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**LA THÈSE A ÉTÉ
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SYNTHESIS OF CHIRAL LIQUID CRYSTALLINE SIDE-CHAIN POLYMERS:

A NEW APPROACH

By

Kevin Charles Taylor

A thesis submitted to the School
of Graduate Studies in partial fulfillment
of the requirements for the degree of
Master of Science in Chemistry

Department of Chemistry
University of Ottawa, Ottawa, Ontario, Canada

Prof. J.M.J. Fréchet
Research Supervisor

Kevin C. Taylor

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in memory of
my father,
Charles Ernest Taylor

ABSTRACT

Liquid crystalline polymers containing a chiral smectic C phase can exhibit ferroelectric behavior, making them of great commercial interest in the development of flat electro-optic display devices. While the ferroelectric phase is well known in non-polymeric liquid crystals, display cells are difficult to produce because the material must be contained in a layer one to three microns in thickness. Polymeric liquid crystals are readily cast into very thin, uniform, dimensionally stable films, thus greatly simplifying the manufacture of large display cells. To date there is only one reported example of a liquid crystalline polymer exhibiting ferroelectric properties.

The goal of this work was to make new, potentially ferroelectric, liquid crystalline polymers. However, it soon became obvious that reported synthetic methods were inadequate in terms of utility and efficiency. Accordingly, a new methodology was developed which greatly simplifies the synthesis of a variety of side-chain liquid crystalline polymethacrylates.

In the final synthetic step, the dicyclohexylcarbodiimide coupling of 10-methacryloyloxydecanoic acid with an alkyl 4-hydroxyphenyl 4-carboxy benzoate efficiently gives a methacrylate monomer which is readily polymerized by standard methods. The benzoate moiety can readily be substituted for other hydroxy terminated molecules that promote liquid crystalline phases. The previously unreported 10-methacryloyloxydecanoic acid was prepared in excellent yield from 10-hydroxydecanoic acid using a highly selective benzyl ester protection scheme. Four new polymers and one methyl

methacrylate copolymer were prepared in this manner.

Using the methodology developed in this work, a novel liquid crystalline polymethacrylate incorporating a chiral paired mesogen was prepared. To date, only a single achiral paired mesogen side-chain polymer has been reported. The corresponding methyl methacrylate copolymer was also prepared in this work.

Thus, a new synthesis of side-chain liquid crystalline polymethacrylates has been developed which offers significant advantages over previously reported methods. It has been used to prepare new chiral liquid crystalline polymers including a novel chiral paired mesogen polymer.

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LIST OF ABBREVIATIONS

AIBN	2,2'-azo-bis-isobutyronitrile
DCC	dicyclohexylcarbodiimide
DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
DSC	differential scanning calorimetry
Et	ethyl
HMPA	hexamethylphosphoramide
HPLC	high pressure liquid chromatography
IR	infrared
Me	methyl
NMR	nuclear magnetic resonance
PTC	phase transfer catalysis
R_f	retention factor
T_g	glass transition temperature
THF	tetrahydrofuran
TLC	thin layer chromatography

INTRODUCTION

The liquid crystalline state was first discovered in 1888 by Reinitzer in his studies of cholesteryl benzoate (1). It was not until 1971, however, that the first polymeric liquid crystals were reported (2). Since that time, a tremendous amount of research in polymeric liquid crystals has been fueled by both industrial and academic interest. Industrial applications include high strength fibers such as Dupont's Kevlar[®], based on poly(p-phenylene terephthalamide) (3), while academic interest has been driven by the theoretical significance of the structural order in fluid phases. More recently, the discovery of liquid crystals with potential ferroelectric properties has created a new research thrust. Of particular interest is the synthesis of liquid crystalline polymers with potential ferroelectric properties, the area in which this thesis is concerned.

In order to properly understand the liquid crystalline phases possible in polymers, it is necessary to first discuss these phases in low molecular weight liquid crystals. This will be followed by a discussion of the principles involved when connecting liquid crystal molecules to a polymer, and finally by a summary of the synthetic routes known in the preparation of liquid crystalline polymers.

The liquid crystalline state occurs primarily with rod-shaped molecules which are anisotropic in some property. Liquid crystalline phases, or mesophases, which occur in solution are called lyotropic mesophases, while those that form in the solid state upon heating or cooling are called thermotropic mesophases. Thermotropic liquid

crystalline compounds are further classified depending on the stability of the mesophase. If the mesophase is observed directly on heating, it is thermodynamically stable and is called enantiotropic. If the mesophase is observed on cooling only, it is metastable and thus monotropic.

Thermotropic liquid crystalline compounds, or mesogens, are usually rod-shaped, with rigid aromatic units connected by rigid central linkages such as $-\text{COO}-$, $-\text{CH}=\text{CH}-$, or $-\text{N}=\text{NO}-$, and with an aliphatic tail on both ends. Cholesteric liquid crystals are an exception. Examples are shown in Figure 1. Lyotropic liquid crystalline compounds include combinations such as sodium dodecyl sulfate/water/1-alkanol.

Two major types of mesophases, the nematic and smectic states, exist for thermotropic liquid crystalline compounds. In both states the major molecular axes are approximately parallel, but only in the smectic state do molecular layers occur. In the nematic phase there is a high degree of long range orientational order but no long range translational order (Figure 2). The liquid crystal molecules slide easily past one another, but more or less retain their parallelism. In some nematics regions of about one hundred molecules, called cybotactic groups, may be arranged in layers (4).

The cholesteric mesophase is a nematic type of liquid crystal in which the mesogens are optically active. On a local scale, ordering is very similar between nematic and cholesteric mesophases, but on a larger scale a helical packing of the mesogens is evident in the latter (Figure 3). This helical packing is periodic with a characteristic pitch. With optically active molecules the pitch has a

Figure 1

Examples of Liquid Crystalline Molecules

Liquid Crystalline
Temperature Range °C

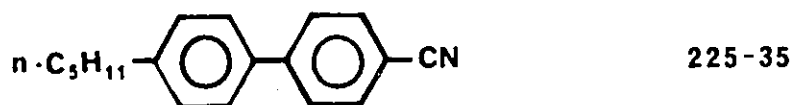
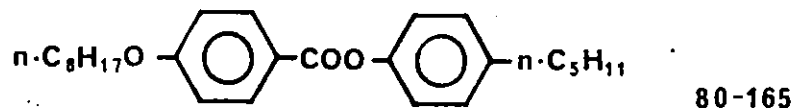
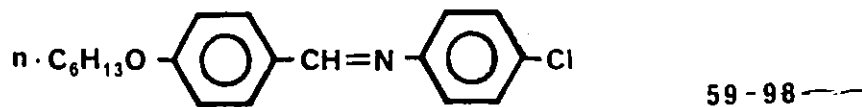
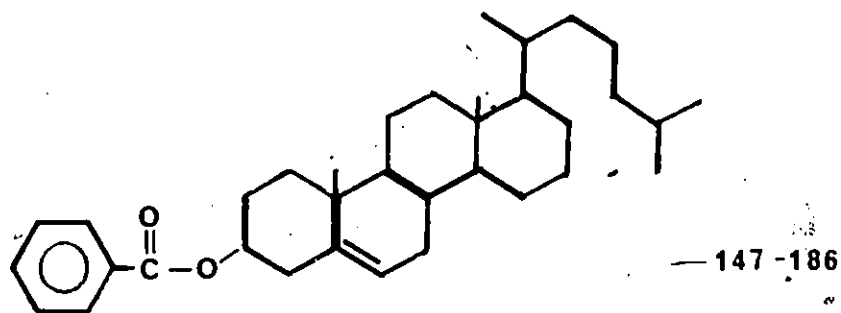
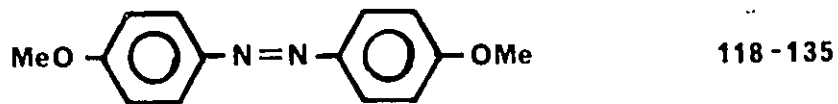


Figure 2

Transitional Order

CRYSTAL



NEMATIC



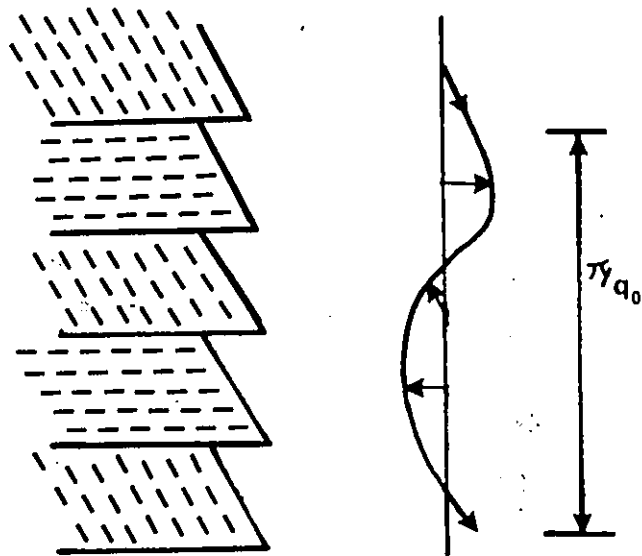
ISOTROPIC



Transition in packing from a highly ordered crystalline state to the nematic liquid crystalline state to an unordered isotropic liquid.

Figure 3

Cholesteric Order of Mesophase of Pitch q_0



finite value and leads to the cholesteric mesophase. With optically inactive or racemic compounds the pitch is infinite and results in the nematic mesophase. The energy difference between cholesteric and nematic mesophases is very small (5), so that addition of small amounts of a cholesteric liquid crystal molecule to a nematic mesophase generally results in a cholesteric mesophase (6).

Historically, the cholesteric mesophase was named because it was first discovered in cholesteric esters. For non-steroidal optically active mesogens forming this mesophase, the term chiral nematic is more appropriate, and also emphasizes the relationship between the nematic and the cholesteric mesophases.

The second major type of mesomorphic order occurs in the smectic state. This mesophase retains the approximate parallelism of major molecular axes, but has the added presence of molecular layers. These layers are similar to the monolayers formed by long chain fatty acids in water. The additional order in the smectic phase makes it generally more viscous than the nematic phase. There are at least eight smectic mesophases, varying in the organization of mesogens in the layers.

In the smectic A phase, the molecules are randomly tilted in each layer, with the tilt direction averaging to zero. Mesogens can move around easily in the layer, but no long range order in the layer occurs (Figure 4a).

The smectic C phase is very similar to the smectic A phase, except for a uniform tilting of the molecular axes in each layer (Figure 4b). Tilt angles of up to 45° may occur, and in some cases the tilt angle varies with temperature.

Figure 4

Order in Smectic A and C Phases

a. Smectic A

b. Smectic C

The remaining smectic phases B, D, E, F, G, H, I are classified based on the order present and the tilt direction, if present, within each layer. Excellent reviews on the subject have been published (7,8).

For example, the smectic B phase is characterized by a layer arrangement of the mesogens in a hexagonally close-packed array in which their long axes are perpendicular to the plane of the layer. The closely related smectic G phase has similar hexagonal packing but the liquid crystal molecules are tilted relative to the plane of the layer.

Of particular interest in tilted smectic phases are the ferroelectric properties that they can exhibit when the liquid crystal molecules are optically active. It is important to remember that in an optically active, tilted smectic phase, the structural asymmetry of the liquid crystal molecules causes a twist of the tilt direction as one moves from layer to layer. In each layer, the optically active liquid crystal molecules are arranged so that their net dipole moments all point in the same direction. This leads to a net dipole moment, making each layer ferroelectric. The macromolecular helical arrangement, however, leads to a cancellation of ferroelectric properties in the bulk phase. In theory such properties are possible for the smectic C, I, and F phases. Ferroelectric behavior was first suggested for smectic C phases by Meyer and co-workers in 1975 (9).

The ferroelectric phase has very important applications as a fast-switching, bistable electro-optic display (10,11). Such phases, when oriented with the layers perpendicular between electrode cell plates, can switch from light transmitting to non-transmitting and




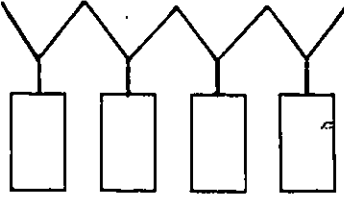
vice versa in microseconds following low voltage pulses. The device is bistable, meaning that it remembers the last on-off state in the absence of an electric field. Possible applications of such a device include flat television display screens, CRT screens, and information storage devices. While the ferroelectric phase is now well known for liquid crystals, display cells remain difficult to produce because bistable operation can only occur in devices that are 1 to 3 microns thick (12). Creating large cells of a uniform thickness of these dimensions provides severe technical problems. For this reason, polymeric liquid crystals are of interest, as the technology already exists for forming such thin, uniform films. Once formed they would be dimensionally stable.

With such promising applications it is tempting to examine the synthetic routes to polymers showing smectic C mesophases. First, however, the factors involved in connecting liquid crystal molecules to a polymer backbone must be discussed.

There are two general methods by which mesogenic moieties can be incorporated into a polymer. Figure 5 illustrates a main chain polymer in which the monomer units, containing the mesogen, are linked head to tail. The rigid, rod-like monomers create a rigid, rod-like macromolecule. The resulting main chain polymeric liquid crystal is of interest primarily for its mechanical properties, as very high strength fibres may be formed (13). Main chain liquid crystal polymers generally have very high temperature liquid crystalline phases (14) and so are not of great interest for display devices, where a mesophase at room temperature is desired. These polymers have been extensively reviewed (15).

Figure 5

Types of Liquid Crystalline Phases

MONOMER UNIT	POLYMER	PHASE BEHAVIOR
	 <p>main chain</p>	thermotropic or lyotropic
	 <p>side chain</p>	thermotropic

Mesogenic monomers may also be linked in a head to head arrangement, where the mesogenic moieties are attached to a polymer as pendant groups (Figure 5). Such macromolecules are known as side-chain or comb polymers. It was soon discovered that linking a mesogenic moiety directly to a polymer backbone rarely produced polymers with a liquid crystalline phase, even though the monomers themselves existed in the liquid crystalline state (16,17). Apparently, attaching the mesogen directly to the polymer greatly reduces its range of motion, and makes parallel alignment of mesogens difficult. This and steric interaction results in stiffening of the polymer chain and an increase in the glass transition temperature (T_g). The T_g is usually so high that only a monotropic liquid crystalline phase is observed, if one is observed at all.

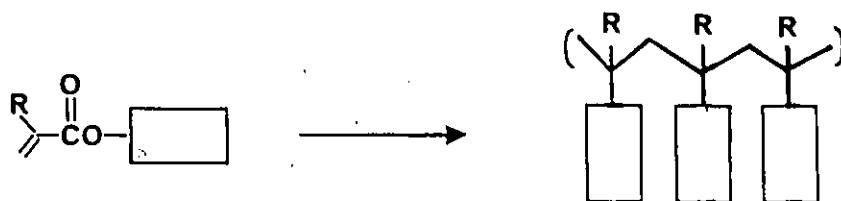
This problem was overcome by Finkelmann in 1978 by the introduction of a flexible spacer chain, typically n-alkyl, between the mesogenic moiety and the polymer backbone, thus partially decoupling the polymer motion from the motion of the mesogenic side group (18,19). This allows the polymer to adopt a statistical chain conformation while the mesogenic groups can adopt an anisotropic ordering. Complete decoupling, of course, does not occur and polymer properties are dependent on spacer length.

Side-chain liquid crystalline polymers can show mesomorphic behavior at temperatures close to room temperature. For this reason they are of much more interest as materials for electro-optic display devices than their main-chain counterparts. Typically, they are made by two general methods: addition polymerization or polymer modification (Figure 6).

Figure 6

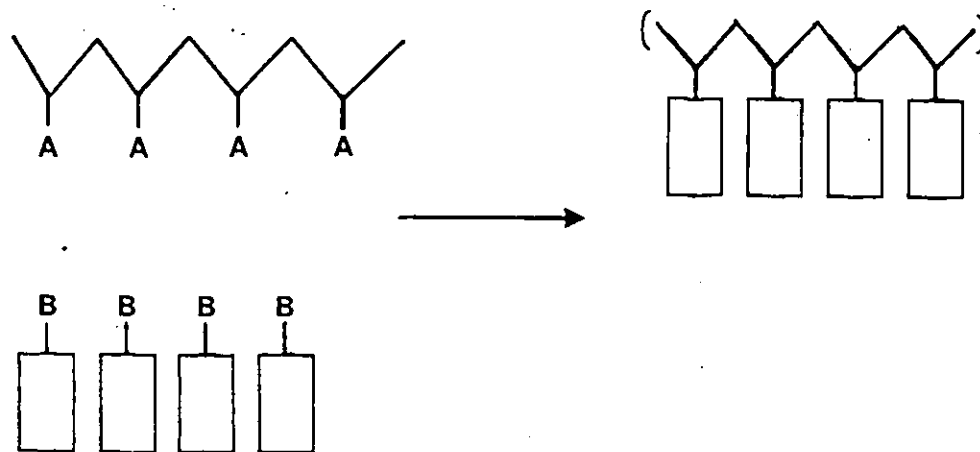
Side-Chain Liquid Crystalline Polymers

ADDITION POLYMERIZATION



R = H, Me, Cl

POLYMER MODIFICATION



 = Mesogenic group

The first examples of polymer modification involved the reaction of poly(acryloyl chloride) with 4-hydroxybiphenyl or 4-hydroxy azobenzene (20,21,22). Polymer quality was generally poor due to side reactions, and this type of route is seldom used at present.

Polymer modification has been used extensively for the synthesis of side-chain polysiloxanes from poly(oxy(methylsilylene)) and vinyl substituted mesogenic monomers in the presence of a platinum (IV) catalyst (23-26). Figure 7 outlines the reagents used, and some selected examples. Polysiloxane side-chain polymers tend to have the lowest T_g values when compared to other polymers with similar side-chains. Yields have not been reported in syntheses published to date, shedding doubt on the utility of the synthetic routes employed.

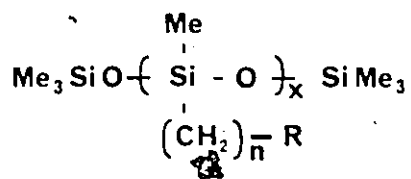
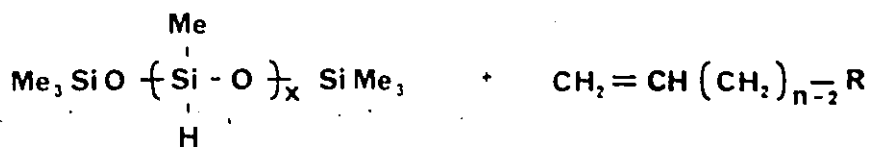
Polymer modification using phase-transfer catalysis has been explored by Keller. He has reacted ω -bromoalkyl esters with sodium polyacrylate (27), sodium polyitaconate (28) and poly(methyl vinyl ether-co-disodium malate) (29) under phase-transfer conditions to obtain polymers with liquid crystalline properties. The polyacrylate synthesis is shown in Figure 8. Yields for these phase-transfer reactions range from 15 to 25%.

Recently, addition polymerization of epoxide-containing monomers has produced poly(ethylene oxide) oligomers with side-chain mesogenic groups (30). Degree of polymerization is very low, however, with the oligomers containing a maximum of about twelve repeating units.

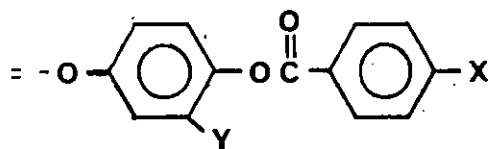
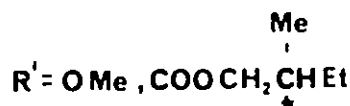
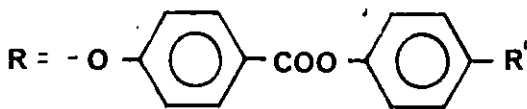
Acrylates, methacrylates, and 2-chloroacrylates are the most extensively used monomers for the synthesis of side-chain liquid crystalline polymers because they are readily transformed into high molecular weight polymers with low T_g values (31).

Figure 7

Polymer Modification of Poly(oxy(methylsilylene))



$n = 3, 4, 5, 6, 10, 11$

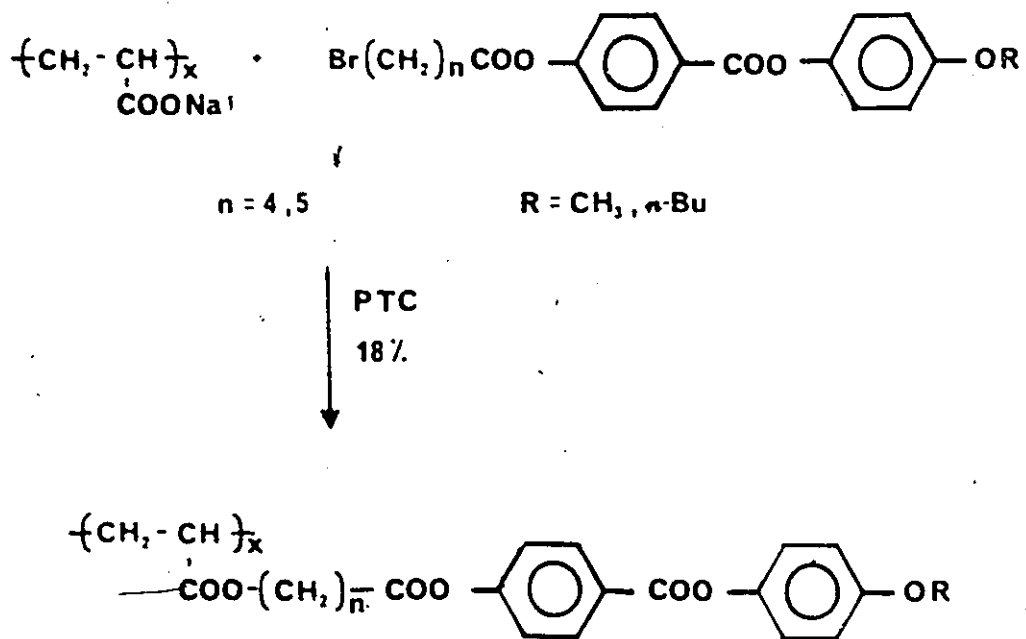


Y = H, Me

X = CN, OMe

Figure 8

Polymer Modification by Phase-Transfer Catalysis

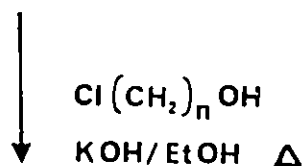
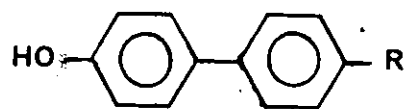


The first monomer synthesis incorporating a spacer chain was reported by Finkelmann in 1978 (18). A biphenyl moiety acted as the mesogenic group, separated by either a 2 or 6 carbon spacer chain from poly(methyl methacrylate). The synthetic route, which is outlined in Figure 9, was reported without yields or product characterization and is not repeated in the literature. A similar route has been reported by Shibaev (32) and is shown in Figure 10. Reported yields are from 60 to 70%, but the method is applicable only to mesogens which are stable to strongly basic conditions, such as p-alkoxy substituted biphenyls. Several other synthetic routes exist for the synthesis of biphenyl mesogenic monomers (32,33). Both involve at least five reaction steps, each of generally poor or unreported yields, and include reaction conditions so harsh as to prevent the incorporation of most other types of liquid crystal mesogens. These conditions include Friedel-Crafts acylation, reduction with lithium aluminum hydride, and Wolff-Kischner reduction of ketones. Thus, these reaction sequences are of very limited use in the synthesis of other types of mesogen containing side-chain polymers.

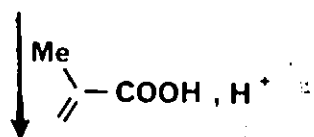
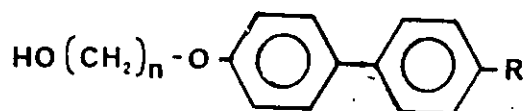
More attention has been paid to synthetic routes involving the phenoxy benzoate mesogen. Figure 11 outlines the synthetic route developed by Ringsdorff for acrylates (34), which has been used in later work for methacrylates and 2-chloroacrylates (35,36). In this case, the mesogen is attached to the spacer chain by an ether linkage. Shibaev (37) claims to have attached phenoxy benzoates to the spacer chain via an ester linkage (Figure 12). The resulting 6-bromo hexanoate ester is reacted with sodium acrylate or lithium acrylate (38) to give the acrylate monomer. However, yields are not reported

Figure 9

Liquid Crystal Acrylate Polymers Containing Biphenyl Mesogens



n = 2, 6



R = H, OMe, OEt, OC₆H₁₃

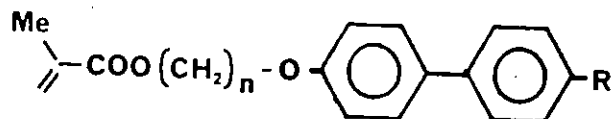


Figure 10

Liquid Crystal Acrylate Polymers Containing Biphenyl Mesogens

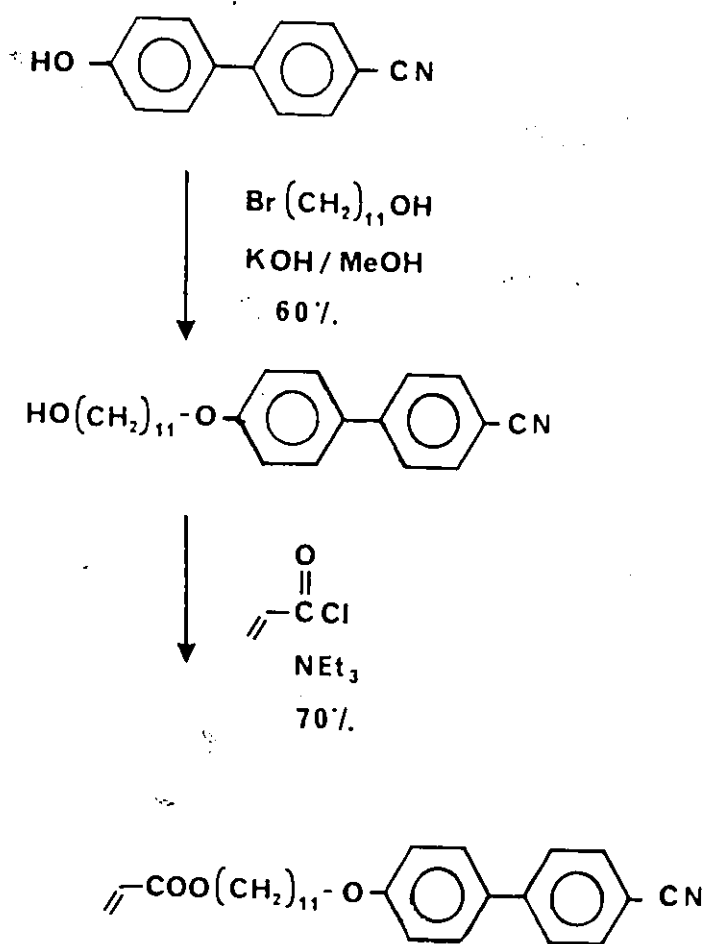


Figure 11

Liquid Crystal Acrylate Polymers with Phenyl Benzoate Mesogens

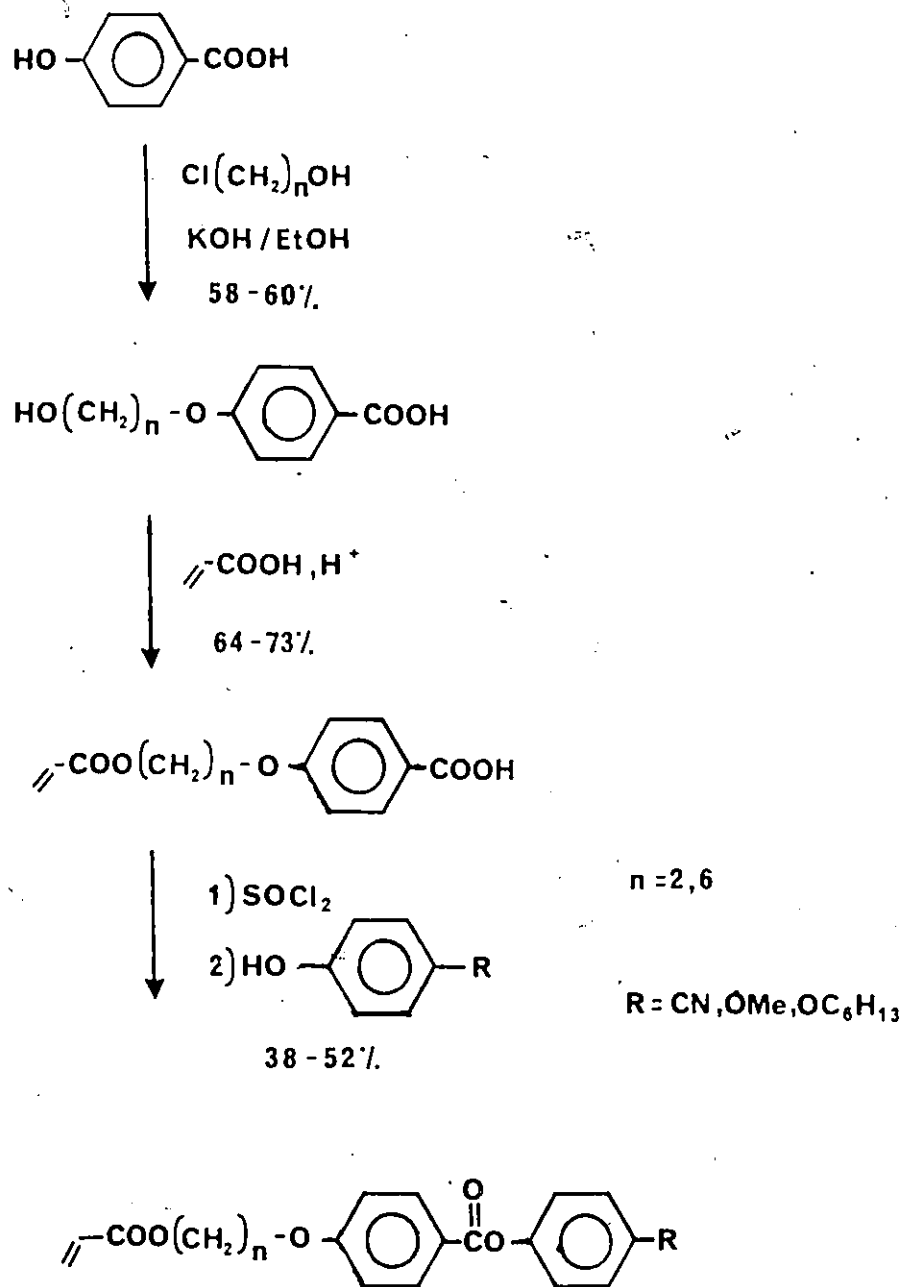
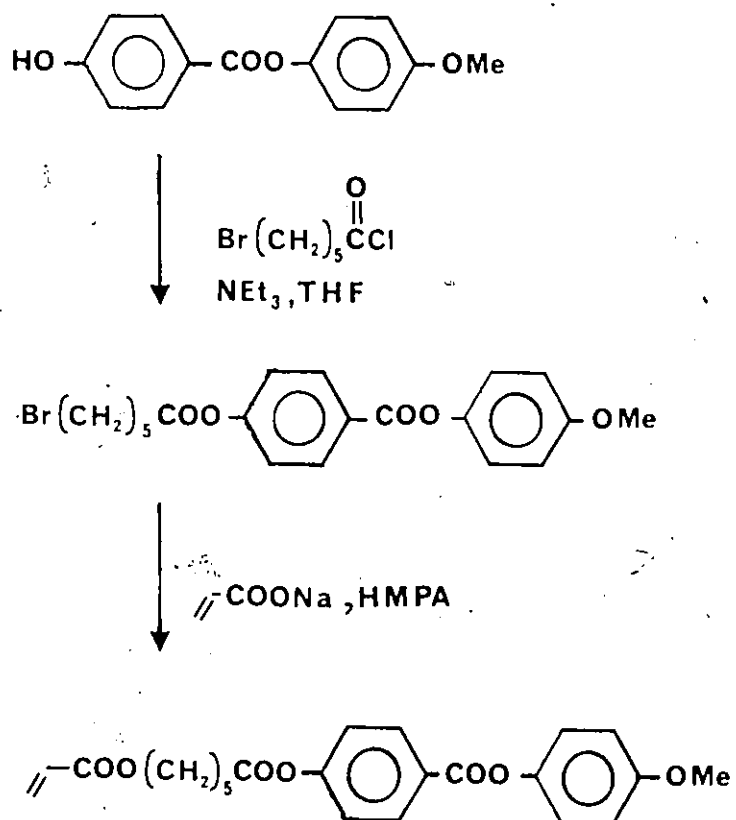


Figure 12

Mesogen Attached to Spacer Chain by Ester Linkage



and experimental details are incomplete. In a later paper by Shibaev (32), a similar reaction sequence using 4-hydroxy-4'-cyanobiphenyl and 11-bromoundecanoyl chloride gave an overall yield of 23% for the two synthetic steps.

Up to this point the phase behavior of side-chain polymers has not been discussed. In this work we are interested in obtaining polymers with smectic mesophases, and will concentrate on structures that favor the smectic state. The type of polymer, length of spacer chain, and structure of the mesogen are three important areas in the determination of mesophase type. All three areas have been reviewed extensively (39,40,41), but a summary is in order. The type of polymer employed is significant primarily in the glass transition temperature that it produces, as the liquid crystal polymer must be above the T_g to exhibit true liquid crystalline properties. With long spacer groups, the polymer chain itself usually makes up less than 20% of the total weight of the polymer, making the T_g value largely dependent on the mesogenic group. For instance, the T_g value of liquid crystalline polymethacrylates were found to be only 10 to 20°C higher than those of the corresponding polyacrylates, with a six carbon spacer group (34). In comparison, poly(methyl methacrylate) and poly(methyl acrylate) have T_g values of 105 and 10°C, respectively (42).

Polysiloxane liquid crystalline polymers generally have the lowest T_g values. Thus, main chain flexibility has an influence on T_g and the temperature range of the liquid crystalline phase, but little influence on the type of mesophase. Typically, as the degree of polymerization increases, both the glass transition temperature and

the clearing temperature increase, but a point is reached after which no significant increase occurs in either of them (43). The clearing temperature and the glass transition temperature do not increase at an equal rate as the degree of polymerization increases, so that high molecular weight polymers tend to have the greatest liquid crystalline temperature range.

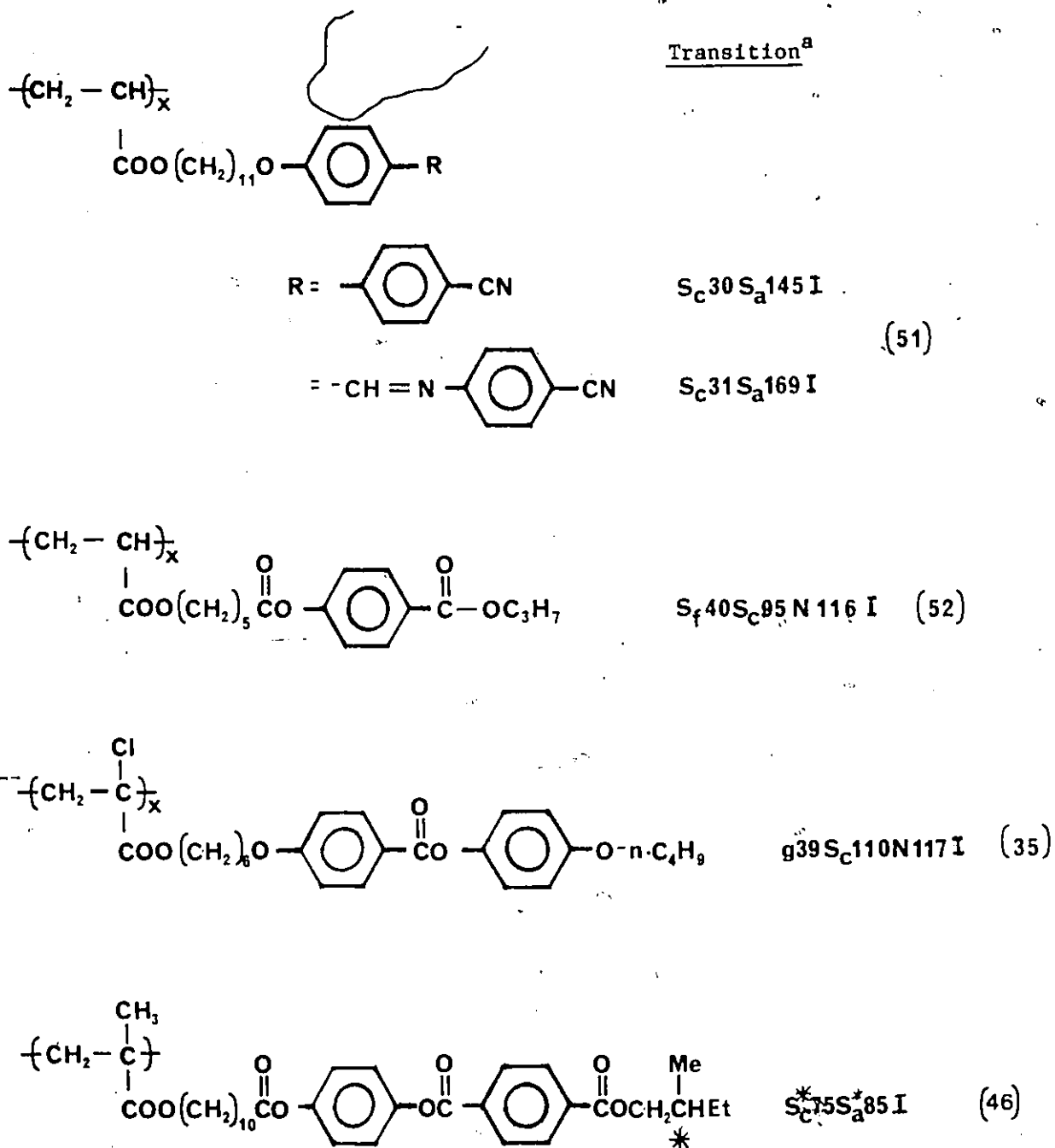
Spacer groups in liquid crystalline polymers are typically straight chain alkyl groups, although oligoethylene oxide spacers have been used with some success (44). Several important trends occur on increasing the spacer length. One of these is a decrease in the T_g of the polymer due to a plasticizing effect, while another is the influence on mesophase type. Spacers with more than 4 to 6 methylene units favor smectic mesophases over nematic ones in similar systems (39). Flexibility of the spacer chain is also important. For example, the lower flexibility of oligoethylene oxide spacers generally results in a smaller liquid crystalline range.

The mesogenic group, of course, plays the most important role in the determination of mesophase type. Correlation between mesogen structure and mesophase has been reviewed and empirical relationships exist (45). Mesophase prediction based on structure is not yet possible, however.

While the smectic C phase is the most common of the tilted polymeric smectic phases, it is relatively rare when compared to smectic phases in general. Polymeric liquid crystals exhibiting smectic C phases are shown in Table I. The great commercial potential of chiral smectic C phases has very recently led to two reports of this mesophase (46,47). Shibaev (46) reports ferroelectric behavior

Table 1

Polymeric Liquid Crystals Exhibiting a Smectic C Phase



a. The first letter represents initial state (K, crystalline; L, liquid crystalline; I, isotropic), while the numbers represent the temperature at which the state changes.

similar to low molecular weight liquid crystalline ferroelectrics, but as usual provides no experimental detail or conclusive evidence to support his claims.

The synthetic routes outlined for the synthesis of side-chain liquid crystalline polymers are usually specific to certain types of mesogens and of generally poor yield. Clearly, a need exists for a synthetic route that is of general utility and of high chemical yield, while at the same time being simple to carry out. With these characteristics in mind, the synthetic strategy of this work will be discussed.

RESULTS AND DISCUSSION

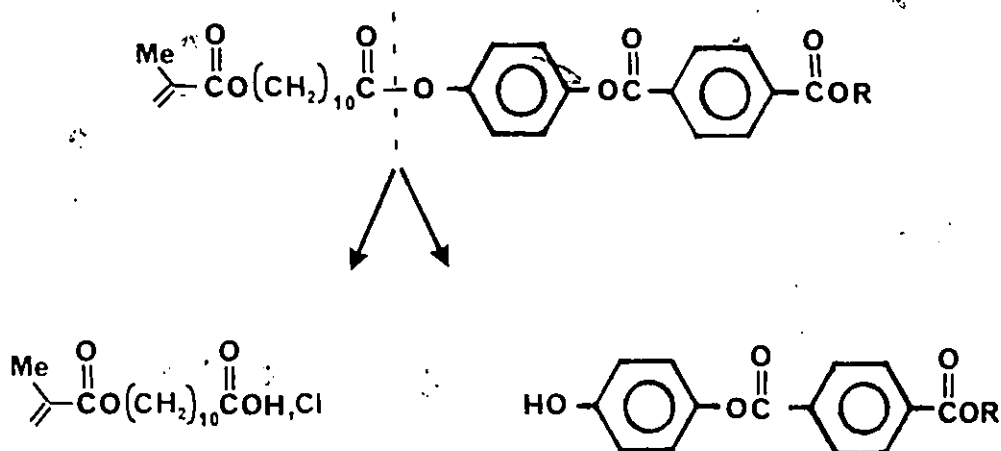
I. Synthesis of Monomers

The initial synthetic target chosen for this work was the polymer claimed by Shibaev (46) in 1984 (Table 1). This polymer contains a chiral 2-methyl butyl group and is said to have a low temperature smectic C phase and ferroelectric behavior. Unfortunately, these claims remain unsubstantiated because of a complete lack of chemical characterization of the polymer and its precursors. In fact, no experimental detail or even a synthetic scheme are supplied. Until very recently (47) this was the only reported polymeric liquid crystalline material exhibiting a chiral smectic C phase. A further incentive for the choice of this target structure was the unusual mesogen incorporated into the polymer: an alkyl 4-hydroxyphenyl 4-carboxy benzoate. To my knowledge, this mesogenic group had not previously been incorporated in any reported polymeric liquid crystals, primarily because it is not stable to the synthetic methods which are typically used. The incorporation of such a group is thus of interest because it opens a vista to the use of other acid or base sensitive mesogenic groups.

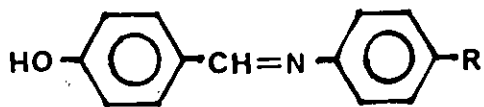
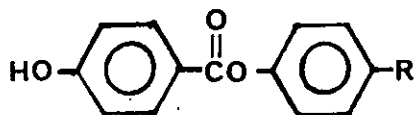
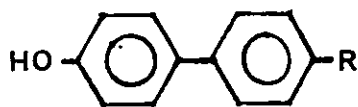
A desirable retro-synthetic scheme from the monomer is shown in Figure 13. In such an approach, the monomer would be produced by coupling the mesogen to a polymerizable spacer chain. Polymerization itself would be carried out later using standard conditions. This method has never been reported and is very attractive in its versatility. Many different types of mesogenic groups could be incorporated into the monomer in the last synthetic step since all

Figure 13

Monomer Retro-Synthesis



Alternative Mesogens



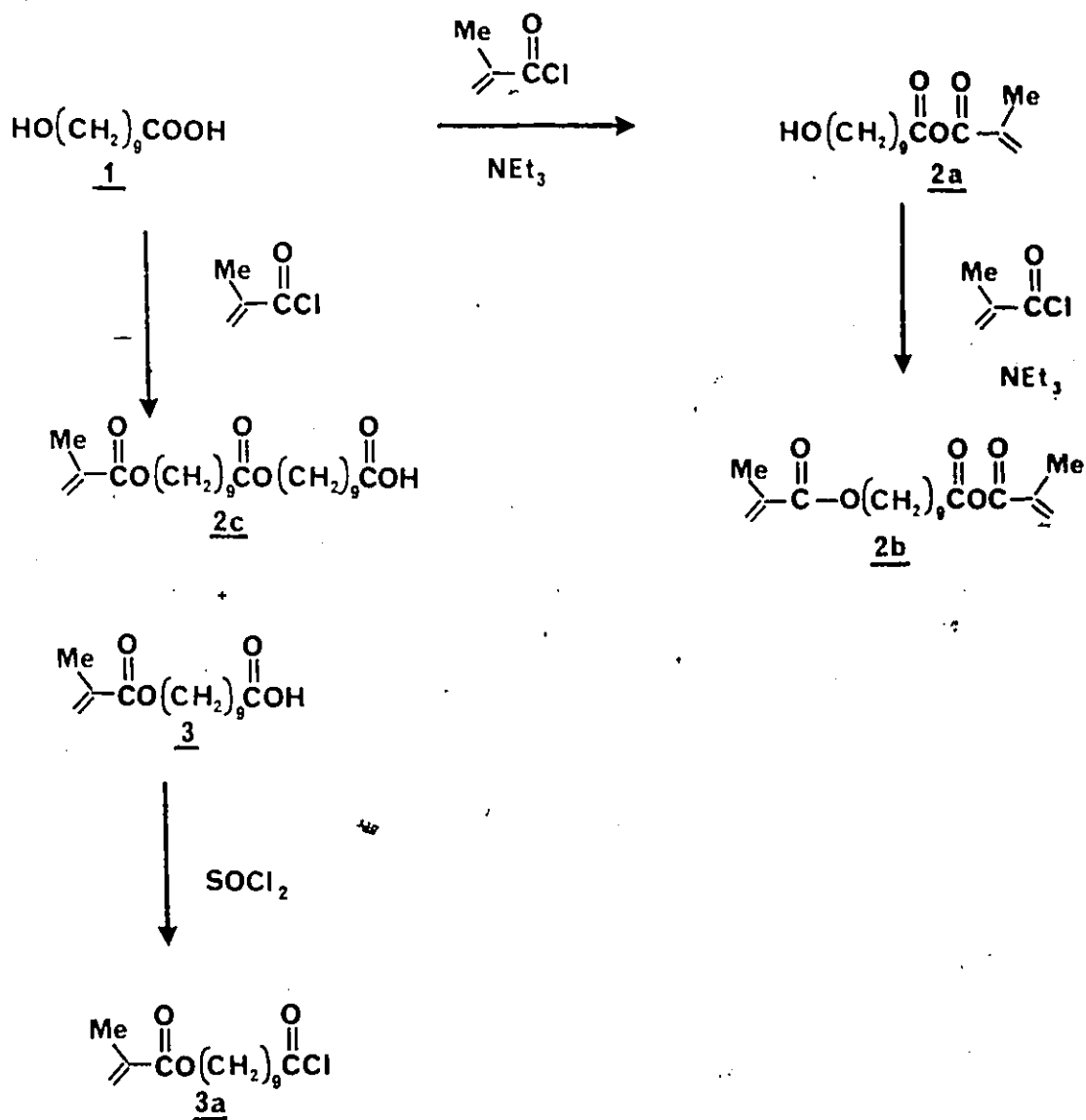
that would be required is a terminal hydroxy group. Examples include 4'-hydroxybiphenyls (50), p-hydroxy benzoates (51), p-hydroxyazomethines (52) and of course the target mesogenic group. The synthesis of the latter is simple and will be described later.

The polymerizable spacer chain is much more difficult to obtain and no methacrylate compounds of this type have been described previously. However, a similar compound, 10-acryloyloxydecanoic acid, has been reported by Diamond (53). In his procedure 10-hydroxydecanoic acid 1 is allowed to react with acryloyl chloride in chloroform in the absence of an acid acceptor. The crude acid is treated directly with oxalyl chloride or thionyl chloride, then distilled in a wiped-film still at 170 °C and 0.02 mm Hg giving the desired acid chloride in 43% yield. These conditions are rather severe, but served as a starting point for this work. Diamond's ten carbon spacer chain was chosen over the eleven carbon spacer chain claimed in the paper of Shibaev based on convenience only, as high purity 10-hydroxy decanoic acid is readily obtained from the alkaline cleavage of castor oil (54).

Figure 14 outlines the various results of the reaction of 1 with methacryloyl chloride. In the absence of an acid acceptor, high resolution proton NMR shows that both the desired product 3 and the dimer 2c were formed, as confirmed by the presence of the two clearly resolved methylene signals of 2c. The two compounds were not readily separated by chromatography or crystallization, but by forming the acid chlorides, 3a could be obtained in 22 to 30% yield following Kugelrohr distillation. Such poor yields and the difficult experimental conditions which were involved led me to search for a

Figure 14

Spacer Chain Reactions



more acceptable synthetic route to 3.

First, addition of an acid acceptor to the reaction was considered. In the presence of triethylamine, the reaction of 1 with one equivalent of methacryloyl chloride produced the anhydride 2a in excellent yield. Further reaction with methacryloyl chloride gave the ester-anhydride 2b. The possibility of using the methacrylate anhydride as a protecting group was considered, and selective hydrolysis of the anhydride in 2b was attempted. The methacrylate anhydride group is remarkably hindered and in all cases polymerization or ester hydrolysis occurred before anhydride hydrolysis was complete. The use of a more readily hydrolyzed anhydride, such as that derived from chloroacetic acid, was considered. The reaction of chloroacetyl chloride with 1 in the presence of an acid acceptor completely favored ester over anhydride formation.

The introduction of reactive site selectivity was attempted by use of the dianion of 1. It was reasoned that the alkoxy anion, having higher pKa, would react preferentially with methacryloyl chloride. However, the reaction of 1 with one equivalent of sodium hydride and one equivalent of triethylamine in tetrahydrofuran, followed by addition of one equivalent of methacryloyl chloride at -78°C gave both 2a and 2b, among other products. Clearly, such lack of selectivity was not acceptable.

These failures led to serious consideration of a protecting group strategy for the synthesis of 3. Restrictions in the nature of such a protecting group are severe, as it must readily functionalize the carboxylic acid in the presence of a primary alcohol, be stable to the

conditions used in the functionalization of that alcohol, and most importantly, it must be cleaved selectively in the presence of both an ester group and the readily polymerized methacryloyl moiety. Since at least three synthetic steps would be required, they must all be of high yield.

A paper by Olah (55) revealed a potential solution to the problem. He reported that benzyl esters are cleaved in four hours with sodium iodide and chlorotrimethylsilane in acetonitrile at room temperature, while cleavage of methyl esters requires 30 to 58 hours in refluxing acetonitrile. This tremendous difference in reactivity is due to the relative stabilities of benzyl and methyl carbocations in the reaction sequence.

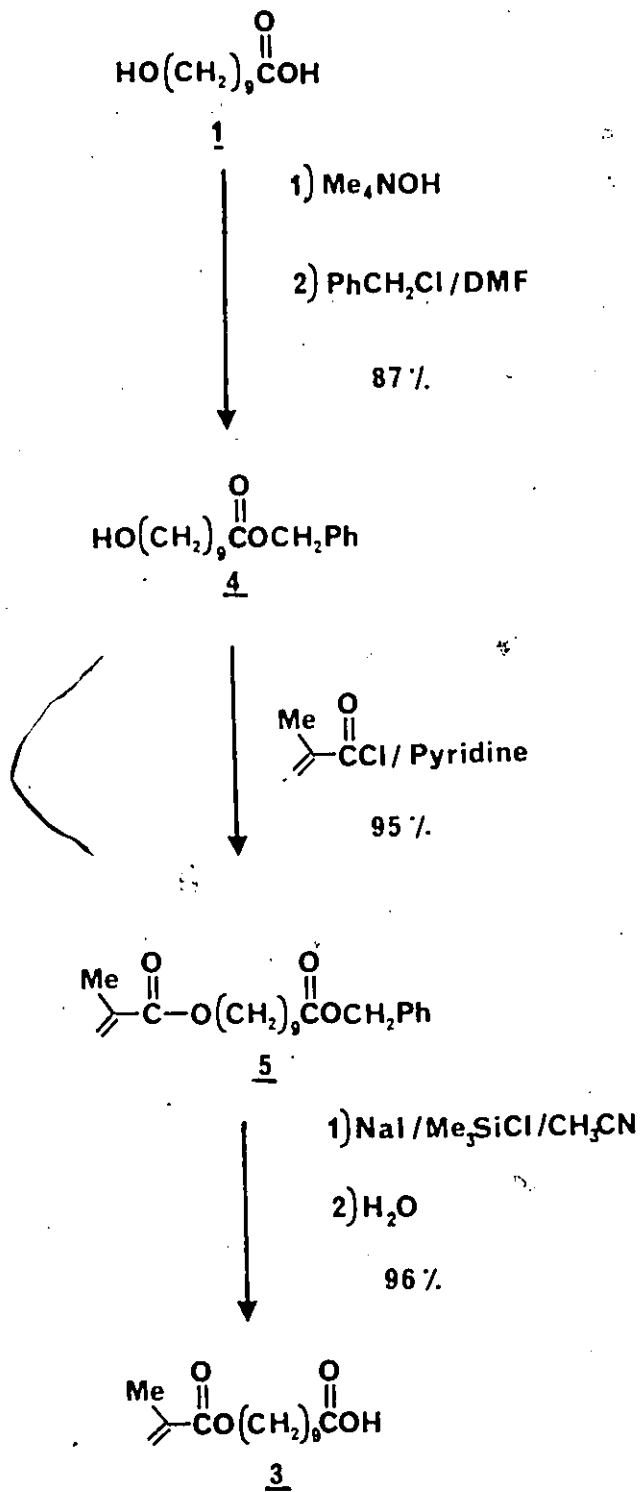
With this remarkable selectivity in hand, an efficient benzyl ester synthesis was needed that would work in the presence of a primary alcohol. The method of Wagenknecht (56), in which the tetramethylammonium salt of a carboxylate undergoes an S_N2 reaction with benzyl chloride in dimethylformamide, was found to be suitable.

The resulting synthetic scheme is shown in Figure 15. Benzyl ester protection of 1 was achieved in 87% yield to give 4, which was treated with methacryloyl chloride in the presence of pyridine to give 5 in 95% yield. Selective benzyl ester cleavage gave the desired polymerizable spacer chain 3 in 96% yield. The reaction sequence is easily carried out on a fifty millimole scale.

It must be pointed out that although proton and carbon-13 NMR and chemical ionization mass spectroscopic analyses were completely satisfactory for 3, elemental analysis was not. Drying of 3 was very difficult, especially as heating above 40 °C often caused

Figure 15

Spacer Chain Reaction Sequence



polymerization. In fact, the elemental analysis obtained is consistent with a hydration number of almost one, making this a likely cause of the problem. As will be seen, if a small amount of water is present it does not cause a significant problem in the subsequent reaction.

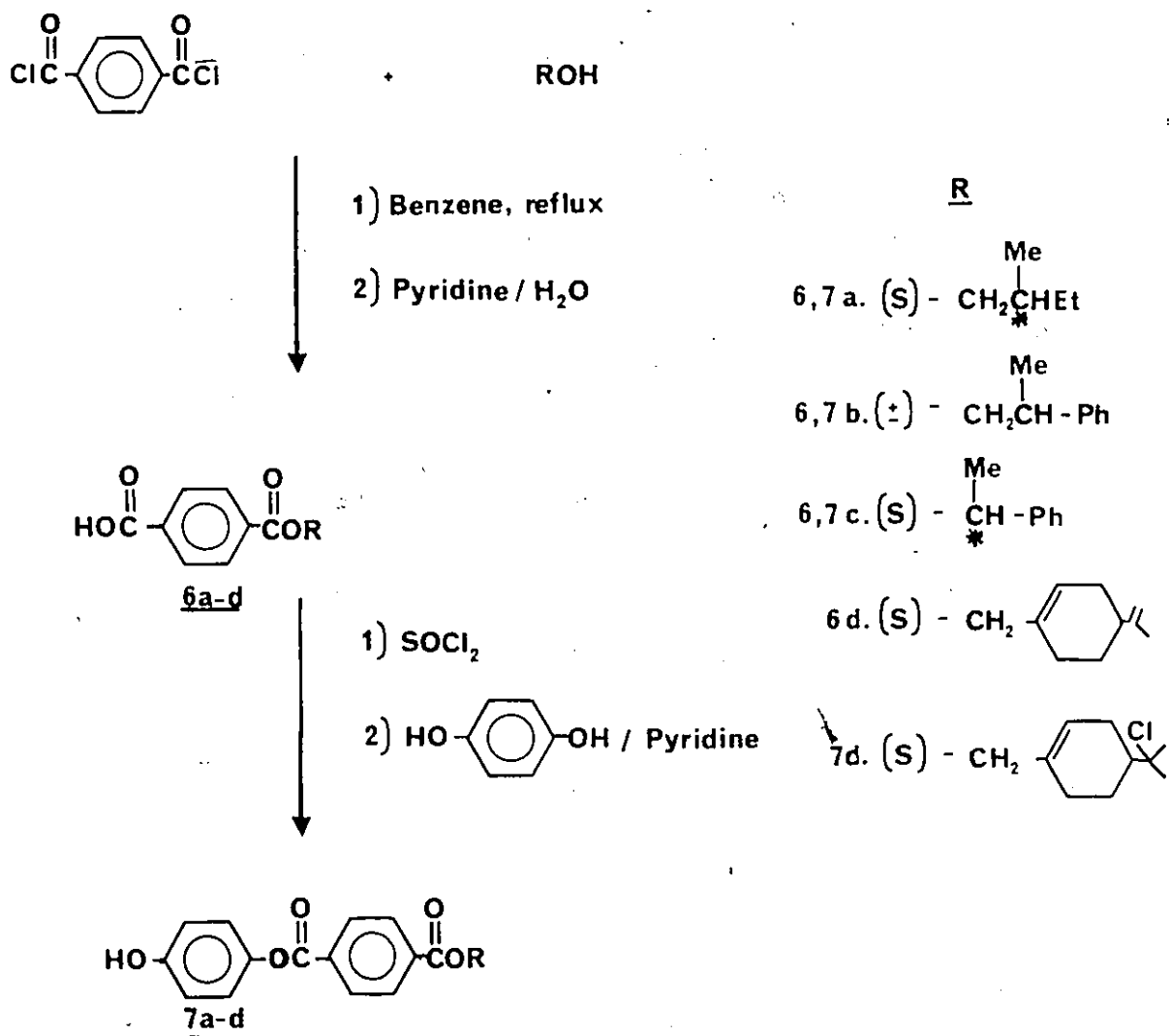
At this point it is appropriate to describe the synthesis of the hydroxy-terminated mesogenic group. Figure 16 outlines the classical methods used to make the mesogenic groups reported in this work. Since there are at present no efficient routes to monoterephthalate esters, the method of Dewar (57) was used, to give 6a-d in yields of 18 to 30%. In each case, however, the major co-product was the corresponding dialkylterephthalate, from which the alcohol starting material could be recovered by base hydrolysis.

Formation of the acid chlorides of 6a-d and reaction with excess hydroquinone in pyridine gave 7a-d in yields of 58 to 72%. These compounds have not been described in the literature.

The selection of the alkyl end groups of 7a-d was based on the use of readily available optically active or potentially optically active alcohols structurally similar to 2-methyl-1-butanol. Compound 7b was made from (+)-sec-phenethylalcohol, essentially replacing the ethyl group in 7a with phenyl. Synthesis of (+)-sec-phenethylalcohol by lithium aluminum hydride reduction of (-)-2-phenylpropionic acid has been reported (58) but was not carried out in this work. In compound 7c, derived from (S)-(-)-1-phenylethanol, the methylene spacer between the chiral center and the terephthalate was eliminated. To prepare 6d, (S)-(-)-perillyl alcohol was used as one of many natural product alcohols available as a low cost chiral center. This

Figure 16

Synthesis of Mesogenic Part of Monomer



is important in the synthesis of optically active liquid crystalline polymers, as suitable chiral alcohols are often expensive. Unfortunately, compound 6a reacted with one equivalent of hydrogen chloride on conversion to 7d. Similar reactions are known (59,60). This reduced the desirability of this end-group since the additional bulkiness of the tertiary chloride can be expected to reduce the likelihood of producing a liquid crystalline phase.

The final step of the monomer synthesis involved the coupling of the polymerizable spacer chain to compounds 7a-d. This was first attempted using the acid chloride 3a. However, no reaction occurred between 3a and 7a in pyridine. Phase-transfer catalysis in the presence of potassium carbonate as base was also unsuccessful. Using sodium hydroxide as the base (61), the monomer 8a was finally produced in 82% yield. Unfortunately, the monomer produced by this method was prone to gel formation on polymerization. It was speculated that due to the presence of base in the reaction medium, small amounts of hydroquinone may have been formed by base hydrolysis of 7a, which would have then reacted readily with 3a to form the bifunctional cross-linking agent 17 (Figure 17). This compound was prepared separately and was found to have an R_f value almost identical to that of the monomer. Since gel formation can be accomplished with very low concentrations of cross-linking agent, and removal of 17 from the product was not feasible, an alternate route was chosen.

This alternate route consisted of the reaction of acid 3 with compounds 7a-d in the presence of dicyclohexylcarbodiimide (DCC) with 4-dimethylaminopyridine (DMAP) as catalyst (62), (Figure 18). Yields of 83 to 89% for monomers 8a-c and 69% for monomer 8d were

Figure 17
Cross-Linking Agent

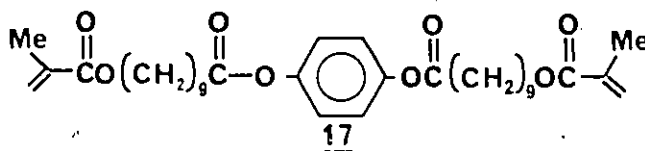
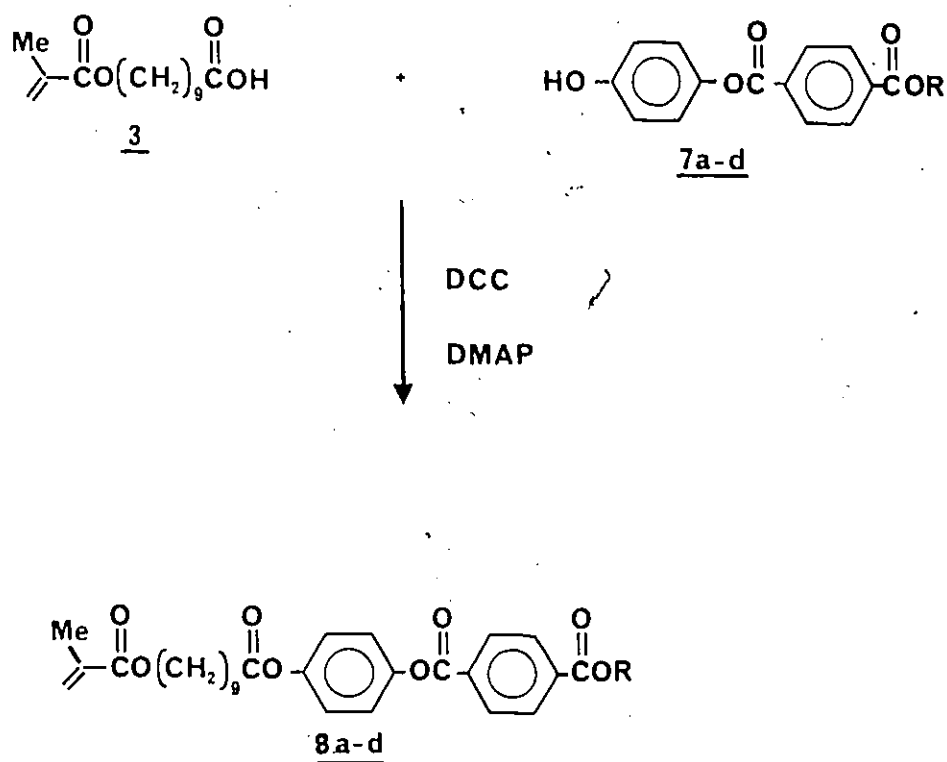


Figure 18
Monomer Synthesis



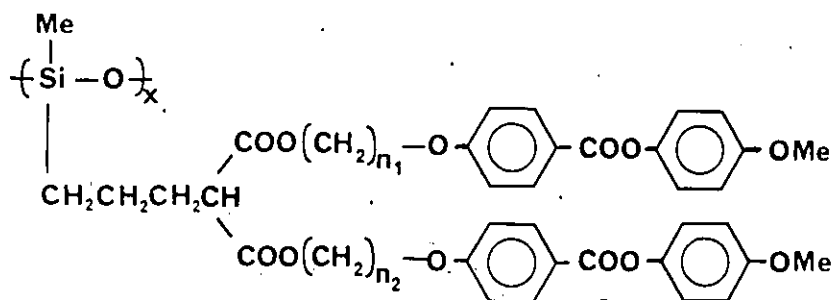
obtained. These monomers were fully characterized and were found to be completely satisfactory. The high field proton NMR spectrum of each monomer is included in Appendix A.

A novel fifth monomer with two parallel mesogenic groups was also prepared. To date there is only one reported example of such a paired mesogen, which was made as a side-chain polysiloxane (63), (Figure 19). Paired mesogens are of interest because of the relative increase in concentration of mesogenic groups in the polymer, making mesophase formation more likely to occur. It was thus of interest to prepare a paired mesogen containing chiral centers. The synthesis, based upon the methods developed for the monomers 8a-d, is shown in Figure 20.

The DCC coupling of 3 with L-malic acid dibenzyl ester 9 was carried out in 77% yield. The sodium iodide/chlorotrimethylsilane cleavage of 10 resulted in the diacid 11 which was not fully purified and characterized due to separation problems. Its high field proton NMR spectrum indicated the desired product as well as small amounts of malic acid and other unidentified impurities. The crude diacid 11 was coupled with 7a using DCC to give the paired mesogen monomer 12. Although the yield was low, the reaction was easily carried out and the readily purified monomer 12 was fully characterized.

Figure 19

Polysiloxane Paired Mesogen

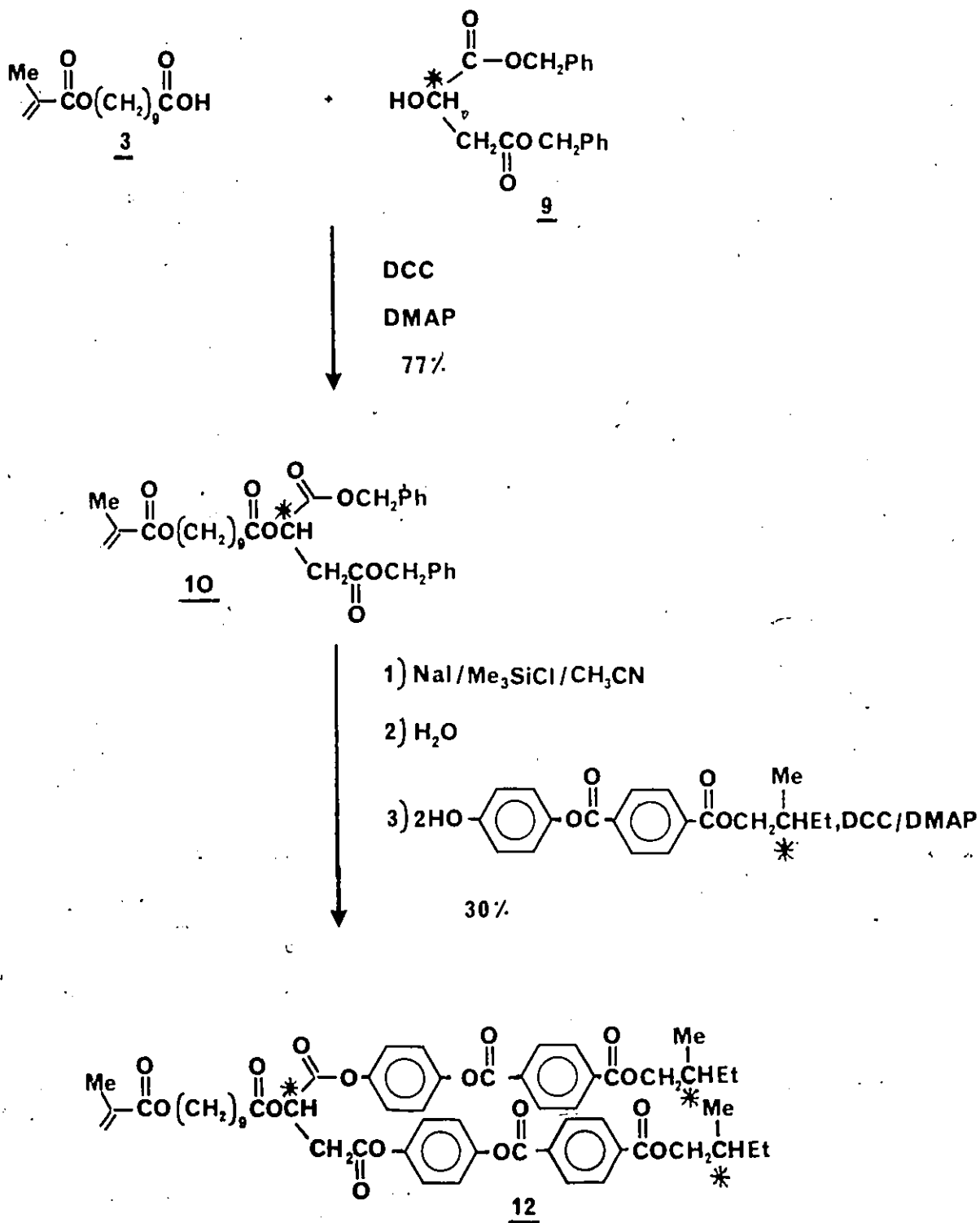


$n_1 = n_2 = 2, 6$

$n_1 = 2, n_2 = 6$

Figure 20

Synthesis of Chiral Paired Mesogen Monomer



II. Polymers and Copolymers

All monomers were polymerized in toluene at 70 °C with 0.5 mole percent each of 2,2'-azo-bis-isobutyronitrile (AIBN) and 1,1'-azo-bis-cyclohexanenitrile over a two day period. The latter initiator was chosen due to its longer half-life at the polymerization temperature. Thus it can prolong the period of radical formation and increase conversion. Copolymers with methyl methacrylate were prepared from the monomers 7a and 12. Figure 21 lists the polymers prepared in this work. Table 2 shows yields and molecular weights of these polymers. For polymers 13c and 13d low yields are reported, which represent only the soluble fraction of the polymer recovered from the gel that was produced. The cross-linking agent 17 appeared to arise from hydroquinone, which had not been completely removed from compounds 7c and 7d. Thus it is important to insure removal of hydroquinone from the hydroxy-terminated mesogens prior-to monomer formation.

Membrane osmometry showed all the polymers to have similar molecular sizes. The apparently low molecular weight of copolymer 15 can be accounted for by the large proportion of methyl methacrylate present in the polymer. The degree of polymerization and thus chain length are all comparable.

It should be noted here that no attempt was made to prepare materials with very high molecular weights. Since molecular size is limited both by the percentage and nature of the initiator used, a compromise is required. The longer-lived initiator used in this work favors increased conversion at the expense of molecular size, as the likelihood of termination by radical recombination increases with reaction time.

Figure 21

Polymers and Copolymers Prepared

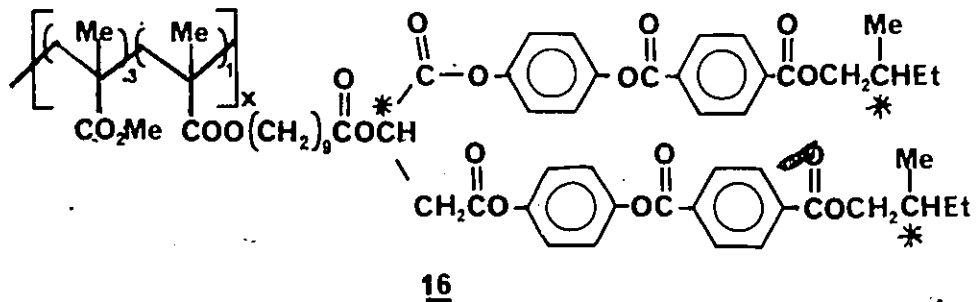
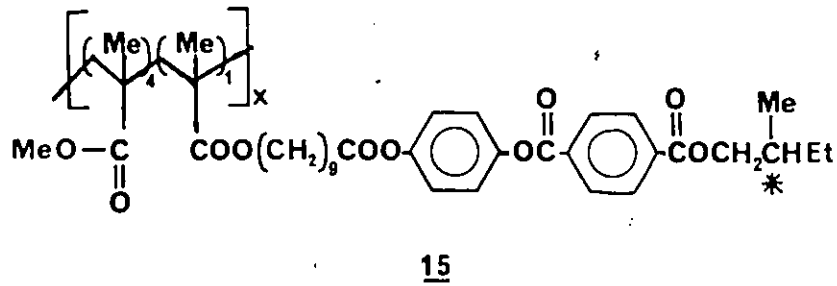
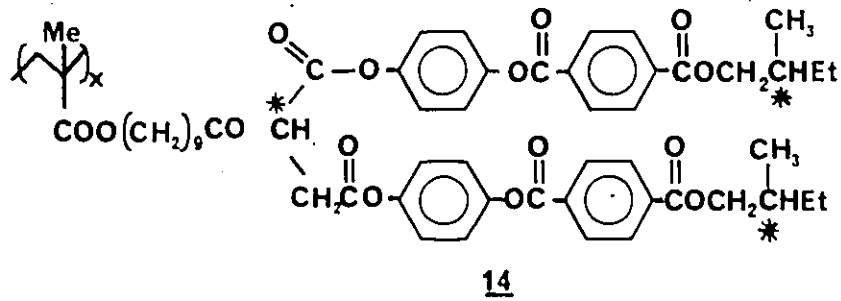
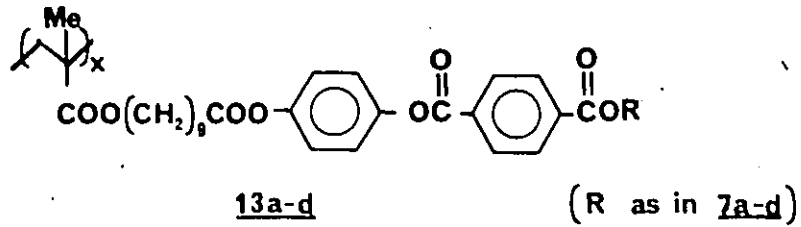


Table 2
Polymers and Copolymers

Compound	Yield % ^a	Molecular Weight ^b	Optical Rotation (g/dL, chloroform)
<u>13a</u>	89	157,000	+2.5° (4.6)
<u>13b</u>	92	238,000	-
<u>13c</u>	36 ^a	232,000	+30.6° (1.3)
<u>13d</u>	32 ^a	104,000	-20.2° (2.3)
<u>14</u>	75	141,000	-5.5° (3.6)
<u>15</u>	78	30,600	+1.5° (3.3)
<u>16</u>	61	75,700	-6.2° (3.1)

a. soluble polymer recovered from gel.
b. determined by membrane osmometry.

III. Phase Behavior

All of the monomers, polymers, and copolymers were analyzed by differential scanning calorimetry (DSC) and polarized light microscopy to determine their phase behavior. Photographs are displayed in Appendix B while DSC curves are shown in Appendix C. Results are summarized in Table 3. Glass transitions sometimes occurred with partial crystallization. For monomer 8a, the glass transition was very broad and not readily observed. This is known for other polymethacrylate liquid crystalline compounds (35).

It should be mentioned that unambiguous mesophase identification of side-chain liquid crystalline polymers can only be done by X-ray diffraction measurements. This technique involves obtaining an X-ray diffraction pattern from an oriented polymer sample. These techniques have recently been published for side-chain liquid crystalline polymers (64,65), but were found to be beyond the scope of this work. Thus only the existence of a mesophase can be demonstrated, while the specific type of mesophase can only be inferred.

Monomers 8a and 12 were found to have a monotropic liquid crystalline phase. This means that the liquid crystalline phase is stable only below the melting point of the compound, and is observed on supercooling only. Monomer 8b displayed an enantiotropic mesophase. All three monomers exhibited a similar birefringence pattern by polarized light microscopy. Using the excellent guides of Gray (7), and Demus (8), the nematic mesophase was indicated for all three compounds.

Only the polymers obtained from liquid crystalline monomers formed a mesophase. Polymers 13a and 13b showed enantiotropic phase

Table 3
Phase Behavior

Compound	T _g	Phases Observed			
		Heating ^a	H	Cooling	H
<u>8a</u>	-	K33.2I	45.8	I23L13.6K	9.5/28.1
<u>8b</u>	-	K26L36L58I	45/0.3/27	I36L24K	1.5/2.5
<u>8c</u>	-	K52I	65.5	I-12.6K	9.4
<u>8d</u>	-	K27I	37.8	I-12K	25.3
<u>12</u>	-	K92I	60.8	I52L48K	48.6
<u>13a</u>	5-20	L89I	11.8	I84.5L	13.2
<u>13b</u>	25-45	L104I	3.3	I102L	3.1
<u>13c</u>	30-45	-		-	
<u>13d</u>	35-50	-		-	
<u>14</u>	40-50	L158I		I150.5L149L	7.6/2.8
<u>15</u>	45-60	-		-	
<u>16</u>	30-50	-		-	

a. The first letter represents initial state (K, crystalline; L, liquid crystalline; I, isotropic), while the numbers represent the temperature at which the state changes.

behavior with almost identical birefringence patterns. The Schlieren texture observed for both is very characteristic of the smectic C mesophase.

The paired mesogen polymer 14 was the only other polymer to exhibit a mesophase. It was a highly unusual phase however, as it appeared to be of very similar stability to a crystalline phase. In microscope observation at 150 °C, the liquid crystalline phase could be initiated in the isotropic melt by brief application of pressure to the glass slide, or by annealing at 150 °C for several hours. Both a crystalline phase and a mesophase were able to occur in adjacent droplets, as the photograph in Appendix B clearly shows.

Neither of the copolymers showed liquid crystalline behavior. The paired mesogen copolymer, in which methyl methacrylate units made up only 23 percent of the polymer units, did not exhibit a mesophase. Apparently the extra polymer backbone present destabilizes the mesophase, and does not act as a simple diluent.

IV. Conclusion

Polymers 13a-d and 14-16 were synthesized and characterized by infrared spectroscopy, proton NMR, DSC, polarized light microscopy, and elemental analysis. All polymers except 13b contained optically active centers. Polymers 13a-b and 14 were found to have liquid crystalline properties.

The new synthetic method developed in this work is very versatile and leaves many options open for further work. For example, polymerizable spacer chains of different lengths could be made to study the effect of length on mesophase characteristics. Other polymerizable end groups could be incorporated to vary the glass transition temperature of the polymer. Many hydroxy-terminated mesogenic groups are available which have not been incorporated into polymers. These include mesogenic groups which previously were too sensitive to the reaction conditions available. Expansion into this area could produce many new mesomorphic polymers of interest. The effect of copolymer ratios on liquid crystalline properties is an obvious area of interest, given the failure of the copolymers 15 and 16 to produce a mesophase.

The synthetic route to the novel paired mesogen polymer 14 could be exploited in a similar large number of ways.

EXPERIMENTAL SECTION

I. Materials and Equipment

All the starting materials used in this work were commercially available in 98% or higher purity and used without further purification unless otherwise stated.

Melting points were measured in capillaries using a Gallenkamp Melting Point Apparatus equipped with a calibrated thermometer. Values are reported in degrees centigrade and are uncorrected.

Infrared spectra were recorded on a Nicolet 10 DX FT-IR spectrometer, either as potassium bromide discs or as films on sodium chloride plates.

Except where stated otherwise, nuclear magnetic resonance (NMR) spectra were measured on a Varian XL-300 spectrometer. Chemical shifts (δ) are reported in parts per million from tetramethylsilane. The following conventions are used: s, singlet; d, doublet; t, triplet; q, quartet; bs, broad singlet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; m, multiplet.

Optical rotations were measured using a Perkin-Elmer Model 241 digital polarimeter with the D-line of a sodium lamp. All measurements were made at room temperature with chloroform as solvent using a one dm, one mL sample cell.

High pressure liquid chromatography (HPLC) was carried out on a Waters preparative LC model 500A.

Mass spectroscopic analyses were performed on a VG Analytical model 7070E double focusing instrument.

Molecular weights of polymers and copolymers were determined in

toluene using a Wescan Instruments Ltd. model 231 "Athena" Membrane Osmometer.

Birefringence patterns were observed using an Olympus BH-2 microscope with BH2-KPA polarizer and Leitz model 350 microscope heating hot stage. Photographs were taken with a camera attachment using Polaroid 667 black and white film.

The alkaline cleavage of castor oil was performed using a Parr 300 mL reactor with stirrer, heater, and glass insert, supplied by the Parr Instrument Company, Moline, Illinois.

Differential scanning calorimetry was carried out using the Mettler TA3000 system with DSC 20 cell and a Kelvinator three cubic foot upright freezer.

Microanalyses were performed by M-H-W Laboratories, P.O. Box 15149, Phoenix, Arizona, U.S.A. 85018.

II. Procedures

A. Spacer-Chain

10-hydroxydecanoic acid 1

To a slurry of powdered sodium hydroxide (14.7 g, 0.37 mol) in absolute ethanol (85 mL) was added castor oil (40 g, 0.041 mol, assuming a molecular weight of 980). The mixture was placed in a glass-lined 300 mL Parr reactor and heated with slow stirring to 195 °C. Initial pressure at that temperature was 240 psi. After heating for 19 hours, a pressure of 400 psi was reached and the reactor was allowed to cool. The resulting waxy white solid was dissolved in 300 mL of distilled water and extracted with diethyl ether (3 x 50 mL) to remove 2-octanol. The solution was then acidified with 6N

hydrochloric acid, and the resulting organic phase was separated. The remaining aqueous phase was extracted with ether (3 x 50 mL) and the extracts were combined with the previous organic phase. The combined extracts were washed with saturated brine solution (2 x 50 mL) then dried over magnesium sulfate. Evaporation of the ether gave 32.2 g of a clear yellow oil. The oil was dissolved in warm ethyl acetate (85 mL), and hexane was added (90 mL). After standing overnight at -5 °C, the mixture deposited 13.9 g of a white powder which on recrystallization from benzene (100 mL) gave 13.4 g of 1 (67% yield based on a ricinoleic ester content of 87% in castor oil), mp 73-75 °C (lit(54) 73-75).

IR (KBr disc): 3200, 2914, 1685, 1469, 1310, 1286, 1047 cm^{-1} .

Proton NMR ($\text{CDCl}_3/\text{DMSO-d}_6$): δ 3.58 (t, 2H), 2.29 (t, 2H), 1.58 (t, 2H), 1.51 (t, 2H), 1.14 (s, 10H).

C-13 NMR (DMSO-d_6): δ 174.5 (s), 60.80 (t), 33.72 (t), 32.60 (t), 29.07 (t), 29.00 (t), 28.83 (t), 28.66 (t), 25.57 (t), 24.57 (t).

Analysis: calculated for $\text{C}_{10}\text{H}_{20}\text{O}_3$: C, 63.80; H, 10.71; O, 25.49.

Found: C, 64.00; H, 10.72.

Benzyl 10-hydroxydecanoate 4

To 1 (24 g, 128 mmol) was added tetramethylammonium hydroxide solution (20 weight percent in methanol) to neutrality (about 70 mL). Methanol was evaporated at 50 °C under aspirator vacuum. To the resulting viscous liquid was added dimethylformamide (500 mL) with stirring, and benzyl chloride (15.0 g, 130 mmol). After stirring at room temperature for sixteen hours, the mixture was poured into distilled water (500 mL) and extracted with diethyl ether (4 x 100

mL). The combined extracts were washed with distilled water (2 x 100 mL) and 5% sodium bicarbonate solution (2 x 100 mL). The sodium bicarbonate extract was acidified, extracted with ether, dried over sodium sulfate, filtered, and solvent was evaporated to give unreacted 1, 0.7g. The combined extracts were then washed with distilled water (2 x 100 mL) and saturated brine solution (2 x 100 mL), then dried over sodium sulfate. The dried ether solution was filtered and solvent was evaporated under aspirator vacuum to give 32.4 g of a clear oil, which was dissolved in 1 L of 5% ethyl acetate in hexane, and left at -5 °C overnight. The resulting crystals were filtered and dried to give 27 g of 4. A further 3.8 g of product was obtained as a second crop on evaporation of crystallization solvent and recrystallization of the residue. Yield 30.8 g (87%), mp 35-37 °C.

IR(KBr disc): 3316, 2927, 1796, 1169, ~~747~~, 686 cm^{-1} .

Proton NMR (CDCl_3): δ 7.30 (m, 5H), 5.06 (s, 2H), 3.59 (t, 2H), 2.30 (t, 2H), 1.56 (m, 4H), 1.24 (s, 10H).

C-13 NMR (CDCl_3): δ 173.67, 136.10, 128.51, 128.13, 66.06, 63.01, 34.30, 32.75, 29.34, 29.29, 29.11, 29.05, 25.67, 24.91.

Analysis: calculated for $\text{C}_{17}\text{H}_{26}\text{O}_3$: C, 73.34; H, 9.41; O, 17.24.

Found: C, 73.54; H, 9.22.

Benzyl 10-methacryloyloxydecanoate 5

To 4 (15.0 g, 54 mmol) in anhydrous diethyl ether (150 mL) under a nitrogen atmosphere was added 2,6-dimethylphenol (50 mg) and pyridine (9.1 mL, 108 mmol, distilled from KOH). To the stirred solution was added dropwise freshly distilled methacryloyl chloride (5.4 mL, 55 mmol) in anhydrous ether (20 mL). After stirring for 22

hours, the mixture was filtered through celite, extracted with 0.6N HCl (2 x 50 mL), distilled water (1 x 50 mL), 5% sodium bicarbonate solution (2 x 50 mL), distilled water (1 x 50 mL), and saturated brine solution (2 x 50 mL), then dried over sodium sulfate. The dried solution was filtered and the solvent evaporated under aspirator vacuum. Drying under vacuum over phosphorus pentoxide for sixteen hours at 40 °C yielded 5 as a clear oil, 17.7 g (95%).

IR(film): 2929, 1738, 1720, 1639, 1455, 1165, 687 cm^{-1} .

Proton NMR (CDCl_3): δ 7.30 (m, 5H), 6.05 (s, 1H), 5.49 (s, 1H), 5.04 (s, 2H), 4.08 (t, 2H), 2.30 (t, 2H), 1.88 (s, 3H), 1.60 (dt, 4H), 1.23 (s, 10H).

C-13 NMR (CDCl_3): δ 173.60, 167.51, 136.51, 136.10, 128.49, 128.40, 128.13, 125.08, 66.02, 64.75, 34.27, 29.25, 29.11, 29.06, 29.01, 28.55, 25.91, 24.88, 18.30.

Analysis: calculated for $\text{C}_{21}\text{H}_{30}\text{O}_4$: C, 72.80; H, 8.73; O, 18.47.

Found: C, 72.99; H, 8.58.

10-methacryloyloxydecanoic acid 3

To 5 (17.7 g, 51.2 mmol) dissolved in dry acetonitrile (120 mL) was added sodium iodide (30.7 g, 205 mmol) with stirring under a nitrogen atmosphere. Chlorotrimethylsilane (26.0 mL, 205 mmol) was added dropwise over a ten minute period, and the mixture was left to stir for 24 hours at room temperature. It was then poured into distilled water (300 mL) and extracted with diethyl ether (4 x 100 mL). The combined ether extracts were washed with water (3 x 50 mL), 10% sodium thiosulfate solution (2 x 50 mL), water (2 x 50 mL), 5% sodium bicarbonate solution (2 x 50 mL), and extracted with 10% sodium

carbonate solution (4 x 50 mL). The combined sodium carbonate extracts were washed with ether (2 x 50 mL), acidified with 6N hydrochloric acid, and extracted with ether (4 x 100 mL). The combined ether extracts were washed with water (1 x 50 mL) and saturated brine solution (2 x 50 mL), then dried over sodium sulfate for 24 hours. The mixture was filtered, solvent was evaporated under aspirator vacuum, and the residue was dried over phosphorus pentoxide at 40 °C and 2 mm Hg to give 12.6 g of 3 as a clear oil (96%).

IR(film): 2800-3600, 2928, 1718, 1696, 1297, 1166, 939, 815 cm^{-1} .

Proton NMR (CDCl_3): δ 6.04 (s,1H), 5.50 (s,1H), 4.08 (t,2H), 2.30 (t,2H), 1.88 (s,3H), 1.60 (m,4H), 1.25 (s,10H).

C-13 NMR (CDCl_3): δ 180.08, 167.58, 136.51, 125.17, 64.80, 34.03, 29.24, 29.12, 29.06, 28.97, 28.53, 25.91, 25.83, 24.62, 18.30.

Analysis: calculated for $\text{C}_{14}\text{H}_{24}\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$: C,63.37; H,9.49; O,27.13.

Found: C,63.20; H,8.68.

MS (chemical ionization): 257 (m+1).

10-methacryloyloxydecanoyl chloride 3a

To 1 (0.50g, 2.7 mmol) and hydroquinone (0.1g) in ethanol-free chloroform (20 mL) at 50 °C was added rapidly with stirring freshly distilled methacryloyl chloride (0.60g, 5.5 mmol). The solution was heated at reflux until proton NMR showed the disappearance of the triplet at δ 3.60, about 2 hours. High resolution NMR showed the following: 6.02 (s,1H), 5.48 (s,1H), 4.06 (t,2H), 3.98 (t,1.6H), 2.28 (t,2H), 2.22 (t,1.6H), 1.86 (s,3H), 1.56 (m,7H), 1.12 (s, 17.2H). This spectrum is consistent with 20 to 25% of the product having structure 2a and 75 to 80% having structure 2c. The cooled solution

was treated with thionyl chloride (0.40 mL, 5.5 mmol) and then heated to 50 °C for 90 minutes. Solvent and excess thionyl chloride were removed by distillation under aspirator vacuum at 50 °C, to give a residual yellow oil which was distilled in a Kugelrohr apparatus at 0.07 mm Hg and 120 °C to give 210 mg of 3a as a clear oil (28%).

IR(film): 2982, 1799, 1718, 1297, 1166, 944 cm^{-1} .

Proton NMR (CDCl_3): δ 6.04 (s,1H), 5.49 (s,1H), 4.08 (t,2H), 2.82 (t,2H), 1.88 (s,3H), 1.62 (m,4H), 1.24 (s,10H).

C-13 NMR (CDCl_3): δ 173.74 (s), 167.46 (s), 136.48 (s), 125.09 (t), 64.68 (t), 47.03 (t), 29.11 (t), 29.03 (t), 28.91 (t), 28.52 (t), 28.30 (t), 25.85 (t), 24.97 (t), 18.26 (q).

B. Alkyl 4-Carboxy Benzoates 6a-d

The method of Dewar (57) was used, and is illustrated for compound 6a.

To terephthaloyl chloride (60 g, 0.29 mol) dissolved in dry benzene (300 mL) was added (S)-(-)-2-methyl-1-butanol (27 g, 0.31 mol) with stirring under a nitrogen atmosphere. The solution was heated at reflux for two hours, then cooled. The stirred solution was treated with aqueous pyridine (44 mL pyridine in 200 mL water) then stirred for two hours. Benzene was evaporated at 40 °C under aspirator vacuum to give a white semi-solid, which was washed with 0.15N hydrochloric acid (4 x 50 mL) and water (1 x 50 mL). It was then stirred vigorously with 10% sodium carbonate solution (400 mL) for 6 hours. The mixture was filtered and the solution was acidified with 6N hydrochloric acid with stirring in a 2L beaker. The precipitate was filtered, washed with distilled water (200 mL) and dissolved in

diethyl ether to form a cloudy solution which was dried over sodium sulfate. The dried solution was filtered through celite and solvent was evaporated under aspirator vacuum to give a white solid. This solid was dissolved in chloroform and filtered through celite. The filtered solution, free of terephthalic acid, was evaporated under aspirator vacuum to give 22.7 g of crude product. This was dissolved in a minimum of diethyl ether and hot petroleum ether (500 mL) was added. After standing overnight at 0 °C the mixture deposited 14.8 g of crystals. Evaporation of solvent and repetition of the recrystallization procedure produced another 5.8 g of product. Total yield of 6a was 20.6 g (30%).

Tabulated Data for 6a-d

Compound	Yield %	Optical Rotation in chloroform (g/dL)	melting point °C
<u>6a</u>	30	+5.01° (3.7)	153-154
<u>6b</u>	19	0	156-157
<u>6c</u>	18	+57.3° (3.5)	103-106
<u>6d</u>	23	-45.7° (1.4)	137-142

Further Characterization of 6a-d

(S)-(+)-2-methylbutyl 4-carboxy benzoate 6a

IR(KBr disc): 2400-3200, 2963, 1711, 1684, 1276, 1104, 848, 733 cm⁻¹.

Proton NMR (CDCl₃): δ 8.11 (m, 4H), 4.16 (dq, 2H), 1.84 (m, 1H), 1.50 (m, 1H), 1.27 (m, 1H), 0.97 (d, 3H), 0.91 (t, 3H).

C-13 NMR (CDCl₃): δ 171.40 (s), 165.69 (s), 135.00 (s), 132.87 (s), 130.11 (d), 129.52 (d), 70.04 (t), 34.20 (d), 26.08 (t), 16.42 (q), 11.21 (q).

Analysis: calculated for $C_{13}H_{16}O_4$: C,66.09; H,6.83; O,27.09.

Found: C,66.28; H,6.63.

(+)-2-phenylpropyl 4-carboxy benzoate 6b

IR(KBr disc): 2400-3200, 1718, 1684, 1268, 732, 702 cm^{-1} .

Proton NMR ($CDCl_3$): δ 8.06 (2d,4H), 7.26 (m,5H), 4.40 (m,2H), 3.23 (q, 1H, J=7.6 Hz), 1.36 (d, 3H, J=7.6 Hz).

C-13 NMR ($CDCl_3$): δ 171.23 (s), 165.55 (s), 142.90 (s), 134.88 (s), 132.93 (s), 130.16 (d), 129.60 (d), 128.57 (d), 127.29 (d), 126.84 (d), 70.36 (t), 39.02 (d), 18.00 (q).

Analysis: calculated for $C_{17}H_{16}O_4$: C,71.82; H,5.67; O,22.51.

Found: C,72.00; H,5.44.

(S)-(+)-1-phenylethyl 4-carboxy benzoate 6c

IR(KBr disc): 2400-3200, 1719, 1690, 1272, 731, 697 cm^{-1} .

Proton NMR ($CDCl_3$): δ 8.10 (s,4H), 7.26-7.42 (m,5H), 6.10 (q, 1H, J=7.0 Hz), 1.64 (d,3H,J=7.1 Hz).

C-13 NMR ($CDCl_3$): δ 171.27, 164.90, 141.31, 135.13, 132.95, 130.14, 129.71, 128.63, 128.09, 126.09, 73.66, 22.29.

Analysis: calculated for $C_{16}H_{14}O_4$: C,71.10; H,5.22; O,23.68.

Found: C,71.37; H,5.43.

(S)-(-)-perillyl 4-carboxy benzoate 6d

(S)-(-)-Perillyl alcohol was first purified by HPLC with 10/90 ethyl acetate/hexane as eluent.

IR(KBr disc): 2400-3100, 1718, 1688, 1272, 1017, 731 cm^{-1} .

Proton NMR (CDCl₃): δ 8.12 (m, 4H), 5.84 (s, 1H), 4.70-4.80 (m, 4H), 2.16 (bs, 4H), 1.8-2.1 (m, 4H), 1.72 (s, 2H), 1.4-1.6 (m, 2H).

C-13 NMR (CDCl₃): δ 171.17 (s), 165.56 (s), 149.47 (s), 134.98 (s), 132.93 (s), 132.31 (s), 130.16 (d), 129.67 (d), 126.27 (d), 108.85 (t), 69.44 (t), 40.77 (d), 30.47 (t), 27.29 (t), 26.46 (t), 20.74 (q).

C. Alkyl 4-Hydroxyphenyl 4-Carboxy Benzoates 7a-d

Typical procedure:

The acid chloride was first obtained by treating the acid 6a-d with an excess of thionyl chloride using pyridine as catalyst. After two to four hours, excess thionyl chloride was distilled under aspirator vacuum to give the acid chloride as a residual product.

Typically 10 mmol of the acid chloride was added to a stirred saturated solution of hydroquinone (50 mmol) in dry pyridine (35 mL). After stirring for 16 hours the solution was poured into 1.1N HCl (400 mL) and 6N HCl was added until the mixture was slightly acidic. The precipitate was filtered, washed with 0.5N HCl (100 mL), distilled water (150 mL) and then dissolved in ethyl acetate. The ethyl acetate solution was diluted by half with ethanol, and solvent was evaporated under aspirator vacuum. Crystals, which usually formed after two thirds of the solvent had evaporated, were filtered and discarded. The filtrate was then evaporated to dryness, and dissolved in 20 mL of ethyl acetate. Silica gel (150 mesh, 3g per gram of compound) was added, and solvent was evaporated. The resulting silica was placed on top of a silica gel column (100 g) and eluted with 20/80 ethyl acetate/hexane. The first product to be eluted was always the by-product diester of hydroquinone, followed by the desired monoester.

Tabulated Data for 7a-d

Compound	Yield %	Optical Rotation Chloroform (g/dL)	Melting Point °C	R _f ^a
<u>7a</u>	72	+4.2° (5.6)	106-107	.35/.55
<u>7b</u>	65	-	113-115	.24/.51
<u>7c</u>	58	+49.3° (0.95)	78-83	.19/.49
<u>7d</u>	62	-26.1° (1.0)	oil	.17/.42

a. R_f using silica TLC with 20/80 ethyl acetate/hexane eluent. First number is value for product, second for diester by-product.

Further Characterization of 7a-d

(S)-(+)-2-methylbutyl 4-hydroxyphenyl 4-carboxy benzoate 7a

IR(KBr disc): 3382, 2960, 1708, 1287, 1267, 1190, 725 cm⁻¹.

Proton NMR (CDCl₃): δ 8.11 (d, 4H), 7.04 (d, 2H), 6.84 (d, 2H), 4.76 (bs, 1H), 4.16 (dq, 2H), 1.86 (m, 1H), 1.50 (m, 1H), 1.25 (m, 1H), 1.96 (d, 3H), 1.90 (t, 3H).

C-13 NMR (CDCl₃): δ 166.08 (s), 165.31 (s), 153.99 (s), 143.81 (s), 134.73 (s), 133.20 (s), 130.14 (d), 129.66 (d), 122.32 (d), 116.21 (d), 70.26 (t), 34.21 (d), 26.09 (t), 16.48 (q), 11.26 (q).

Analysis: calculated for C₁₉H₂₀O₅: C, 69.50; H, 6.14; O, 24.36.

Found: C, 69.73; H, 5.99.

(+)-2-phenylpropyl 4-hydroxyphenyl 4-carboxy benzoate 7b

IR(KBr disc): 3400-3450, 2969, 1732, 1717, 1275, 1237, 1192, 722, 699 cm⁻¹.

Proton NMR (CDCl₃): δ 8.19 (d, 2H), 8.04 (d, 2H), 7.27 (m, 5H), 7.04

(d,2H), 6.83 (d,2H), 4.76 (bs, 1H), 4.40 (m,2H), 3.24 (q,1H, J=7.2 Hz), 1.37 (d,3H, J=7.2 Hz).

C-13 NMR (CDCl₃): δ 165.69 (s), 165.07 (s), 153.73 (s), 144.06 (s), 142.89 (s), 134.59 (s), 133.28 (s), 130.10 (d), 129.65 (d), 128.58 (d), 127.30 (d), 126.85 (d), 122.42 (d), 116.18 (d), 70.43 (t), 39.04 (d), 17.98 (q).

Analysis: calculated for C₂₃H₂₀O₅: C,73.39; H,5.36; O,21.25.

Found: C,73.14; H,5.60.

(S)-(+)-1-phenylethyl 4-hydroxyphenyl 4-carboxy benzoate 7c

IR(KBr disc): 3400-3450, 1718, 1509, 1271, 1249, 1192, 726, 696 cm⁻¹.

Proton NMR (CDCl₃): δ 8.16 (m,4H), 7.26-7.44 (m,5H), 7.40 (d,2H), 6.82 (d,2H), 6.11 (q,1H,J=6.2 Hz), 1.65 (d,3H,J=6.0 Hz), 1.4-1.7 (bs,1H).

C-13 NMR (CDCl₃): δ 165.09, 153.70, 144.08, 141.29, 134.84, 133.30, 130.11, 129.78, 128.64, 128.14, 126.09, 122.41, 116.17, 73.78, 22.32.

Analysis: calculated for C₂₂H₁₈O₅: C,72.92; H,5.01; O,22.08.

Found: C,72.82; H,5.26.

(S)-(-)-1-(4-(2-(2-chloropropyl))cyclohex-1-enyl)methyl 4-hydroxyphenyl 4-carboxy benzoate 7d

IR(KBr disc): 3500, 2928, 1723, 1602, 1510, 1269, 1191, 1018, 727 cm⁻¹.

Proton NMR (CDCl₃): δ 8.16 (2d,4H), 7.03 (d,2H), 6.83 (d,2H), 5.80 (s,1H), 4.72 (s,2H), 1.2-2.4 (m,14H).

C-13 NMR (CDCl₃): δ 165.67 (s), 164.99 (s), 153.70 (s), 144.09 (s), 134.62 (s), 133.34 (s), 132.48 (s), 130.11 (d), 129.74 (d), 125.83 (d), 122.43 (d), 116.14 (d), 74.03 (s), 69.21 (t), 46.18 (d), 30.61 (q), 29.89 (q), 27.23 (t), 26.83 (t), 24.24 (t).

D. Alkyl 4-(10-Methacryloyloxydecanoxy)phenyl 4-Carboxy
Benzoate Monomers 8a-d

Typical procedure:

Compound 7 (5 mmol), compound 3 (5.1 mmol) and 4-dimethylaminopyridine (50 mg) were dissolved in dichloromethane (10 mL) with stirring under a nitrogen atmosphere. A solution of dicyclohexylcarbodiimide (5.5 mmol) in dichloromethane (5 mL) was added, and the solution was left to stir for 24 hours at room temperature. The mixture was filtered to remove dicyclohexylurea and washed with water (2 x 20 mL), 5% acetic acid solution (2 x 20 mL), water (2 x 20 mL) and saturated brine solution (1 x 20 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated to give the crude product, which was purified by column chromatography using 10/90 ethyl acetate/hexane or by HPLC with 5/95 ethyl acetate/hexane.

Tabulated Data for 8a-d

Compound	Yield %	Optical Rotation Chloroform (g/dL)	Melting Point °C	R _f ^a
<u>8a</u>	89	+2.6° (4.4)	44-46 ^b	.45
<u>8b</u>	86	-	56-58 ^b	.49
<u>8c</u>	83	+30.4° (1.6)	48-51	.45
<u>8d</u>	69	-19.7° (3.0)	35-38	.50

a. R_f using silica TLC with 20/80 ethyl acetate/hexane eluent.

b. exhibited liquid crystalline behavior.

Further Characterization of 8a-d

Proton NMR spectra for 8a-d, carried out using deuteriochloroform as solvent, are shown in Appendix A. Chemical shifts are tabulated below.

(S)-(+)-2-methylbutyl 4-(10-methacryloyloxydecanoyloxy)phenyl 4-carboxy benzoate 8a

IR(KBr disc): 2930, 1762, 1734, 1722, 1710, 1507, 1273, 1255, 1180, 1016, 733 cm^{-1} .

Proton NMR (CDCl_3): δ 8.20 (d,2H), 8.12 (d,2H), 7.16 (d,2H), 7.10 (d,2H), 6.04 (s,1H), 5.50 (s,1H), 4.16 (m,2H), 4.08 (t,2H), 2.50 (t,2H), 1.87 (s,3H), 1.84 (m,1H), 1.70 (t,2H), 1.61 (t,2H), 1.49 (m,1H), 1.28 (s,11H), 0.97 (d,3H), 0.90 (t,3H).

C-13 NMR (CDCl_3): δ 172.09 (s), 167.50 (s), 165.66 (s), 164.24 (s), 148.35 (s), 148.00 (s), 136.52 (s), 134.94 (s), 133.02 (s), 130.12 (d), 129.65 (d), 125.14 (t), 122.56 (d), 122.40 (d), 70.06 (t), 64.75 (t), 34.31 (d), 34.25 (t), 29.28 (t), 29.22 (t), 29.15 (t), 29.05 (t), 28.57 (t), 26.14 (t), 25.93 (t), 24.85 (t), 18.34 (q), 16.52 (q), 11.29 (q).

Analysis: calculated for $\text{C}_{33}\text{H}_{42}\text{O}_8$: C,69.94; H,7.47; O,22.59.

Found: C,69.96; H,7.29.

8a From 3a and 7a.

To 7a (0.66 g, 2 mmol) was added tetrabutylammonium hydrogen sulfate (5 mg), 2,6-dimethylphenol (5 mg), powdered sodium hydroxide (0.20 g, 5 mmol) and dry diethyl ether (100 mL) under a nitrogen atmosphere. To the stirred solution at 0 °C was added dropwise 3a (0.66 g, 2.4 mmol). After 55 minutes the mixture was filtered,

solvent was evaporated under aspirator vacuum, and the crude product was purified by column chromatography on silica gel (100 g) with 20/80 ethyl acetate/hexane as eluent to give 0.93 g of 8a as a white solid (82%). TLC (silica, 5/95 ethyl acetate/hexane) showed trace amounts of an impurity of nearly identical R_f which could not be separated by chromatography or by crystallization from absolute ethanol. IR, NMR were identical to those of the previous preparation of 8a, but on polymerization a gel was always produced.

Analysis: calculated for $C_{33}H_{42}O_8$: C, 69.94; H, 7.47; O, 22.59.

Found: C, 70.20; H, 7.27.

**(+)-2-phenylpropyl 4-(10-methacryloyloxydecanoyloxy)phenyl
4-carboxy benzoate 8b**

IR(KBr disc): 2935, 1755, 1737, 1715, 1504, 1258, 1188, 724, 701 cm^{-1} .

Proton NMR ($CDCl_3$): δ 8.16 (d, 2H), 8.02 (d, 2H), 7.32-7.06 (m, 9H), 6.04 (s, 1H), 5.48 (s, 1H), 4.39 (m, 2H), 4.08 (t, 2H), 3.22 (q, 1H), 2.50 (t, 2H), 1.88 (s, 3H), 1.70 (t, 2H), 1.62 (t, 2H), 1.35 (d, 3H), 1.28 (s, 10H).

C-13 NMR ($CDCl_3$): δ 172.10 (s), 167.52 (s), 165.48 (s), 164.21 (s), 148.38 (s), 148.00 (s), 142.90 (s), 136.53 (s), 134.70 (s), 133.07 (s), 130.11 (d), 129.66 (d), 128.57 (d), 127.29 (d), 126.84 (d), 125.15 (t), 122.56 (d), 122.39 (d), 70.33 (t), 64.77 (t), 39.02 (d), 34.31 (t), 29.29 (t), 29.16 (t), 29.03 (t), 28.58 (t), 25.94 (t), 24.86 (t), 18.33 (q), 17.98 (q).

Analysis: calculated for $C_{37}H_{42}O_8$: C, 72.29; H, 6.89; O, 20.82.

Found: C, 72.09; H, 6.72.

**(S)-(+)-1-phenylethyl 4-(10-methacryloyloxydecanoxy)phenyl
4-carboxy benzoate 8c**

IR(KBr disc): 2832, 1758, 1742, 1716, 1506, 1279, 1258, 1183, 761, 730
702 cm^{-1} .

Proton NMR (CDCl_3): δ 8.17 (2d,4H), 7.44-7.26 (m,5H), 7.14 (2d,4H),
6.11 (q,1H), 6.04 (s,1H), 5.50 (s,1H), 4.08 (t,2H), 2.52 (t,2H), 1.88
(s,3H), 1.78-1.56 (m,7H), 1.28 (s,10H).

C-13 NMR (CDCl_3): δ 172.03 (s), 167.44 (s), 164.77 (s), 164.16 (s),
148.32 (s), 147.94 (s), 141.28 (s), 136.47 (s), 134.90 (s), 133.04
(s), 130.04 (d), 129.70 (d), 128.57 (d), 128.03 (d), 126.03 (d),
125.07 (t), 122.51 (d), 122.35 (d), 73.59 (d), 64.70 (t), 34.25 (t),
29.23 (t), 29.10 (t), 28.98 (t), 28.52 (t), 25.88 (t), 24.80 (t),
22.25 (q), 18.27 (q).

Analysis: calculated for $\text{C}_{36}\text{H}_{40}\text{O}_8$: C,71.98; H,6.71; O,21.31.

Found: C,71.72; H,6.70.

**(S)-(-)-1-(4-(2-(2-chloropropyl))cyclohex-1-enyl)methyl
4-(10-methacryloyloxydecanoxy)phenyl 4-carboxy benzoate 8d**

IR(KBr disc): 2931, 1759, 1742, 1721, 1501, 1268, 1181, 1017,
728 cm^{-1} .

Proton NMR (CDCl_3): δ 8.16 (2d,4H), 7.14 (2d,4H), 6.04 (s,1H), 5.81
(s,1H), 5.50 (s,1H), 4.71 (s,2H), 4.08 (t,2H), 2.52 (t,2H), 2.32-1.96
(m,5H), 1.89 (s,3H), 1.86-1.58 (m,6), 1.53 (d,6H), 1.29 (s,10H).

C-13 NMR (CDCl_3): δ 172.01 (s), 167.43 (s), 165.39 (s), 164.13 (s),
148.31 (s), 147.92 (s), 136.46 (s), 134.68 (s), 133.06 (s), 132.47
(s), 130.05 (d), 129.66 (d), 125.71 (d), 125.05 (t), 122.49 (d),
122.32 (d), 73.88 (s), 69.08 (t), 64.68 (t), 46.11 (d), 34.24 (t),
30.54 (q), 29.84 (q), 29.22 (t), 29.09 (t), 28.97 (t), 28.51 (t),

27.16 (t), 26.76 (t), 25.87 (t), 24.79 (t), 24.17 (t), 18.26 (q).

E. Paired Mesogen Monomer

(S)-(-)-dibenzyl 2-hydroxypropandioate 9

To L-malic acid (15 g, 0.11 mol) was added a solution of tetramethylammonium hydroxide in methanol (20 weight percent) until neutral to litmus. Solvent was evaporated from the solution under aspirator vacuum at 50 °C to give a very viscous liquid, which was vigorously stirred in dimethylformamide (200 mL) under a nitrogen atmosphere. Benzyl chloride (29.7g, 0.23 mol) was added, and the mixture was left to stir for 48 hours. Distilled water (200 mL) was added, and the solution was extracted with diethyl ether (4 x 400 mL). The combined ether extracts were washed with water (3 x 100 mL), 2% acetic acid solution (2 x 100 mL), water (1 x 100 mL), 5% sodium bicarbonate solution (1 x 100 mL), water (3 x 100 mL), and saturated brine solution (2 x 100 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated under reduced pressure to give 31.4 g of a pale yellow oil. This crude product was purified in two batches by HPLC with 20/80 ethyl acetate/hexane to give 23.1 g of 9 as a clear oil (67%). R_f (20/80 ethyl acetate/hexane, silica TLC): 0.22. Optical rotation -20.1° ($c=4.1$, chloroform).

IR(film): 3491, 3065, 3034, 2954, 1739, 1455, 1266, 1216, 1166, 1104, 752, 697 cm^{-1} .

Proton NMR (CDCl_3): δ 7.28 (m,10H), 5.13 (s,2H), 5.06 (s,2H), 4.50 (bs,1H), 3.16 (bs,1H), 2.84 (m,2H).

Analysis: calculated for $\text{C}_{18}\text{H}_{18}\text{O}_5$: C,68.78; H,5.77; O,25.45.

Found: C,68.83; H,5.59.

(S)-(-)-dibenzyl 2-(10-methacryloyloxydecanoyloxy)propanoate 10

To 4 (5.0 g, 19.5 mmol) and 9 (6.13 g, 19.5 mmol) in dichloromethane (55 mL) under a nitrogen atmosphere was added 4-dimethylaminopyridine (150 mg) and 2,6-dimethylphenol (100 mg). A solution of dicyclohexylcarbodiimide (4.85 g, 23.4 mmol) in dichloromethane (5 mL) was added with stirring. After sixteen hours of stirring at room temperature, the mixture was filtered and washed with water (3 x 20 mL), 5% acetic acid solution (3 x 20 mL), water (3 x 20 mL), and saturated brine solution (2 x 20 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated under aspirator vacuum to give a brown oil. The oil was dissolved in 40/60 ethyl acetate hexane (100 mL) and filtered again. On evaporation of solvent under aspirator vacuum 12.5g of crude product was obtained, which was purified by HPLC with 7/93 ethyl acetate/hexane as eluent to give 8.3 g of 10 as a clear oil (77%).

R_f (20/80 ethyl acetate/hexane, silica TLC): 0.48.

Optical rotation: -12.4° ($c=3.5$, chloroform).

IR(film): 2935, 1743, 1717, 1696, 1169 cm^{-1} .

Proton NMR (CDCl_3): δ 7.26 (m, 10H), 6.04 (s, 1H), 5.48 (m, 2H), 5.06 (m, 4H), 4.08 (t, 2H), 2.87 (d, 2H), 2.26 (dt, 2H), 1.90 (s, 3H), 1.60 (m, 4H), 1.12 (s, 10H).

C-13 NMR (CDCl_3): δ 172.65 (s), 168.86 (s), 168.73 (s), 167.54 (s), 136.53 (s), 135.36 (s), 135.00 (s), 128.58 (d), 128.47 (d), 128.40 (d), 128.31 (d), 128.23 (d), 125.14 (t), 68.08 (d), 67.42 (t), 66.83 (t), 64.78 (t), 36.18 (t), 33.77 (t), 29.26 (t), 29.17 (t), 29.10 (t), 28.93 (t), 28.58 (t), 25.94 (t), 24.67 (t), 18.33 (q).

Analysis: calculated for $C_{32}H_{40}O_8$: C,69.54; H,7.29; O,23.16.

Found: C,69.27; H,7.32.

(S)-(-)-2-(10-methacryloyloxydecanoyloxy)propanoic acid 11

To 10 (2.1 g, 3.8 mmol) and sodium iodide (4.56 g, 30.4 mmol) in dry acetonitrile (40 mL) stirred under a nitrogen atmosphere was added chlorotrimethylsilane (3.9 mL, 30.4 mmol). After fifteen hours, the reaction mixture was poured into dilute sodium bicarbonate solution (1.68 g, 20 mmol, in 150 mL water). The slightly acidic solution was extracted with diethyl ether (4 x 50 mL). The combined ether extracts were washed with water (2 x 30 mL), 5% sodium thiosulfate solution (2 x 50 mL), water (2 x 30 mL), and saturated brine solution (2 x 30 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated to give an oil which was washed with hexane (4 x 30 mL) until benzyl iodide was no longer detected in the hexane wash by TLC. Solvent was evaporated under aspirator vacuum to give the crude product as a clear viscous oil, 1.3 g, which was used without further purification. The high resolution proton NMR spectrum of crude 11 is shown in Appendix A, and tabulated below.

Proton NMR ($CDCl_3$): δ 6.06 (s,1H), 5.51 (s,1H), 5.48 (t,1H), 4.10 (t,2H), 2.94 (m,2H), 2.36 (t,2H), 1.88 (s,3H), 1.60 (m,4H), 1.24 (s,10H).

**(-)-di((S)-2-methylbutyl 4-phenyl 4-carboxy benzoate)
(S)-(-)-2-(10-methacryloyloxydecanoyloxy)propanoate 12**

To 11 (1.3 g, about 3.5 mmol), 6a (1.5 g, 4.6 mmol), and 4-dimethylaminopyridine (40 mg) dissolved in dichloromethane (20 mL) was added with stirring a solution of dicyclohexylcarbodiimide (1.50 g,

7.3 mmol) in dichloromethane (3 mL). After 48 hours, TLC showed that reaction had taken place but that some 6a still remained. The mixture was filtered, washed with water (2 x 10 mL), 5% acetic acid solution (3 x 10 mL), water (2 x 10 mL), and saturated brine solution (2 x 10 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated under aspirator vacuum. The resulting oil was purified by column chromatography (150 g silica) using 15/85 ethyl acetate/hexane as eluent, to give 0.68 g of 12 as a white solid (30% based on 6a). R_f (20/80 ethyl acetate/hexane TLC on silica): 0.20. Optical rotation -8.3° ($c=3.1$, chloroform).

mp 88-92 °C, exhibiting monotropic liquid crystalline behavior.

IR(KBr disc): 2933, 1757, 1794, 1719, 1507, 1271, 1246, 1183, 1018, 725 cm^{-1} .

Proton NMR (CDCl_3): δ 8.15 (2d, 8H), 7.17 (2d, 8H), 6.02 (s, 1H), 5.74 (t, 1H), 5.48 (s, 1H), 4.16 (m, 4H), 4.06 (t, 2H), 3.27 (m, 2H), 2.42 (t, 2H), 1.90-1.80 (m, 5H), 1.70-1.40 (m, 8H), 1.24 (m, 10H), 0.97 (d, 6H), 0.90 (t, 6H).

C-13 NMR (CDCl_3): δ 172.72 (s), 167.50 (s), 167.43 (s), 167.35 (s), 165.67 (s), 164.17 (s), 148.52 (s), 148.40 (s), 147.87 (s), 147.73 (s), 136.52 (s), 135.00 (s), 132.90 (s), 130.12 (d), 129.67 (d), 125.10 (t), 122.65 (d), 122.62 (d), 122.39 (d), 122.34 (d), 70.10 (t), 67.92 (d), 64.77 (t), 36.34 (t), 34.26 (t), 33.82 (d), 29.25 (t), 29.13 (t), 28.94 (t), 28.55 (t), 26.14 (t), 25.91 (t), 24.77 (t), 18.32 (q), 16.51 (q), 11.26 (q).

F. Polymers 13a-d, 14, and Copolymers 15, 16

Typically, to 1.0 g of monomer in 2.0 mL of dry toluene was added 2,2'-azo-bis-isobutyronitrile (0.5 mole %) and 1,1'-azo-bis-cyclohexanenitrile (0.5 mole %). The latter initiator was made by a known procedure (66). The solution was then heated under a nitrogen atmosphere at 70 °C in an oil bath for 48 hours. It was then diluted with toluene (ten to fifteen mL) and the polymer was precipitated into one liter of distilled hexane. The precipitated polymer was filtered, and the precipitation repeated. Polymers 13c and 13d formed gels from which soluble polymer was recovered by refluxing for two hours in dichloromethane followed by filtration through a medium fritted disc funnel. The recovered soluble polymer was then precipitated twice using distilled hexane.

The copolymers 15 and 16 were treated in an identical manner. Initiators were added based on the total amount of the two monomers present. A 4.0 to 1 mole ratio of methyl methacrylate to monomer 8a resulted in an identical ratio in the copolymer 15, as determined by high resolution proton NMR. A 3.0 to 1 mole ratio of methyl methacrylate to monomer 12 resulted in a ratio of only 0.3 to 1 in copolymer 16. It is possible that the long reaction time required led to a loss of methyl methacrylate by a slow nitrogen purge.

Tabulated Data for Polymers and Copolymers

Compound	Yield %	Molecular Weight ^b	Optical Rotation (g/dL, chloroform)
<u>13a</u>	89	157,000	+2.5° (4.6)
<u>13b</u>	92	238,000	-
<u>13c</u>	36 ^a	232,000	+30.6° (1.3)
<u>13d</u>	32 ^a	104,000	-20.2° (2.3)
<u>14</u>	75	141,000	-5.5° (3.6)
<u>15</u>	78	30,600	+1.5° (3.3)
<u>16</u>	61	75,700	-6.2° (3.1)

- a. soluble polymer recovered from gel.
b. determined by membrane osmometry.

Other Data for Polymers and Copolymers

High resolution proton NMR spectra, carried out using deuteriochloroform as solvent, are shown in Appendix A. Chemical shifts are tabulated below.

Poly((S)-(+)-2-methylbutyl 4-(10-methacryloyloxydecanoyloxy)phenyl 4-carboxy benzoate) 13a

IR(KBr disc): 2931, 1762, 1734, 1724, 1506, 1264, 1184, 1017, 725 cm⁻¹.

Proton NMR (CDCl₃): δ 8.09 (d, 4H), 7.09 (d, 4H), 4.12 (m, 2H), 3.88 (bs, 2H), 2.48 (t, 2H), 1.86-1.40 (m, 11H), 1.28 (s, 11H), 0.94 (d, 3H), 0.88 (t, 3H).

Analysis: calculated for (C₃₃H₄₂O₈)_x: C, 69.94; H, 7.47; O, 22.59.

Found: C, 70.09; H, 7.49.

**Poly((+)-2-phenylpropyl 4-(10-methacryloyloxydecanoyloxy)phenyl
4-carboxy benzoate) 13b**

IR(KBr disc): 2930, 1760, 1724, 1501, 1267, 1182, 1017, 761, 725, 700
cm⁻¹.

Proton NMR (CDCl₃): δ 8.02 (2d,4H), 7.30-7.00 (m,9H), 4.34 (m,2H),
3.88 (bs,2H), 3.16 (q,1H), 2.46 (bs,2H), 1.80-1.44 (m,9H), 1.40-1.20
(m,13H).

Analysis: calculated for (C₃₇H₄₂O₈)_x: C,72.29; H,6.89; O,20.82.

Found: C,72.12; H,6.95.

**Poly((S)-(+)-1-phenylethyl 4-(10-methacryloyloxydecanoyloxy)phenyl
4-carboxy benzoate) 13c**

IR(KBr disc): 2931, 1761, 1740, 1724, 1501, 1266, 1181, 1016, 762,
726, 699 cm⁻¹.

Proton NMR (CDCl₃): δ 8.12 (2d,4H), 7.44-7.20 (m,5H), 7.09 (2d,4H),
6.08 (q,1H), 3.88 (bs,2H), 2.48 (bs,2H), 1.80-1.44 (m,9H), 1.50
(s,3H), 1.27 (bs,10H).

Analysis: calculated for (C₃₆H₄₀O₈)_x: C,71.98; H,6.71; O,21.31.

Found: C,72.04; H,6.84.

**Poly((S)-(-)-1-(4-(2-(2-chloropropyl))cyclohex-1-enyl)methyl
4-(10-methacryloyloxydecanoyloxy)phenyl 4-carboxy benzoate) 13d**

IR(KBr disc): 2931, 1761, 1740, 1725, 1501, 1266, 1181, 1016,
725 cm⁻¹.

Proton NMR (CDCl₃): δ 8.08 (2d,4H), 7.08 (2d,4H), 5.76 (s,1H), 4.66
(s,2H), 3.88 (bs,2H), 2.48 (bs,2H), 2.30-1.82 (m,5H), 1.80-1.10
(m,27H).

Analysis: calculated for (C₃₈H₄₇ClO₈)_x: C,68.40; H,7.10; Cl,5.32; O,19.18.

Found: C,68.42; H,6.88; Cl,5.36.

Poly((-)-di((S)-2-methylbutyl 4-phenyl 4-carboxy benzoate)
(S)-(-)-2-(10-methacryloyloxydecanoyloxy)propandioate) 14

IR(KBr disc): 2963, 2931, 1744, 1723, 1501, 1266, 1179, 1016,
724 cm^{-1} .

Proton NMR (CDCl_3): δ 8.04 (2d,8H), 7.08 (m,8H), 5.66 (t,1H), 4.09
(m,4H), 3.82 (bs,2H), 3.18 (m,2H), 2.36 (bs,2H), 1.78 (m,3H), 1.65-
1.32 (m,12H), 1.20 (bs,10H), 0.92 (d,6H), 0.84 (t,6H).

Analysis: calculated for $(\text{C}_{56}\text{H}_{64}\text{O}_{16})_x$: C,67.73; H,6.50; O,25.78.

Found: C,68.00; H,6.60.

Poly(methyl methacrylate-co-(S)-(+)-2-methylbutyl 4-(10-
methacryloyloxydecanoyloxy)phenyl 4-carboxy benzoate) 15

IR(KBr disc): 2934, 1761, 1728, 1501, 1267, 1248, 1181, 1149, 1017,
749, 727 cm^{-1} .

Proton NMR (CDCl_3): δ 8.14 (2d,4H), 7.13 (2d,4H), 4.15 (m,2H), 3.88
(bs,2H), 3.52 (s,12H), 2.51 (t,2H), 2.00-1.44 (m,18), 1.24 (bs,12H),
0.97 (d,3H), 0.90 (t,3H).

Analysis: calculated for $(\text{C}_{53}\text{H}_{74}\text{O}_{16})_x$: C,65.82; H,7.71; O,26.47.

Found: C,66.09; H,7.81.

Poly(methyl methacrylate-co-(-)-di((S)-2-methylbutyl 4-phenyl
4-carboxy benzoate) (S)-(-)-2-(10-methacryloyloxydecanoyl-
oxy)propandioate) 16

IR(KBr disc): 2931, 1762, 1744, 1724, 1501, 1265, 1179, 1016,
724 cm^{-1} .

Proton NMR (CDCl_3): δ 8.08 (d,8H), 7.11 (bs,8H), 5.68 (bs,1H), 4.10
(m,4H), 3.84 (bs,2H), 3.48 (bs,0.9H), 3.20 (m,2H), 2.38 (bs,2H), 1.80
(m,3H), 1.70-1.36 (m,13H), 1.20 (bs,10H), 0.92 (d,6H), 0.84 (t,6H).

Analysis: calculated for $(C_{57.5}H_{66.4}O_{16.6})_x$:

C, 67.50; H, 6.54; O, 25.96. Found: C, 67.76; H, 6.86.

C. Miscellaneous

1,4-di(10-methacryloyloxydecanoyloxy)benzene 17

To hydroquinone (50 mg, 0.45 mmol), 1 (250 mg, 0.98 mmol) and 4-dimethylaminopyridine (10 mg) in dichloromethane (5 mL) was added a solution of dicyclohexylcarbodiimide (220 mg, 1.1 mmol) in dichloromethane (1 mL). After stirring for 24 hours under a nitrogen atmosphere, the mixture was filtered, washed with distilled water (2 x 15 mL), 5% acetic acid solution (2 x 15 mL), water (2 x 15 mL), and saturated brine solution (2 x 15 mL), then dried over sodium sulfate. The dried solution was filtered and solvent was evaporated under aspirator vacuum to give 300 mg of 17 as a white solid (100%).

IR(KBr disc): 2917, 1748, 1711, 1506, 1194 cm^{-1} .

Proton NMR (60 MHz, $CDCl_3$): δ 7.1 (s, 2H), 6.1 (s, 1H), 5.5 (s, 1H), 4.1 (t, 2H), 2.5 (t, 2H), 1.9 (s, 3H), 1.0-1.7 (m, 14H).

Methacrylic 10-hydroxydecanoic anhydride 2a

To 1 (0.50 g, 2.7 mmol) in diethyl ether (20 mL) was added triethylamine (0.28 g, 2.7 mmol) and freshly distilled methacryloyl chloride (0.26 mL, 2.7 mmol) with stirring under a nitrogen atmosphere. After two hours triethylamine hydrochloride was filtered from the solution, and solvent was evaporated under aspirator vacuum to give 0.72 g of 2a as a clear oil (100%). Proton NMR showed no ester formation. R_f (40/60 ethyl acetate/hexane): 0.34.

IR(film): 3400, 2929, 1806, 1731, 1043 cm^{-1} .

Methacrylic 10-methacryloyloxydecanoic anhydride 2b

To 1 (250 mg, 1.3 mmol) in diethyl ether (10 mL), was added triethylamine (270 mg, 2.6 mmol) and freshly distilled methacryloyl chloride (280 mg, 2.6 mmol) with stirring under a nitrogen atmosphere. After 18 hours the mixture was filtered, extracted with water (3 x 5 mL), dilute hydrochloric acid solution (3 x 5 mL), water (2 x 5 mL), and saturated brine solution (2 x 10 mL), then dried over magnesium sulfate. The dried solution was filtered and solvent was evaporated under reduced pressure to give 330 mg of 2b as an oil (78%). R_f (40/60 ethyl acetate/hexane): 0.69.

IR(film): 2927, 1805, 1784, 1715, 1698, 1040 cm^{-1} .

Proton NMR (60 MHz, CDCl_3): δ 6.1 (s, 2H), 5.7 (s, 2H), 4.1 (t, 2H), 2.4 (m, 2H), 2.0 (s, 6H), 1.3 (m, 14H).

MS(chemical ionization): 325 (M + 1).

10-(2-chloroacetyloxy)decanoic acid

To 1 (0.50 g, 2.7 mmol) in diethyl ether (25 mL) was added triethylamine (0.75 mL, 2.7 mmol) with stirring. After five minutes, chloroacetyl chloride (0.45 mL, 2.8 mmol) was added dropwise over a five minute period. A precipitate formed immediately. After twelve hours the mixture was filtered through celite, and solvent was evaporated under reduced pressure to give 0.72 g of the product as a clear oil (100%). Proton NMR showed the disappearance of the methylene alcohol resonance and the appearance of a methylene ester resonance.

IR(film): 2700-3500, 2926, 1757, 1725, 1216, 1190 cm^{-1} .

CLAIMS TO ORIGINAL RESEARCH

1. The development of a new synthetic route to side-chain liquid crystalline polymethacrylates which offers significant advantages over previously reported methods.
2. The preparation and characterization of three new side-chain polymethacrylates, one of which exhibits liquid crystalline properties.
3. The first reported synthesis of an ω -methacryloyloxyalkanoic acid, specifically 10-methacryloyloxydecanoic acid, which is a very versatile reagent in side-chain polymethacrylate synthesis.
4. The synthesis and characterization of the first chiral paired mesogen liquid crystalline polymethacrylate.
5. Preparation of two mesogen-containing methyl methacrylate copolymers.

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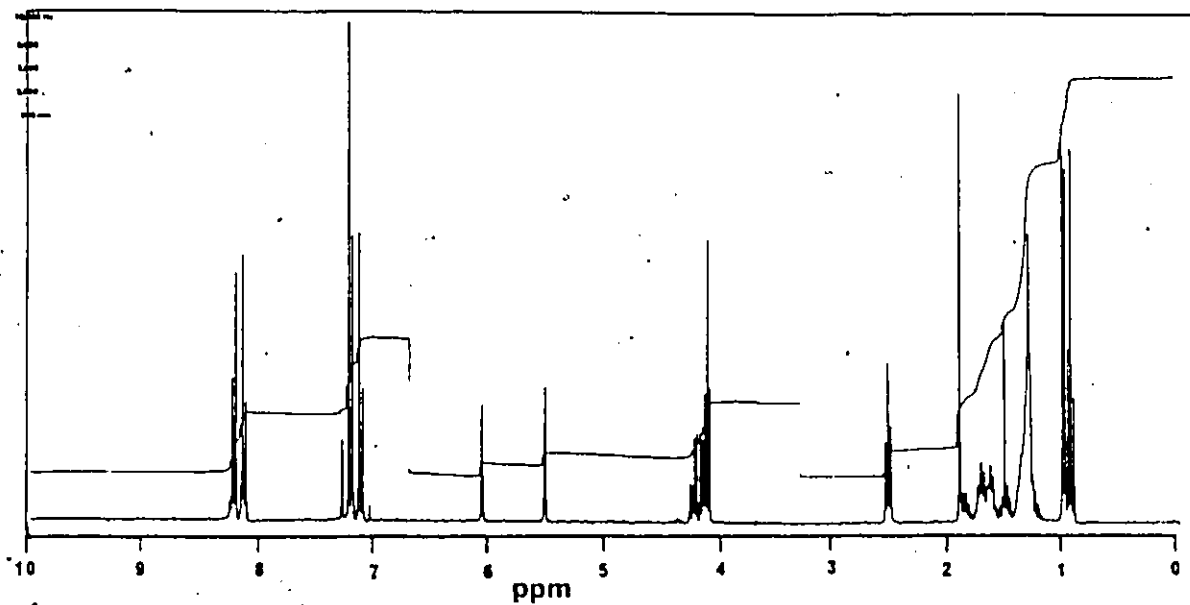
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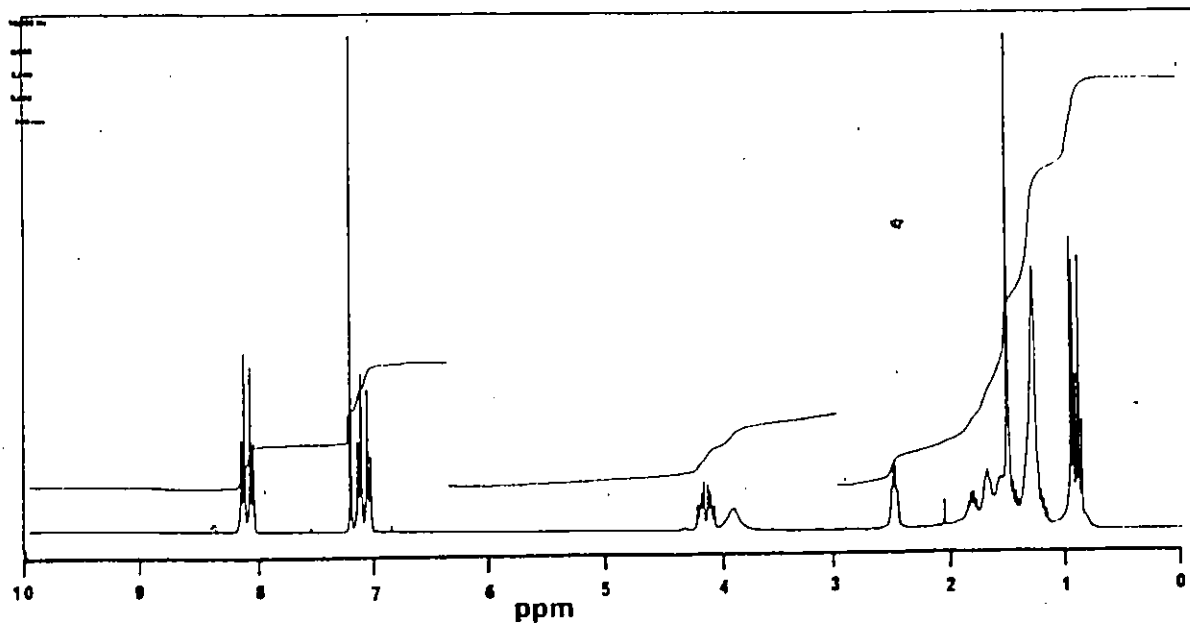
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APPENDIX A

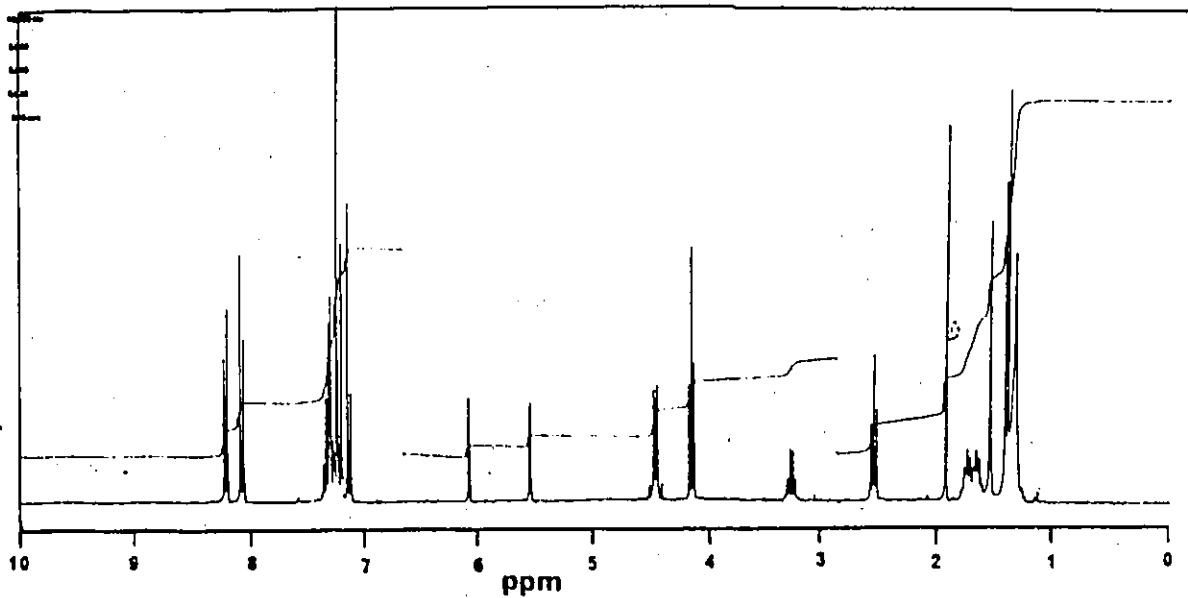
300 MHz Proton NMR Spectra



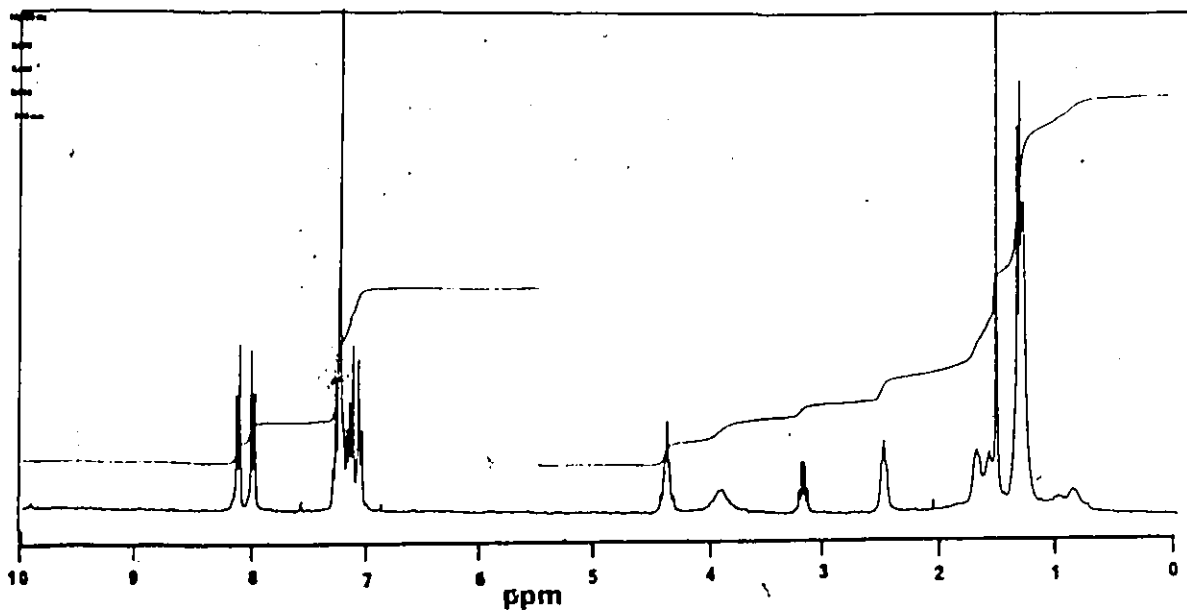
Monomer 8a



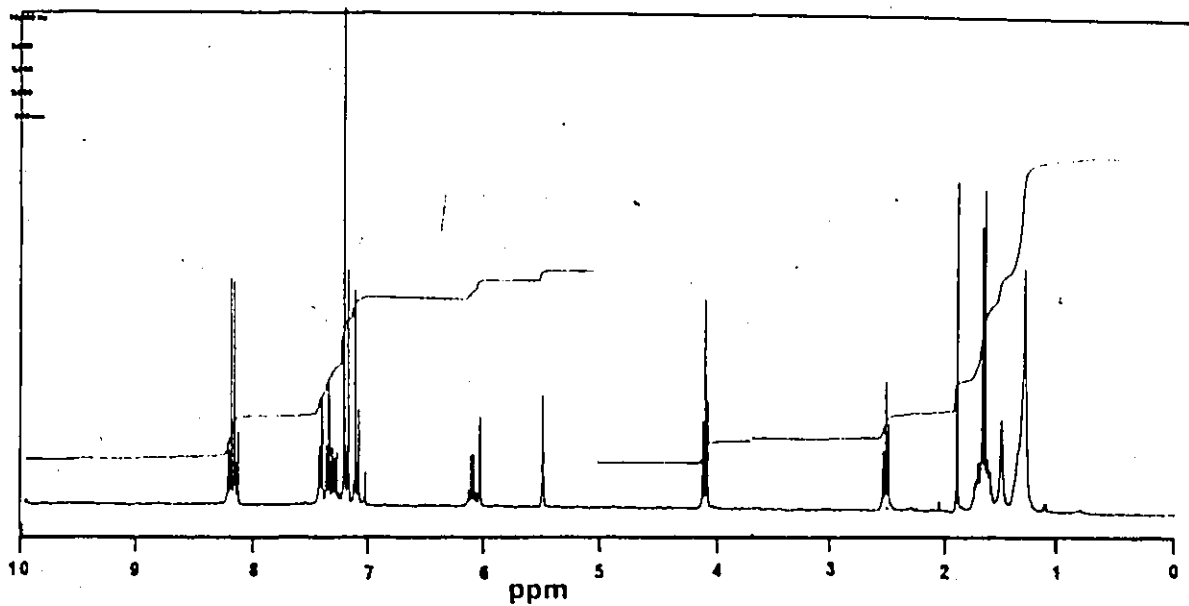
Polymer 13a



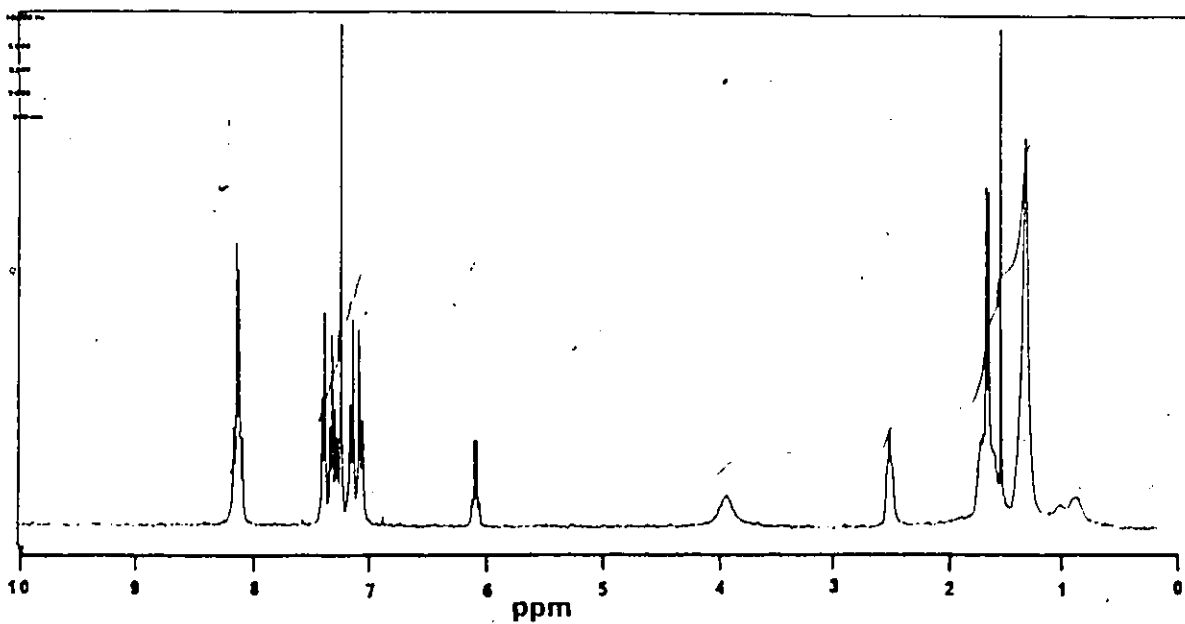
Monomer 8b



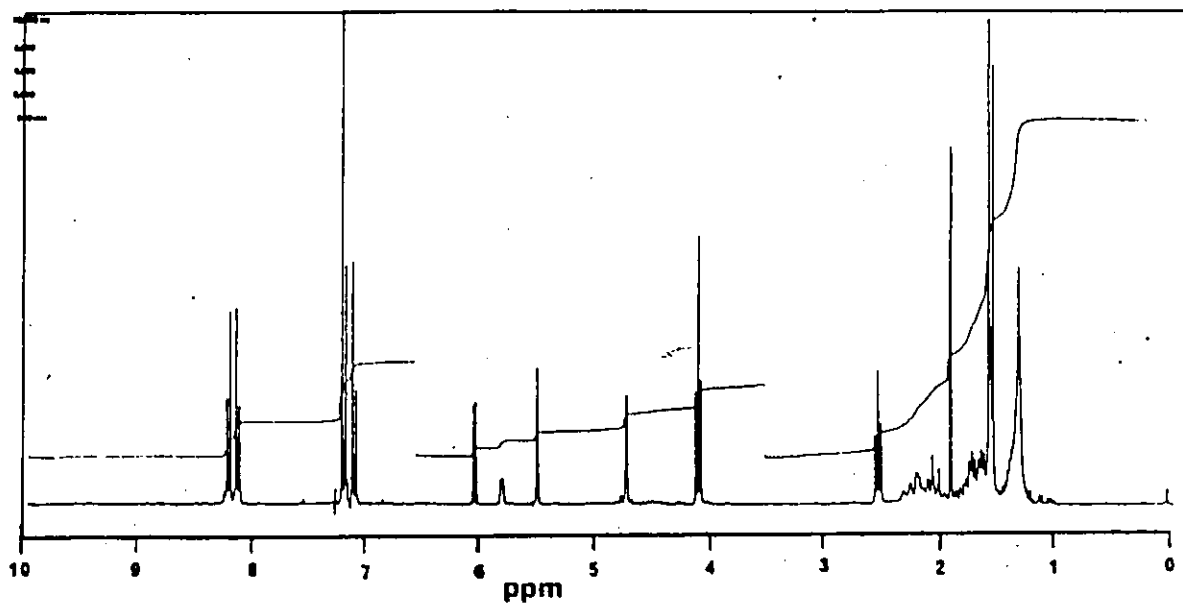
Polymer 13b



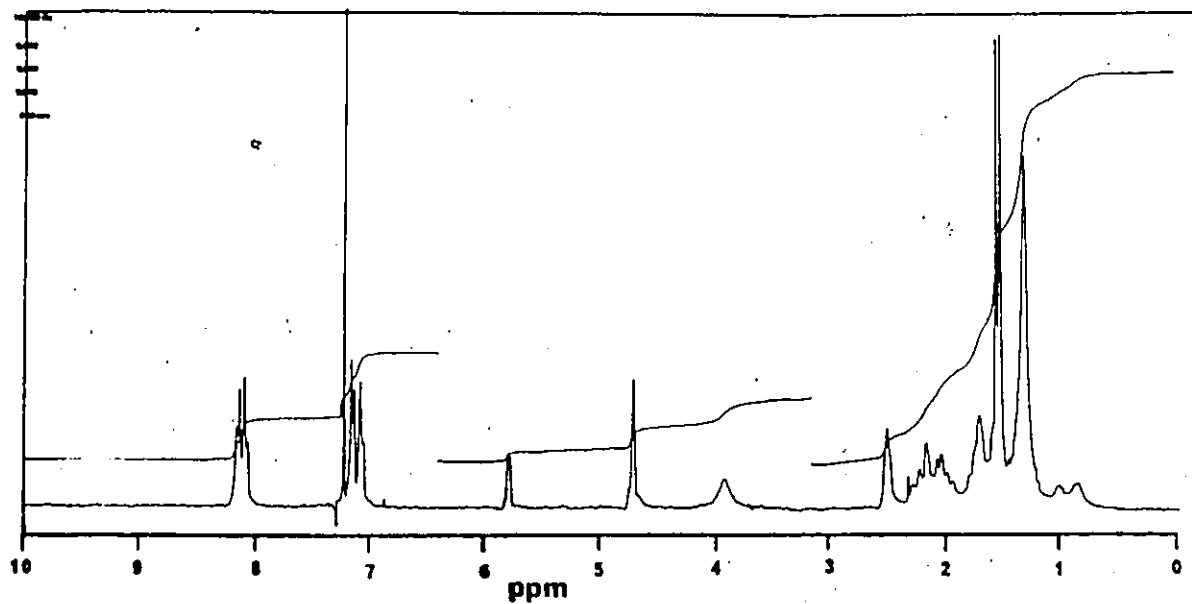
Monomer 8c



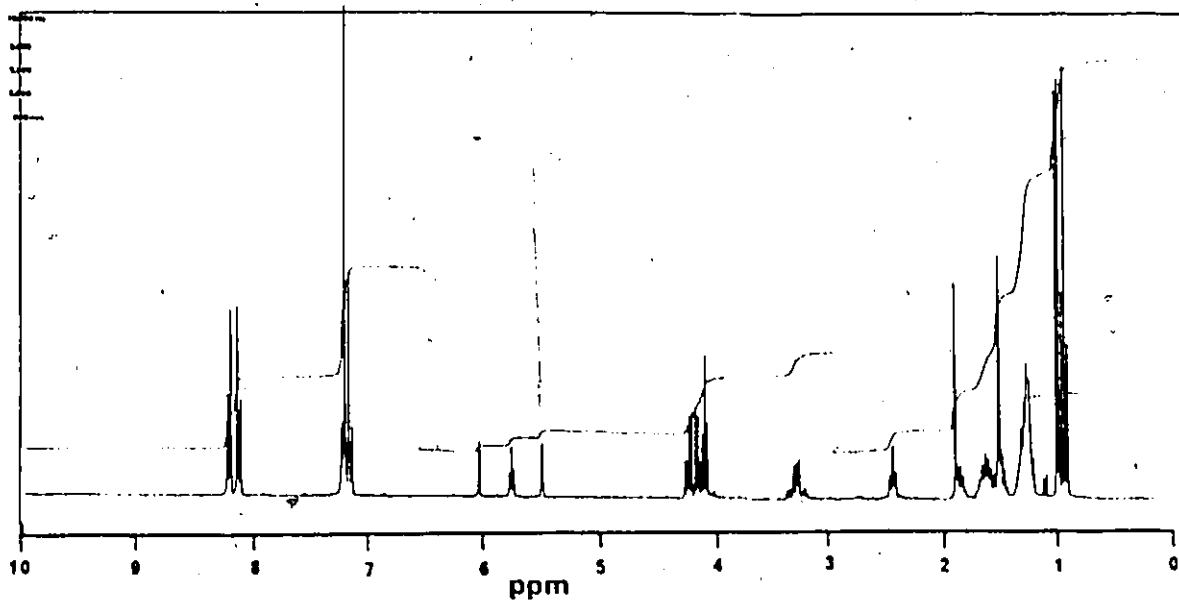
Polymer 13c



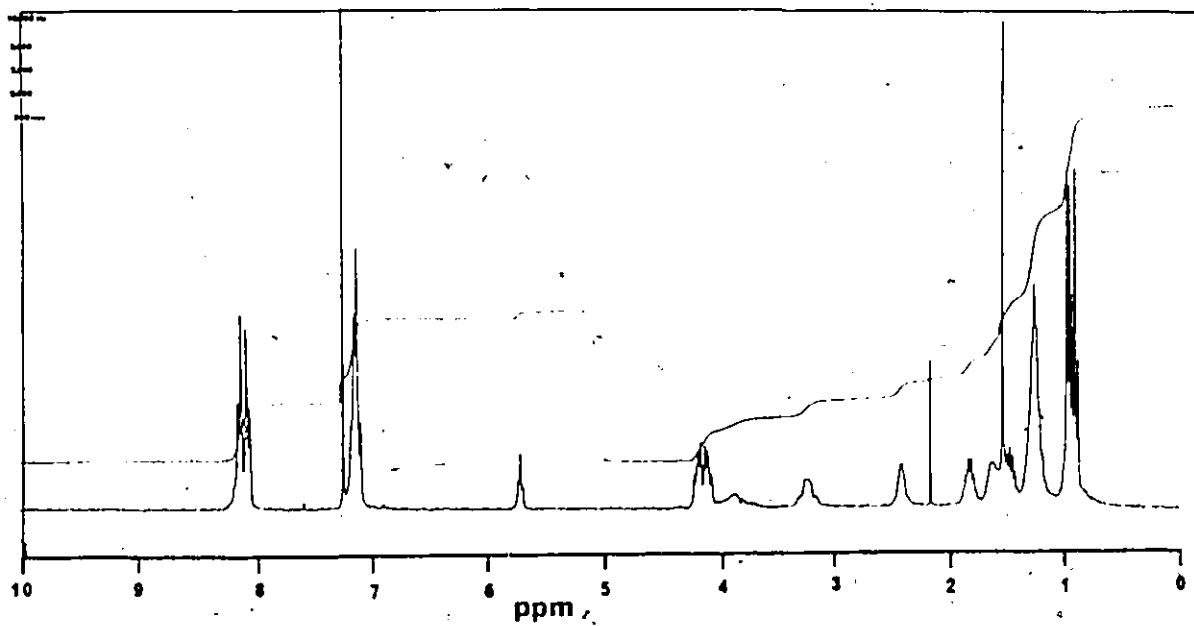
Monomer 8d



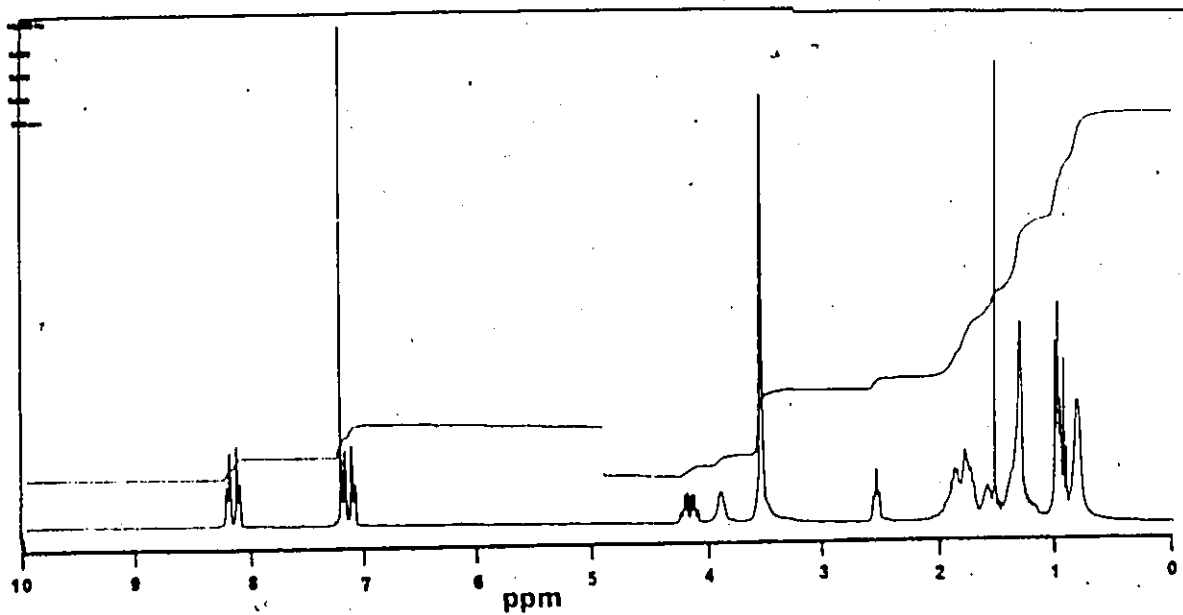
Polymer 13d



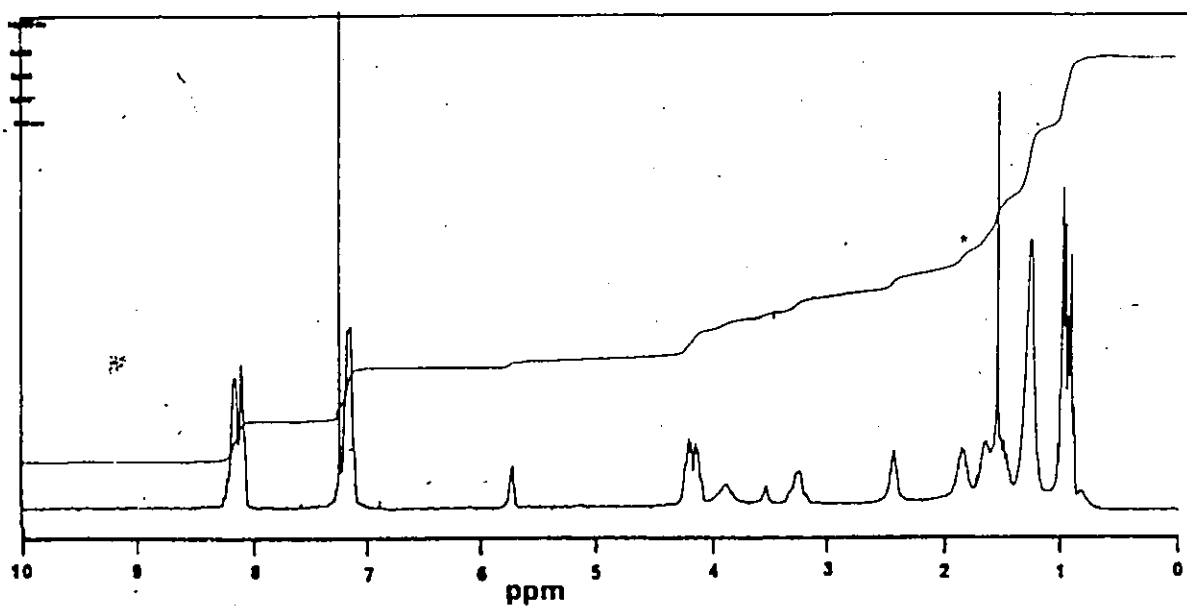
Monomer 12



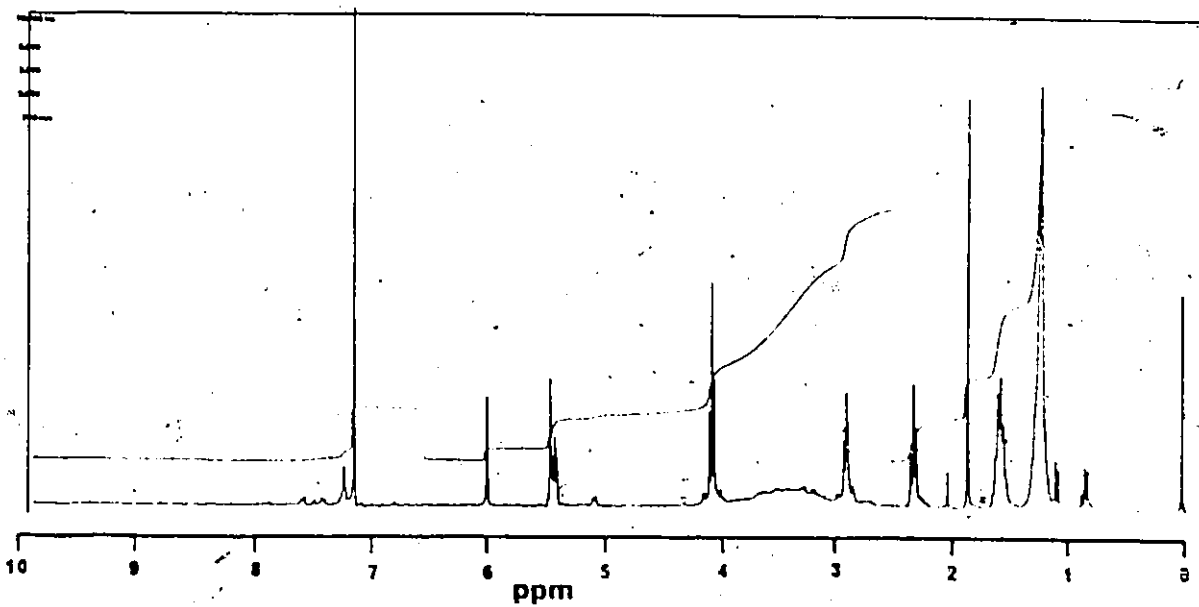
Polymer 14



Copolymer 15



Copolymer 16



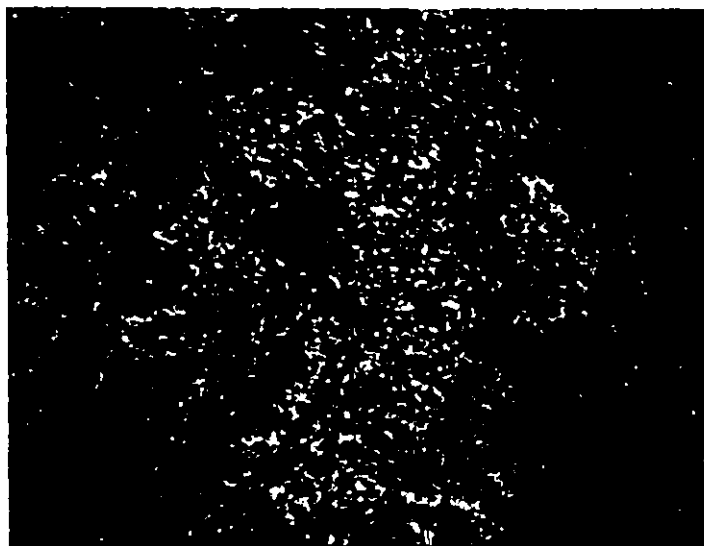
Compound 11

APPENDIX B

Photographs of Birefringence Patterns



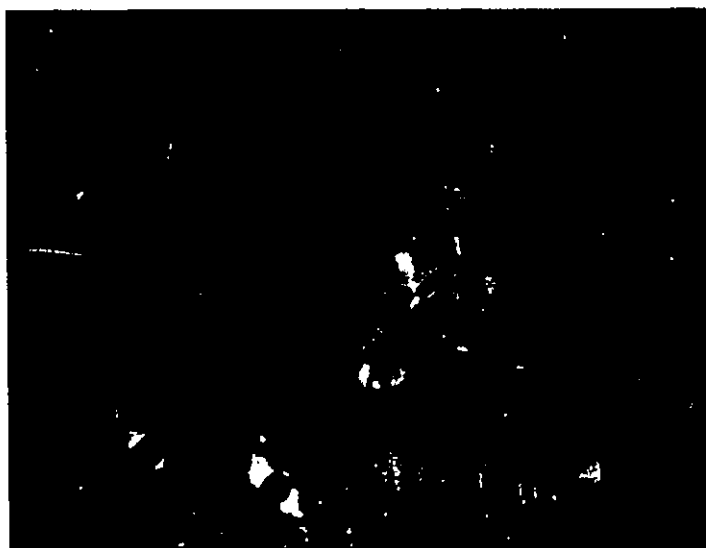
Monomer 8a 50X magnification, crossed polarizers, 18 °C, cooling.
Transition from liquid crystalline to crystal.



Monomer 8b 50X magnification, crossed polarizers, 30 °C, heating.



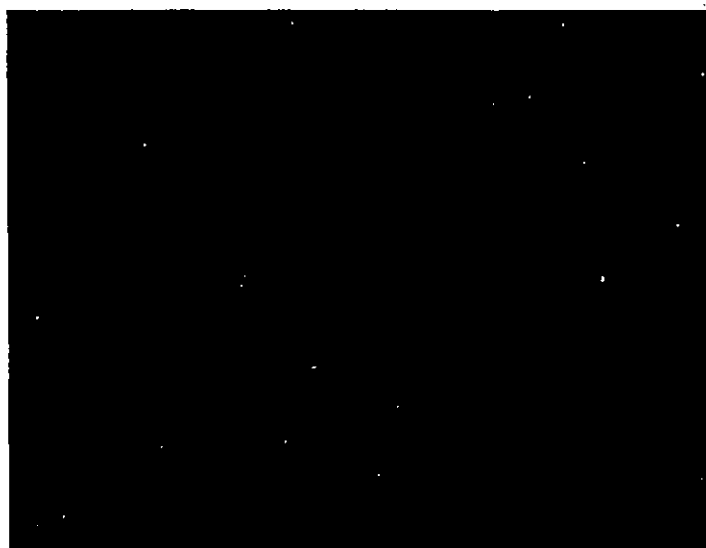
Monomer 12 50X magnification, crossed polarizers, 49 °C, cooling.



Polymer 13a 50X magnification, crossed polarizers, 72 °C.



Polymer 13a 200X magnification, crossed polarizers, 80 °C.



Polymer 13b 200X magnification, crossed polarizers, 99 °C.



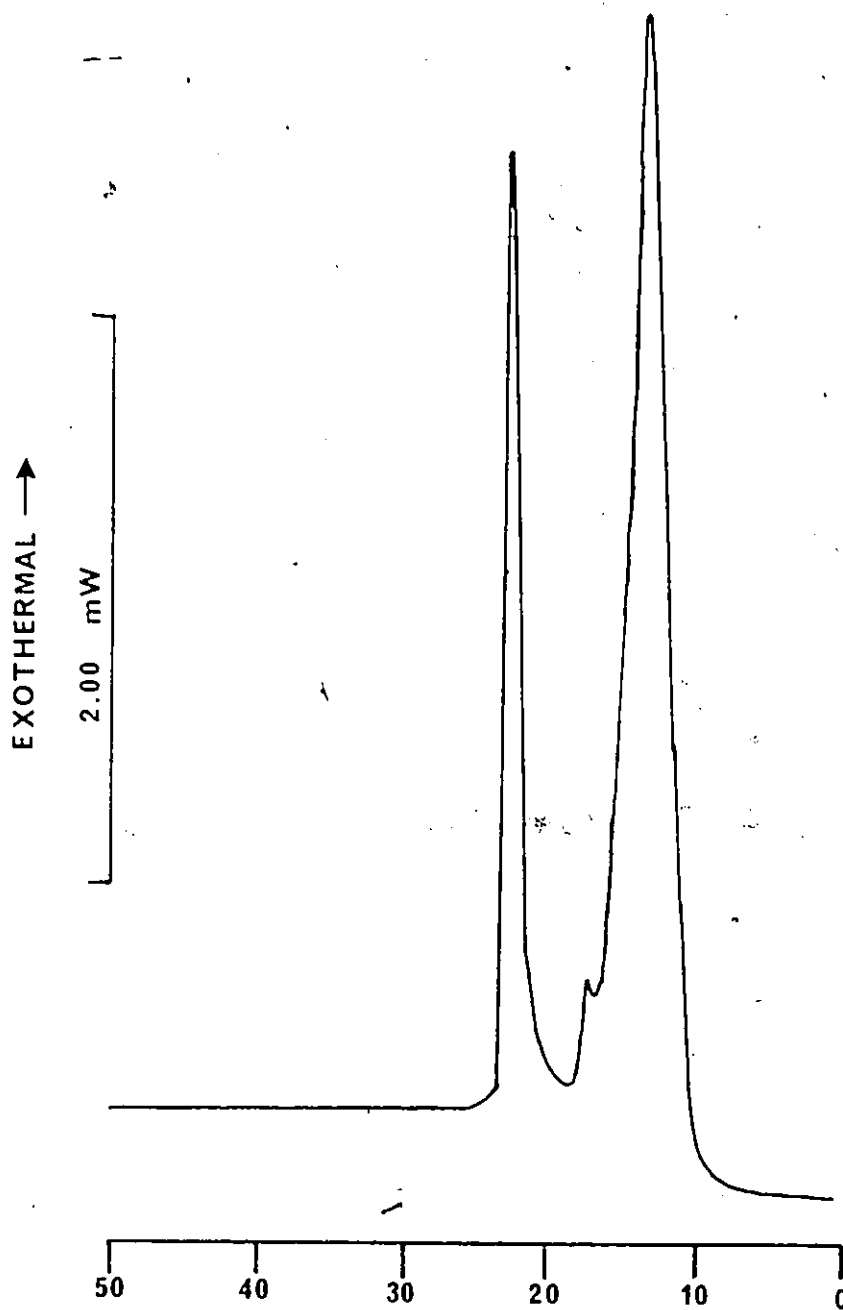
Polymer 14 50X magnification, crossed polarizers, 90 °C.
After cooling from 200 °.



Polymer 14 50X magnification, crossed polarizers, 148 °C.
Shows polymer in two different states, one liquid crystalline and the other crystalline.

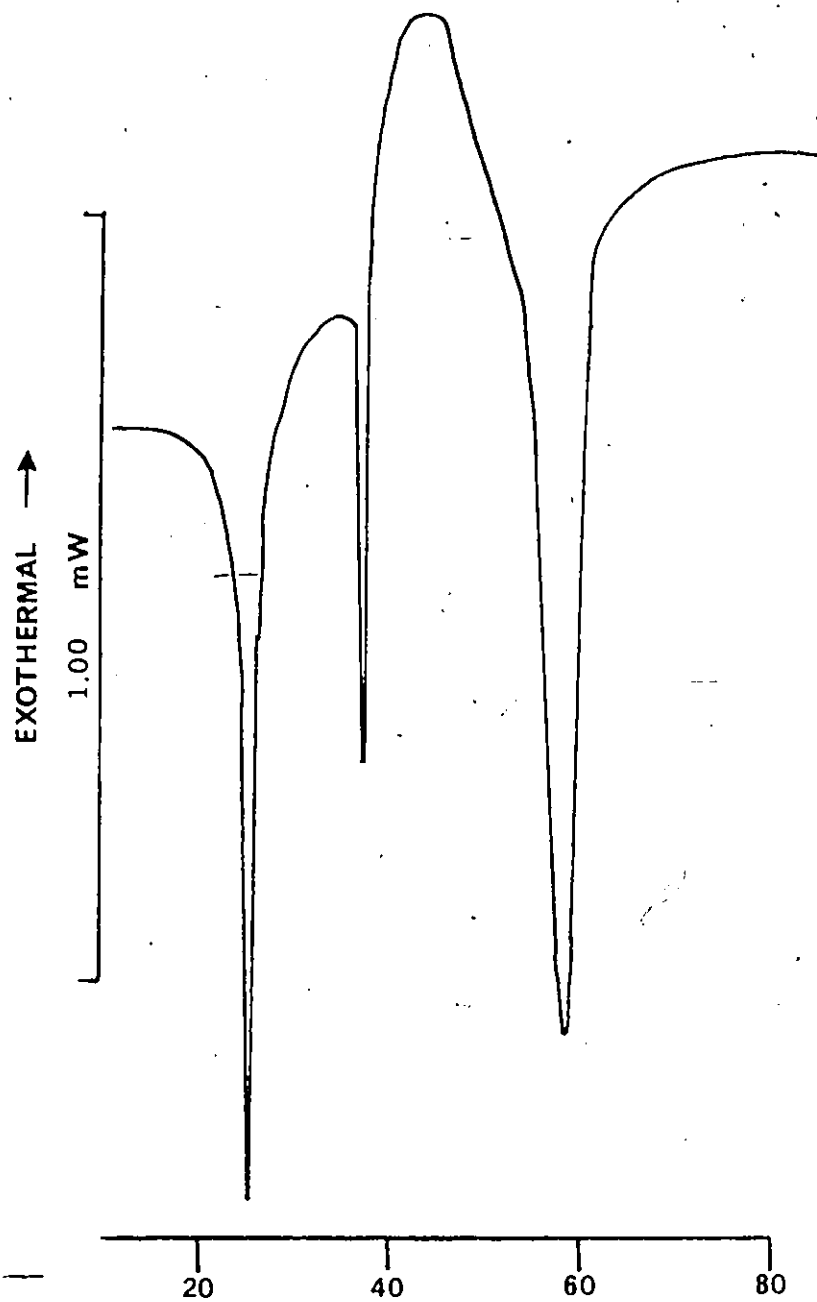
APPENDIX C

Differential Scanning Calorimetry Curves



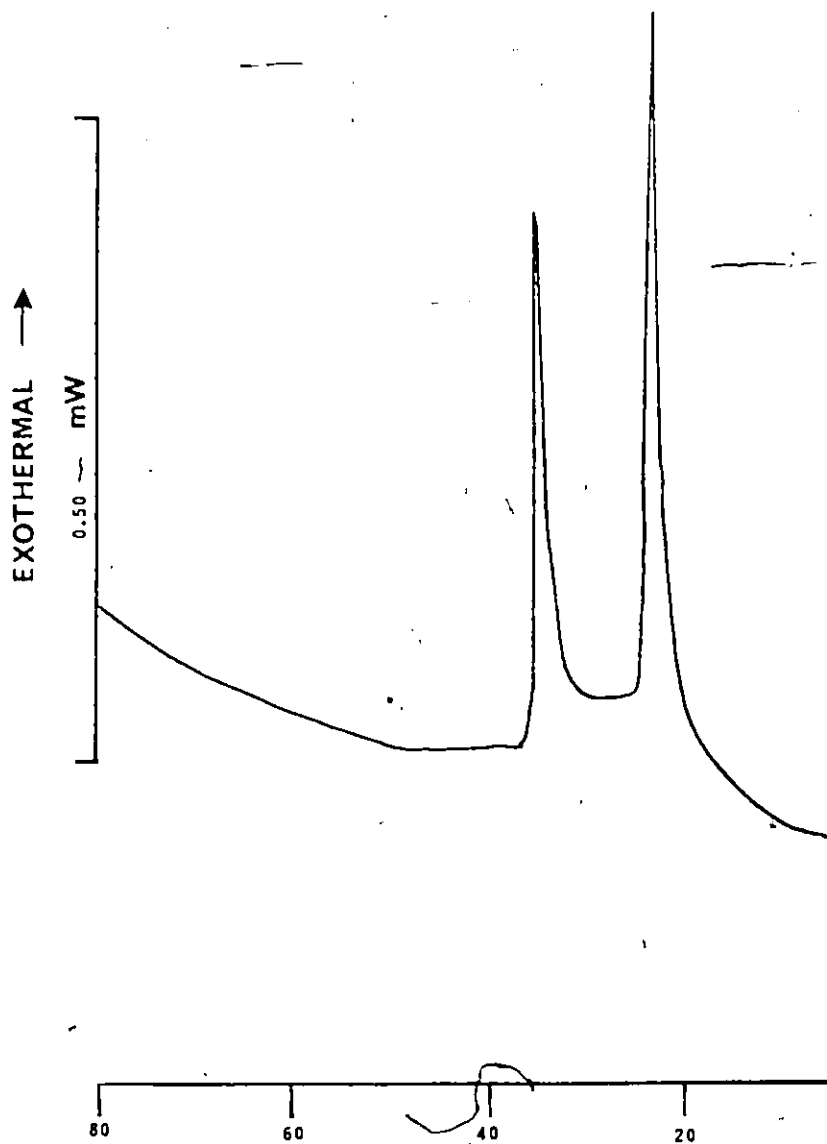
Monomer 8a 5.70 mg, cooling at 5 °C per minute.

Exotherms: 23.0 °C, 9.5 J/g; 13.6 °C, 28.1 J/g.

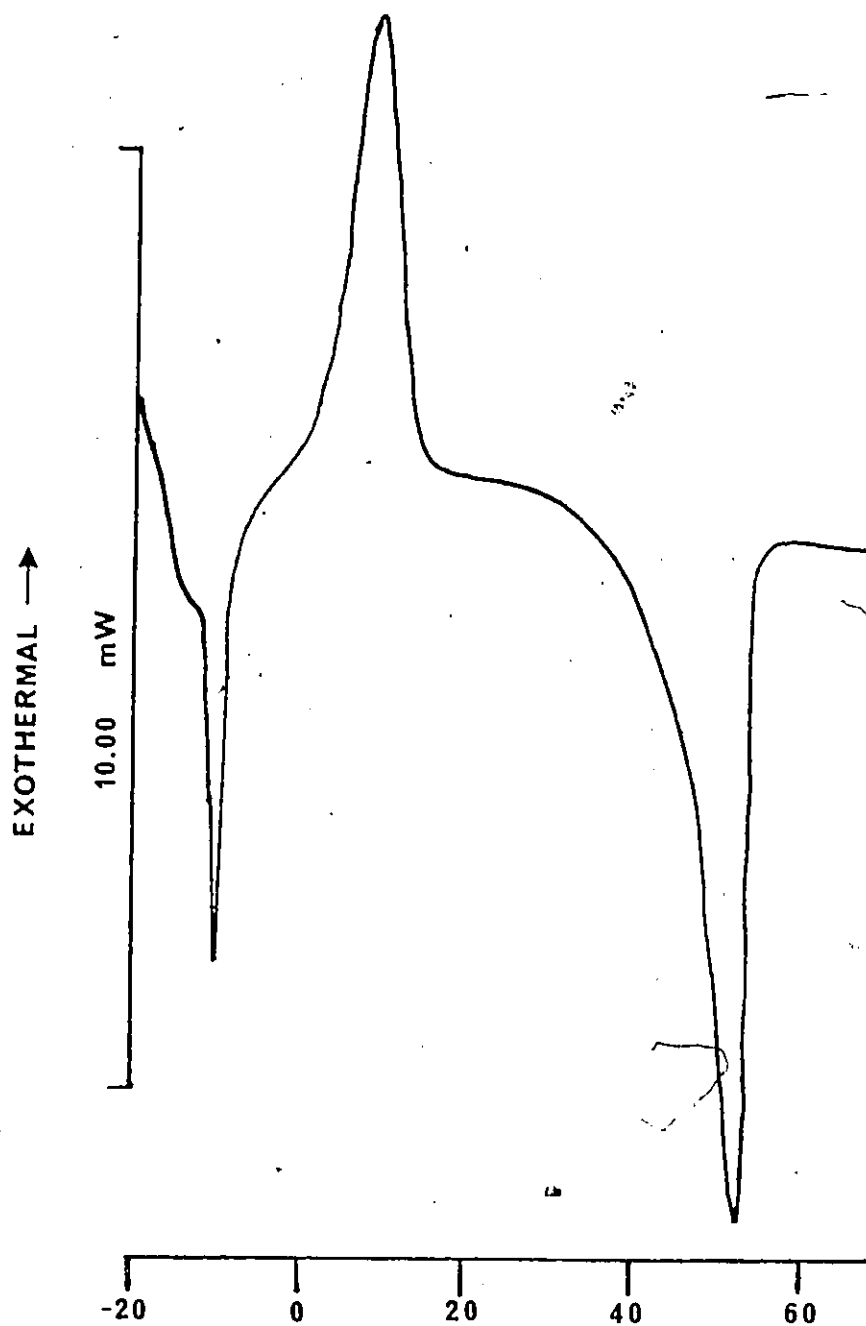


Monomer 8b 4.43 mg, heating at 10 °C per minute.

Exotherms: 26.4 °C, 44.9 J/g; 36.4 °C, 0.8 J/g; 58.4 °C, 27.3 J/g.

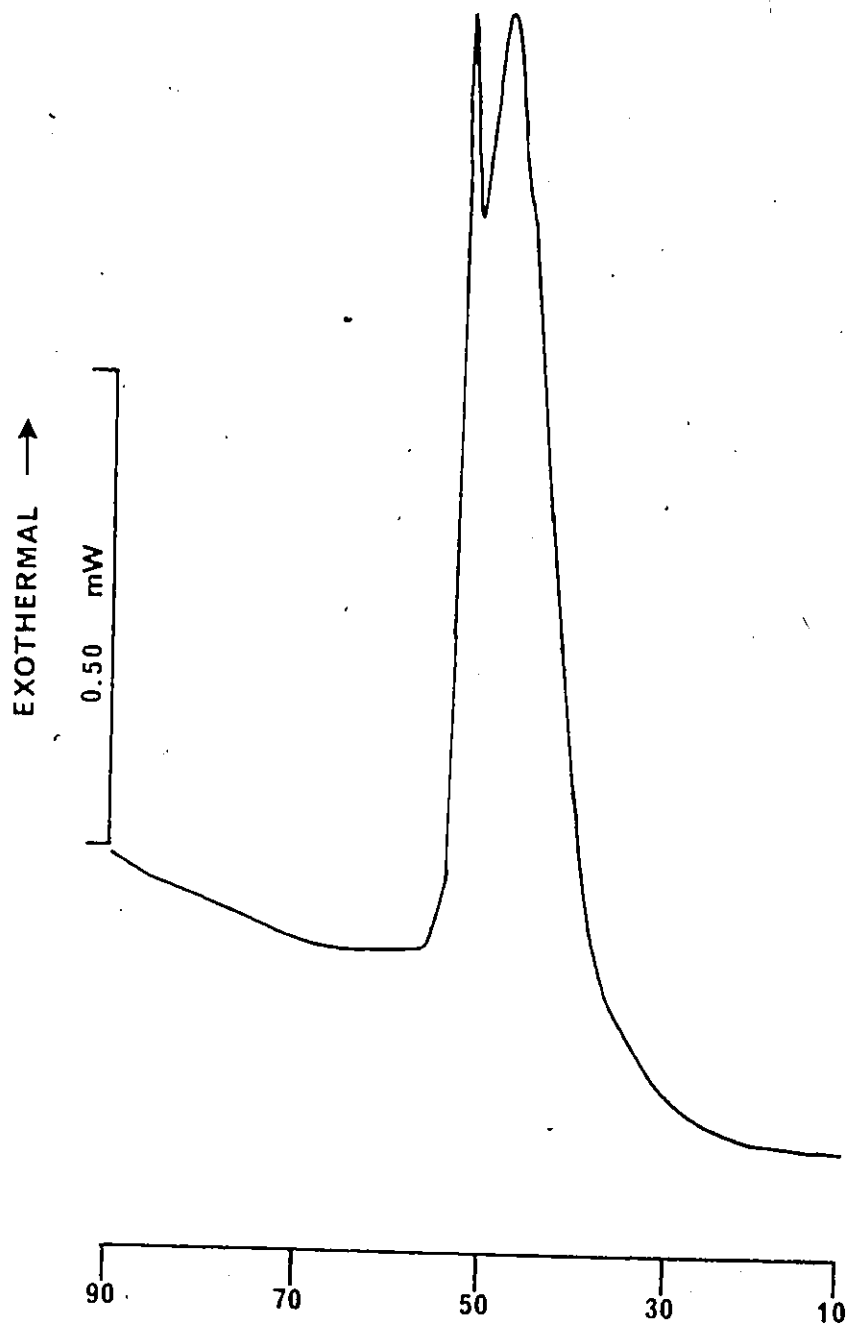


Monomer 8b 4.43 mg, cooling at 5 °C per minute.
Exotherms: 35.7 °C, 1.5 J/g; 23.5 °C, 2.5 J/g.



Monomer 8c 10.60 mg, heating at 5 °C per minute.

Endotherms: -10.6 °C, 17.3 J/g; 51.6 °C, 44.3 J/g.
Exotherm: 10.1 °C, 37.0 J/g.



Monomer 12 2.82 mg, cooling at 5 °C per minute.

Exotherms at 52 and 48 °C, 48.6 J/g total (unresolved).

EXOTHERMAL ↑

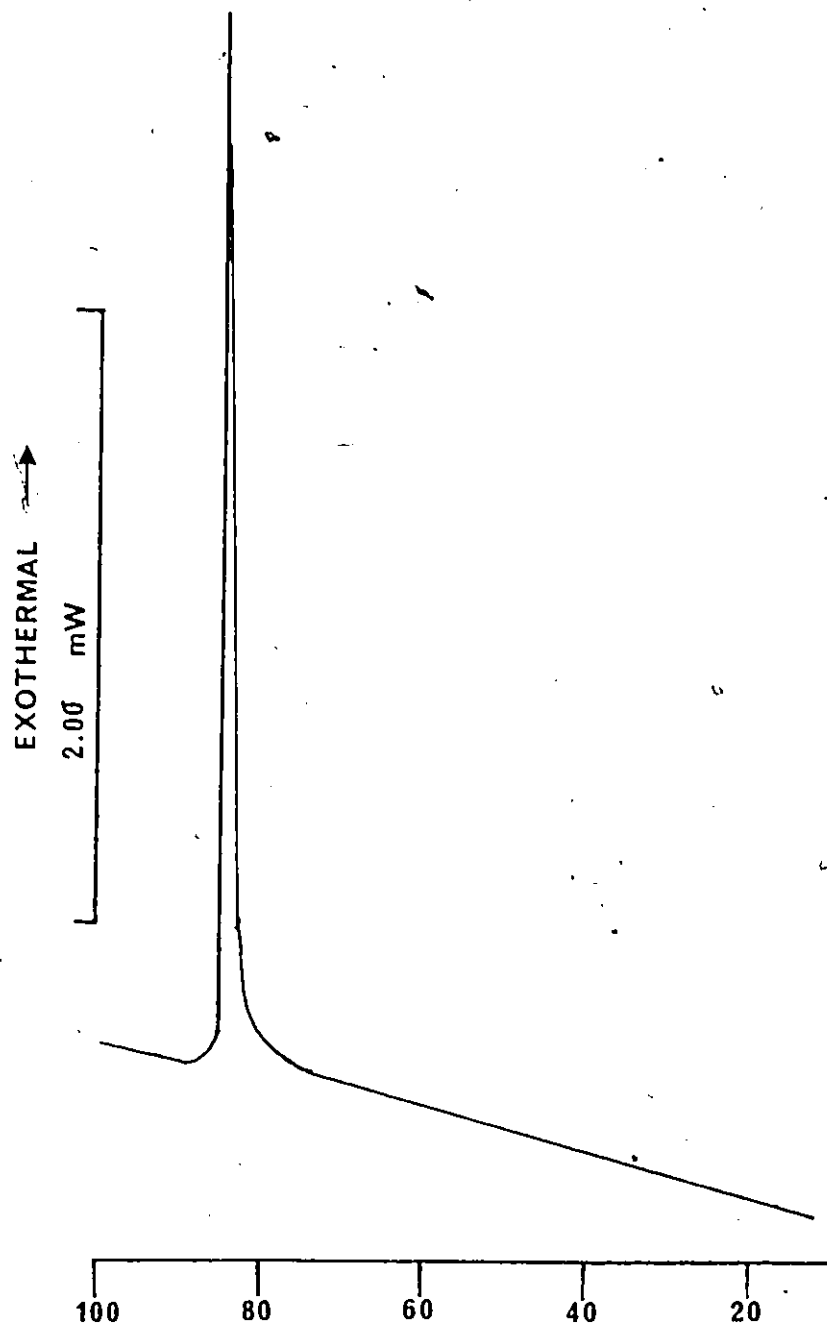
2.00 mW

0 20 40 60 80 100

Polymer I3a 5.15 mg, heating at 5 °C per minute. .

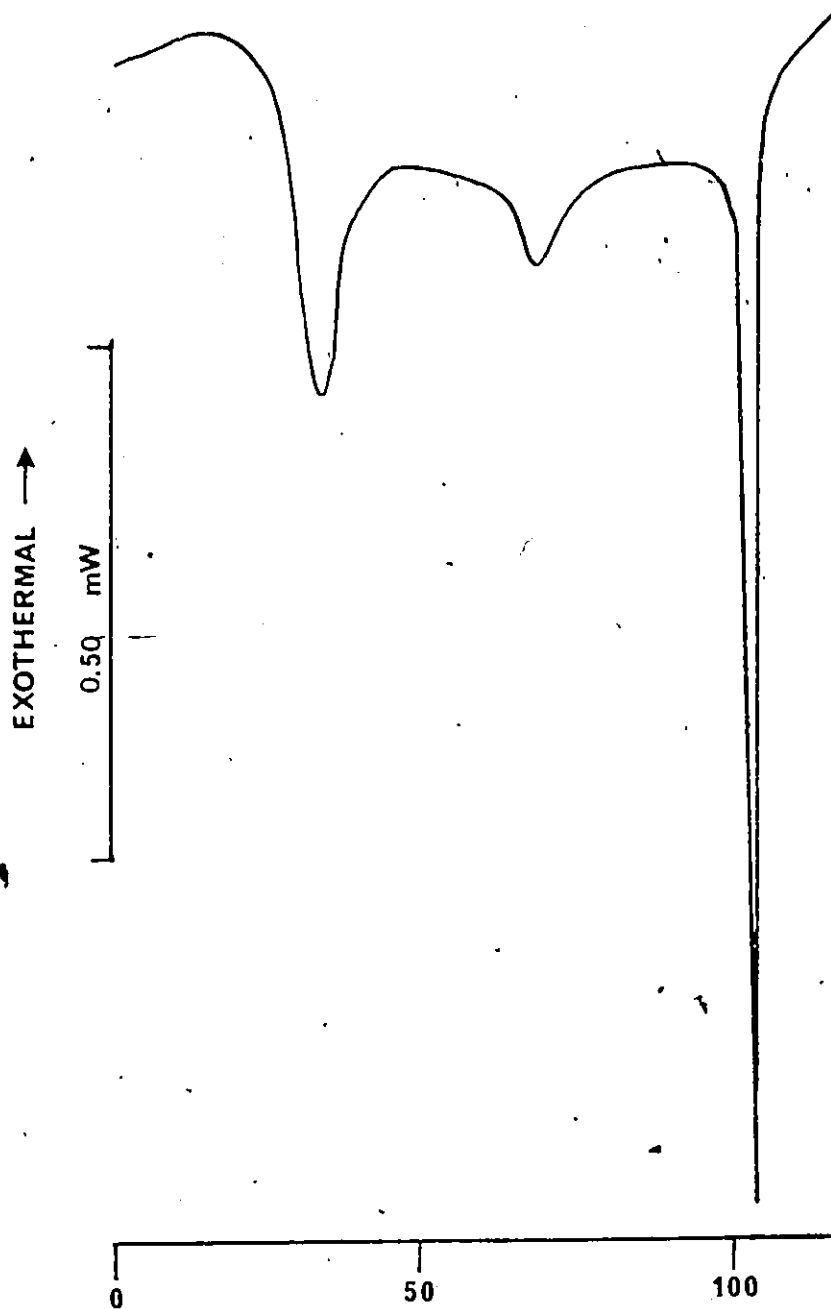
Glass transition: 5-20 °C.

Endotherm 89.2 °C, 11.8 J/g.



Polymer 13a 5.15 mg, cooling at 5 °C per minute.

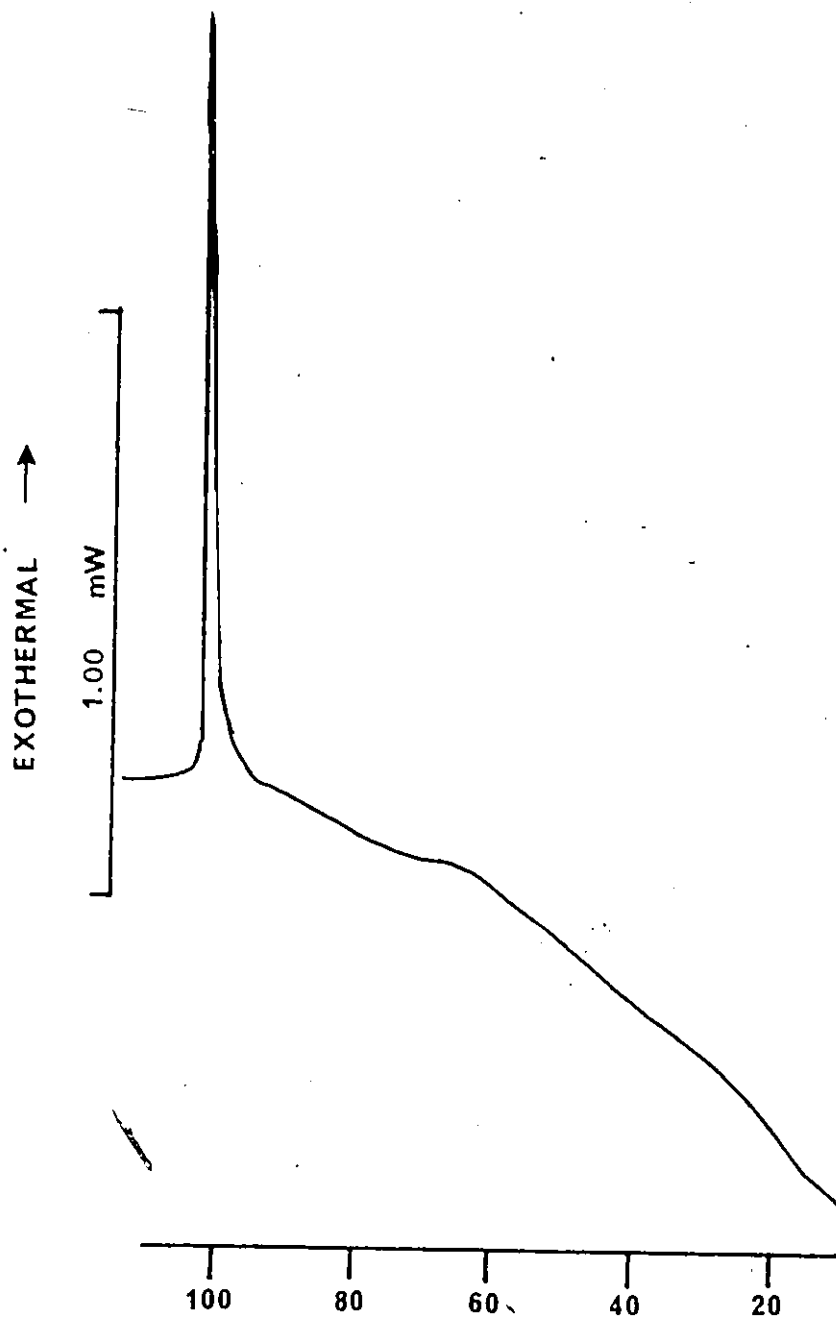
Exotherm: 85.0 °C, 13.2 J/g.



Polymer 13b 7.67 mg, heating at 5 °C per minute.

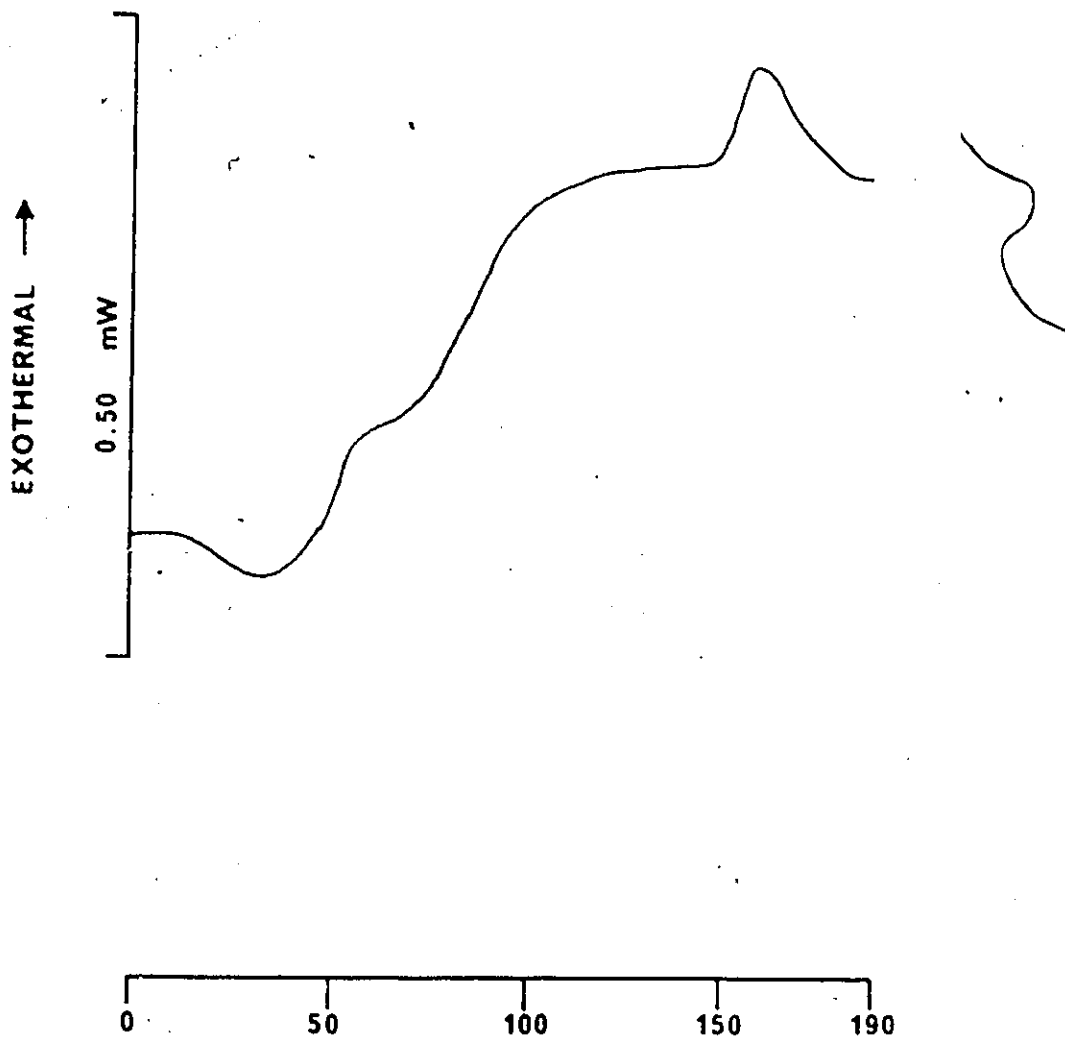
Glass transition (partial crystallization): 25-40 °C.

Endotherms: 70 °C; 103.9 °C, 3.3 J/g.



Polymer 13b 7.67 mg, cooling at 5 °C per minute.

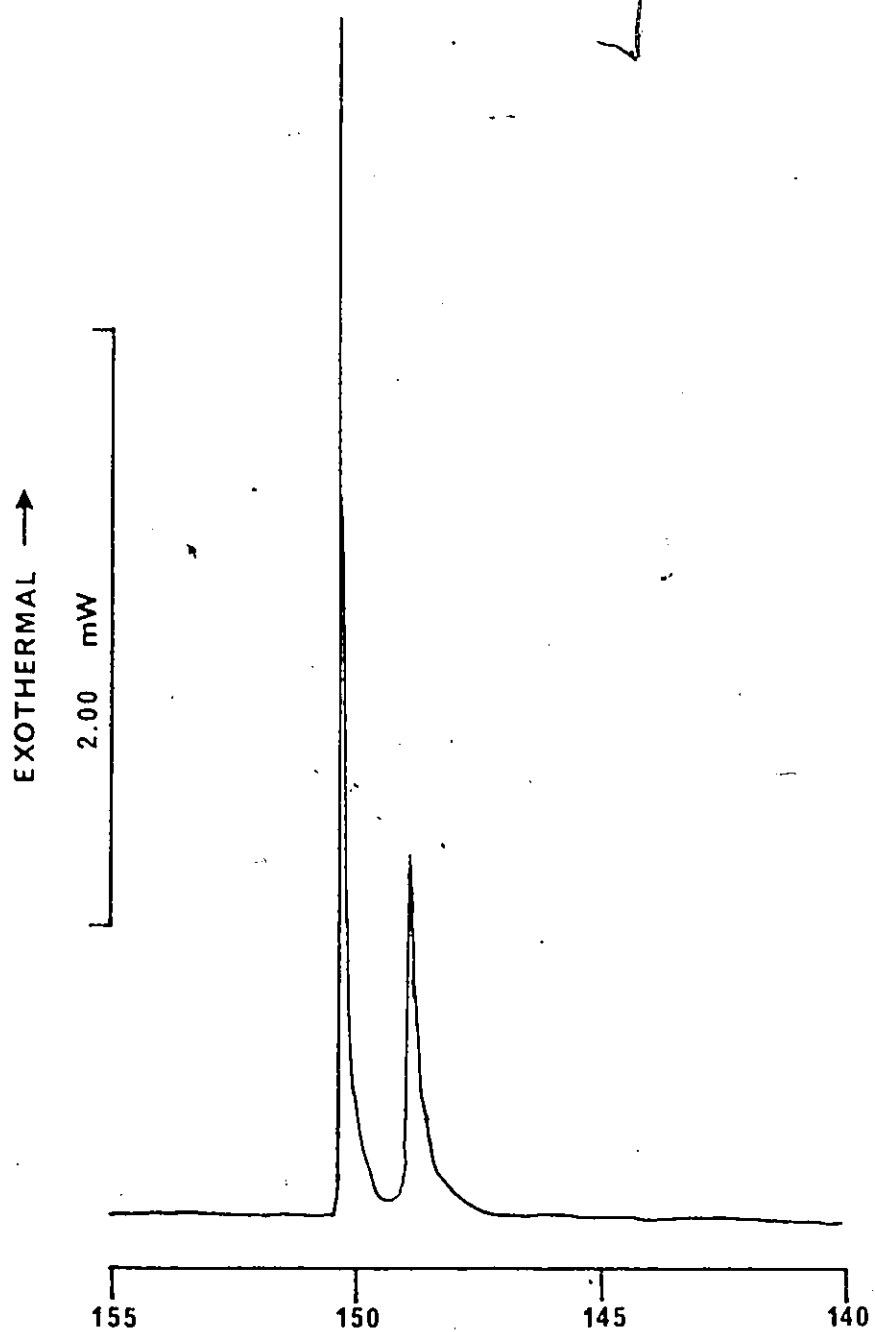
Exotherm: 102.2 °C, 3.1 J/g.



Polymer 14, 5.30 mg, heating at 5 °C per minute.

Glass Transition: 40-50 °C, Δ

Exotherm: 158 °C, 2.33 J/g.



Polymer 14 5.30 mg, cooling at 1 °C per minute.

Exotherms: 150.5 °C, 7.6 J/g; 149.0 °C, 2.8 J/g.

✓

BIOGRAPHY

Kevin Taylor was born in Estevan, Saskatchewan in March, 1960. He completed high school and first year college in Castlegar, B.C. In 1979, Kevin enrolled in the Chemistry co-operative education program at the University of Victoria. During this time he worked for Eurocan Pulp and Paper Ltd., Kaiser Resources Ltd., and Esso Resources Ltd. In addition, he held a Natural Science and Engineering Research Council summer bursary with Dr. Tom Fyles in synthetic organic chemistry.

On graduation in the Spring of 1983, Kevin joined Dow Chemicals Canada Inc. in Fort Saskatchewan, Alberta. He was involved in new product development, and co-authored a patent on the preparation of N-substituted piperazinones.

In the Fall of 1985 Kevin began graduate studies in polymer chemistry with Dr. Jean Fréchet at the University of Ottawa. Kevin was funded by both a Natural Science and Engineering Research Council postgraduate scholarship and a University of Ottawa entrance scholarship.

Kevin is currently working for the Petroleum Recovery Institute in Calgary, Alberta.