOO-); 7.1-8.4 (Ar)

vi) ^{13}C NMR (DMSO-d_6) : 166.6, 163.2, 154.0, 151.4, 149.5, 133.6, 132.7, 131.1, 130.3, 126.9, 125.1, 122.8, 122.2, 121.5, 43.2, 34.2, 15.6 ppm.

3. *Poly[4-[(4-acryloyloxy-2-methylphenyl)azo]benzoic acid]* (**VIIc**): yield 0.67 g (67%); orange powder. Anal. Calcd. for $C_{17}H_{14}N_2O_4$: C, 65.79; H, 4.55; N, 9.03. Found: C, 66.12; H, 3.73; N, 9.21.



(**VIIc**)

i) viscosity : 0.53 dL/g

ii) m.p. (°C) : K 224 N 285 I

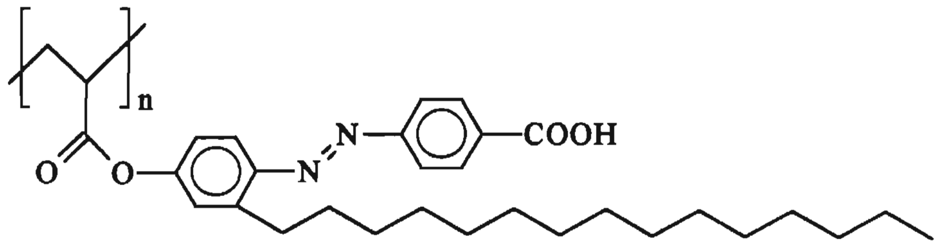
iii) UV-Vis (λ_{max}) : 347 nm (ε_{max} = 25 305 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2980, 2870 (-CH_2- & -CH_3); 1750 (>CHCOOAr); 1690 (ArCOOH); 1610, 1590 (Ar; C=C); 1440 (-CH_2-); 1157 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 1.1-1.4 (-CH_2-); 2.3-2.8 (-CH_3 & >CHCOO-); 7.0-8.3 (Ar)

vi) ^{13}C NMR (DMSO-d_6) : 166.6, 163.5, 154.5, 152.7, 147.6, 140.1, 132.6, 130.4, 127.3, 123.9, 122.8, 122.4, 119.9, 116.3, 46.2, 33.5, 17.0 ppm

4. *Poly[4-[(4-acryloyloxy-2-pentadecylphenyl)azo]benzoic acid]* (**VIId**): yield 0.76 g (76%); red solid. Anal. Calcd. for $C_{31}H_{42}N_2O_4$: C, 73.49; H, 8.35; N, 6.20. Found: C, 72.81; H, 9.81; N, 6.20.



(VIId)

i) viscosity : 0.62 dL/g

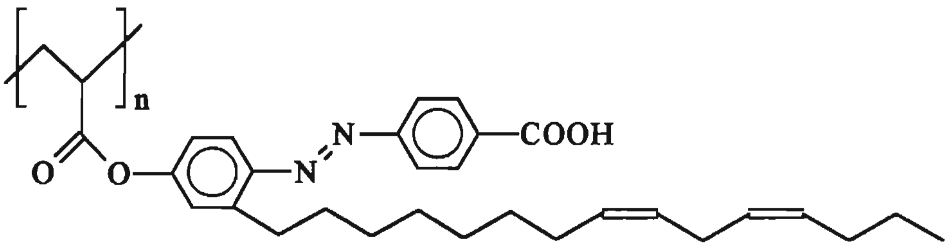
ii) m.p. (°C) : K 175 S_A 202 N 280 I

iii) UV-Vis (λ_{max}) : 348 nm (ε_{max} = 19 039 M^{-1} cm^{-1})

iv) IR (KBr; cm^{-1}) : 2960, 2885 (-CH_2-); 1750 (>CHCOOAr); 1700 (ArCOOH); 1620, 1590 (Ar;C=C); 1425 (-CH_2-); 1150 (-N=N-)

v) ^{1}H NMR (DMSO-d_6) : δ 0.5-4.4 (-CH_2- & >CHCOO-); 7.1-8.5 (Ar)

5. *Poly[4-[(4-acryloyloxy-2-pentadecadienylphenyl)azo]benzoic acid]* (**VIId**): yield 0.68g (68%); red solid. Anal. Calcd. for $C_{31}H_{38}N_2O_4$: C, 74.08; H, 7.62; N, 5.57. Found: C, 75.22; H, 8.45; N, 5.26.



(VIIe)

i) viscosity : insoluble

ii) m.p. (°C) : K 156 N 260 I

iii) IR (KBr; cm^{-1}) : 2960, 2880 ($-CH_2-$); 1740 (>CHCOOAr); 1700 (ArCOOH); 1620, 1600 (Ar;C=C); 1420 ($-CH_2-$); 1156 (-N=N-); 3020, 780 (*cis* -CH=CH-)

6.3 RESULTS AND DISCUSSION

The polyacrylates were prepared by radical polymerization method using benzoyl peroxide initiator. The polymers were precipitated in excess methanol, filtered and washed thoroughly with acetone or methanol and dried. The colour of the polymers are yellow(**VIIa**), orange(**VIIb** & **VIIc**) and red(**VIId** & **VIIe**). The polymers are soluble in highly polar solvents such as DMF, DMSO, *o*-dichlorobenzene etc. The solubility data is tabulated in Table 3. The inherent solution viscosities of the polyacrylates (**VIIa-d**) were in the range of 0.33-0.62 dL/g in DMSO at 28°C. The viscosity data indicates that the polymers are having considerable molecular weight. The viscosity of the polymer **VIIe** could not be obtained due to its insolubility. The melting of polyacrylates followed the typical sequence of LC materials i.e. crystalline → LC → isotropy.

Elemental analysis and IR spectra (Figure 47) support the formation of polyacrylates.[3] The calculated values of elemental analysis are in good agreement with the experimental values. The IR absorbance at 1662-1656 cm^{-1} of acrylate C=C vibration of **VIa-e** decreased largely on polymer formation and the characteristic alkyl polymer chain $-CH_2-$ stretching vibrations appeared at 2980-2960 and 2885-2870 cm^{-1}. The ester peak of polymers **VIIa-e** have been shifted by atleast 10 cm^{-1} on polymerization when compared to their respective monomers and the carboxylic acid hydrogen bonded dimer peak appeared at 1700-1690 cm^{-1}. The characteristic *p*-substituted azobenzene absorption of polymers **VIIa-e** appeared at 1157-1150 $cm^{-1}$and aromatic C=C stretchings at 1620-1590 cm^{-1}.

Table 3: Solubility data of SCLCPs

Polymer Solvent	**VIIa**	**VIIb**	**VIIc**	**VIId**	**VIIe**
$CHCl_3$	X	X	X	∗	∗
THF	X	∗	∗	✓	∗
Acetone	∗	∗	∗	✓	∗
Toluene	X	X	X	∗	∗
o-Dichlorobenzene	✓	✓	✓	✓	∗
DMF	✓	✓	✓	✓	∗
DMSO	✓	✓	✓	✓	∗
CF_3COOH	∗	∗	∗	✓	∗
CH_3SO_3H	✓	✓	✓	✓	∗
H_2SO_4	✓	✓	✓	✓	∗

✓= soluble; X = insoluble; ∗ = swelling

^{1}H NMR spectra also supported the formation of polyacrylates[4] **VIIa-e**. The acrylic multiplets of **VIa-d** were disappeared and the corresponding $-CH_2-$ and >CHCOO- protons appeared in the range of 1.1-1.5 δ and 1.6-2.8 δ respectively (**VIIa**; Figure 48). For polymers **VIIb** (Figure 50) and **VIIc** (Figure 52) the methyl protons were merged with the polymer chain protons. In polymer **VIId** (Figure 54) the long alkyl chain protons masked the identity of the polymer chain protons. The broad resonance peaks of polyacrylates **VIIa-d** are due to the poor relaxation of the protons in polymers. ^{1}H NMR of polymer **VIIe** could not be recorded due to insolubility of the polymer.

The structure of the polymers were further confirmed by ^{13}C NMR spectroscopy and found to be complementary to the conclusions drawn from ^{1}H NMR studies.[5] The $-CH_2-$ and >CHCOO- carbons of polymer backbone of polymers **VIIa-c** resonated in the range of 33.5-36.6 ppm and 46.3-42.2 ppm respectively (**VIIa**; Figure 49). The acrylic resonance peaks of **VIa-c**, in the region of 129.3-128.5 ppm, vanished on polymerization. The carboxylic acid and the carboxylate ester peaks resonated in the range of 166.6 ppm and 163.2-163.7 ppm respectively. The methyl carbons of polymers **VIIb** (Figure 51) and **VIIc** (Figure 53) appeared at 15.6 ppm and 17.0 ppm respectively. The ^{13}C NMR of polymer **VIId** could not be recorded due to the limited solubility of the polymer in DMSO and for polymer **VIIe**, due to insolubility. The UV-Vis spectra (Figure 46) of polyacrylates **VIIa-d** have one absorption peak in the range of 337-348 nm (ε_{max} = 19 037-25 305 M^{-1} cm^{-1}) due to π-π^* transition of azobenzene group.[4]

The viscosity data indicates that the polymers **VIIa-d** are having considerable molecular weight. The viscosity of polymer **VIIe** could not be obtained due to its insolubility which possibly arises from the crosslinking of unsaturations present in the alkyl chain of the -C_{15} substituent. IR spectra shows that the carboxylic acid group is present in dimeric form which introduces a kind of physical crosslinking between polymer chains. This may be the cause for the solubility of polacrylates **VIIa-d** in highly dipolar solvents and higher melting temperatures than that expected for SCLCPs. The presence of substituent increased the solubility in various solvents (see Table 3). The polymer **VIId** containing -C_{15} n-alkyl chain is the most soluble among the polymers studied. Polymer **VIIe** is not soluble in any solvent possibly due to crosslinking of the alkenyl substituent in polymer **VIIe,** but the characteristic swelling of crosslinked polymers is observed.

6.4 STUDY OF LIQUID CRYSTALLINE PROPERTY OF SIDE CHAIN POLYMERS

The DSC thermograms are explained as follows. In general, endotherms in DSC thermograms are assigned to crystal→mesophase and mesophase→isotropic transitions. In the DSC heating cycle, endotherm at the highest transition temperature corresponds to the transition from LC phase to the isotropic phase. The peak maximum was taken as the transition temperature. The cooling curve of the polymers could not be obtained due to decomposition prior to isotropization.

In PLM the temperature of appearance of the phase was taken as the crystal to LC transition and the complete disappearance of phase was taken as LC to isotropic transition. Normally, the identification of the transition temperatures is done by coupling the DSC data with the information obtained by the visual examination of the polymer under PLM[6]. The DSC and PLM data are tabulated in table 4.

1. *Poly[4-[(4-acryloyloxyphenyl)azo]benzoic acid]* (**VIIa**): The DSC thermogram of polymer **VIIa** is given in Figure 55. The polymer showed crystal to mesophase transition at 273°C to nematic mesophase and above 300°C the polymer started degrading as may be seen from the abrupt raise in the baseline. DSC trace did not show any baseline shift characteristic of glass transition (Tg) indicating that the polymer could be crystalline. The polymer melted and exhibited schlieren texture characteristic of nematic mesophase (Figure 56) under PLM at 276°C which remained till 300°C. The polymer started decomposing above 300°C and the sample darkened. DSC and hot stage PLM observations match well with each other.

Table 4: DSC and PLM data of SCLCPs

Poly-mer	Method	Phase transitions (°C)
VIIa	DSC	K 273 N dec.>300
	PLM	K 276 N dec.>300
VIIb	DSC	K 238 N 296 I
	PLM	K 242 N 299 I
VIIc	DSC	K 218 N 280 I
	PLM	K 224 N 285 I
VIId	DSC	K 172 S 198 N 278 I
	PLM	K 175 S 202 N 280 I
VIIe	DSC	K 151 N 258 I
	PLM	K 156 N 260 I

where,
K = crystal
S = smectic A phase
N = nematic phase
I = isotropic

2. *Poly[4-[(4-acryloyloxy-3-methylphenyl)azo]benzoic acid]* (**VIIb**): The DSC thermogram of polymer **VIIb** is given in Figure 57. The mesophase transition of the polymer is observed at 238°C to nematic phase and the isotropization at 297°C. The absence of Tg in DSC trace indicates that the polymer could be crystalline. PLM observation supported the transitions observed in DSC thermogram. The polymer started melting and displayed schlieren texture(Figure 58) characteristic of nematic mesophase from 242°C and the phase remained till 299°C where it isotropized.

3. *Poly[4-[(4-acryloyloxy-2-methylphenyl)azo]benzoic acid]* (**VIIc**): The DSC trace of polymer **VIIc** is given in Figure 59. which showed crystal to nematic phase transition at 218°C and the nematic to isotropic transition at 297°C. The absence of Tg indicates the crystalline nature of the polymer. The hot stage PLM observation agree well with DSC trace. The polymer started melting and exhibited schlieren texture of nematic phase(Figure 60) at 224°C which remained unchanged till the isotropization temperature at 303°C.

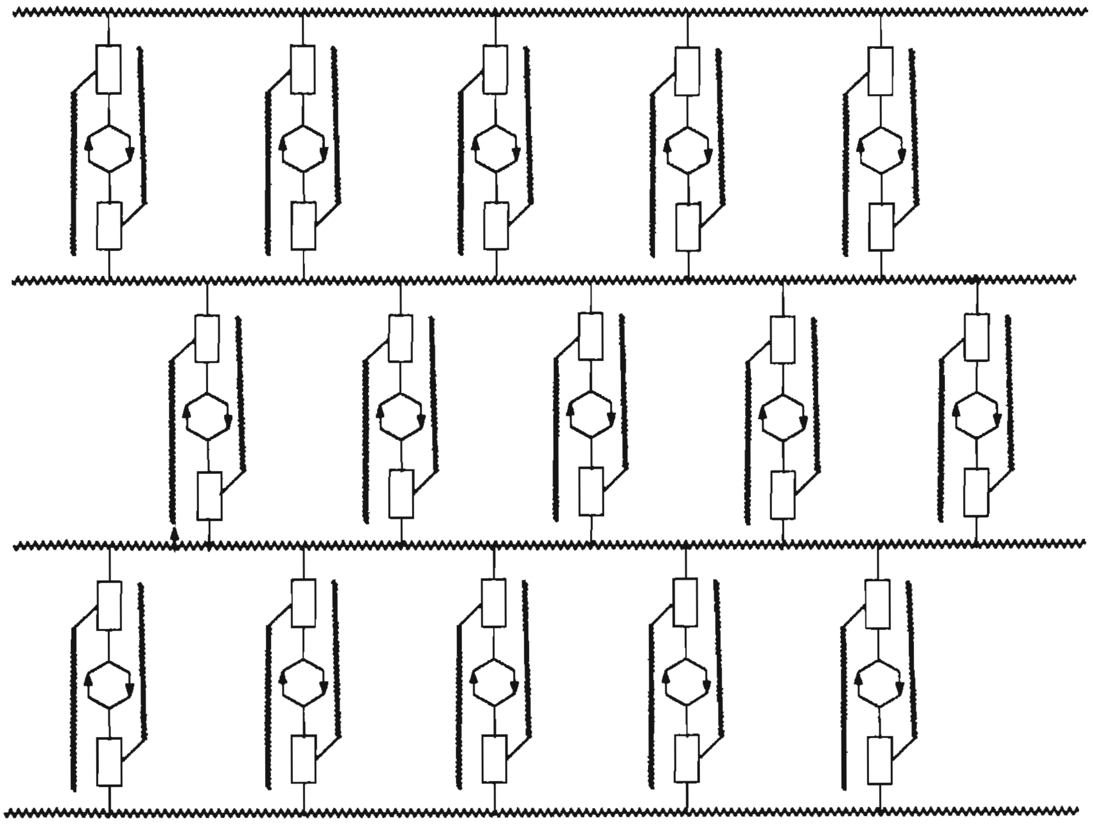
4. *Poly[4-[(4-acryloyloxy-2-pentadecylphenyl)azo]benzoic acid]* (**VIId**): The DSC thermogram (Figure 61) of polymer **VIId** showed three well defined peaks at 172, 198 and 278°C. The transition at 172°C is crystal to smectic A phase transition and the smectic A to nematic phase transition is observed at 198°C. The polymer isotropized at 278°C. There was no Tg observed in DSC trace indicating the crystalline nature of the polymer. Hot stage PLM studies supported the transition temperatures found in DSC trace. The polymer started melting and displayed focal conic texture characteristic of smectic A phase (Figure 62a) at 175°C which turned schlieren texture of nematic phase (Figure 62b) at 202°C and isotropized at 280°C. X-ray diffractogram (Figure 65) of **VIId** was recorded and observed that the

WAXD showed two diffraction peaks at $\theta = 2.5$ and 20°. In WAXD the small angle diffraction ($\theta = 2.5°$)[6] support the existance of layered molecular arrangement the wide angle diffraction indicate that there is a three dimensional order.

5. *Poly[4-[(4-acryloyloxy-2-pentadecadienylphenyl)azo]benzoic acid]* (**VIIe**): The DSC thermogram of polymer **VIIe** is given in Figure 63. which showed an endothermic phase transition at 151°C to nematic mesophase and the polymer isotropized at 258°C. In this case also DSC trace did not show any baseline shift characteristic of Tg indicating that the polymer could be crystalline. The polarized light microscopic observation matched well with the DSC trace. The polymer started melting and showed schlieren texture of nematic phase (Figure 64) at 156°C and isotropized at 260°C. Near to isotropization temperature the polymer started darkening and which may be due to the decomposition of tertiary carbon centers introduced on crosslinking of the long alkyl chain unsaturations.

As can be seen from the preceding discussion, all the polyacrylates exhibited nematic phase except polymer **VIId** which showed smectic A phase in addition to nematic phase. The phase transition temperatures are quite high than expected for SCLCPs. This is due to the interchain dimerization of carboxylic acid (IR spectra: 1690-1700 cm^{-1}) groups through hydrogen bonding which introduces a kind of physical crosslinking leading to higher transition temperatures. The same may be the reason for the crystalline nature of polyacrylates **VIIa-e**. The presence of substituent attached to the pendant side chain has remarkable influence on phase transitions (see table 4). The methyl substituent of polymers **VIIb** and **VIIc** decreases the crystal to nematic phase transition temperature by 35 and 51°C respectively with respect to polymer **VIIa**. Polymers **VIId** and **VIIe** having saturated and unsaturated -C_{15} side chain experienced drastic decrease in transition temperature of about 100 and 122°C respectively of the crystal to nematic phase transition temperature when compared to polymer **VIIa**. The presence of *cis* olefinic double bonds in polymer **VIIe** lowered the transition temperatures much more than that of polymer **VIId** which has saturated n-alkyl chain. The transition temperature difference between polymers **VIIb** and **VIIc** is about 20°C. The cause for this difference is discussed in chapter - VII. The isotropization temperatures of polyacrylates **VIIa-e** also follow the same trend of crystal to mesophase transition temperatures but the temperature differences are not high.

A very interesting observation in this study is the formation of smectic A phase by polymer **VIId.** It is well known that the formation of smectic phases require enough flexibility and the mesogens have to be decoupled from the backbone motion by introducing spacers[1]. Moreover, Finklemann et al.[7] have described that the homogenous spacer distribution leads to smectic phase and the inhomogenity leads to nematic phase. In the present case the mesogen is directly attached to the backbone and a -C_{15} n-alkyl substituent is present which may be supporting the formation of smectic layers as shown in scheme 23. Though polymer **VIIe** has the similar structural features as in polymer **VIId**, the formation of smectic phase will be prevented by inhomogeneous distribution of n-alkyl chains containing *cis* olefinic double bonds and interchain crosslinking. The layered smectic structure as given in scheme 23 can be formed by polymers **VIIa-c** also. But the temperature at which the crystal to mesophase transition occur for polymers **VIIa-c** may be high enough to cause random motion of mesogens and breaking of carboxylic acid dimer hydrogen bonds as observed for polymer **VIId** where at higher temperature the smectic phase collapse to form nematic phase. A similar kind of observation is reported by Gray et al.[8] for low molar mass LCs.



Scheme 23 : The probable smectic layer arrangement in **VIId** (the rigid rod units are carboxylic acid dimers of **VIId**)

From the above observations it can be concluded that the formation of smectic phase require enough flexibility, homogeneous spacer distribution irrespective of the mode of introduction of flexibility and the temperature lower enough to restrict the randomization of mesogens in order to maintain the layered structure of smectic phases.

6.5 CONCLUSION

Five novel polyacrylate SCLCPs (**VIIa-e**) were prepared by radical polymerization of their respective monomers. The polymers are yellow, orange and red coloured solids. The inherent viscosities of the polyacrylates were in the range of 0.33-0.62 dL/g. The polymers **VIIa-d** are soluble in dipolar solvents. polymer **VIIe** is insoluble in any solvent but swells in most of the solvents indicating that the polymer is crosslinked. The structure of polymer **VIIa-d** were confirmed by IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy. The LC behaviour of SCLCPs were studied using DSC and PLM. All the polymers exhibited nematic phase except polymer **VIId**, which showed smectic A phase in addition to nematic phase. This is an exception to the general observation, that the direct attachment of the mesogen to polyacrylate backbone does not always lead to LCPs due to steric hinderances[1]. The possibility for the smectic phase formation is explained. The presence of substituent altered the transition temperatures and the lowest being polymer **VIIe**. As in the case of monomers, polymers also show higher transition temperatures due to the interchain hydrogen bonded carboxylic acid dimers. Absence of Tg in DSC traces indicates that the polymers could be crystalline.

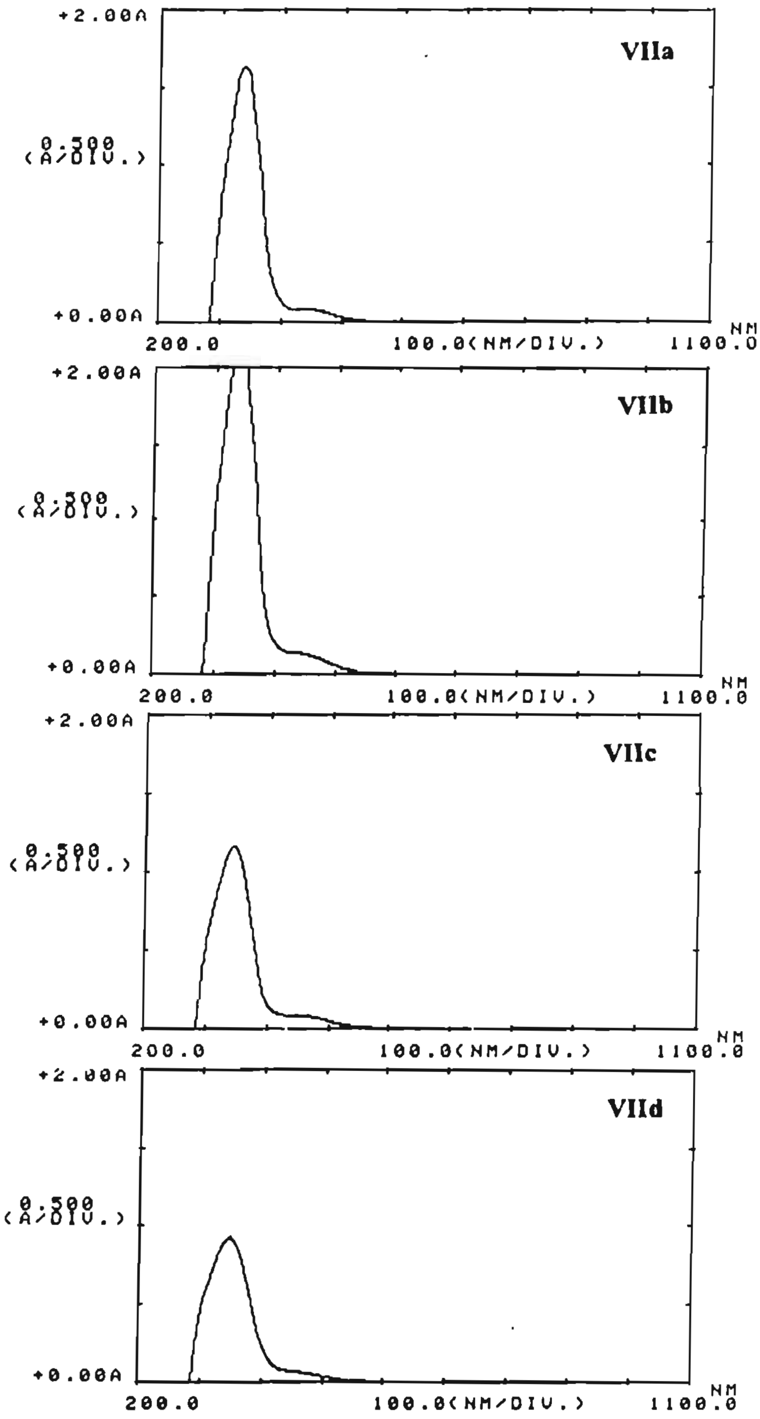


Figure 46: UV-Vis spectra of polyacrylates (**VIIa-d**)

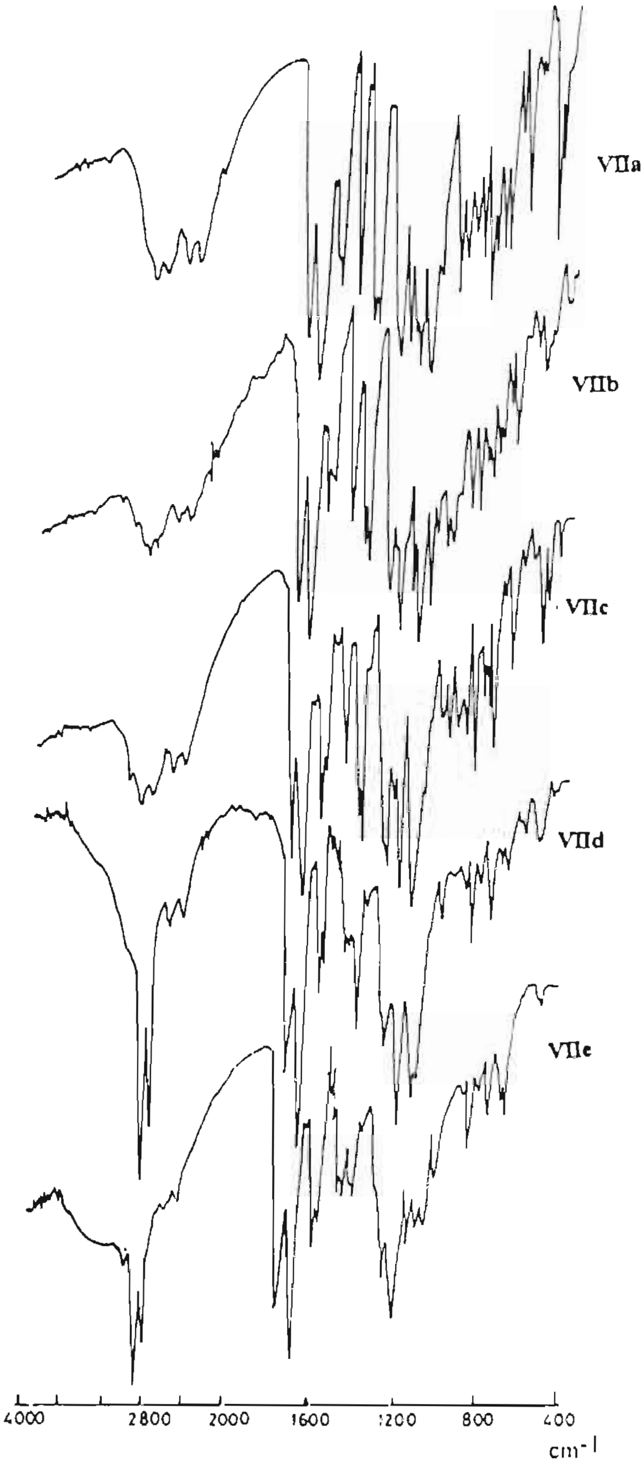


Figure 47: IR spectra of polyacrylates (VIIa-e)

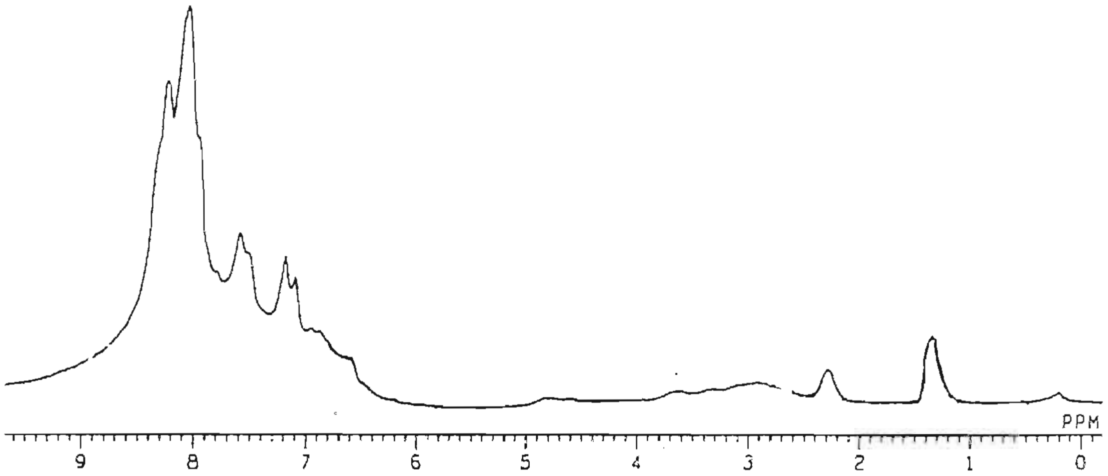


Figure 48: ${}^1H$ NMR spectrum of polyacrylate **VIIa**

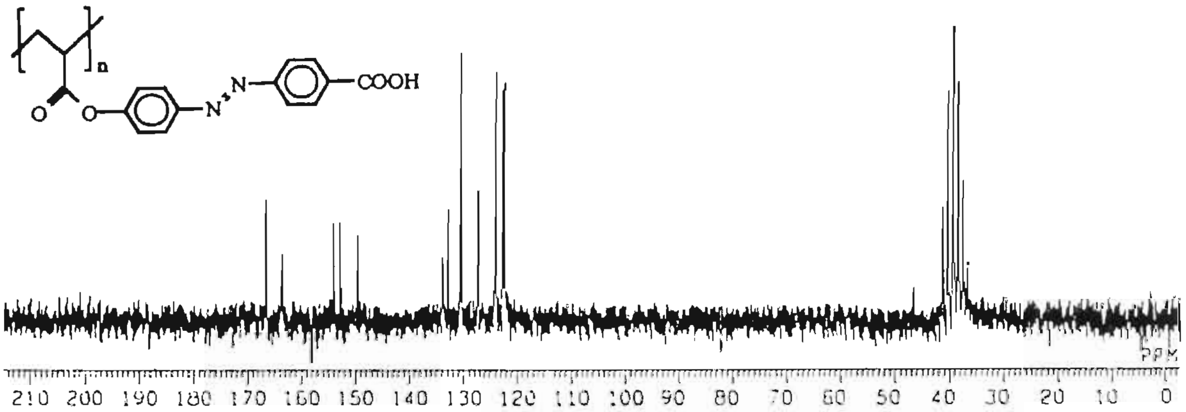


Figure 49: ${}^{13}C$ NMR spectrum of polyacrylate **VIIa**

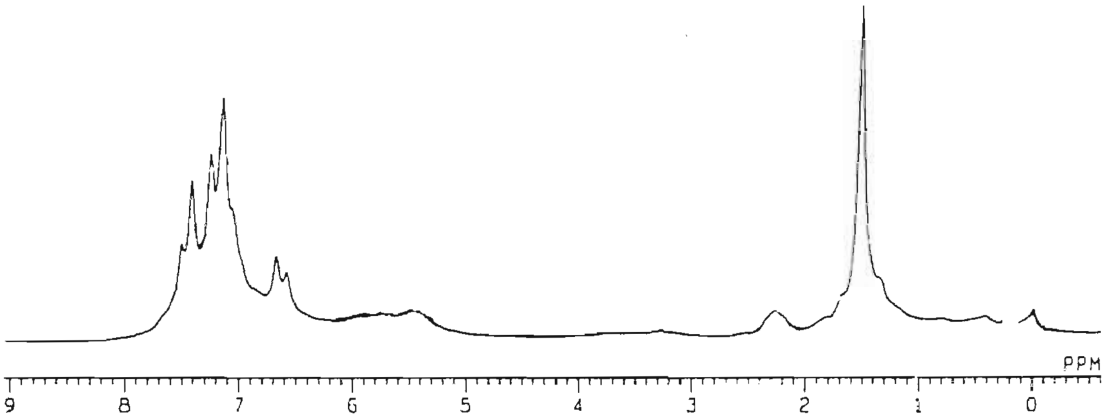


Figure 50: ^{1}H NMR spectrum of polyacrylate **VIIb**

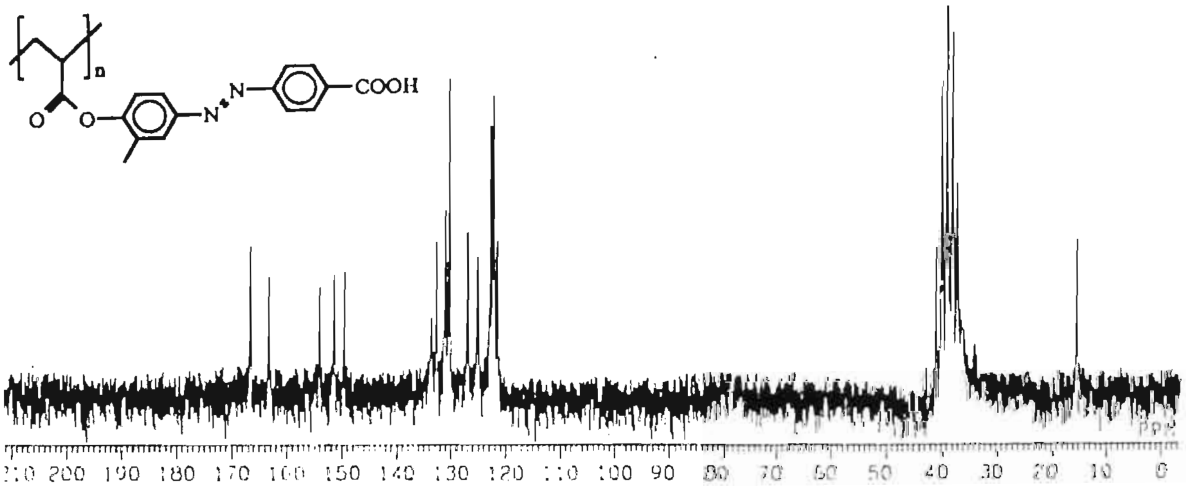


Figure 51: ^{13}C NMR spectrum of polyacrylate **VIIb**

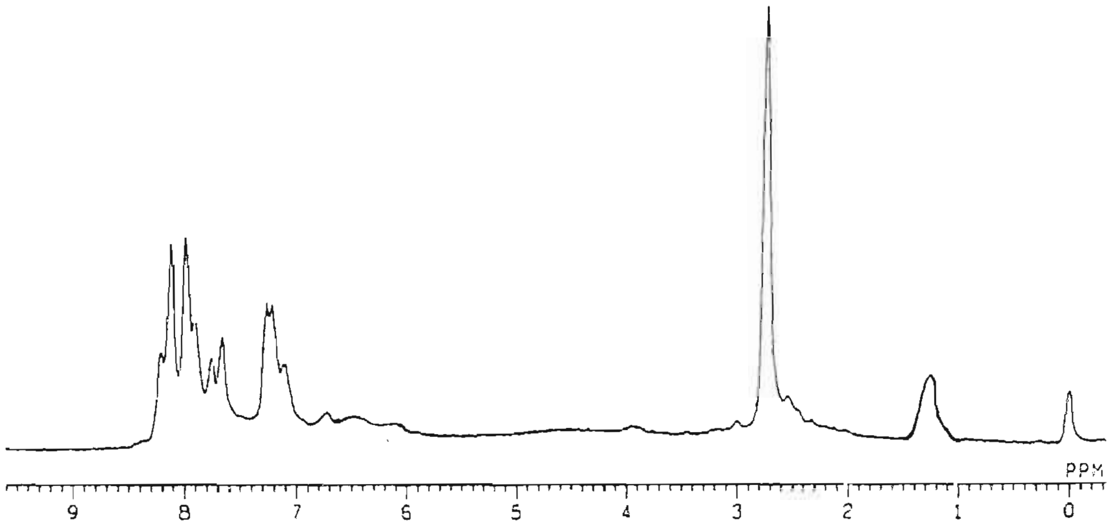


Figure 52: ^{1}H NMR spectrum of polyacrylate **VIIc**

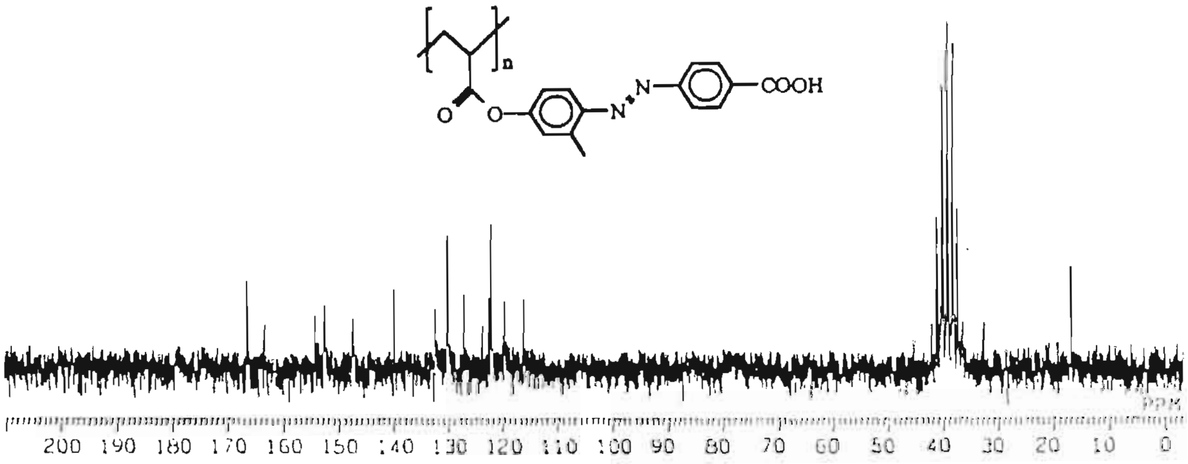


Figure 53: ^{13}C NMR spectrum of polyacrylate **VIIc**

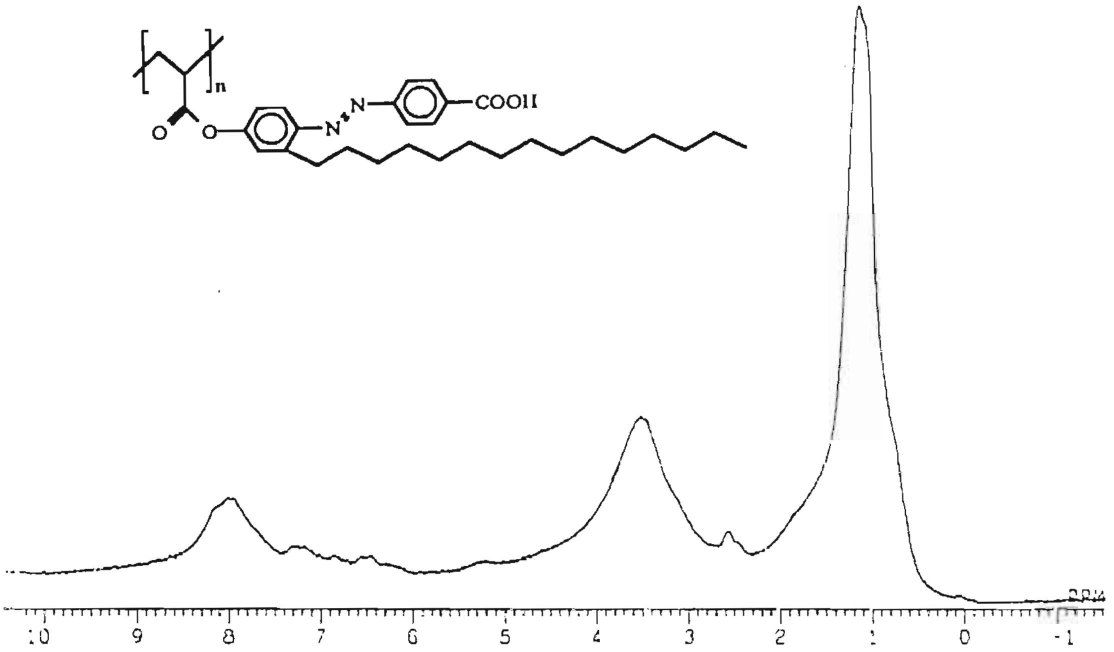


Figure 54: ^{1}H NMR spectrum of polyacrylate **VIId**

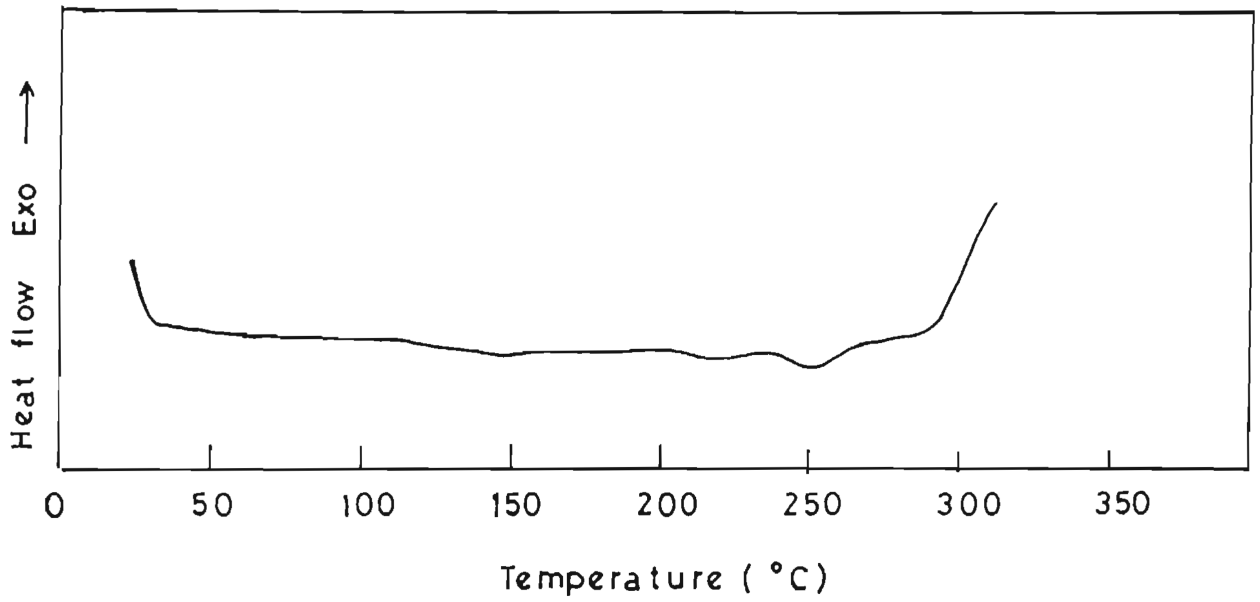


Figure 55: DSC thermogram of polymer **VIIa**

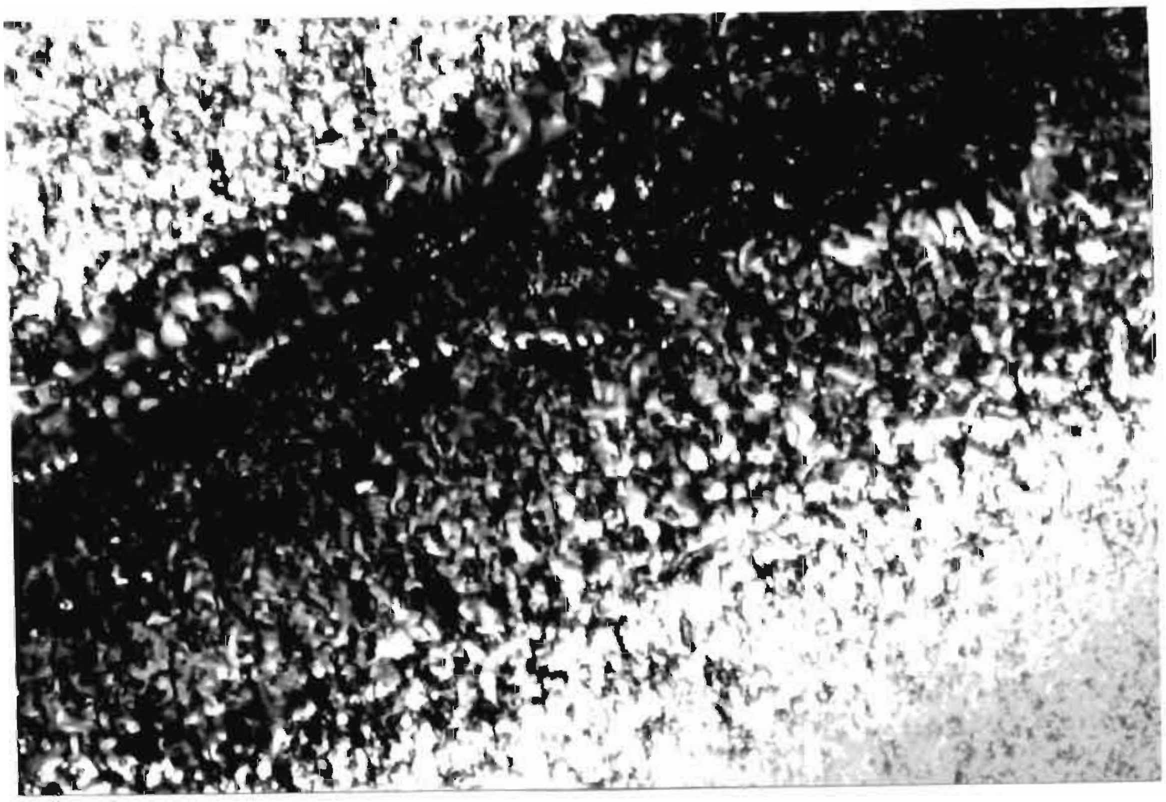


Figure 56: Schlieren nematic texture of polymer **VIIa** at 280°C (X 200)

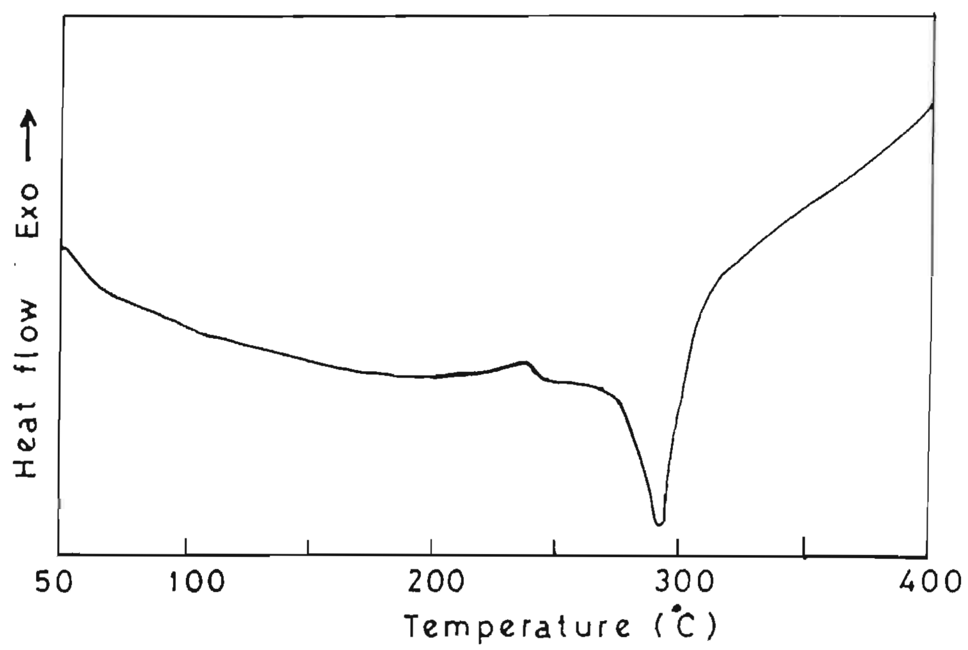


Figure 57: DSC thermogram of polymer **VIIb**

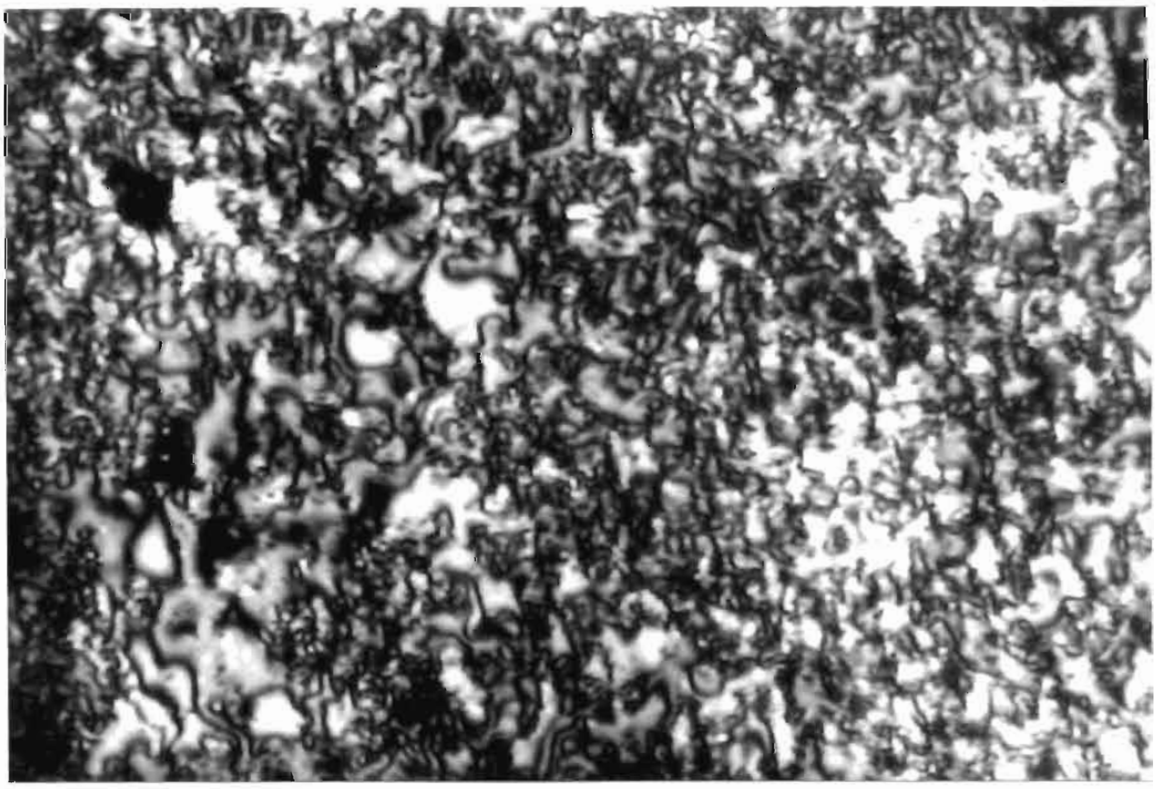


Figure 58: Schlieren nematic texture of polymer **VIIb** at 245°C (X 200)

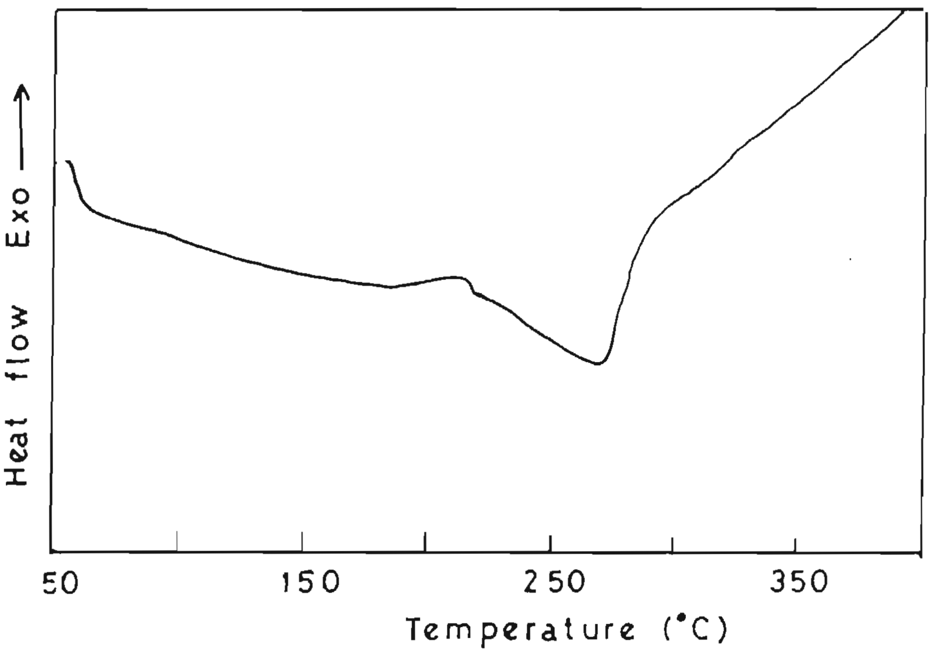


Figure 59: DSC thermogram of polymer **VIIc**

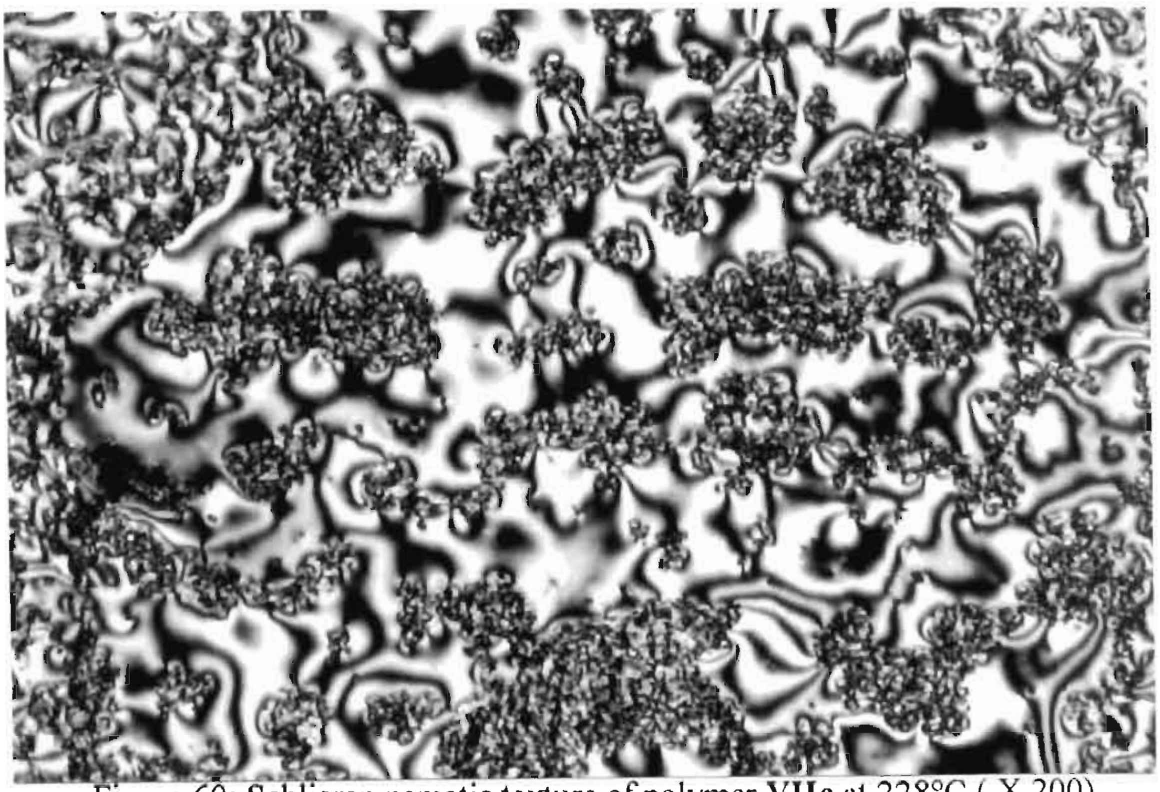


Figure 60: Schlieren nematic texture of polymer **VIIc** at 228°C (X 200)

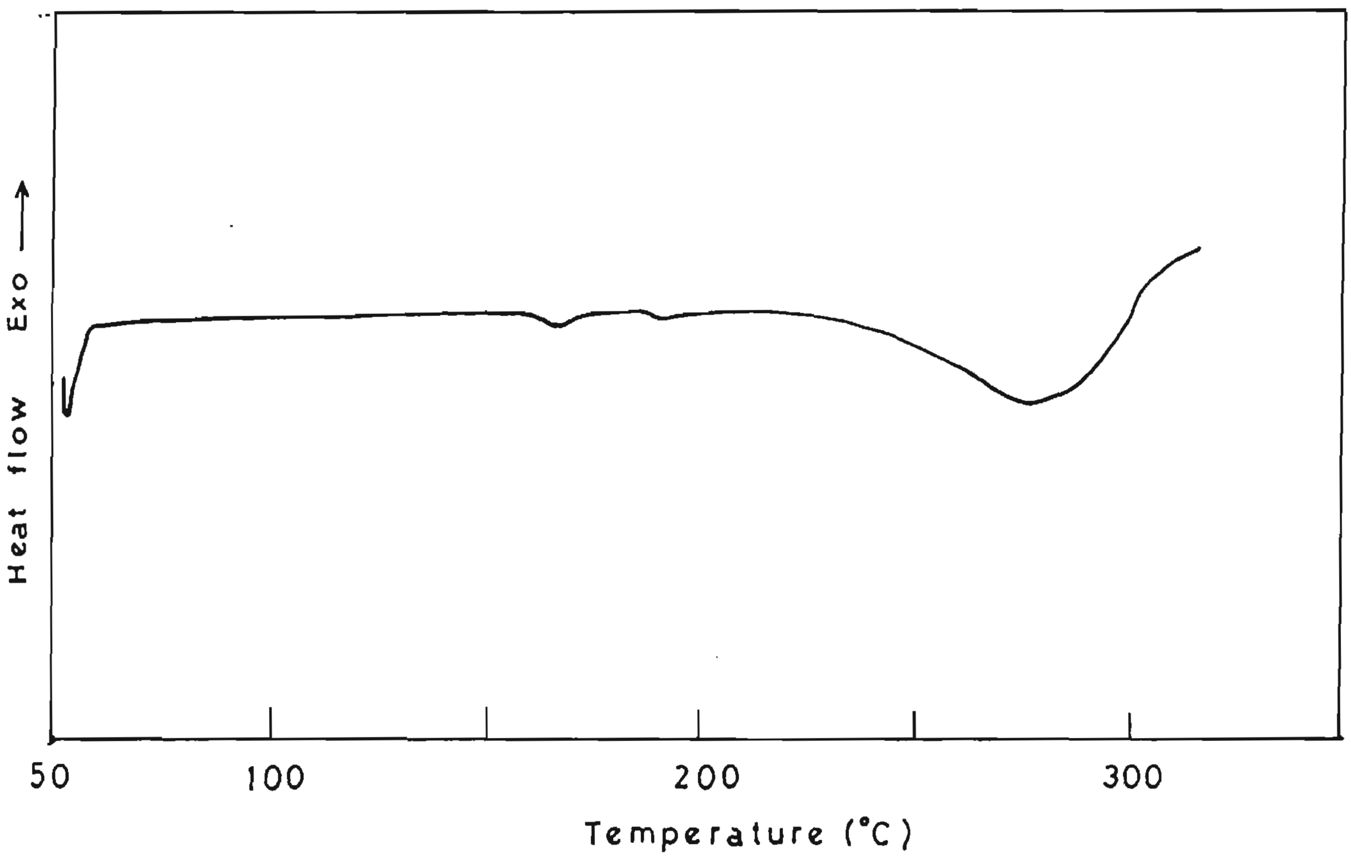


Figure 61: DSC thermogram of polymer **VIId**

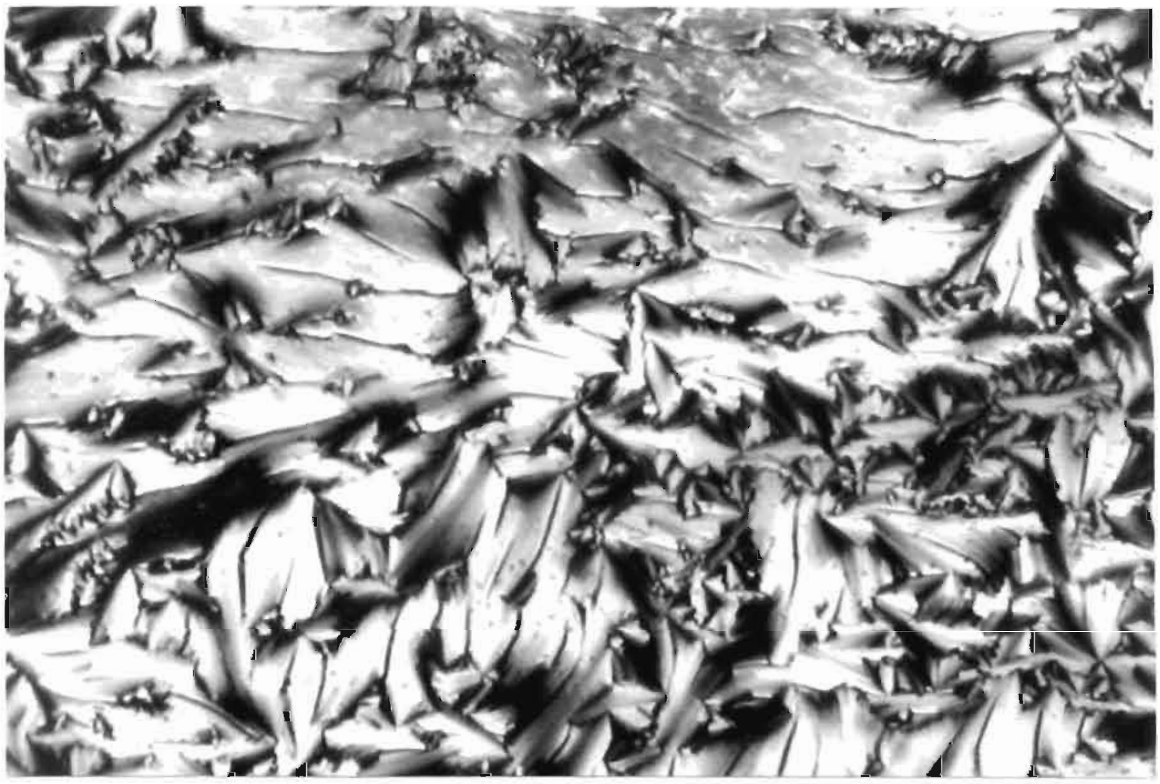


Figure 62a: Focal conic texture of smectic A phase of polymer **VIId** at 180°C (X 200)

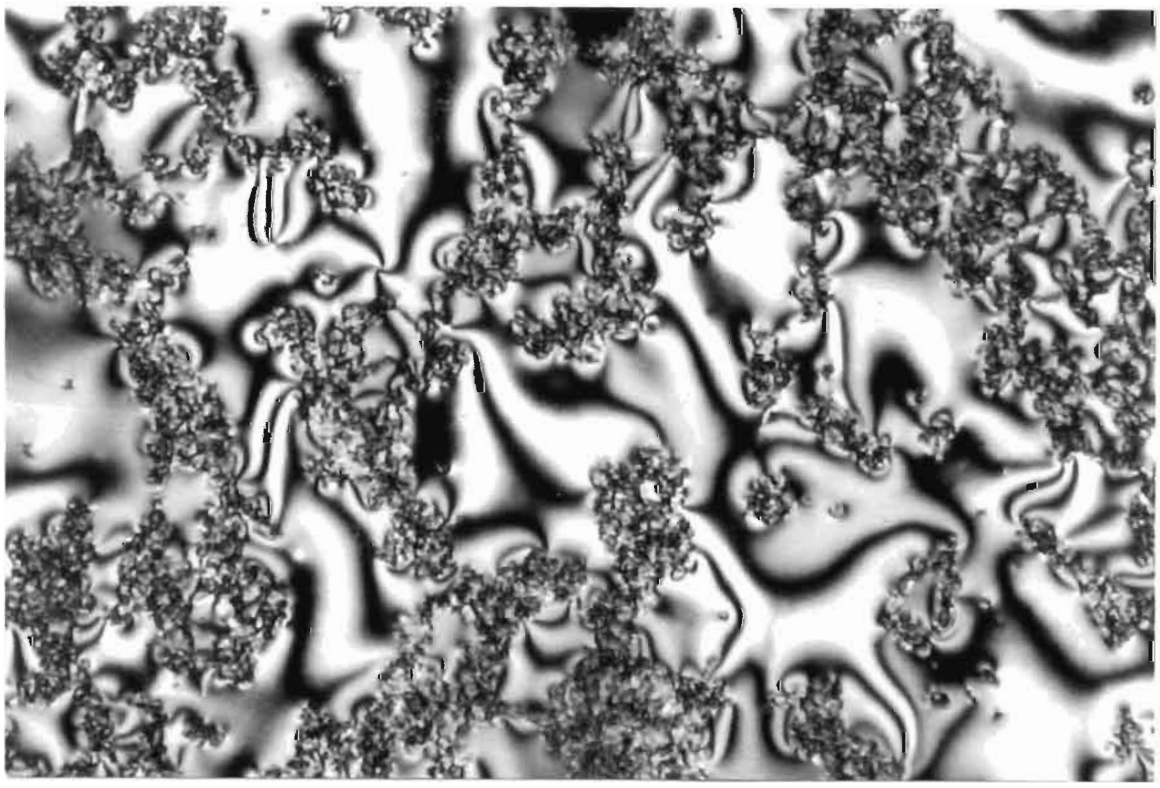


Figure 62b: Schlieren nematic texture of polymer **VIId** at 210°C (X 200)

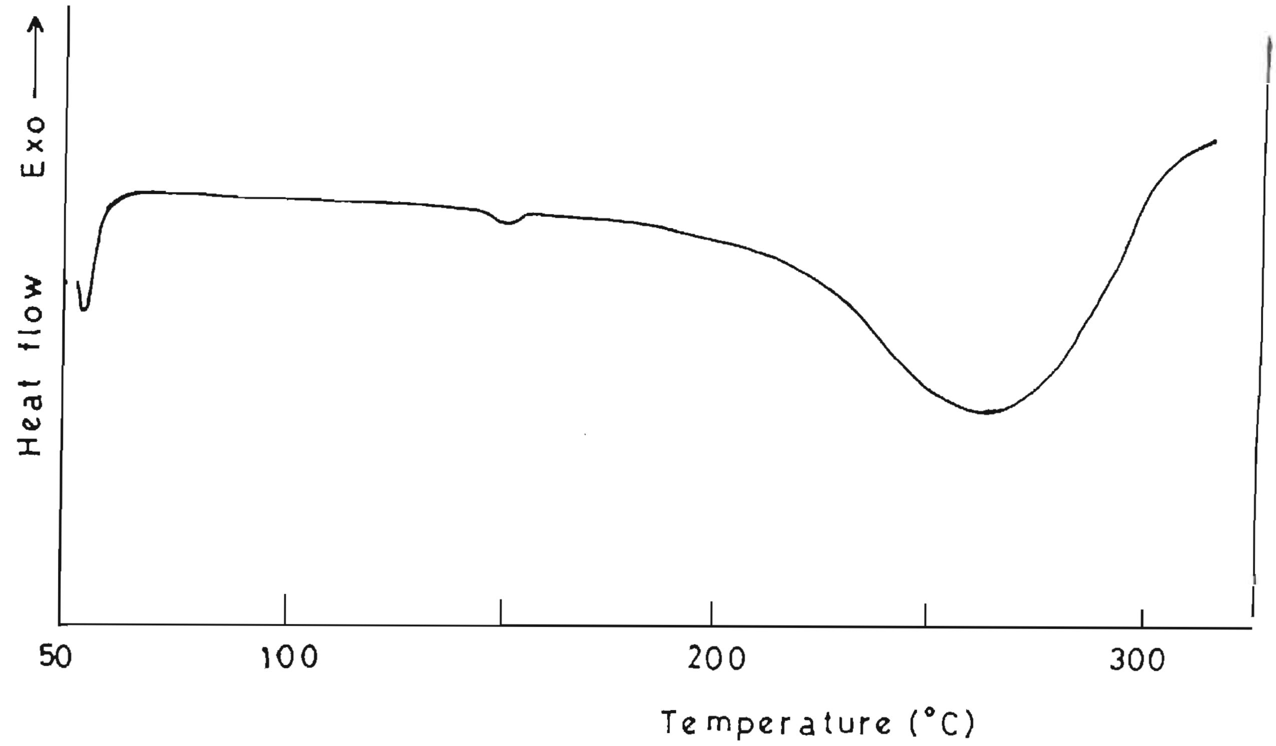


Figure 63: DSC thermogram of polymer **VIIe**

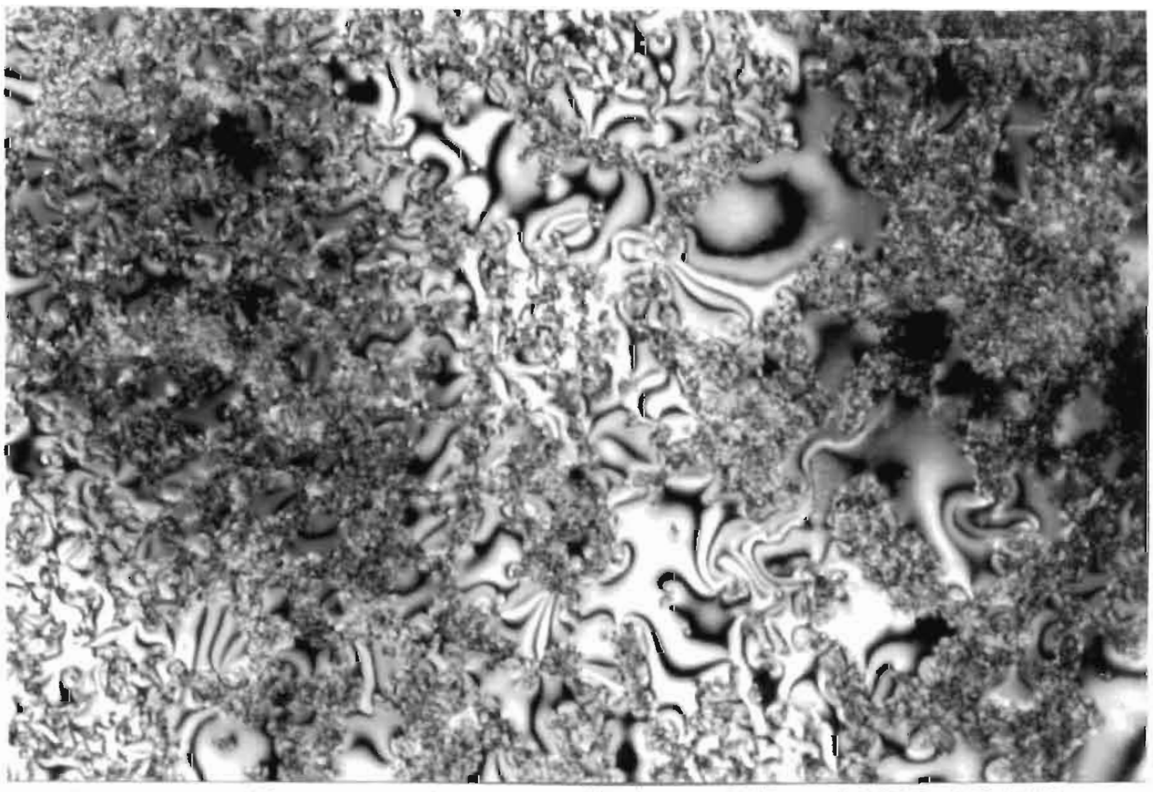


Figure 64: Schlieren nematic texture of polymer **VIIe** at 160°C (X 200)

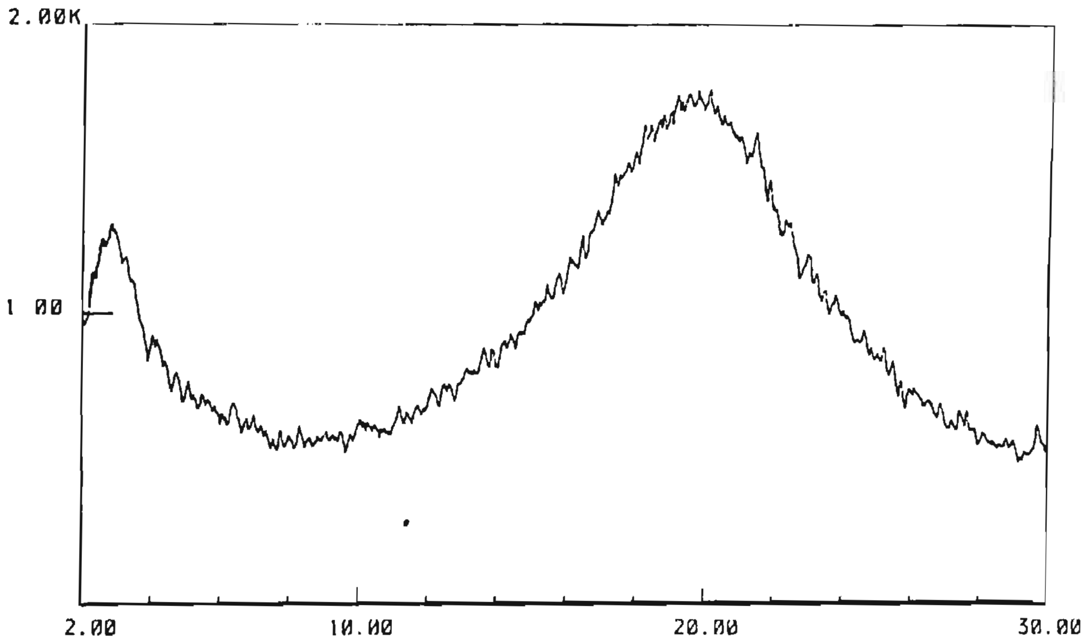


Figure 65: A representative WAXD of polymer **VIId**

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CHAPTER - VII

A COMPARISON ON THE EFFECT OF SUBSTITUENTS ON TRANSITION TEMPERATURES AND A STUDY ON NON-LINEAR OPTICAL PROPERTY

7.1 INTRODUCTION

It is well known that the presence of substituents in liquid crystal polymer backbone tend to reduce the transition temperatures and the same is observed in the present study also.[1] Substituents are introduced to bring down the transition temperatures of otherwise intractable LCPs to the processable range where the study on various substituents on transition temperatures become inevitable. Hence, it would be worthwhile to compare the substituent effect on the phase transition temperatures of MCLCPs and SCLCPs, which would throw light on the structure - property relationship of these materials is important. The data presented in Chapter -IV and VI are used here for the comparison study.

This section deals with a comparative study on the effect of substituents on phase transition temperatures of main chain and side chain LCPs. A study on non-linear optical (NLO) behaviour of the monomers and polymers based on UV-Vis spectroscopy is also presented. This chapter also includes the synthesis and characterization of a novel LC polymer.

7.2 DISCUSSION

The data obtained from PLM observation is selected for the comparison of effect of substituents on transition temperatures of MCLCPS and SCLCPs. This study mainly focuses on the effect of substituent on crystal → LC → isotropic transitions and hence the the results of PLM would be more straight forward for discussion than DSC where the transitions which are difficult to explain also occur (eg. crystal → crystal transition). The PLM results of MCLCPs and SCLCPs are tabulated in Table 5.

Table 5: PLM data of MCLCPs and SCLCPs

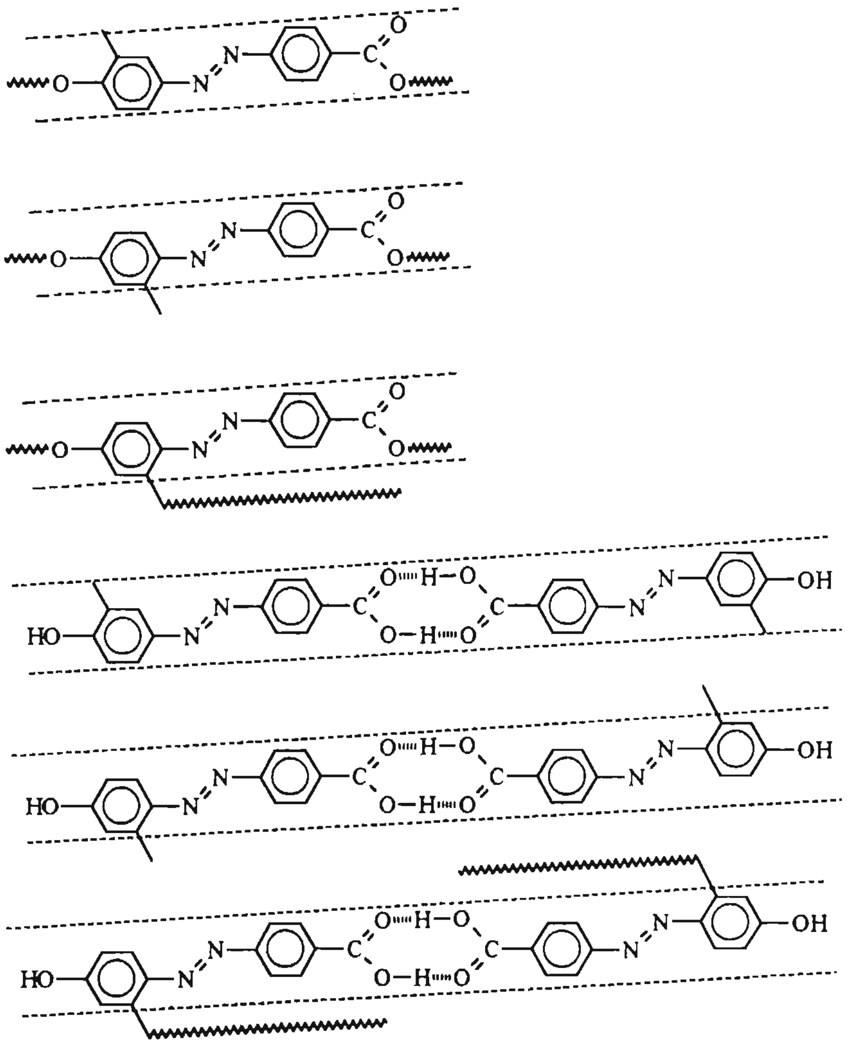
Set	Polymer	Phase transitions (°C)
1	**Va**	K 265 N 382 I
	VIIa	K 276 N dec.>300
2	**Vb**	K 258 N dec.>300
	VIIb	K 242 N 299 I
3	**Vc**	K 228 N dec.>320
	VIIc	K 224 N 285 I
4	**Vd**	K 135 N 262 I
	VIId	K 175 S 202 N 280 I
5	**Ve**	dec.> 200; (N)#
	VIIe	K 156 N 260 I

where,
K = crystal
N = nematic phase
I = isotropic
# obtained by rapid melting

Table 5 provide the PLM data of MCLCPs (polymers **Va-e**) and SCLCPs (polymers **VIIa-e**). The polymers are divided into five sets in Table 5 based on the type of substituent. Set 1 represents the polymers having no substituent. Polymers of Set 2 and 3 are having a methyl substituent attached to (a) the carbon atom adjacent to ester group, (b) the carbon atom adjacent to azo group respectively. Both set 4 and set 5 represents the polymers having $-C_{15}$ n-alkyl substituent attached to the carbon atom adjacent to azo group. However, the $-C_{15}$ substituent of set 4 polymers is saturated chain while the substituent of set 5 is having olefinic unsaturation.

From this table it can be noted that the crystal → mesophase transitions of SCLCPs are close to or more than that of MCLCPs. The higher transition temperatures for SCLCPs can be explained as due to the physical crosslinking introduced by the free carboxylic acids in SCLCPs which is absent in MCLCPs. As all the polymers have the necessary molecular rigidity and structural anisotropy, the only phase observed for all polymers is nematic mesophase except for polymer **VIId** which showed smectic A phase also (see chapter - VI). However, the nematic phase width of MCLCPs are much higher than that of SCLPCs except for the set 5. This is because, in MCLCPs the mesogens form the backbone which when oriented once will maintain the order till isotropization occurs whereas in SCLCPs, at high temperatures segmental motion of the polyacrylate backbone is high enough to break the orientational order required to maintain the nematic phase and hence the early isotropization. But the isotropization temperature of MCLCPs, except for polymers **Vd** and **Ve**, are higher than that of SCLCPs and this may be explained as due to the higher phase stability of MCLCPs. It is difficult to compare the polymers Ve and VIIe (set 5 in table 5) because of the inhomogenity in olefinic unsaturations of the substituent and the presence of crosslinks. However, it can be seen that the extent of crosslinking is higher in MCLCP than in SCLCP and this may be due to the orientation of -C_{15} substituent along the nematic rods^2 leading to more crosslinking in MCLCP. This type of orientation will be difficult in SCLCP. In polymer set 4 of Table 5 the influence of substituent on the type of phase formed is demonstrated by polymer **VIId**. But the forces involved in the mesophase formation of polymers **Vd** and **VIId** are different. In the case of polymer **VIId** the -C_{15} substituent brought down the mesophase transition temperature low enough to maintain the smectic layers formed by hydrogen bonded carboxylic acid dimers (see scheme 23 in chapter - VI) . Whereas in polymer **Vd**, though there is reduction in mesophase transition temperature, the smectic layers cannot be formed due to the energetic preference for orientation along the nematic rods (see scheme 24). The similar observation have been reported by Lenz et al.[2]

Apart from comparing the substituent effect on transition temperatures of MCLCPs and SCLCPs, it would also be interesting to compare the substituent effect on transition temperatures within each class between regio isomers. The regio isomers in MCLCPs are polymers **Vb** and **Vc** in which the methyl substituent is attached to different position and in SCLCPs, polymers **VIIb** and **VIIc**. In polymers **Vb** and **Vc**, though the viscosity difference is mariginal, the mesophase transition temperature differ by 30°C and same is the case with polymers **VIIb** and **VIIc** where the viscosity of polymer **VIIc** is higher than that of polymer **VIIb** but the LC transition temperature is low by about 20°C. This can be explained from the point that, as in naphthalene systems reported by Gray[3], the replacement of hydrogen atom by a substituent X does not broaden the molecule (when molecular perimeter is defined by the dashed line) and alter the transition temperature when the space is effectively filled. It can be noted from Scheme 24 that the methyl group in polymer **VIIb** effectively fill the space whereas in polymer **VIIc**, at its most stable conformation, the methyl group is projecting outside the molecular perimeter thereby broadening the molecule. Moreover, the transition temperatures of the polymers with $-C_{15}$ substituent are not reduced so much as expected for $-C_{15}$ substituent when compared to the methyl group substituted polymers. It is reported by Noel et al.[4] that the reduction in transition temperatures are low for long chain substituents than expected. This phenomenon can be explained as due to the orientation of n-alkyl chain along the molecular long axis of the polymer thereby causing minimum disruption to the LC alignment. In effect, the long alifatic substituents favours the stabilization of LC phase.



Vb

Vc

Vd

VII

VIIc

VII

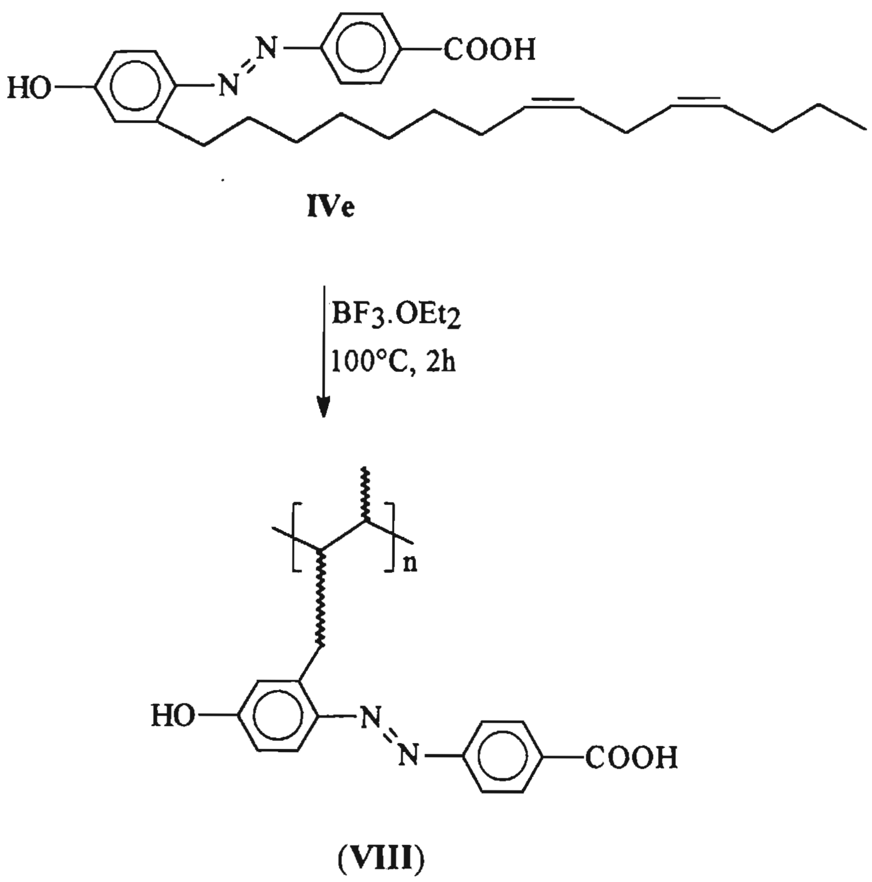
Scheme 24 : The effect of subtituent on transition temperatures

7.3 SYNTHESIS AND CHARACTERIZATION OF A NOVEL LIQUID CRYSTAL POLYMER CONTAINING IN-BUILT SPACER.

As a continuation of the synthesis of SCLCPs, it is also proposed to carry out the synthesis and characterization of a SCLCP containing in-built spacer unit from 4-[(4-hydroxy-2-pentadecadienylphenyl)azo]benzoic acid (**IVe**) by cationic polymerization of side chain olefinic unsaturations. This is interesting from the point that the monomer is obtained from cardanol which is a renewable natural product obtained from the plant Anacardium occidentale L. It has been shown that cardanol has interesting structural features for chemical transformation and polymerization into high performance polymers.[5-9] The chemical modification of cardanol into **IVe** was given in chapter - II. **IVe** was polymerized using boron trifluoride - diethyl etherate ($BF_3.OEt_2$) and found that the polymer show LC property. [In order to avoid confusion, **IVe** will be called as 4-cardanylazobenzoic acid (**IVe**) and the polymer as poly(4-cardanylazobenzoic acid) (**VIII**)]. The of synthesis of polymer **VIII** is illustrated in the scheme 25.

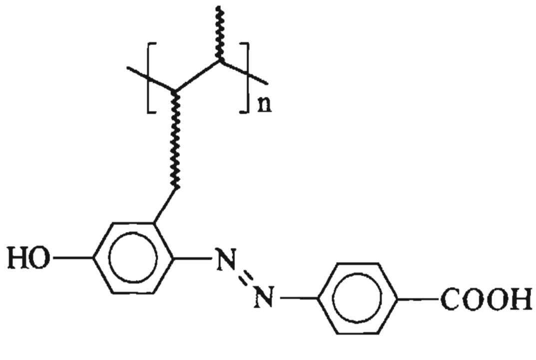
7.3.1 EXPERIMENTAL

4-cardanylazobenzoic acid(**IVe**) was polymerized using $BF_3.OEt_2$ catalyst at 100°C. The polymer was characterized by elemental analysis and spectral methods. IR spectra was recorded using Perkin-Elmer 882 infrared spectrometer and ^1H & ^{13}C NMR from Jeol JNM-EX 90 FT NMR system. UV-Vis spectra was obtained in DMF using Shimatzu UV-160A spectrophotometer. The inherent solution viscosities(η_{inh}) of the polymer was measured using Ubbelode suspended level viscometer at 28°C using o-dichlorobenzene as solvent. The solution concentration used was 0.5 g/dL. The studies on LC properties of **VIII** was performed using DSC and hot stage polarized light microscope (PLM). The DSC used was Du Pont DSC V2.2 A 9900 system under nitrogen and PLM by Leitz 1350 hot stage coupled cross- polarized light microscope. The heating rate used was 20°C/min.



Scheme 25: Synthesis of poly(4-cardanylazobenzoic acid)

Synthesis of poly[4-cardanylazobenzoic acid] (**VIII**) by cationic polymerization: 1 g of monomer **IVa** was dissolved in *o*-dichlorobenzene and 10 mg (1wt%) of $BF_3.OEt_2$ was added. The reaction was continued for 2h at 100°C on an oil bath. The polymer was precipitated in excess carbon tetrachloride, filtered and washed thoroughly with chloroform and dried at 80° C for 12h in a vacuum oven. Yield 0.80 g (80%); dark red solid. Anal. Calcd. for $C_{28}H_{37}N_2O_3$: C, 74.8; H, 8.29; N, 6.23. Found: C, 75.34; H, 7.3; N, 7.12.



(VIII)

i) viscosity : 0.24 dL/g

ii) m.p. (°C) : K 134 N 242 I

iii) UV-Vis (λ_{max}) : 371 nm (ε_{max} = 21 783 $M^{-1}cm^{-1}$)

iv) IR (cm^{-1}) : 3320 (Ar-OH); 3020, 790 (cis -CH=CH-); 2960, 2880 ($-CH_2-$); 1700 (ArCOOH); 1620, 1600 (Ar;C=C); 1440 ($-CH_2-$); 1158 (-N=N-)

v) ^1H NMR (DMSO-d_6) : δ 0.7-3.3 ($-CH_2-$); 4.9-5.5 (-CH=CH-); 6.7-8.3 (Ar)

vi) ^{13}C NMR (DMSO-d_6) : 166.8, 161.6, 155.1, 146.3, 143.0, 131.6, 130.4, 129.8, 129.4, 121.9, 116.8, 116.2, 114.6, 114.1, 31.6, 31.1, 30.8, 29.1, 28.7, 28.6, 28.3, 26.9, 26.6, 25.8, 25.1, 22.1, 13.8 ppm.

7.3.2 RESULTS AND DISCUSSION

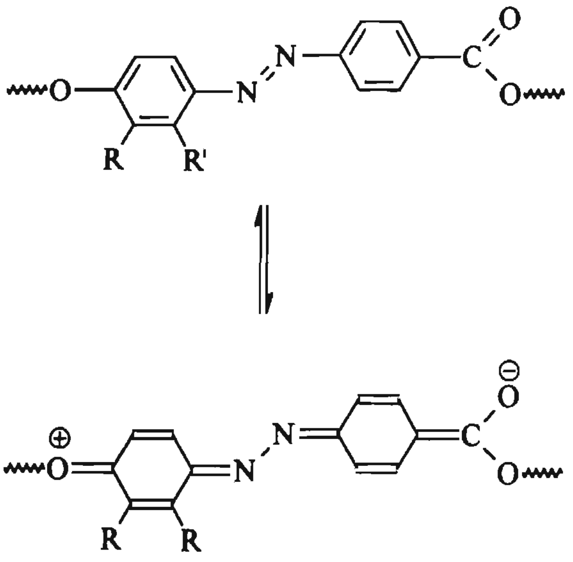
Polymer **VIII** was prepared by cationic polymerization of **IVe** using modified procedure of Rosy et. al.,[9] and was precipitated in carbontetrachloride because the polymer is freely soluble in methanol which is a common solvent for most of the polymer precipitation. The unreacted monomer and oligomer were removed by washing the polymer with chloroform. The polymer is soluble in polar solvents such as methanol, acetone, ether, DMF, *o*-dichlorobenzene, pyridine, triethylamine etc., and swells in solvents like chloroform, aromatic hydrocarbon solvents etc. The inherent viscosity of polymer **VIII** in *o*-dichlorobenzene at 28°C was found to be 0.24 dL/g (concentration : 0.5 g/dL).

The formation of polymer **VIII** was supported by elemental analysis, IR, ^1H & ^{13}C NMR spectroscopy. The calculated values of elemental analysis agree well with the experimental value. IR spectra (Figure 67) of polymer **VIII** showed[10] the characteristic hydroxyl group peak at 3320 cm^{-1} and alkyl $-CH_2-$ vibrations at 2960 and 2880 cm^{-1}. The aromatic group frequencies and carboxylic acid peak appeared at 1620, 1600 and 1700 cm^{-1} respectively. Though there is decrease in *cis* olefinic peaks at 3020 and 790 cm^{-1}, the change is not so large which indicates that not all double bonds are used-up on polymerization. The ^1H NMR peaks (Figure 68)broadened on polymer formation[11] but the olefinic resonance peaks did not vanish completely due to the presence of unreacted double bonds. However, the conclusive evidence of polymer formation is provided by ^{13}C NMR spectroscopy (Figure 69). When compared[12] to the ^{13}C NMR of **IVe**, polymer **VIII** has five new peaks in the region of 32-12 ppm indicating five different, new carbon centers have been produced on polymerization. The increase in the number of carbon centers can be possibly attributed to the formation of saturated carbon centers. Moreover, when compared to **IVe,** there is no Friedel-Crafts type substitution to aromatic ring under Lewis acidic condition is apparent from the unaltered aromatic carbon resonances. The UV-Vis spectroscopy of polymer **VIII** (Figure 68) have one absorption peak at 371 nm (ε_{max} = 21 783 M^{-1} cm^{-1}).[11]

The DSC thermogram of polymer **VIII** is given in Figure 70 which showed two endothermic and an exothermic peaks.[13] The first endotherm at 130°C is the crystal to mesophase transition which is immediately followed by an exotherm at 140°C which may be due to the crosslinking of olefinic unsaturations under organized environment. The second endotherm at 230°C corresponds to isotropization. The polymer started degrading soon after isotropization which is clear from the steep raise in base line. PLM observation[13] agree well with DSC trace. The polymer started melting at 134°C and exhibited schlieren texture characteristic of nematic phase (Figure 71). The polymer isotropized at 236°C and darkened soon after isotropization. It is reported[14] that the method of crosslinking is used to freeze the relaxation of LC orientation. It is expected that this polymer can also be used for such studies where the freezing of LC orientation in crosslinked structure is required.

7.4 A STUDY ON NON-LINEAR OPTICAL (NLO) PROPERTY OF AZOBENZENE COMPOUNDS

The technology of non-linear optics requires materials that interact with light in a non-linear fashion when they are illuminated by high intensity radiation. Oscillating electric field of an incident light beam causes electron clouds in the non-linear materials to move in response forming an oscillating dipole. This creates a secondary field that oscillates not just at the original frequency but also at multiples of frequency; the so called second and third hormonic and so on.[15,16] Organic compounds containing dipolar groups in a push-pull arrangement are found to exhibit non-linear optical(NLO) behaviour. Hall et al.[17] reported that the UV-Vis spectroscopy can be used as a method to predict the NLO property of a material and stated that the absence of absorbance, in an UV-Vis spectra of a compound, above 600 nm indicate that the compound may be NLO active. It can be seen from the UV-Vis spectra of all azobenzene monomers and soluble polymers, presented in this study, showed no absorbance above 500 nm. This is a positive indication that these monomers and polymers may exhibit NLO property. NLO copolymers containing similar azobenzene unit have been reported by S'hreen et al.[18] Moreover, all the monomers and polymers have the structural features expected for NLO materials as shown in scheme 26. The typical UV-Vis spectrum is given in Figure 68.



Scheme 26: dipolar structure of the azobenzene compounds

7.5 CONCLUSION

The effect of substituents on phase transition temperatures of MCLCPs and SCLCPs have been compared. The cause for the alteration in transition temperatures of regio isomeric azobenzene polymers is also discussed. A novel side chain polymer containing in-built spacer unit was prepared by cationic polymerization and characterized using elemental analysis, spectral methods such as IR, ^{1}H &^{13}C NMR spectroscopy and viscosity. The solubility studies showed that the polymer is soluble in almost all polar solvents. The polymer is mesomorphic and showed schlieren texture characteristic of nematic phase. The probable existance of NLO activity, in all the monomers and polymers used for this study, based on their UV-Vis spectroscopy is highlighted.

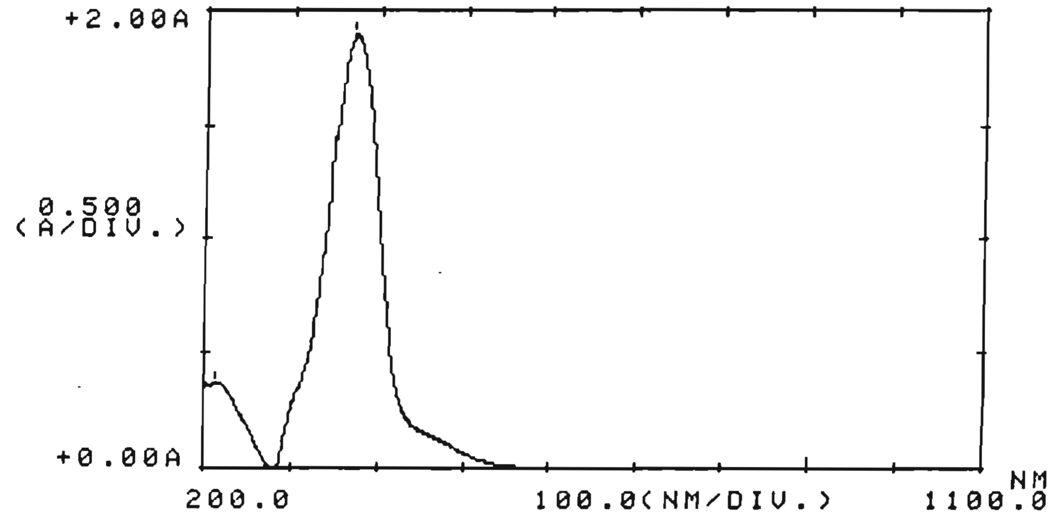


Figure 66: UV-Vis spectrum of polymer VIII

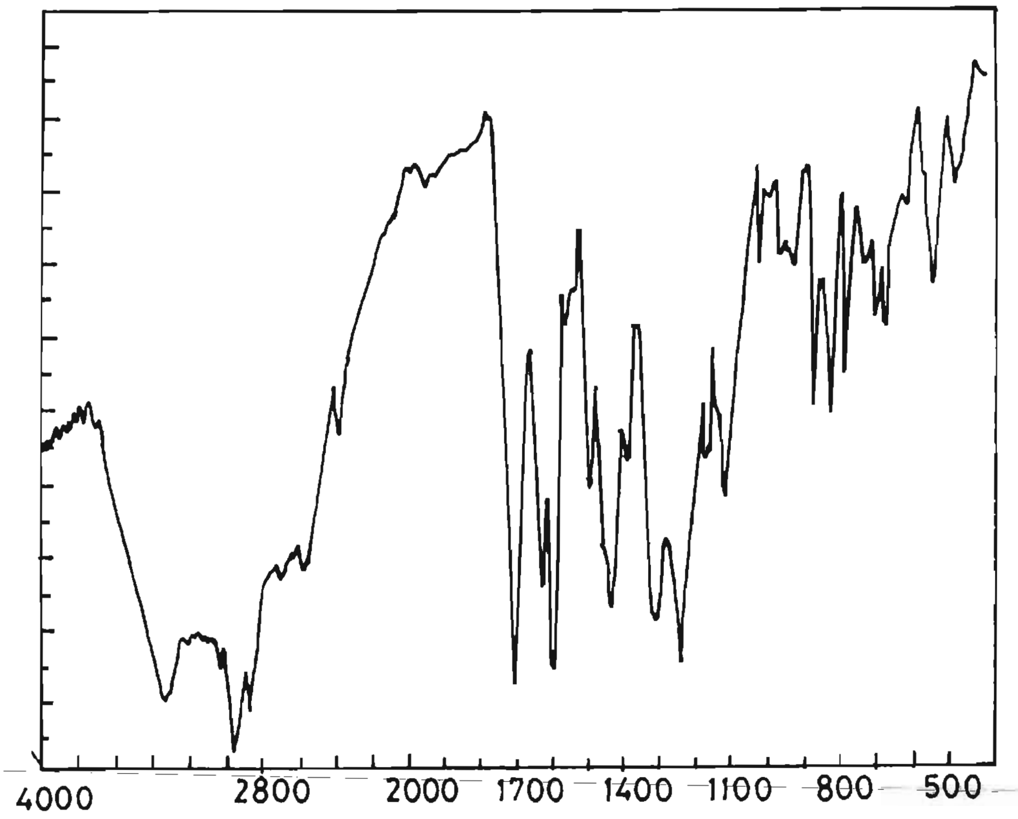


Figure 67: IR spectrum of polymer VIII

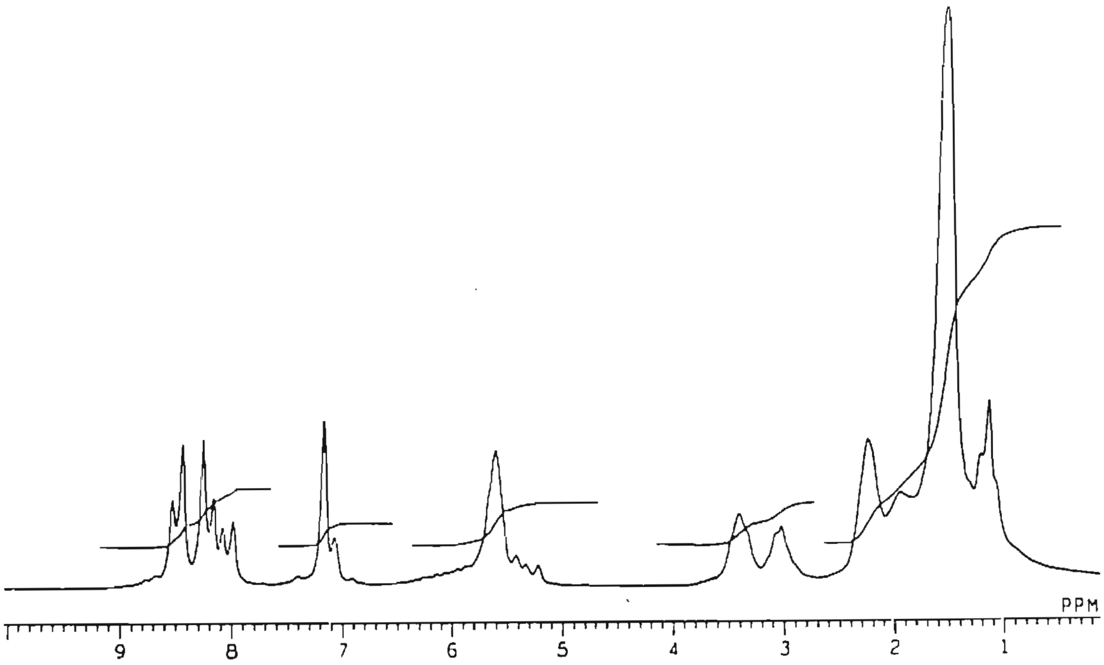


Figure 68: ^{1}H NMR spectrum of polymer **VIII**

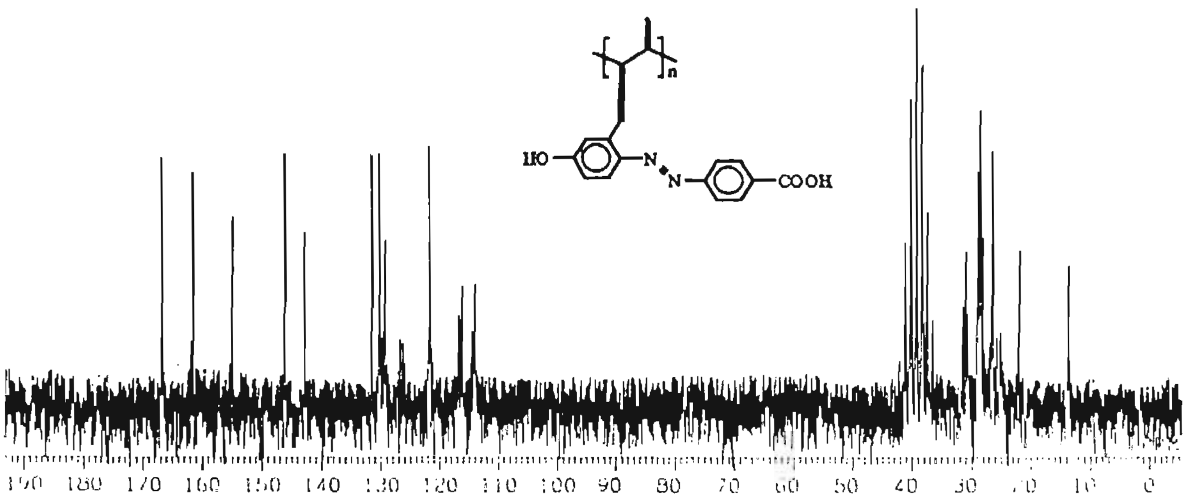


Figure 69: ^{13}C NMR spectrum of polymer **VIII**

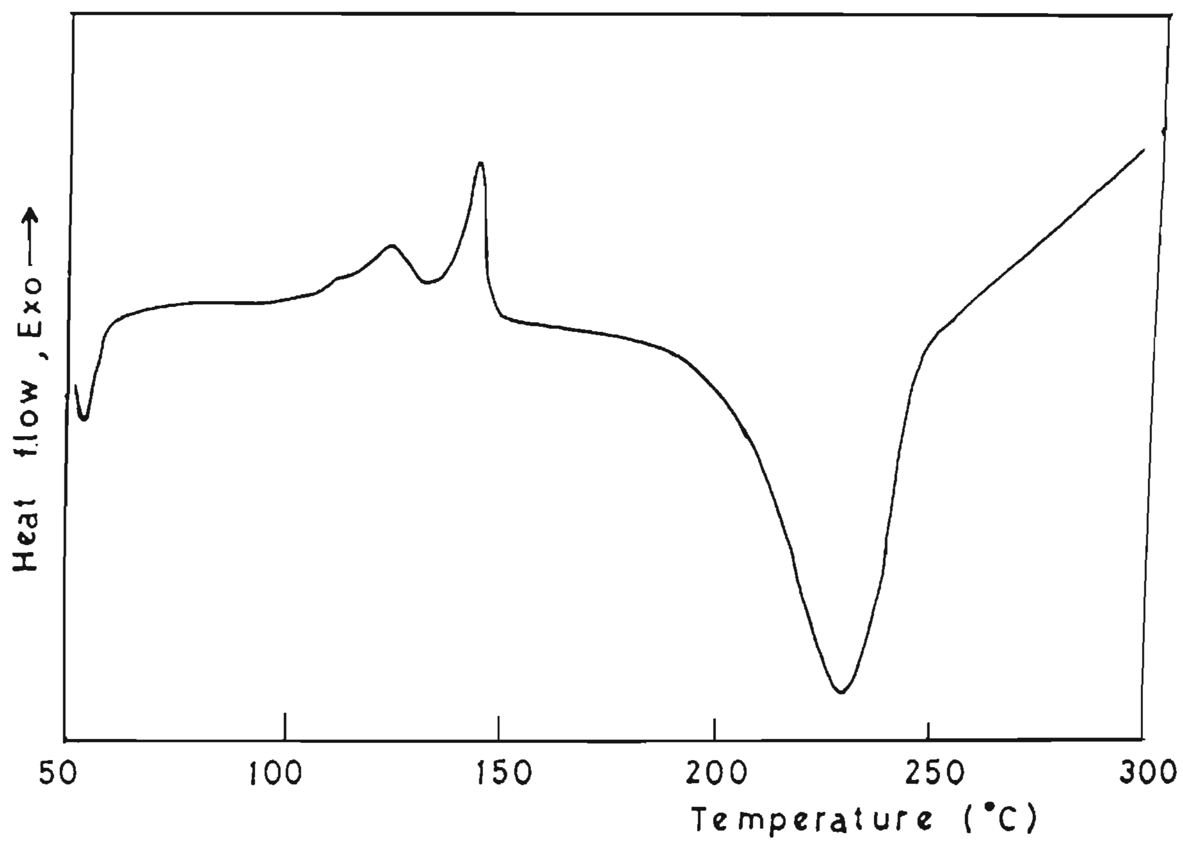


Figure 70: DSC thermogram of polymer VIII

Figure 71: Schlieren nematic texture of polymer VIII at 138°C (X 200)

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SUMMARY AND OUTLOOK

Azobenzene rigid rod monomers and liquid crystal polymers offer vast scope for production of speciality products. This is evident from the large number of scientific publications and patents emerging in this area. Azobenzene compounds can be prepared conveniently with required structural features for intended applications. Thus, p-hydroxyphenylazobenzoic acid derivatives without and with substiutents have been synthesized. The monomers were self polycondensed to obtain main chain LCPs. The monomers were further functionalized with acrylate group and polymerized using radical initiator to obtain side chain LCPs. The monomers were characterized by elemental analysis, IR, UV-Vis, ^{1}H &^{13}C NMR etc., and found that the data agree with the assinged structure. Main chain liquid crystal polymers were characterized using inherent viscosity, elemental analysis and IR spectroscopy. Solubility of these polymers are limited to acidic solvents such as conc.sulphuric acid except for the polymer having saturated -C_{15} side chain which is soluble in polar solvents. All the main chain polymers showed nematic phase only and the presence of substituents have pronounced impact on phase transition temperatures. Thermal stability of these polymers are high except for polymers having long alkyl substituent. With the exception of a polymer with unsaturated olefinic substituent, all the other polymers are crystalline.

Side chain polyacrylates were characterized by solubility, viscosity, IR, UV-Vis, ^{1}H & ^{13}C NMR spectroscopy. Polymers are soluble in dipolar solvents such as DMSO, DMF etc. All the side chain polymers exhibited nematic phase except the polymer having saturated -C_{15} n-alkyl substituent which showed smectic A phase in addition to nematic phase. The probable mechanism for the formation of smectic A phase is explained. As in the case of MCLCPs, the substituents showed notable influence on transition temperatures.

The solubility of MCLCPs are poor when compared to side chain polymers. But the transition temperatures of SCLCPs are higher than that of their respective MCLCPs, this is explained as due to the interchain hydrogen bonded carboxylic acid dimers of SCLCPs. In both the cases, polymers having -C_{15} substituent showed better solubility and lower transition temperatures. The probable reason for the difference in transition temperatures between polymers containing methyl substituents, at different positions, is explained.

A novel side chain LC polymer was obtained by cationic polymerization of a monomer containing olefinic unsaturations in -C_{15} alkyl chain and characterized by usual spectral methods and viscosity. This polymer is soluble in almost all polar solvents. The study on the LC behaviour of polymer showed the texture charcteristic of nematic mesophase. The possibility of stabilization of the LC phase in a crosslinked structure is anticipated here.

The possibility of these monomer and polymers to exhibit nonlinear optical behaviour, due to the presence of hydroxy donor and carboxyl acceptor groups in push-pull arrangement, is highlighted based on the UV-Vis spectroscopic study.

The present study shows that

1. Novel rigid rod monomers and liquid crystal polymers containing azobenzene group can be synthesized in high yields.
2. Introduction of substituents improved solubility and brought down the transition temperatures to the processable range.

3. In MCLCPs even the long n-alkyl substituent could not bring down the temperature and alter the type of LC phase as expected for a -C_{15} side group (due possibly to the orientation of the chain along the long molecular axis).

4. In the case of SCLCPs, the polyacrylate containing-C_{15} saturated n-alkyl substituent tend to give smectic A phase in addition to nematic phase is due to the presence of inter chain hydrogen bonded carboxylic acid dimers which give rise to the layered structure of smectic A phase.

5. SCLCPs show better solubility in a range of dipolar solvents whereas MCLCPs are soluble only in highly acidic solvents except the polymer with long alkyl substituent which is soluble in polar solvent. But the transition temperatures of SCLSPs are higher than that of their main chain analogues.

6. These monomers and polymers are expected to exhibit nonlinear optical property as seen from their UV-Vis spectra.

7. The polymer obtained by cationic polymerization, of olefinic side chain, showed nematic phase only and this may be due to the inhomogenous distribution of in-built spacer group.

Hence the possibilities for the future developments are:

1. The novel azobenzene monomers of p-hydroxybenzoic acid type used in this study are amenable to modification to obtain new monomers and polymers with speciality properties such as LC behaviour, light modulations, NLO properties etc.

2. Introduction of chiral groups, either in main chain and/or in the side chain, would give rise to polymers exhibiting chiral smectic phases and cholesteric phase which are used in high technology areas such as telecommunications, high speed data processing etc.

3. Physico-mechanical properties of copolymers containing LC azobenzene groups can be altered by light of specific wave lengths thereby the polymers can find use in smart materials development.

4. As the azobenzene group can undergo *cis-trans* photoisomerization, there is a strong possibility for the development of materials for information storage devices, holography etc.

In summary, the data generated in this present work indicate that high performance materials with improved properties could be developed from the polymers containing azobenzene group with polymerizable functional groups. It would thus strengthen the base for the future development of this class of polymeric materials for advanced applications.