The synthesis and characterization of some liquid crystalline polyesters based upon the oxybenzoate-terephthalate mesogenic unit.

C. K. Ober

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THE SYNTHESIS AND CHARACTERIZATION OF SOME LIQUID CRYSTALLINE POLYESTERS BASED UPON THE OXYBENOZATE-TEREPHALATE MESOGENIC UNIT

A Dissertation Presented
By
CHRISTOPHER K. OBER

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of
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May 1982
Polymer Science and Engineering
THE SYNTHESIS AND CHARACTERIZATION OF SOME LIQUID CRYSTALLINE POLYESTERS BASED UPON THE OXYBENZOATE-TEREPHTHALATE MESOGENIC UNIT

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Dedicated to my wife
Patricia and our families.
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I would like to thank all the students and faculty at UMASS for making these years so enjoyable, and especially my committee members, Professors Lenz, Stein and Porter for their part in it. In particular, I would like to thank Professor Lenz for opening up so many opportunities to me.

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ABSTRACT

THE SYNTHESIS AND CHARACTERIZATION OF SOME LIQUID CRYSTALLINE POLYESTERS BASED UPON THE OXYBENZOATE-TEREPHTHALATE MESOCENIC UNIT

May 1982

Christopher K. Ober

B.Sc., University of Waterloo
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Directed by: Dr. R.W. Lenz

Several series of thermotropic polyesters were prepared by solution polymerization methods using various specially prepared diols and diacid chlorides. The effect that different flexible spacers and mesogenic units based on oxybenzoate terephthalate dyads and triads had on liquid crystallinity was studied by microscopic and thermal analysis techniques.

Polymers combining triad aromatic mesogenic groups and polymethylene flexible spacers in the main chain were shown to possess a single mesophase. The transition temperatures of the homologous series were determined by polarized-light microscopy, differential scanning calorimetry (DSC), and thermal-optical analysis (TOA), and were shown to follow an even-odd relationship. Those polymers with less than seven methylene groups in the spacer possessed nematic mesophases while those polymers with seven or more methylene groups showed the optical textures of smectic mesophases.
Other polymers were prepared based upon the mesogenic triad and either a poly(ethylene oxide) (PEO), or a poly(propylene oxide) (PPO) flexible spacer. Some polymers with spacers of PEO exhibited two mesophase transitions. Polymers with PPO spacers showed a single mesophase and no melt transition. More than 50 weight-% spacer led to mesophase loss.

Polymers with flexible spacers and mesogenic dyads were prepared which showed either a random or alternating placement of the dyads. All of the liquid crystalline polymers containing the mesogenic dyad were nematic, and the arrangement of the dyads in the polymer chain was important, because two polymers with decamethylene spacers and differing dyad sense had different melt behaviors.

A final series of polyesters was prepared by melt-transesterification that contained the mesogenic elements described above. In order to incorporate oxybenzoate groups into the polymer chain, it was necessary to use terephthalate copolymers that contained ethylene glycol in addition to a second diol. These materials were found to be more "weakly" liquid crystalline than the other polymers with mesogenic aromatic dyads and triads.
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CHAPTER I
LOW MOLECULAR WEIGHT AND
POLYMERIC LIQUID CRYSTALS

Introduction

Polymers and low molecular weight compounds which show a
degree of order in the melt or in solution which is intermediate
between the crystalline solid and the isotropic liquid states are
called liquid crystalline. Alternative terms for this state are
mesomorphic and mesophasic. In the polymeric form, the high degree
of order of these materials imparts unusual properties not possessed
by more conventional amorphous or semi-crystalline polymers so that
when properly treated, such polymers can give oriented materials of
extremely high strength and modulus.\(^1\) Additionally, their capacity
for spontaneous ordering is also expected to have possible applica-
tions in biological and biomedical areas.\(^2\)

After the development of high modulus fibers based on lyotropic
nematic polyamides,\(^3\) attention focussed on the preparation of
thermotropic polymers that would possess similar properties but
without the practical difficulties of the solvent-based lyotropic
systems. The first recognized thermotropic polymer reported in the
patents was a polyester based on poly(ethylene terephthalate) modified
with p-hydroxy benzoic acid.\(^4\)
More recently, the number of polymers showing thermotropic behavior has increased tremendously. Mesogens have been polymerized in cross-linked systems in order to trap in the mesophase structure.\(^{(5)}\) By placing the mesogenic unit in a side chain, greater freedom of movement is allowed, and polymers have been prepared showing smectic, cholesteric, and nematic mesophases.\(^{(6-10)}\) Polymers with the entire main chain acting as a mesogen, that is, rigid-rod type polymers,\(^{(11-13)}\) and polymers with both mesogenic units and flexible spacers in the main chain have also been prepared.\(^{(14-20)}\) Some of these polymers are shown schematically in Figure 1.

In order to understand polymeric liquid crystals, a review of low molecular weight liquid crystals in general would be useful. For this reason, the next section is devoted to a brief discussion of the possible structures and properties of low molecular weight liquid crystals. Subsequent sections are concerned with the different types of liquid crystalline polymers with primary interest being limited to thermotropic compounds.

**Low Molecular Weight Liquid Crystals**

The structure of liquid crystalline polymers in the mesophase is very similar to that of low molecular weight liquid crystals in the melt. A major difference for polymers is that mesogenic units are covalently bonded together in a chain, whereas the low molecular weight mesogens are free to act independently. This leads to differences in their properties, but it is still useful to look at
Figure 1. Schematic structures of thermotropic polymers

- Cross-linked LC polymers

- Side-chain LC polymers

- Main-chain LC polymers

mesogenic unit
the behavior of low molecular weight mesophases in order to gain insight into the organization of polymer melts.

The first liquid crystalline compound was discovered by Reinitzer about 90 years ago when cholesteryl benzoate was found to generate an unclear, turbid melt from the solid crystal at $145^\circ C$ which upon further heating gave the expected isotropic melt at $179^\circ C$. The intermediate phase, or mesophase, possessed both the anisotropy of the solid crystal and the fluidity of the liquid and hence was termed a liquid crystal. Since the mesophase appeared with changes in temperature it was called thermotropic to differentiate it from mesophases generated in the presence of solvent (lyotropic).

Friedel in his early work on these materials found that when a liquid film was placed on a microscope with cross polarized light, the mesophases gave birefringent patterns or textures. These textures were characteristic of the organization of the mesophase, and he could define three basic types.

i) Nematic phases. Structurally, the least complex of the mesophases is the nematic phase which is characterized by orientation of the long axis of the molecules, and a random arrangement of the centers of gravity of the molecules, as shown in Figure 2a. The outstanding characteristic of this form when texture observations are made is the appearance of thread-like structures, referred to as a Schlieren texture. This feature of the nematic state in fact gives the nematic phase its name, which is based on the Greek
Figure 2. Schematic drawing of the mesophase. (a) Nematic (b) Smeectic A.
Figure 2. (cont'd) (c) Cholesteric mesophase showing the characteristic helical twist.
"nematos", meaning threads. A typical nematic texture appears in Figure 3 which shows the Schlieren texture of p-azoxyanisole at 125°C. In this photomicrograph there is also a series of brushes connected to point defects, and an interesting trait of these brushes is that they can be used to positively identify the nematic phase provided that only two brushes share a common point defect. However, it is important to note that the presence of four brushes from a common defect can indicate either nematic or smectic states, the latter being another kind of mesophase.(25)

Orthoscopic and conoscopic observations can be made on liquid crystalline materials. As a result of the orientation of the molecules, the refractive index of the mesogen is different in the directions along the chain and perpendicular to it.(26) From conoscopic measurements, the sample can be studied for positive or negative optical sign. If the refractive index is greater along the long axis, as usually occurs, the mesophase is said to be positive, and as seldom happens, if the refractive index is greater perpendicular to the long axis of the mesogen, then the mesophase is negative. From orthoscopic measurements the birefringence of a sample can be measured, and from this the degree of orientation could be measured. In practice this has not been done because of the liquid nature of the mesophase.(27)

Occasionally, when liquid crystalline compounds in the nematic state are observed under the polarizing microscope, the texture observed is that of the isotropic melt; in other words, the sample
Figure 3. Photomicrograph of the nematic phase of p-azoxyanisole at 130°C. Magnification equals 400x.
appears non-birefringent.\(^{27}\) This appearance can occur when the long axes of the molecules are oriented in the direction of the polarized light. Since the center of gravities of the molecules are arranged in a random fashion, there is no birefringence and the sample appears black. Even the smectic A mesophase can exhibit this texture, because the mesogen layers are perpendicular to the light beam.\(^{30}\)

This pseudo-isotropic texture is also known as the homeotropic texture, and can be caused in several ways. Usually it is caused by the interaction of the liquid crystals with the glass surfaces involved in holding the samples under the microscope. Homeotropism can be eliminated by use of glass slides covered by a layer of obliquely evaporated SiO\(_2\).\(^{31}\) Other means of generating the texture are by the use of electric or magnetic fields which align the molecules in the direction of the polarized light beam.\(^{32}\)

The optical properties of these materials are a function of their orientational order; therefore, the spontaneous ordering of the material can be detected by X-ray diffraction techniques. A crystalline solid will give a series of sharp rings when observed in a powder scattering pattern. If a single crystal is studied, distinct points are observed; however, if this crystal were to melt to a mesophase, these points would change to a diffuse ring resembling in some respects the powder pattern.\(^{28}\) Since the basic repeat unit in the nematic state is the inter-chain spacing, this ring usually corresponds to a separation of about 4-5 Å. Its
Diffuseness is typical of the amorphous nature of liquids, but the fact that rings can be seen also demonstrates that order is present in the system. In the isotropic liquid the diffuse rings give way to an amorphous halo characteristic of complete disorder. Typical diffraction patterns are shown in Figure 4.

Another aspect of liquid crystalline materials is the polarity of the molecule. Generally, the molecules have a lathe-like shape often composed of aromatic rings connected by short polar links. Therefore, the molecules possess a dipole moment that can interact with an electric or magnetic field. If a field is applied, the molecular dipoles orient, and it is this process that is used so effectively in liquid crystal displays (LCD). While liquid crystals are ordered on a microscale, larger sections of the sample exist in separate mesophase domains, and the relative orientations of these domains are disordered. It is for this reason that the X-ray pattern shows rings. It is possible to orient these domains so that their major axes are in a common direction by some external means, and when this occurs, these rings become arcs.

The thermodynamic properties of mesophases are also rather interesting. From thermal and volumetric measurements it has been proved that both the change from solid crystal to mesophase and the change from mesophase to isotropic melt are first order transitions. The melting from solid crystal to nematic phase represents quite a substantial decrease in order which can be seen by measuring the values for the change of entropy ($\Delta S$). For this transition, they
Figure 4. Schematic diagram of X-ray diffraction of liquid crystals. (a) nematic, (b) smectic A, (c) oriented nematic, and (d) oriented smectic A. Arrow indicates direction of magnetic or electric field induced alignment.
are of the order of 20-50 cal/mol-K. However, the clearing transition from the nematic phase to the isotropic melt has a much lower value of ΔS than the melting transition and is generally 10% of that of the melt.\(^{(35)}\) This relationship indicates a much lower change in order, and hence the degree of randomness of the mesophase is much closer to that of the isotropic melt than to the solid.

Most liquid crystalline compounds show complete reversibility of both the melting and clearing temperatures as well as the various liquid crystal-liquid crystal transitions. There are however certain examples of liquid crystal compounds that possess a particular mesophase only on cooling. This property is referred to as monotropic behavior, whereas those that have both reversible melting and clearing transitions are referred to as enantiotropic in nature.\(^{(22)}\)

The prediction of which compounds will be enantiotropic and which will be monotropic is not yet possible, but certain mesogenic units are known to favor the latter.\(^{(27)}\) These structures are described in a subsequent section of the introduction.

The order in the liquid crystalline state is reflected in various spectroscopic methods. While the methods just discussed (X-ray diffraction, optical microscopy, and thermal analysis) are used routinely with liquid crystals, other spectroscopic methods can be used to detect characteristics unique to mesophases.

Infrared spectroscopy can be used to measure frequencies, intensities and band shapes, but it is sensitive only to short range interactions, except in certain crystalline systems, such as
polyethylene. Unless the mesophase is brought into macroscopic alignment as discussed above there exist only small oriented regions, and these have refractive index discontinuities between them which can cause multiple scattering,\(^{33}\) and lead to difficulties in interpreting IR spectra.

Most of the data that appears in the literature concerns the infrared spectra of nematic mesophases, and essentially deals with band assignment. In these data little change in the spectra is seen on clearing, except when the vibrations associated with alkyl chain ends were studied in compounds containing such substituents. Plots of intensity versus temperature show drops in intensity on passing through the crystal-nematic and nematic-isotropic transitions.\(^{36}\) The orientation function of an externally oriented sample can be calculated using the infrared dichroism of mesogens or labels placed in a sample.

Another technique, small angle light scattering (SALS), has been used with liquid crystals and is similar in principle to X-ray diffraction. Since a longer wavelength is involved, the scattering unit is bigger. Very few samples have been examined by this technique, but very interesting scattering patterns have been observed.\(^{37}\) From these it could be implied that at the clearing temperature \((T_{\text{c}})\) a spherical scattering particle is formed in at least some cases. Measurements in other systems showed the presence of rod-like entities in the mesophase. Such measurements can give useful indications of the degree of order in the system.\(^{38}\)
ii) Cholesteric phases. The cholesteric mesophase was actually the first to be recognized and was given this name because the first liquid crystalline compound was a cholesteryl ester. This phase is structurally different from the nematic phase because of its twisted-layer structure. Each individual layer contains a nematic alignment with the long axes of the molecules parallel, but the layers are stacked on top of each other with a periodic twist or helical arrangement of the alignment axis; hence, this state is also called the twisted nematic phase. The structure of this mesophase is illustrated in Figure 2c. The helical twist is responsible for the optical properties observed in both ordinary and polarized light.

Different wavelengths of light can be reflected by the cholesteric mesophase depending on the twist of the helix and the repeat distance between successive layers with the same orientation. This repeat length, or pitch, is the distance for one complete rotation of the molecular layers. The wavelength of reflected light, \( \lambda_p \), is related to the average refractive index, \( \bar{n} \), and the pitch, \( p \), by the following equation:

\[
\lambda_p = \bar{n} \cdot p
\]

Electric and magnetic fields when applied to cholesteric mesophases can orient the layers in such a way that a nematic phase occurs in which the domains are oriented in more or less a common direction when the fields are of sufficient power.

The pitch is very sensitive to temperature, pressure, electric
and magnetic fields and also to the chemical environment (eg. to the presence of solvent or diluent). This behavior is the basis for the use of cholesteric liquid crystals to indicate temperature change and for pressure sensing materials as well as for other applications.

iii) Smectic phases. The smectic state shows two-dimensional order. There is directional order when all the mesogen long axes are parallel, but unlike the mentioned mesophases, there is also lateral order resulting from a layered structure of the molecules. Possible arrangements are shown in Figure 2b. Various smectic states are possible depending on the position of the mesogen in the layers. These states have been designated as Smectic A to H states, the letter subscript having been determined by the order of discovery.\(^{30}\)

Orientation of the mesophase is reflected in the microscopic texture observed for the different variants of the mesophase. The micrographs in Figure 5 show the appearance of the smectic A, and smectic C mesophases between crossed polarizers for the compound TBBA having the following structure:

\[
\text{TBBA} \quad \text{Bu}-\bigcirc-N=\text{CH}-\bigcirc-\text{CH}=\text{N}-\bigcirc-\text{Bu}
\]

These photographs show the fan and Schlieren textures of the A and C phases, respectively.

The higher degree of order for the smectic phase is clearly seen
Figure 5. Photomicrographs of two of the smectic mesophases of TBBA. The structure of TBBA is shown in the text, and the magnification is 400x.

a) The smectic A mesophase of TBBA at 196°C. (above)

b) The smectic C mesophase of TBBA at 155°C. (below)
in X-ray diffraction spectra of such compounds, see Figure 4. A somewhat diffuse outer ring of approximately 4-5 Å is due to the intermolecular spacing within the layer, and the sharp inner ring corresponds to the interlayer spacing. If the sample is oriented by mechanical means, or in an electric or magnetic field, then the two rings become arcs. \(^{(28)}\)

The greater order in the smectic state is also shown by the increased entropy of clearing. On passing through the clearing transition both directional and layered ordering is lost from the smectic state whereas only directional order is lost when the nematic state goes to the isotropic state. Again using TBBA as an example the values for the various entropies of transition are as follows:

<table>
<thead>
<tr>
<th>Transition</th>
<th>K - S(_B), S(_B) - S(_C), S(_C) - S(_A), S(_A) - N, N - I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta S) (cal/mol-K)</td>
<td>10.9 2.1 - 0.35 0.41</td>
</tr>
</tbody>
</table>

While there is as yet no clear-cut relationship between the molecular structure of the mesogenic unit and the type of mesophase it forms, several generalizations can be made. Gray\(^{(27)}\) has divided these factors into how the molecular structure a) is conducive to liquid crystal formation, b) affects the thermal stability of the mesophase, and c) favors the occurrence of smectic versus nematic/cholesteric liquid crystals.

Since the molecules are geometrically anisotropic, a stage-wise breakdown of the crystal might occur. For example, as a smectogen
melts, the interlayer forces may also act to preserve the structure. As well as having the appropriate cohesive forces, the molecule must be sufficiently rigid that in the melted state flexing does not occur. For this reason, most substances that give mesophases are of aromatic character. By substitution in the para position and connecting at least two rings by a rigid group, a rod-like group is formed. Many of these fall into the general category shown below:

![Diagram of mesogen structure]

where X and Y are terminal groups and n can be one or more. Figure 6 shows some of the linking groups that can lead to mesogen formation. In three of the linking groups shown, ($\text{C}^0_2\text{O}$, $\text{OCH}_2\text{CH}_2\text{O}$, and $\text{CHO}_2\text{CHO}_2$) a linear mesogen is maintained, but these groups are more flexible than other linking groups so a less thermally stable mesophase is formed. When n is 1, these linking groups often give monotropic mesophases, the general thermal characteristics of which have been explained earlier.

If more than two rings are connected ($n \geq 2$), then the liquid crystalline properties are enhanced, especially if conjugation or direct linkage of benzene rings is involved. This type of structure leads to both higher transition temperature and increased LC stability as demonstrated by a wider temperature range for mesophase behavior,
Figure 6. Possible linking groups that lead to liquid crystalline behavior in low molecular weight compounds.
termed the thermal stability of the mesophase. Linkages through the ortho or meta positions will destroy liquid crystallinity by destroying molecular linearity, and linear structures with substituents in these positions usually have lower LC thermal stability. In general, mesophase behavior can be affected greatly by modifying both rigidity and the length of the mesogen, which is generally described in terms of the length-to-width ratio of the molecular structure of the mesogen.

Other cyclic structures can also be used to give linear mesogenic structures, some of which are also rigid, such as the 1,4-bicyclo-[2,2,2]-octane ring, but these units give lower transition temperatures and mesophase stability. Therefore, the polarizability and conjugative effects of the π-system seem to be important.

In low molecular weight liquid crystals, terminal groups are important in determining the LC nature of the system. For example, highly polarizable terminal groups tend to favor interactions along the long axis of the mesogen, (between the ends of aligned units rather than laterally between units) and as a result these groups tend to enhance the formation of a nematic mesophase. Conversely, groups that tend to reduce terminal interaction and enhance lateral interaction instead, will increase the tendency to form a smectic mesophase. Therefore, for example, in many model systems, terminal -OME, -CN and -NO2 groups have a greater tendency to form nematic mesophases, while halogens tend to favor smectic phases.

Another general effect of structure on the mesophase thermal
properties occurs when alkyl end groups are used. Studies on numerous homologous series of compounds have shown that an alternating even-odd relationship occurs between the clearing temperature and the number of methylene units, exactly as it does for melting temperatures. Usually, as the size of the n-alkyl group is increased, the clearing temperature decreases in a steady way. The clearing temperatures typically alternate and two smooth lines can be drawn in a plot of clearing temperature versus number of methylene groups, one for the higher melting compounds with an even-numbered chain and the other for the lower melting odd-numbered chains. This behavior also holds for n-alkyl ether terminal groups, but when these are n-alkyl esters the effect is just the opposite. As the alkyl series length increases, the even-odd effect slowly disappears, and the relationship between transition temperatures and chain length levels off.

Liquid crystalline behavior can also be modified by the addition of lateral substituents, as mentioned above. The substituents can have either of two effects, a) either they increase intermolecular attractions through changes in molecular polarizability, or b) they act to separate the long axes of the mesogens through steric interactions. Of course, these factors depend on the size and type of substituent and the mesogen involved. The position of the substituent is also important, and in certain cases an added substituent can either create a mesogen from a non-mesogen or destroy the liquid crystallinity.\(^{(26)}\) Other factors controlling liquid
crystallinity exist, such as the branching of end groups, optical activity of the compound, etc., and these will be discussed where appropriate.

**Polymeric Liquid Crystals**

Originally, deGennes proposed that polymers with a liquid crystalline structure could be prepared by taking a difunctional liquid crystalline monomer and cross-linking it in the mesomorphic state, as shown in Figure 1. The product of this reaction was expected to be a rubber with unusual properties, because at that time it was assumed that liquid crystalline behavior could not exist unless it was chemically frozen in by the cross-linking reaction. This arrangement was found not to be necessary, and a large number of linear liquid crystal polymers have been prepared, as discussed below.

i) Cross-linked polymers. Several examples of this type exist and many of them have been covered in a review by Shibaev. Generally, the monomers contained two terminal vinyl groups, and polymerization by free radical initiation was carried out at a temperature within the liquid crystalline range of the monomer (monomers 1 to 3, Table I). Early work by Liebert showed that the mesophase order of the monomer was often preserved in the polymer provided that polymerization was fast and there was a high degree of cross-linking. If these conditions did not exist, then a certain amount of relaxation
would occur and order could be lost.

When polymerization of these monomers was carried out in the isotropic melt, a polymer with no anisotropy was formed, and polymerization in a magnetic field produced highly oriented polymers but not of a liquid crystalline morphology. Proper treatment by swelling of the amorphous polymer could recover on anisotropic structure for the latter case. \(^{(47)}\)

Blumstein and coworkers showed that neither monomer mesomorphism nor cross-linking was necessary for the development of mesophases in polymers. Using divinyl monomers 1,2 and 5, \(\text{(Table I)}\) with mesogens containing Schiff bases, they were able to prepare by free radical means, polymers with either smectic or nematic melts. One monomer polymerized rapidly when heated to the nematic state forming a smectic phase. \(^{(48)}\) By copolymerizing with a vinyl monomer, the mobility of the system was increased, and when polymerized in a magnetic field, the order parameter \(f\), of the nematic state was found to be 0.70, where the order parameter can be defined as:

\[
f = \frac{1}{2} \left( 3 \cdot <\cos^2 \phi> - 1 \right)
\]

and \(\phi\) is the angle the long axis of the mesogen makes with the magnetic field.

In the case of a smectic structure, an interlayer distance of about twice the length of the repeat unit, as estimated from molecular
models, was initially present. When sufficient cross-linking occurred, the interlayer distance became one repeat unit thereby confirming that cross-linking had taken place. Another interesting feature of their work was the measure of the anisotropy of thermal expansion in the intermesogen direction. These values were found to be slightly smaller than for low molecular weight smectics.\(^{49}\)

ii) Side-chain LC polymers. Work in the area of cross-linked systems has slowly given way to work on sidechain liquid crystals since the discovery was made that they too could show mesomorphic character. In most cases, the vinyl group was of the acrylic or methacrylic acid type, but substituted styrenes or acrylamides were also used. Several monomers are shown in Table 1; many of these appear in Shibaev's review.\(^{44}\) In this manner a wide variety of mesogens can be attached to a polymeric main chain. Of course, copolymerization as well as the use of stereospecific catalysts are possible, and both of these produce very interesting materials.\(^{8,50}\)

Blumstein and coworkers prepared polymers in bulk and solution in order to see what effect an isotropic solution state had on the final polymer. The products of monomer 6, Table 1 were nematic and soluble.\(^{44}\)

Another monomer which was reacted with a radical initiator (monomer 7, Table 1) in both the bulk state and isotropic solution formed polymers that were crystalline and amorphous, respectively. However, by proper treatment both of these forms could be interconver-
ted through the smectic mesophase. The ability to form a glass shows the low mobility of pendent mesogens when they are connected directly to the main chain.\(^{(41)}\)

Other polymers with mesomorphic side groups for which the nature of molecular and segmented order has been reliably established generally show layered arrangements, and are listed as monomers 8 to 10, Table 1. Within the layers, the side group in these polymers usually are oriented at an angle to the plane formed by the main chain. It was concluded from this observation that the presence of strong transverse dipoles (such as in carboxy groups) leads to well-defined lamellar organization of the smectic type. Conversely, the presence of strong longitudinal dipoles favored nematic polymers.\(^{(44)}\)

The X-ray diffraction patterns of all these polymers showed intermesogen spacings of about 4-5 Å, and the smectic polymers showed an interlayer repeat spacing of twice the approximate mesogen length.\(^{(48)}\)

The transition temperatures and mesophase structures were very much dependent on the mesogen used. However, the inherent disorder of the polymer main chain influenced the melt structure as well because the main chain tended to coil. A method of removing this effect was to place a so-called "flexible spacer" between the main chain, and the mesogenic unit. This group decoupled the rigidity of the polymer backbone from the side group and allowed greater freedom of the latter for the formation of a mesophase,\(^{(51)}\) in Figure 7.

Ringsdorf and coworkers have specialized in the synthesis of
• Direct linkage of mesogenic unit

• Linkage through flexible spacer

• Possible smectic structures in LC polymers with side-chain mesogenic groups

Figure 7. Structures of LC polymers with side-chain mesogenic units.

Figure 8. Structures of LC polymers with mesogenic units inserted in the main chain.
side-chain liquid crystalline polymers, and were quick to realize
the usefulness of flexible spacers for decoupling the motions of the
main and side chains. Very few polymers with a spacer-free pendent
mesogen show mesophase forming capabilities. The polymers prepared
by Ringsdorf and coworkers were based on acrylic and methacrylic
acid ester with flexible spacers of polymethylene chains and various
mesogens including biphenyl and the aromatic esters and Schiff bases
shown in Table 1, monomers 12 to 14.(6)

It was found that the flexible spacer allowed enough ordering
of the pendent mesogen that smectic phases were preferentially formed.
To reduce this tendency, copolymers were made with monomers of differ-
ext flexible spacer lengths, and this approach was found to success-
fully give the twisted nematic state when chiral mesogenic units were
used.(6) Other polymers with the cholesteric state were prepared
by using mesogens that included cholesteryl derivatives (monomer 15,
Table 1) or copolymers made with both a biphenyl benzoate derivative
(monomer 14) known to give nematic polymers and a chiral component
known to be non-mesophase forming.(131) This result again shows the
strict analogy between low molecular weight mesogens, and LC polymers.

When the authors compared polymers with the same mesogen but
different alkyl or alkoxy substituents, two effects were found.
Mesophase stability was greater for polymers with alkoxy substituents;
an increase in substituent length caused a higher clearing temperature.
When the biphenyl group replaced the phenyl esters, the resulting
polymers had a broader mesophase temperature range which extended up
to quite high temperatures. (52)

It was found that some of the polymers prepared had unusual optical properties, even though by DSC and microscope they appeared identical in nature to low molecular weight (MW) nematics. The authors used X-ray measurements, dye probes and birefringence measurements to try to clarify these discrepancies. (53)

A study of mobility in an electric field was also made of polymers with some cyano-containing mesogens, see Table 1, monomers 15 and 16. In low MW liquid crystals, these polar groups were used to increase the response to electric fields. It was found that alignment with the field was fastest with the longest flexible spacer and was in the range of 200 ms. (54)

To further lower the glass transition temperature of these polymers Finkelmann attached to a polysiloxane main chain the same mesogenic units (monomers 11, 12, 16, 17 and 18) used previously with polymethylacrylates. The properties of these polymers were found to be very much dependent on the pendent mesogen. According to their results, the type of LC phase was determined by the substituents of the mesogenic moiety. (55)

By cross-linking the polysiloxane main chain Finkelmann and coworkers were able to prepare a liquid crystalline elastomer. Even though the system was cross-linked, the pendent mesogenic groups were still free enough to have liquid crystalline order and show a clearing transition, but the presence of a cross-linking agent lowered both $T_g$ and $T_i$ of the polymer. A cholesteric phase could be induced by
the addition of a low molecular weight chiral molecule in the mesophase and the resulting mixture had an opalescent quality.\textsuperscript{(56)}

Studies were made of some of the methacrylate polymers using PVT measurements to determine if the observed transitions were analogous to conventional materials. The Clausius-Clapeyron equation was found to describe the clearing transition of both the LC polymer and the model compound. The $T_g$ of the LC polymer showed a smaller pressure dependence than did poly(methyl methacrylate), PMMA.\textsuperscript{(57)}

The polysiloxane backbone polymers were used to determine the effect which flexible spacers had on the liquid crystallinity. Polymers with induced cholesteric mesophases were studied optically to see the effect of structure on relative helical twisting power (htp). It was found that the shorter spacer chains led to greater twisting powers, which nearly equalled those of very high htp, low molecular weight compounds.\textsuperscript{(58)} More recently the interests of this research group have expanded to include polysiloxane spacers in polymers with the mesogen in the main chain,\textsuperscript{(59)} see polymers 22, 28-30, Table 2.

An important property of side chain mesogen polymers is their potential for copolymerization of almost any side group. Therefore the mesogen used need not be limited to rigid rod-like groups as was done with cross-linked LC polymers, but instead more unusual groups such as cholesterol esters can be added. In fact, this group has been included in several types of main chain polymers with various
flexible spacer lengths, and has led to the formation of polymers with cholesteric, smectic and nematic mesophases.

Shibaev and coworkers have concentrated on preparing polymers of cholesteryl derivatives, the low molecular weight analogs of which have extensive applications. Cholesteryl and other groups were attached to acrylate or methacrylate groups through ω-amino carboxylic acids containing between 2 and 11 methylene groups separating the mesogen from the vinyl group, monomers 19 to 21, Table 1. Homopolymers and copolymers with n-alkyl acrylates were prepared from these mesogenic monomers.

The cholesteryl monomers with short spacers polymerized rapidly when heated to the melt, and all monomers formed metastable monotropic mesophases for all spacer lengths (monomer 19, Table 1). The values of \( T_g \) of the polymers were lowest for those with the longest spacer, and X-ray diffraction data show that the mesophase structure was preserved even in the glass. The X-ray diffraction spectra were interpreted as showing a layered structure where side chains were arranged at 90° to the main chain. However, the authors believed that the mesophase formed by the homopolymers was cholesteric. Copolymers of cholesteryl esters were found to be amorphous and did not show any birefringence when copolymerized in 50:50 mixtures.

In another publication, this author studied monomers and polymers made from a hydroquinone benzoyl ester with the same spacer and vinyl type as used before (monomer 21, Table 1). In the melt, these monomers polymerized rapidly, but without a spacer, only an amorphous
polymer with a liquid crystalline state was obtained. Increasing the spacer length allowed greater freedom of mobility of the mesogenic group, and so crystallinity went up accordingly. The structure of the crystalline solid was felt to consist of mesogens placed at right angles to the main chain with each chain slightly displaced from the next.\(^{(61)}\) This basic structure was possibly carried over into the mesophase.

By employing infrared spectroscopy, Shibaev tried to determine what part the flexible spacer and the mesogenic group played in forming the crystalline and liquid crystalline states. A series of polymers were studied where the samples contained the same spacer but different "anisodiametric" terminal groups. The infrared spectra of these compounds were then observed as a function of temperature. The feature most sensitive to structural changes was the intensity of certain bands including those of the aromatic rings in the mesogen and the methylene atoms in the spacer. A monotonic decrease of the intensity of the spacer bands with increased temperature showed that the spacer did not take part in crystallization.\(^{(62)}\) Along with the benzene ring bands, the ester groups in the 1050-1300 cm\(^{-1}\) region were sensitive to phase transitions of the LC state. The authors concluded that the mesogenic group alone was responsible for formation of the thermotropic state and that the ester group acted as a hinge to connect the mesogen to the polymer chain.

Recently, this group has studied the electro-optical effect of side chain polymers with a cyano substituted biphenyl mesogen (mono-
mer 22, Table 1). Below T_g no change in the sample birefringence occurred even in very high electric fields. Above T_g, the birefringence dropped to almost zero and the rate of the decrease depended on the applied voltage. Such results showed that the side groups either acted independently of the main chain or could easily influence its conformations.\(^{(63)}\)

iii) Main-chain LC polymers. Main chain liquid crystalline polymers were perhaps the first type to be prepared, but they certainly were the last recognized type of mesophase forming polymers.\(^{(64)}\) Inclusion of mesogenic structures in the main chain requires that condensation polymerization techniques be employed, and this leads in many cases to polymers that have only moderate molecular weight and low solubility.

Here again flexible spacers can be used, so there are essentially two types of polymers with the mesogen in the main chain; that is, the rigid-rod polymers with a flexible spacer used to couple mesogenic groups, see Figure 8. In the latter case, this allows improved solubility, lower transition temperatures, and greater mobility for better ordering.\(^{(65)}\)

The rigid-rod polymers have been reviewed by Jin and co-workers\(^{(66)}\) and are usually high melting-point polyesters with a large aromatic content. These thermotropic polymers are analogous to the Kevlar\(^{®}\) class of lyotropic polymers except that the linking unit in the former is typically an ester rather than an amide group. A decrease in rigidity or linearity will lower the transition
temperature of this class of compounds without destroying liquid
crystallinity, and for this reason, three approaches have been used
to affect polymer properties: a) dissymmetric substitution of the
aromatic groups; b) the use of non-linear aromatic comonomers; and
c) the inclusion of flexible units in the main chain.

The use of asymmetrically-substituted hydroquinones with tereph-
thalic acid leads to the formation of melt spinnable polymers, whereas
the analogous non-substituted polymers are generally so high melting
as to be unsuitable for fiber spinning. These polymers still pos-
sessed a mesophase of the nematic type, and by inclusion of non-
linear diphenols, both the solubility of the products improved and
melting temperature decreased. Of the comonomers used, bisphenol
A affected the liquid crystallinity the most, and only 40 mole-% of
this monomer could be copolymerized before LC behavior was lost. (66)

The inclusion of flexible units in the main chain is a relatively
recent approach to melt behavior modification. The first polymer with
a main-chain mesogen and very short flexible spacer that was recognized
in the literature as liquid crystalline (others were reported earlier
in patents) was that prepared by using the melt-transesterification
technique with poly(ethylene terephthalate) and p-acetoxy benzoic
acid, (4) see Figure 38, Chapter V. The resulting copolymer was ne-
matic provided that it contained from 40-70% oxybenzoate residue.
Above this limit the polymer was insoluble and infusible and took
on the properties of poly(p-oxybenzoate) itself, but below this limit
the polymers resembled poly(ethylene terephthalate).
The mechanical strength of molded samples increased to a maximum and then decreased with increasing oxybenzoate content when measured in the direction of orientation. Minimum melt viscosities and maximum mechanical properties were found with copolymers with 60-70% oxybenzoate content, and this composition also corresponded to the greatest flexural moldulus, tensile strength, and impact strength. These results were explained on the basis of the formation of a liquid crystalline melt in which mesogenic units became highly oriented under shear. McFarlane and coworkers have shown that the polyester with 60 mole-% oxybenzoate formed a nematic melt according to wide-line NMR data. Similar samples have been shown to be nematic by miscibility studies and by optical and electron microscopy.

Other copolymers have been prepared using ester interchange reactions on preformed poly(ethylene terephthalate), PET, to incorporate various aromatic groups in the chain. Non-linear comonomers such as isophthalic acid destroyed thermotropic potential. Symmetrically substituted co-units raised the melting temperature, while dissymmetric substitution lowered $T_m$.

Feichtinger studied copolymers of PET with mesogenic comonomer units composed of $p$-oxybenzoate units substituted in the 3- and 3,5-positions, as shown below:

$$
\begin{align*}
\{-O\begin{array}{c}
\raisebox{0.3em}{\text{C}}\end{array}\begin{array}{c}
\raisebox{0.3em}{\text{O}}\end{array}R'\}x\{-O\begin{array}{c}
\raisebox{0.3em}{\text{C}}\end{array}\begin{array}{c}
\raisebox{0.3em}{\text{O}}\end{array}CH_2CH_2\begin{array}{c}
\raisebox{0.3em}{\text{O}}\end{array}\begin{array}{c}
\raisebox{0.3em}{\text{C}}\end{array}R\}y
\end{align*}
$$

$R = H, Cl; R' = Cl, OMe$
The principal goals were to determine the average sequence length of oxybenzoate block needed to generate a mesophase, and to study the crystallization induced reactions of the copolymers\(^{(71)}\). More will be said about the polymers produced by melt transesterification in Chapter V.

Following the work of Kuhfuss and Jackson\(^{(4)}\), many different polymers have been produced with a variety of mesogens. The mesogenic units most often used are those which are also found in low molecular weight liquid crystals, as shown in Figure 9. These units include Schiff bases, trans-stilbene, biphenyl, terphenyl and diphenyl azo residues as well as dyad and triad aromatic esters. Flexible spacers have included polymethylene, poly(ethylene oxide), and polysiloxane chains and are also shown in Figure 9. The research investigations of different authors are usually concentrated in only a few mesogens, so this review will be partially organized according to the reports of individual research groups. As a result of the recent development of main-chain liquid crystal polymers with flexible spacers, no comprehensive review yet exists for these polymers.

Roviello and Sirigu initiated the systematic synthesis of LC polymers with main-chain mesogens. Their work was centered on the stilbene and phenyl azide types of polymers and copolymers with polymethylene flexible spacers of different lengths\(^{(14,73)}\). Their studies were based mostly on thermal and X-ray diffraction characterization of these polymers. For example, polymers 1 to 3 in Table 2 was nematic and showed polymorphic behavior in the solid and liquid
Mesogenic Units

Flexible Spacers

Figure 9. Various mesogenic units and flexible spacers that have appeared recently in the literature.
state. A monotropic smectic phase was also detected, which is a somewhat rare feature in polymers.

Their second series of polymers 4 and 5, Table 2 showed a nematic mesophase, but crystallized so quickly that a quenching technique could not freeze in the liquid crystalline state. Co-polymers of different spacer lengths were used to try to suppress the crystallization, and the X-ray diffraction maxima of these solids were at the same spacing as that of the prevalent monomer.(73) A series of model compounds were also prepared where the end group lengths differed by one methylene unit.(102) This series showed an even-odd relationship of the melting temperatures much like that of the series of low molecular weight liquid crystals prepared by Gray.(74) Another series of polymers used a polyethylene glycol spacer and these also gave mesophases.(93)

The work by Strzelecki and coworkers on main chain polymers followed their earlier work on cross-linked and side chain mesogen systems. In their newer studies, they investigated various mesogens based upon aromatic acids and phenols in conjunction with alkyl flexible spacers, see polymers 19, 27, 33 and 34, Table 2. Using transesterification, they were able to produce polymers with a reasonably well-defined mesogen, and all of these polymers were studied by DTA and microscopy.(75)

The various polymers prepared showed both the often observed even-odd relationship for polyesters, and the expected decrease in the transition temperatures with increased spacer size, as shown in
Figure 10. They also showed that the melting temperature increased with mesogen size and, for the case of polymers with nonamethylene spacers, the $T_m$ was about $200^\circ$C for that with a mesogen of $\approx 13\sigma$ in length and $350^\circ$C with a mesogen of $\approx 25\sigma$ in length. Other work in their laboratories has included the preparation of polymers with a mesogenic unit in the main chain and a chiral group in the flexible spacer. These polymers, however, were not claimed to be liquid crystalline.\(^\text{(76)}\)

The most interesting work of this group to date has been the preparation of a series of polymers based on mesogen 19 Table 2 which showed two mesophases in the melt, presumably smectic and nematic. Unpublished X-ray diffraction results were quoted as supporting the existence of these phases. Another polymer based on mesogen 33 (Table 2) was the subject of an X-ray study which showed the existence of a nematic phase and the possibility of orientation in a magnetic field.\(^\text{(77)}\)

Using the azomethine linkage, several interesting thermotropic polymers have been produced by Skoulios and coworkers. Their initial work was intended to show that increasing the size of the mesogen also increased polymer transition temperatures. The mesogen structures are listed in Table 2, polymers 42 and 43.\(^\text{(78)}\) Due to the sensitivity of this composition to heat, a substituted polymer was made in order to lower transition temperatures to a more stable range. This polymer was prepared along with the unsubstituted polymer and also with several model compounds with different chain lengths.\(^\text{(79)}\)
Figure 10. Plot of transition temperature versus the number of methylene groups in the spacer. Reference 104.
Using a nematic solvent, the materials were mixed and plots of transition temperatures as a function of composition were made but very poor mixing occurred in most cases. They showed that, where the solute-solvent transition temperatures were close, the solution could show a very extended nematic range.

Later, by introducing a flexible spacer in a related structure, a high melting poly-Schiff base was prepared that was shown to be smectic by the use of X-ray diffraction methods. Hot stage microscopy was not useful, because of the high melting temperatures of these polymers.\(^{80}\)

Slight alteration of the mesogen structure allowed the preparation of a soluble, lower melting range polymer. In some cases, two mesophases were observed in the melt, a smectic and a nematic mesophase.

Other polymers prepared by Fayolle and coworkers have also exhibited dual mesophases. Noel characterized these polymers by conventional microscopy and thermal analysis techniques, and also applied the mesophase miscibility test to them. This method is usually employed with low molecular weight materials, but there are reservations by some other workers about the applicability of this technique to polymers.

The polymers studied included both rigid types and polymers with flexible spacers, and examples of both types are listed in Table 2, polymers 6, 16, 17 and 43.\(^{18}\) Polymers 43 and one of the polyesters of Kuhfuss and Jackson were found to be isomorphic in
the nematic state. In an earlier publication, the rigid polymer 43 had been shown to be nematic by the same method using a nematic model compound.\(^{81}\)

Another interesting feature of liquid crystals in general is their ability to be transformed to the twisted state upon the physical addition of a low molecular weight compound with a chiral center. In the present case, the nematic state of polymer 43 was converted to the cholesteric state, and polymer 17 was changed to a twisted smectic C from the smectic C state.

Other mesogens that have been studied include those containing biphenyl and trans-stilbene moieties, also shown in Table 2. Spacers used included polymethylene and polyethylene oxide (PEO) sequences. Multiple melting endotherms were found in polymers with polymethylene spacers, but a single melting peak was found in the polymers with PEO spacers.\(^{18}\)

A comparison of the thermal behavior of samples with the same mesogen but different spacers showed that spacer length was important as expected. However, both PEO and polymethylene spacers gave polymers with roughly the same transition temperatures when different spacers of the same molecular length were used.

Supercooling of the crystallization temperature occurred with all polymers investigated, and as the authors pointed out, this property is quite common in many low molecular weight liquid crystalline compounds. While melting points of the polymers were higher than those of the model compound, the change in entropies and
enthalpies upon melting were lower. These lower values were the result of either a highly ordered smectic mesophase or of lower crystallinity in the solid. Lastly, it was shown that a spacer of sufficient length or weight caused loss of liquid crystallinity of the polymer, and that this occurred when the spacer constituted approximately 50 weight percent of the repeating unit.

The work of Griffin and Havens on main chain LC polymers has been limited to one mesogen type, see polymer 35, Table 2, with various combinations of flexible spacer lengths.\(^{(19)}\) Their polymers were modelled on the thermotropic polyesters of Jackson and Kuhfuss except that in their case the mesogen used was a hydroquinone oxybenzoate dyad. Polymers and copolymers were prepared with mixed spacer lengths, and then characterized by DSC, miscibility studies, and microscopy.

It was shown that the copolymer containing both a hexamethylene and decamethylene spacer was miscible with both model compound I and TBBA (the structure of which was shown earlier) in the nematic range, which confirmed earlier work on this type of melt structure determination. It was also pointed out that the higher viscosity of their polymers led to slowed spontaneous ordering.\(^{(72)}\) Consequently, the lack of identifiable textures in these polymers might be expected, so reports by others of polymers with characteristic textures were really dealing with oligomers. The molecular weights
of their polymers were in the 15,000 range, and so texture identification was difficult.

Thermal studies showed that all polymers in their series had at least two endotherms. The clearing transitions were broad and corresponded to the nematic-isotropic transitions. Most polymers showed a structured melt endotherm presumably due to reorganization during the melting process. Supercooling of the mesophase to form a crystalline phase occurred, but this was not significant for the transition of the isotropic state to mesophase. There is a good analogy here with low molecular weight liquid crystals. By comparing the entropy change on melting to that of clearing for both model compounds and polymers, the authors also showed that the relative difference in order in the solid and the mesophase was much less in the case of the polymer than for model compounds.

Until recently, Blumstein and coworkers have concentrated their efforts on polymers with mesogenic side chains, but their efforts now are centered on the preparation and study of polymers with mesogenic units and flexible spacers in the main chain.

Contrary to their expectations, many of these polymers were found to be smectic in nature. Structures of the mesogens and spacers in these polymers are given as polymers 7, 8, 13, 14 and 15 in Table 2. The thermotropic nature of the compounds were determined only by DSC, and microscopy, since the X-ray diffraction patterns of the unoriented nematic polymers were often too diffuse. In order to overcome this problem, samples that had been oriented in
the melt by a magnetic field were studied by X-ray techniques.\(^{(84)}\)

An important development by Blumstein was the incorporation of a chiral center into the flexible spacer. In analogy with small molecules, these polymers formed cholesteric phases.\(^{(15)}\) Similar work by Strzelecki resulted in the formation of only semi-crystalline polymers, so the choice of the mesogen is evidently critical. By synthesis of copolymers with chiral and achiral spacers, it was shown that the pitch of the cholesteric helix decreased with increasing chiral content.

In work by Lenz and coworkers, only mesogenic units composed of aromatic groups connected by ester linkages have been studied.\(^{(85)}\) One of the polymers prepared was similar in structure to those of Strzelecki.\(^{(75)}\) Different polymers were made in which the central part of the mesogen was also mono- and disubstituted in order to be able to adjust the polymer melting and clearing transitions. Various spacer lengths were also used for the same purpose of transition temperature adjustment.

The polymers with mesogen 31 in Table 2 showed the same even-odd relationships observed previously by others. The polymer melts showed typically nematic, threaded-Schlieren textures. Some also had textures that contained point singularities with values of S equal to either one-half or one.

Small-angle light scattering studies showed generally circular scattering patterns except for the polymer with a decamethylene spacer, which produced a \(\pm 45^\circ\) crossed four-leaf-clover type of
pattern. These results suggested that the scattering elements of the melts of most of the polymers in the study were spherical, but those for the latter polymer were rod- or disklike in shape. This result might have been due to the ability of the longer spacer to form rodlike assemblies. The interchain spacings of all of these polymers were about 4.5 Å by X-ray diffraction showing no difference by this technique as to mesophase structure.

All polymers showed broad clearing endotherms which were obscured by decomposition of polymers with shorter flexible spacers because of their very high melting points. The broadness of the transition was probably due to the polydispersities of the polymers. The entropies of clearing of these polymers increased with increasing spacer length and became larger than those for the model compounds. If equal values of entropy can be assumed for the isotropic melts of all polymers regardless of structure (i.e., equal degrees of disorder), then the nematic state of the polymers with longer flexible spacer was more ordered than either polymers with shorter spacers or than the model. (85)

The second series of polymers (mesogen 24, Table 2) was studied for the effect of substitution of the mesogen on the crystalline mesophase properties. Monosubstitution improved solubility as well as lowering the melting temperature. Liquid crystalline melts all showed textures typical of the nematic state; however, others have observed possible smectic mesophases for the unsubstituted polymer in this series. (66)
The clearing transitions in this series of polymers possessed a higher change in the entropy of clearing than in the previous series. This result was attributed to the possibility of coplanar geometry of the mesogenic units which contained central hydroquinone moieties. In contrast to this possibility, the central terephthaloyl units would be forced to twist to reduce the steric interactions between the carboxyl oxygens and the protons in the ortho position. The larger value of $\Delta S$ for the monosubstituted samples was believed to be due to a locking-in effect between the substituents on neighboring mesogenic units that inhibited molecular mobility.

Other work by this group has explored the effect of large aromatic substituents attached to the mesogenic moiety of the polymer, polymers 23, 26 and 27, Table 2. The mesogenic unit in this series was structurally related to that in the second series of polymers discussed above. For example, the use of a rigid biphenyl instead of a phenylene group, which increased the long axis of the mesogenic element in the polymer chain, increased both the melt transition and the liquid crystalline thermal stability. Any attachment of bulky phenyl groups as substituents led to a decrease in melt temperature and a greatly reduced LC temperature range. It was concluded that the increased rigidity of the mesogenic groups favored formation of a higher melting, more thermally stable mesophase. In contrast, bulky side groups resulted in reduced melting temperature and thermal stability presumably because of the increased separation of mesogens in the LC melt through steric repulsions.
A polymer with a siloxane spacer was also prepared, and the greater flexibility of this group was expected to greatly depress the melting point of this polymer, but it was found to be only "weakly" liquid crystalline. However, a copolymer with both a siloxane and a decamethylene spacer had a considerably lower melting temperature although the mesophase thermal stability of this copolymer was that of the homopolymer with the decamethylene spacer, see polymers 25 and 32, Table 2. Koide and coworkers prepared azoxy and azo unit polymers in which the mesogenic moieties were almost identical to those used by Blumstein except for an altered sense in the orientation of the ester links. Direct comparison of the effect of this reversal was not possible because of the use of a spacer based upon ethylene oxide oligomers, polymer 12, Table 2 but the properties of these two series of polymers were quite similar. Koide has also reported on the synthesis of liquid crystalline polyurethanes.

The misconception could exist that there has been equal activity in all areas of research into liquid crystals but in fact, the popular aspects of this research have recently changed. Commercial research has been limited to the rigid-rod polymers, primarily for use in melt-spinnable fibers so that products with properties similar to Kevlar could be made. In contrast, academic research has until recently concerned itself with the study of polymers with side-chain mesogenic units. However, when these materials were found to be no better than low molecular weight materials for possible applications,
and when LC polymers with flexible spacers were shown to be possible, interest in many research groups focussed on this latter type of polymer.

The advantages of polymeric liquid crystals with flexible spacers lies in the orientation of the mesogen with respect to the main chain and the lower melting temperature of the polymer. Polymers with mesogenic side chains show orientation of the pendant groups perpendicular to the main chain. This property would not matter for LC display purposes, but would be detrimental in the case of fiber applications because a tensile force on the sample would be borne by non-covalent bonds. Rigid-rod polymers would have the mesogenic groups in the direction of the force as would, presumably, LC polymers with spacers, but the latter also have reduced melting temperatures and increased solubility which make processing much simpler. Uses that require rapid rearrangement of the mesogenic unit need the freedom of the side chain mesogenic group. Since the mesogenic groups in polymers with main chain mesogens are encumbered by the rest of the chain, probably only slow rearrangement is possible for these polymers in external fields.

Other work in the literature which could have been covered, but which does not apply directly to the purposes of the present study includes the investigations by Cser(90) and by Americk(91) on polymerization reactions in the liquid crystalline state, as well as the work by Magagnini(92) on α-substituted ethylenes and ethylene oxides. With the rapid increase in the number of research workers in this
area, it is to be expected that many new papers will appear in the near future that will shed light on the understanding of liquid crystalline polymers and liquid crystals in general.
Table 1. Monomers of liquid crystalline polymers with mesogenic units in the side chain.

Structure of monomer

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) H₂C=CH-OO-CH=N-CH=N=CH-OO-CH=CH₂ R=H,Cl</td>
<td>5,48</td>
</tr>
<tr>
<td>2) H₂C=CH-OO-CH=N-CH=N=CH-OO-CH=CH₂</td>
<td>45,49</td>
</tr>
<tr>
<td>3) H₂C=CH-OO-CH=N-CH=CH₂</td>
<td>46</td>
</tr>
<tr>
<td>4) H₂C=CH-OO-CH=N-CH=CH₂</td>
<td>5</td>
</tr>
<tr>
<td>5) H₂C=CH-N=CH-CH=N-CH=CH₂</td>
<td>49</td>
</tr>
<tr>
<td>6) H₂C=CH-C-O-CH=N-CH=CH₂</td>
<td>48</td>
</tr>
<tr>
<td>7) H₂C=CH-C-OH</td>
<td>41</td>
</tr>
<tr>
<td>8) H₂C=CH-C-O(CHO₂)₂₆-C₂H₅</td>
<td>48</td>
</tr>
<tr>
<td>9) H₂C=CH-N=CH-C-O(CHO₂)₂₆-C₂H₅</td>
<td>48</td>
</tr>
<tr>
<td>10) H₂C=CH-N=CH-C-CN</td>
<td>48</td>
</tr>
<tr>
<td>11) H₂C=CH-C-O(CHO₂)ₙ-C-O-CO-O(CHO₂)ₙ-OMe n=2,6</td>
<td>6</td>
</tr>
<tr>
<td>12) H₂C=CH-C-O(CHO₂)ₙ-C-C-CN-OMe n=6</td>
<td>7</td>
</tr>
<tr>
<td>13) H₂C=CH-C-OH-CH=N-C-OH-OMe</td>
<td>51</td>
</tr>
</tbody>
</table>
14) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_2\text{O} \text{Me} \text{O} \text{C} \text{=N-CH-CH=CH=CH} \text{2} \text{Q Me}\text{O}$

15) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-CO-OMe}$ $n=2,6$ 131

16) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-CN}$ $n=2,6$ 54

17) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-O(CH}_2\text{)}_5\text{-Me}$ 55

18) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-Cholesterol}$ 55

19) $H_2C=C\text{-NH(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-Cholesterol}$ $n=2-11$ 60

20) $H_2C=C\text{-NH(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-CH}_2\text{O}$ 10

21) $H_2C=C\text{-NH(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-O(CH}_2\text{)}_5\text{-Me}$ $n=2-11$ 61

22) $H_2C=C\text{-CO(}\text{CH}_2\text{)}_n\text{O} \text{Me} \text{O} \text{C} \text{-CN}$ $R=H, Me; n=2-11$ 63
Table 2. Liquid crystalline polymers with main chain mesogenic groups and flexible spacers.

<table>
<thead>
<tr>
<th>Mesogenic Unit</th>
<th>Flexible Spacer</th>
<th>n</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) -(\text{O}^\text{-(C=\text{N-N}-\text{C-(\text{O})}})&lt;sub&gt;(\text{CH}_3)&lt;/sub&gt;(\text{CH}_3)</td>
<td>-(\text{OCO}(\text{CH}_2)\text{-OCO-})(_n)</td>
<td>6,8,10,12</td>
<td>17,73</td>
</tr>
<tr>
<td>2) &quot;</td>
<td>-(\text{OCO}(\text{CH}_2\text{CH}_2\text{O})\text{-CO-})(_n)</td>
<td>2,3,4</td>
<td>93</td>
</tr>
<tr>
<td>3) &quot;</td>
<td>-(\text{OC}(\text{CH}_2)\text{-CO-})(_n)</td>
<td>8,10,12</td>
<td>14</td>
</tr>
<tr>
<td>4) -(\text{O}^\text{-(C=\text{H-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>&quot;</td>
<td>6,8,10,12</td>
<td>102,122, 123</td>
</tr>
<tr>
<td>5) &quot;</td>
<td>-(\text{O}^\text{-(C(O))}}\text{-CO-})(_n)</td>
<td>2,3,4</td>
<td>93</td>
</tr>
<tr>
<td>6) -(\text{O}^\text{-(C=\text{H=CH-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>-(\text{O}(\text{CH}_2)\text{-O-})(_n)</td>
<td>5,6,10</td>
<td>18</td>
</tr>
<tr>
<td>7) -(\text{O}^\text{-(C=\text{H=CH-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>-(\text{O}(\text{CH}_2)\text{-O-})(_n)</td>
<td>10</td>
<td>84</td>
</tr>
<tr>
<td>8) -(\text{O}^\text{-(C=\text{H=CH-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>&quot;</td>
<td>10</td>
<td>84</td>
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<tr>
<td>9) -(\text{O}^\text{-(C=\text{N=N-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>-(\text{O}(\text{CH}_2)\text{-O-})(_n)</td>
<td>4,6,8,10, 12,16</td>
<td>40</td>
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<tr>
<td>10) &quot;</td>
<td>-(\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{-O-})(_n)</td>
<td>2,3,4</td>
<td>88</td>
</tr>
<tr>
<td>11) -(\text{O}^\text{-(C=\text{N=N-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>-(\text{O}(\text{CH}_2)\text{-O-})(_n)</td>
<td>4,6,8,10, 12,16</td>
<td>40</td>
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<tr>
<td>12) &quot;</td>
<td>-(\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{-O-})(_n)</td>
<td>2,3,4</td>
<td>88</td>
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<tr>
<td>13) -(\text{O}^\text{-(C=\text{N=N-(\text{O})}})&lt;sub&gt;(\text{CH}_3)(\text{CH}_3)</td>
<td>-(\text{OCO}(\text{CH}_2)\text{-CO-})(_n)</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>14) -(\text{O}^\text{-(C=\text{N=N-(\text{O})}})&lt;sub&gt;(\text{Me})(\text{Me})</td>
<td>&quot;</td>
<td>10</td>
<td>124</td>
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15) -O-O-

16) \(-\text{C}-\text{O}-\text{O}-\text{C}-\)

17) \(-\text{C}-\text{O}-\text{O}-\text{C}-\)

18) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

19) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

20) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

21) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

22) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

23) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

24) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

25) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

26) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

27) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

28) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

29) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)

30) \(-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\)
<table>
<thead>
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<th>No.</th>
<th>Structure</th>
<th>Description</th>
<th>Ranges</th>
<th>Refs.</th>
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<td>31</td>
<td><img src="image1" alt="Structure 31" /></td>
<td>(-\text{O}(\text{CH}_2)\text{-O-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
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<td>32</td>
<td>&quot;</td>
<td>(-\text{O}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>--</td>
<td>87</td>
</tr>
<tr>
<td>33</td>
<td><img src="image2" alt="Structure 33" /></td>
<td>(-\text{OC}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>3-12,14,20</td>
<td>103,75,77</td>
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<td>34</td>
<td>&quot;</td>
<td>(-\text{O}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>4,5,6,8,9</td>
<td>75</td>
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<tr>
<td>35</td>
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<td>&quot;</td>
<td>6,8,10</td>
<td>19,72</td>
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<td><img src="image3" alt="Structure 36" /></td>
<td>(-\text{OC}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>2-10,12</td>
<td>66</td>
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<tr>
<td>37</td>
<td>&quot;</td>
<td>(-\text{O}(\text{CH}_2\text{CH}_2\text{O})\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>2,3,4,6,13</td>
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<tr>
<td>38</td>
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<td>(-\text{OC}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
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<td>39</td>
<td>&quot;</td>
<td>(-\text{O}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
<td>2,6,10</td>
<td>96</td>
</tr>
<tr>
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<td><img src="image5" alt="Structure 40" /></td>
<td>&quot;</td>
<td>2,6,12</td>
<td>79</td>
</tr>
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<td>41</td>
<td><img src="image6" alt="Structure 41" /></td>
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<td>12</td>
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<td>&quot;</td>
<td>--</td>
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<tr>
<td>43</td>
<td>(-\text{OC}(\text{CH}_2)\text{-0-}\text{Me} \text{-O}-\text{Me-CH}_2-\text{Si-0-Si-CH}_2-)</td>
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CHAPTER II
TRIAD THERMOTROPIC POLYESTERS WITH
MAIN CHAIN POLYMETHYLENE SPACERS

Introduction

The study of liquid crystalline (LC) polymers with both flexible spacers and well-defined mesogenic groups in the main chain is a relatively new area in polymer science. It was only in 1975 that the first polymer of this type was reported in the literature, \(^{(14)}\) and because of its recent appearance many of the structural characteristics that lead to liquid crystallinity in polymers are not well understood.

The commercialization of this class of polymeric materials has been limited to applications involving high orientation of the polymer chains in forms such as fibers. Unlike low molecular weight LC compounds, polymers with mesogenic groups in the main chain are slow to rearrange in external electromagnetic fields and may not be useful in LC displays, but advantage could be taken of the mesophase structure to lead to anisotropic properties in the final state. Another possible way to exploit such high structural order might be in the preparation of liquid crystal dialysis membranes that would duplicate the separation properties of a cell wall. \(^{(94)}\) Therefore the preparation of polymers suitable for this kind of application was
among the factors inspirational to this research.

One of the features that unifies the work reported in this thesis is the use of the oxybenzoate-terephthalate mesogenic unit. The utilization of these mesogen elements was introduced to this laboratory by the study of crystallization induced reaction (CIR) on polymers containing statistical distributions of oxybenzoate-terephthalate components in the main chain. Our initial work on the preparation of polymers with mixed flexible spacers is reported in Chapter V of this dissertation, and the preparation and physical properties of polymers of that type are described there in detail.

A possible arrangement for a mesogenic unit composed of oxybenzoate and terephthalate groups would be the "triad" formed from a terephthalate group flanked by two oxybenzoate groups. The triad can be more generally defined as any 3 aromatic groups linked by ester groups in the para position. This structure has been used before to produce low molecular weight liquid crystalline compounds in which the terminal groups were alkyl chains. By connecting both ends of these alkyl chains to mesogenic units, a polymer of the structure shown below can be prepared with both the mesogenic group and the flexible spacer located in the main chain,

Polymers of this structure were prepared using flexible spacers
with 2 to 10 and 12 methylene units, and one polymer substituted
with chlorine in the 3-position of the oxybenzoate ring was prepared
with a decamethylene spacer. This latter polymer was made to see
what effect alteration of the mesogenic unit might have on the be-
behavior of the polymer.

The polymers were prepared by synthesis of the diphenols shown
in Figure 11. This sequence of reactions involved blocking, and
deblocking reactions of the oxybenzoate groups. The diphenol was
then reacted with terephthaloyl chloride in the presence of pyridine
in a reaction that both formed the polymer and created the mesogenic
triad.

A large number of LC polymers have been prepared using a wide
variety of mesogens. However, very few have been studied systemati-
cally by preparing a homologous series of polymers. These few
include polymers reported by Strzelecki,(103) Meurisse,(18) Grif-
fin,(83) and Roviello,(73) and their coworkers which were listed in
Table 2. However, even these series left considerable gaps so
that the exact behavior of the missing polymers could only be in-
erred. For this reason, the preparation of a homologous series
would give the opportunity to determine the effects that a poly-
methylene spacer has on changes in the liquid crystallinity of
polymers.

The synthetic route used to include different spacer lengths
and types dealt with a diphenol that was polymerized in solution
with terephthaloyl chloride. Some of the reasons for choosing this

Fig. 11. Synthetic route for the preparation of polymers with triad mesogenic units and poly(methylene) flexible spacers.
synthetic route include the desire to prepare a product with a well-defined mesogen structure, the greater reactivity of the diphenol than alkyl diols with acid chlorides, and the inherent ease of the preparation of this series of diphenols.

The synthesis of polymers compositionally similar to those discussed in this chapter can also be performed by melt-transesterification techniques; however, these polymers have a very poorly defined mesogenic structure as shown in Chapter V, Figure 39. One of the causes for forming several possible types of structures is the use of high reaction temperature, which is necessary for polymerization and which can lead to CIR reorganizations. The need for a low temperature polymerization, therefore, required the use of the Schotten-Baumann reaction either in solution or by means of the interfacial method.

To obtain the well-defined mesogenic group needed for these structure-property studies, two routes were chosen for use here and to make the polymers reported in Chapter III, see Figure 20. The major advantages of the diphenol route are that phenols are known to be more reactive to acid chlorides and terephthaloyl chloride is readily available. However, a disadvantage was that each new polymer required the preparation of a different monomer by a route with no fewer than four synthetic steps.\(^{(66,96)}\)

The discussion section of this chapter has been organized into several parts: the first section deals with monomer preparation properties and polymerization because several of the monomers are
new compounds, and the remaining sections deal with the resulting polymers and their properties.

**Experimental**

**Synthesis of monomers and polymers.**

*p*-Carbethoxybenzoic acid, I. This compound was prepared by the addition of ethyl chloroformate (50 ml) in three portions to a cool (5°C) stirred solution of *p*-hydroxybenzoic acid (60 g, 0.434 mol) and sodium hydroxide (38.0 g, 0.955 mol) in 900 ml of distilled water. After reaction, the final mixture was acidified with 2 N HCl, and the precipitate was filtered and washed with excess water. The product was recrystallized without drying from an acetone-water mixture. Yield, 95% (white needles); mp, 157-158°C.

α,ω-Bis(p-ethoxycarbonyloxybenzoyloxy)polymethylene, III. The carbethoxybenzoic acid (I) was converted to the corresponding acid chloride (II) by a reaction with thionyl chloride in the presence of DMF. On the assumption that a 90% yield was obtained for the acid chloride, a 20% functional excess of the diol was used. Dry α,ω-alkanediol was then added to the solution of the acid chloride (20 g) in 50 ml of 1,2-dichloroethane. The mixture was refluxed with stirring overnight, cooled, poured into 300 ml of a 0.5N-Na₂CO₃ solution in ice water. The product was extracted into chloroform, and after drying with magnesium sulfate, the product was isolated on a rotary evaporator, dried under vacuum, and recrystallized in...
ethanol. (126) Listed below are some of the physical constants found for the compounds not listed in the literature; that is, for those having 7 or more methylene groups (n) in the diol chain. Other abbreviations are CI for compounds chlorinated in the 3-position of the oxybenzoate group, and DEG for diethylene glycol which connects the oxybenzoate groups. Some other properties can be found in Table 3.

7: \( \text{IR(KBr): } 2940 (\text{m}), 1760 (\text{C}=\text{O}), 1715 (\text{C}=\text{O}), 1605, 1365, 1250 (\text{broad}), 1160, 1100 (\text{m,broad}), 770; \int^1 \text{H-NMR(CDC1}_3 \int \delta 8.15 (d,2,2.6-\text{oxybenzoate}), 7.3 (d,2,3.5-\text{oxybenzoate}), 4.4 (m,4,\text{CH}_2), 1.45 (m,8, \text{CH}_2 \text{ chain } + \text{ CH}_3). \)

8: \( \text{IR(KBr): } 2940 (\text{m}), 1770 (\text{C}=\text{O}), 1755 (\text{C}=\text{O}), 1610, 1365, 1270 (\text{broad}), 1165, 1125, 780, 730; \int^1 \text{H-NMR(CDC1}_3 \int \delta 8.15 (d,1,2,6-\text{oxybenzoate}), 7.3 (d,1,3,5-\text{oxybenzoate}), 4.4 (m,2,\text{CH}_2), 1.45 (m,4.5,\text{CH}_2 \text{ chain } + \text{ CH}_3). \)

9: \( \text{IR(KBr): } 2910, 1765 (\text{C}=\text{O}), 1715 (\text{C}=\text{O}), 1605, 1500, 1460, 1370, 1220 (\text{broad}), 1165, 1125, 995, 770; \int^1 \text{H-NMR(CDC1}_3 \int \delta 8.15 (d,2,2.6-\text{oxybenzoate}), 7.3 (d,2,3.5-\text{oxybenzoate}), 4.4 (m,4,\text{CH}_2), 1.45 (m,10,\text{CH}_2 \text{ chain } + \text{ CH}_3). \)

10: \( \text{IR(KBr): } 2940, 2860, 1765 (\text{C}=\text{O}), 1710 (\text{C}=\text{O}), 1600, 1500, 1460, 1410, 1370, 1230 (\text{broad}), 1160, 1120, 1050, 1010, 995, 855, 770; \int^1 \text{H-NMR(CDC1}_3 \int \delta 8.2 (d,1,2.6-\text{oxybenzoate}), 7.35 (d,1,3.5-\text{oxybenzoate}), 4.4 (m,2,\text{CH}_2), 1.4 (m,5.5,\text{CH}_2 \text{ chain } + \text{ CH}_3). \)

12: \( \text{IR(KBr): } 2920, 2850, 1770 (\text{C}=\text{O}), 1715 (\text{C}=\text{O}), 1605, 1510, 1470, 1420, 1370, 1250 (\text{broad}), 1160, 1120, 995, 905, 775; \int^1 \text{H-NMR (CDC1}_3 \int \delta 8.15 (d,1,2.5-\text{oxybenzoate}), 7.35 (d,1,3.5-\text{oxybenzoate}),
Table 3. Properties of Monomers and Monomer Precursors.

\[
\text{Et-OC-O-CO-(CH}_2\text{)}_n\text{-OC-O-CO-Et}
\]

a) Carbethoxy Blocked Diphenols

<table>
<thead>
<tr>
<th>Compound(^(*)) No.</th>
<th>Yield (%)</th>
<th>Recryst. Solvent</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-2A</td>
<td>56</td>
<td>95% EtOH</td>
<td>102</td>
</tr>
<tr>
<td>II-3A</td>
<td>72</td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>II-4A</td>
<td>72</td>
<td></td>
<td>68</td>
</tr>
<tr>
<td>II-5A</td>
<td>84</td>
<td></td>
<td>48-50</td>
</tr>
<tr>
<td>II-6A</td>
<td>79</td>
<td></td>
<td>73-73</td>
</tr>
<tr>
<td>II-7A</td>
<td>93</td>
<td>90% EtOH</td>
<td>35-40</td>
</tr>
<tr>
<td>II-8A</td>
<td>77</td>
<td></td>
<td>72-73</td>
</tr>
<tr>
<td>II-9A</td>
<td>62</td>
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<td>55-57</td>
</tr>
<tr>
<td>II-10A</td>
<td>91</td>
<td></td>
<td>70-72</td>
</tr>
<tr>
<td>II-10(C1)A</td>
<td>88</td>
<td></td>
<td>61-63</td>
</tr>
<tr>
<td>II-12A</td>
<td>67</td>
<td></td>
<td>58-59</td>
</tr>
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</table>

b) Diphenols

<table>
<thead>
<tr>
<th>Compound(^(*)) No.</th>
<th>Yield (%)</th>
<th>Recryst. Solvent</th>
<th>(T_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-2B</td>
<td>89</td>
<td>MeOH</td>
<td>245</td>
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<tr>
<td>II-3B</td>
<td>90</td>
<td>&quot;</td>
<td>198</td>
</tr>
<tr>
<td>II-4B</td>
<td>92</td>
<td>90% EtOH</td>
<td>190</td>
</tr>
<tr>
<td>II-5B</td>
<td>88</td>
<td>MeOH</td>
<td>110</td>
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<tr>
<td>II-6B</td>
<td>83</td>
<td>80% EtOH</td>
<td>176</td>
</tr>
<tr>
<td>II-7B</td>
<td>85</td>
<td>70% MeOH</td>
<td>138</td>
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<tr>
<td>II-8B</td>
<td>90</td>
<td>90% EtOH</td>
<td>185</td>
</tr>
<tr>
<td>II-9B</td>
<td>44</td>
<td>70% MeOH</td>
<td>108</td>
</tr>
<tr>
<td>II-10B</td>
<td>80</td>
<td>90% EtOH</td>
<td>165</td>
</tr>
<tr>
<td>II-10(C1)B</td>
<td>79</td>
<td>70% MeOH</td>
<td>89</td>
</tr>
<tr>
<td>II-12B</td>
<td>81</td>
<td>60% EtOH</td>
<td>147</td>
</tr>
</tbody>
</table>

\(^(*)\) Compound number indicates number of methylene groups in diol used.
4.4(m,2,CH$_2$), 1.4(m,6.5, CH$_2$ chain + CH$_3$).

10(Cl): IR(KBr): 2950, 2860, 1765(C=O), 1720(C=O), 1480, 1410, 1375, 1280(broad), 1245(broad), 1120, 1040, 990, 950, 885, 765, 745, 720; $^1$H-NMR(CDC$_3$) δ 8.1(m,2,2.6-oxybenzoate), 7.4(d, 1,5-oxybenzoate), 4.35(m,4,CH$_2$), 1.35(m,13,CH$_2$ chain + CH$_3$).

DEG: IR(KBr): 3000, 2910, 1755(C=O), 1705(C=O), 1610, 1590, 1505, 1480, 1445, 1420, 1360, 1275(broad), 1160, 1110, 995, 945, 860, 770, 690; $^1$H-NMR(CDC$_3$) δ 8.15(d,2,2.6-oxybenzoate), 7.3(d,2, 3.5-oxybenzoate) 4.5(m,4,CH$_2$), 3.9(q,2,CH$_2$,ether), 1.45(t,3, CH$_3$).

DEG(C1): IR(KBr): 2950(broad), 1770(C=O), 1730(C=O), 1600, 1580, 1495, 1445, 1400, 1370, 1230(broad), 1120, 1045, 995, 770; $^1$H-NMR(CDC$_3$) δ 8.1(m,2,2.5-oxybenzoate), 7.4(d,1,5-oxybenzoate), 4.5(m,4,CH$_2$), 3.95(q,2,CH$_2$ ether), 1.5(t,3,CH$_3$).

$\alpha$,\$\omega$-Bis(p-hydroxybenzoyloxy) polymethylene, IV. The carbonate ester intermediates were hydrolyzed to the corresponding phenols following the literature method.(126) The intermediates, III, were dissolved in a water/ethanol mixture (300 ml/700 ml) and after addition of 4 equivalents of sodium hydroxide, the mixture was refluxed for one half hour. After cooling, the reaction medium was acidified with acetic acid, and the ethanol was removed with a rotary evaporator. Addition of approximately 200 ml of water caused the product to precipitate, after which, the product could be recrystallized in the solvent system shown in Table 3.

The spectral properties of the compounds not previously reported
in the literature are given below where the number before the data refers to the number of methylene groups in the parent diol. Other abbreviations are the same as those used for the carbethoxy derivatives.

7: Anal. calcd. for C\textsubscript{21}H\textsubscript{24}O\textsubscript{6}: C, 67.7; H, 6.5. Found: C, 67.3; H, 6.5. IR(KBr): 3390(OH), 2940, 2860, 1685(C=O), 1605, 1590, 1510, 1375(broad), 1164, 1100, 852, 774, 695; \textsuperscript{13}C-NMR(dioxane) δ (ppm) 166.2(C=O), 161.9(4-ϕ), 132.3(2,6-ϕ), 122.9(1-ϕ), 115.6(3,5-ϕ), 64.9(CH\textsubscript{2} ester), 29.6(CH\textsubscript{2}), 29.4(CH\textsubscript{2}), 26.6(CH\textsubscript{2}).

8: Anal. calcd. for C\textsubscript{22}H\textsubscript{26}O\textsubscript{6}: C, 68.4; H, 6.8. Found: C, 68.3; H, 6.9. IR(KBr): 3365(OH), 2920, 2860, 1675(C=O), 1610, 1590, 1295(broad), 1170, 970, 860, 775, 695, 620; \textsuperscript{1}H-NMR(TFA) δ 8.15 (d,1,2.6-oxybenzoate), 7.10(d,1,3.5-oxybenzoate), 4.6(t,1, CH\textsubscript{2} ester), 1.65(m,3,CH\textsubscript{2} chain).

9: Anal. calcd. for C\textsubscript{23}H\textsubscript{28}O\textsubscript{6}: C, 68.9; H, 7.1. Found: C, 67.2; H, 7.1. IR(KBr): 3290(OH), 2920, 2850, 1680(C=O), 1610, 1520, 1460, 1440, 1390, 1280(broad), 1160, 1130, 1090, 1010, 940, 850, 780; \textsuperscript{1}H-NMR(d\textsubscript{6}-acetone) δ 9.15(s,1,H\textsubscript{O}), 8.03(d,2,2.6-oxybenzoate), 7.0(d,2,3.5-oxybenzoate), 4.3(t,2,CH\textsubscript{2} ester), 1.45(m,3,5,CH\textsubscript{2} chain).

10: Anal. calcd. for C\textsubscript{24}H\textsubscript{30}O\textsubscript{6}: C, 69.6; H, 7.3. Found: C, 69.3; H, 7.3. IR(KBr): 3390(OH), 2930, 2905, 2860, 1674(C=O), 1605, 1580, 1510, 1470, 1400, 1280(broad), 1160, 1120, 980, 935, 850, 770, 700, 620; \textsuperscript{1}H-NMR(d\textsubscript{6}-acetone) δ 8.9(s,1,H\textsubscript{O}), 7.8(d,2,2.6-oxybenzoate), 6.8(d,2,3.5-oxybenzoate), 4.07(t,2,CH\textsubscript{2} ester),
1.1(m,4,CH₂ chain).

12: Anal. calcd. for C₂₆H₃₄O₆: C, 70.6; H, 7.7. Found: C, 71.1;
H, 7.3. IR(KBr): 2920, 2840, 1770(C=O), 1720(C=O), 1600, 1505,
1470, 1410, 1370, 1250(broad); ^1H-NMR(d₆-acetone) δ 7.9(d,1,
2.6-oxybenzoate), 6.9(d,1,3.5-oxybenzoate), 4.2(t,1,CH₂), 1.3(m,
5,CH₂).

10(C1): Anal. calcd. for C₂₄H₂₈O₆Cl₂: C, 59.6; H, 5.8. Found: C,
59.9; H, 6.1. IR(KBr): 3340(broad,OH), 2920, 2860, 1690, 1604,
1580, 1520, 1430, 1390, 1260(broad), 1130, 1050, 960, 900, 830,
770, 710, 630; ^1H-NMR(d₆-acetone) δ 7.8(m,2,2.6-oxybenzoate),
7.0(d,1,5-oxybenzoate), 4.15(t,2,CH₂ester), 1.2(m,8,Cl₂ chain).

DEG: Anal. calcd. for C₁₈H₁₈O₇: C, 62.4; H, 5.2. Found: C, 61.4; H,
5.0. IR(KBr): 3300(OH), 2980, 1705(C=O), 1680(C=O), 1610, 1590,
1520, 1440, 1380, 1265(broad), 1165, 1085, 940, 850, 765;
^1H-NMR(d₆-acetone) δ 7.85(d,1,2.6-oxybenzoate) 6.72(d,1,3.5-
oxybenzoate), 4.23(q,1,CH₂ ester), 3.7(q,1,CH₂ ester).

DEG(C1): Anal. calcd. for C₁₈H₁₆O₇Cl₂: C, 52.1; H, 3.9; Cl, 17.1. Found:
C, 50.7; H, 4.2; Cl, 15.9. IR(KBr): 3150(broad,OH), 1690(C=O),
1600, 1580, 1510, 1470, 1450, 1430, 1380, 1280, 1120, 1080,
1030, 830, 760; ^1H-NMR(d₆-acetone) δ 7.8(m,2,2.6-oxybenzoate),
6.9(d,1,5-oxybenzoate), 4.3(q,2,Cl₂ ester), 3.7(q,2,Cl₂ ether).

I(C1):* Anal. calcd. for C₁₀H₉O₅Cl: C, 49.1; H, 3.7; Cl, 14.5. Found:
C, 49.3; H, 3.8; Cl, 14.2. IR(KBr): 2900(very broad), 1770, 1690,
1600, 1425, 1375, 1240(broad), 1045, 1000, 875, 770, 740, 715,*

*(C1) refers to the 3-chloro-4-carbethoxybenzoic acid.
60, 560; $^1$H-NMR(d$_6$-acetone) $\delta$ 8.25(m,2,2.6-oxybenzoate), 7.65(d,1,5-oxybenzoate), 4.45(q,2,CH$_2$), 1.45(t,3,CH$_3$).

**Polymers.** The monomer, IV, which had traces of water removed by azeotropic distillation in benzene or toluene, was dissolved in a minimum amount of pyridine, and to this was added a solution of terephthaloyl chloride in 1,1,2,2-tetrachloroethane (about 2 g polymer in 50 ml). The mixture was stirred at room temperature for between 24 to 48 hours. The reaction mixture was poured into 300 ml of acetone or methanol, stirred for 1 hour, filtered, and dried. This product was ground up, and stirred in a dilute HCl solution for one hour, then dilute NaHCO$_3$ for the same time, and finally filtered and washed with dilute HCl and water. The product was dried under vacuum at 50°C, and was generally a white powder.

The two copolymers were prepared from equimolar mixtures of the diphenols, IV, having $n = 2$ and 7, (2/7 in the Table), and $n = 2$ and 10(2/10 in the Table) using the same method as described above for the preparation of the homopolymers.

**Reagents.** The research reported in this thesis was performed in two countries, and as a result, several different suppliers of chemicals were used. Generally, Aldrich chemicals were employed, but other suppliers include Fluka, Hoechst and Carlo Erba. Solvents were dried over sodium, unless they were chlorinated in which case they were dried with P$_2$O$_5$ and then distilled. Pyridine was dried over NaOH and distilled from barium oxide. Bulk solvents were obtained from the stockrooms at the University of Massachusetts, and
the University of Pisa.

Characterization of monomers. Melting points of monomers and intermediates were measured on a Fisher-John melting point apparatus. Elemental analyses was determined by the Microanalytical Services Group of the University of Massachusetts. Spectral measurements were performed on instruments made available through the Materials Research Laboratory (MRL) and included a Varian CFT-20 C-13 FTNMR, a Varian T-60, a Perkin-Elmer R-32 (all NMR spectrometers) and a Perkin-Elmer IR-238 infrared spectrometer. For NMR studies, all blocked monomers (III) were studied in d-chloroform (Aldrich), and all monomers were measured in d$_6$-acetone (Aldrich) where TMA was used as reference in both cases. Infrared measurements were done on powder samples pressed in a KBr (Aldrich) matrix.

Polymer characterization. Viscosity measurements were made in a Cannon-Ubbelohde viscometer using p-chlorophenol at 45°C at concentrations of 0.5 g/dl. Temperature was maintained using a Tamsen thermostated water bath (±0.1°C). The values of solution viscosity reported are single point inherent viscosity measurements.

Microscopic observations were made using a Leitz Ortholux polarized light microscope using either the Leitz hot stage, or a Mettler FP-5 programmable temperature controller with an FP-52 hot stage. Photographs were taken with the camera attachment and were made using Kodak Ektachrome ASA 160 Tungssten color slide film.

Thermal studies of the polymers were performed either on a DSC-1B or a DSC-2 with scanning auto zero, and heats of transition,
and temperatures were calibrated using indium as standard. After equating a certain peak area with the value for the heat of melting of indium, the heats of melting and clearing for the polymers could be calculated. When sub-ambient measurements were made, a dry ice-isopropanol bath was used. All DSC runs were performed under dry nitrogen atmosphere using a pre-weighed sample with an empty sample pan and lid as reference. Methods for DSC operation and measurement calculation can be found in the manual supplied with the instrument.

The heats of transition were measured by equating peak area with the weight of tracings cut out from albanene paper. Indium standard was used, and from this the number of calories of transition per gram of tracing paper was calculated. Knowledge of the weight of the sample and the grams per mole-repeat of sample then permitted the computation of the molar heats of transition of the polymers. The following equation describes the values needed for computation of the enthalpies of transition.

\[
H(\text{cal/mole-repeat}) = \frac{(\text{cal/mg-paper}) \times (\text{mg paper}) \times (g/mole-repeat)}{(g\text{-sample})}
\]

The following diagram shows the areas of the curves used in a representative heating run showing the melt and clearing transitions. Also shown are the transition temperatures taken at the peak maxima, and used for calculation of the entropies of transition of the compounds. These values could then be used with the
heats of transition to calculate changes of entropy as shown in the discussion, equation II-1.

Thermal optical analysis (TOA) was performed using an American Optical Microstar microscope with a photocell substituted for one of the eye-pieces. The photocell was attached to a specially equipped Mettler FP-5 temperature controller which registered both the birefringent light intensity as well as the temperature.

Studies of the X-ray diffraction patterns of the samples were made both in the solid and in the liquid crystalline melt. Those in the solid were made at room temperature with 1.5 cm diameter x 1.0 mm polymer pellets pressed in a KBr press, and were measured with a Sieman D-500 diffractometer with a monochromater and Cu radiation. Spectra in the melt were made with Siemens source of Cu radiation and a Ni filter using a Wahrus camera and heating cell. Samples were held in a 0.5 mm O.D. glass capillary tube, sealed at both ends. The camera was operated under reduced pressure to decrease the amount of air scatter.

Any other spectral measurements used the equipment and techniques
outlined for the characterization of the monomers.

**Results and Discussion**

**Monomer and polymer preparation.** Each monomer was prepared in the manner described in the Experimental section of this chapter, and some of the properties of these monomers are reported in Table 3. The synthetic method used was based on that of Wilkinson and co-workers, and monomer II-2A to -6A have been previously reported by them. Those monomers with alkyl diols with seven or more methylene groups (monomers II-7A to -12A) were synthesized for the first time as reported here. Some representative $^1$H-NMR spectra and IR spectra of these new compounds are shown in Figure 12 to 15.

For each new monomer, a new carbethoxy blocked diphenol (I) was prepared, see Figure 11. The characteristic spectral features of the former were due to its carbonyl functional groups. In the infrared spectra, a series of bands due to the alkyl group appeared at roughly 2900 cm$^{-1}$, and of course two carbonyl peaks could be observed, the one due to the ester appearing at 1710 cm$^{-1}$, and that of the carbethoxy carbonyl at 1765 cm$^{-1}$. The absence of any carboxylic acid or alcoholic -OH's in the 3500 - 2500 cm$^{-1}$ range was taken as an indication of the satisfactory preparation of the monomer precursors, which could also be substantiated by their NMR spectra which showed these features; two sets of doublets due to the oxybenzoate group centered at $\delta$ equals 8.2 and 7.3, a multiplet at 4.4,
Figure 12

\[
\text{HO-} \overset{\text{a+b}}{\overset{\text{CO(CH}_2)_2}{\overset{\text{O}}{\text{O}}} \overset{\text{a+b}}{\overset{\text{C}}{\overset{\text{OH}}{\text{OH}}}} \\
\]

\[\text{a+b} \quad \text{c+d} \quad \text{a+b} \]

Figure 13

\[
\text{EtOCO-} \overset{\text{c+d}}{\overset{\text{CO(CH}_2)_2}{\overset{\text{O}}{\text{O}}} \overset{\text{c+d}}{\overset{\text{O}}{\text{O}} \overset{\text{c+d}}{\overset{\text{Et}}{\text{C}}}} \\
\]

\[\text{c+d} \quad \text{a+b} \quad \text{c+d} \quad \text{a+b} \quad \text{c+d} \]

60 MHz $^1$H-NMR spectra of (above) $\alpha,\omega$-bis(p-hydroxybenzoyloxy)-decane, and (below) $\alpha,\omega$-bis(p-ethoxycarbonyloxybenzoyloxy)decane.
Infrared spectra of (above) bis(p-hydroxybenzoyloxy)decane and (below) bis(p-ethoxy-carbonyloxybenzoyloxy)decane.
from the methylene groups, and a multiplet at 1.5 due to the remaining methyl and methylene groups.

After hydrolysis of the carbethoxy groups, the infrared spectrum showed the presence of a very sharp phenolic peak at 3380 cm\(^{-1}\), and only one carbonyl at 1675 cm\(^{-1}\). Likewise, the removal of the blocking groups could be demonstrated by the NMR spectrum where again two sets of doublets could be observed at \(\delta\) equals 7.9, and 6.8 due to the oxybenzoate group. Also present were a triplet at \(\delta\) equals 4.2 and a large peak at \(\delta\) equals 1.4 due to the ester methylene and the remaining chain methylenes respectively. Elemental analysis of the new compounds was performed which showed that the compounds produced had the compositions expected from hydrolysis of the two blocking groups.

The melting temperatures of all of these compounds were determined with a Fisher-Johns melting point apparatus, and in some cases by DSC, and both methods gave the same values for the melting temperatures which have been reported in Table 3. The diphenol monomers showed an even-odd relationship in their melting temperatures which is a common feature of many homologous series of compounds, and this property was retained by the polymers produced from these monomers. Careful observation under the polarized light microscope showed that all of these compounds melted directly to an isotropic melt and were, therefore, not liquid crystalline.

The series of polymers discussed in this chapter was prepared by solution polycondensation of the monomer diphenols just discussed
and terephthaloyl chloride. The structure formed (shown in Figure 11) consisted of a polymethylene flexible spacer and a triad mesogenic unit that was based upon a terephthalate group flanked by two oxybenzoate groups.

Pyridine was used as proton acceptor for the reaction, which took place in chlorinated solvents at ambient temperature. No effort was made to optimize the polymerization reaction; instead the conditions used were essentially those that had been employed successfully with similar systems and reported in the literature. In an effort to compare the possible differences that might occur if the interfacial polymerization technique was used, monomer II-2A was polymerized by both the interfacial and solution methods. The product made by the solution method had a somewhat higher molecular weight as measured by inherent viscosity and also higher transition temperatures, but was otherwise similar to that from the interfacial method. For this reason, all other polymers in the series were made by the solution polymerization technique. All polymers precipitated out of the reaction mixture while the reaction proceeded, so the final polymer molecular weight may have been dependent on polymer solubility.

Polymer characterization. The properties of the triad polymers are tabulated in Table 4. Yields of the different polymerization reaction were less than 100 per cent, and as would be expected, the molecular weights of the polymers were relatively low as shown by their low inherent viscosities. These viscosities were in the
Table 4. Properties of the Triad Series of Polymers with Polymethylene Flexible Spacers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Spacer Length</th>
<th>Yield</th>
<th>( \eta_{\text{inh}} )</th>
<th>( T_m )</th>
<th>( T_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>II- 2</td>
<td>2</td>
<td>80</td>
<td>.18</td>
<td>342</td>
<td>365&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>II- 3</td>
<td>3</td>
<td>94</td>
<td>.26</td>
<td>240</td>
<td>315&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>II- 4</td>
<td>4</td>
<td>91</td>
<td>.23</td>
<td>285</td>
<td>345&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
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<td>253</td>
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<td>8</td>
<td>66</td>
<td>.20</td>
<td>197</td>
<td>220</td>
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<tr>
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<td>55</td>
<td>.28</td>
<td>174</td>
<td>233</td>
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<tr>
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<td>10</td>
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<td>.34</td>
<td>220</td>
<td>267</td>
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<tr>
<td>II-12</td>
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<td>94</td>
<td>.48</td>
<td>212</td>
<td>245</td>
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<tr>
<td>II-10Cl</td>
<td>10</td>
<td>74</td>
<td>.31</td>
<td>h)</td>
<td>167</td>
</tr>
<tr>
<td>II-2,7</td>
<td>2/7</td>
<td>63</td>
<td>.22</td>
<td>252</td>
<td>335</td>
</tr>
<tr>
<td>II-2,10</td>
<td>2/10</td>
<td>45</td>
<td>.23</td>
<td>200</td>
<td>290</td>
</tr>
</tbody>
</table>

a) inherent viscosity in p-Chlorophenol at 45°C
b) decomposition temperature h) heating c) cooling
range of 0.15-0.45 dl/g.

The polymers were characterized by differential scanning calorimetry (DSC), polarized-light microscopy, and thermal optical analysis (TOA). The latter technique involved the measurement of birefringent light intensity as a function of temperature and was very useful when used in conjunction with the other two methods.

Figure 16 shows how DSC and TOA can be used together for the heating and cooling curves of polymer 11-10, which contains the decamethylene spacer, after an initial heating and cooling cycle. Initially, the heating curve showed some crystallization followed by a sharp, and somewhat structured melting peak at 220°C. A rather broad clearing transition followed at 267°C, and at the same time the birefringence dropped to zero intensity, (that is, the sample became isotropic and appeared black under crossed-polars). The slight increase in birefringence that occurred upon melting should also be noted.

During cooling, a broad structured exotherm occurred at 253°C upon nucleation of the mesophase, and at the same time there was a sharp jump in the amount of birefringence. This transition was followed by crystallization of the polymer with a sharp exotherm at 157°C, and a slight decrease in birefringence. The undercooling of the liquid crystalline melt that occurred before crystallization is common to many LC compounds, both the polymeric and low molecular weight types.

The study of these compounds by the use of a polarizing
Figure 16. Thermal-optical analysis (TOA) and differential scanning calorimetry (DSC) of the triad polymer with the decane spacer. a) Heating and b) cooling.
microscope proved to be very useful when combined with the other two methods. The transitions of thin films of the molten polymers were studied on the polarizing microscope using a variable-temperature hot stage. These observations often enabled the identification of the mesophase present according to the type of liquid crystalline texture observed. Examples of the different textures present for this series of polymers are shown in Figure 17a) to e). The polymers with short spacers had melting temperatures which were too high for the mesophases of polymers II-2 to II-4 to be observed. Presumably, they had nematic mesophases like polymers II-5 and II-6, and would have exhibited the typical nematic Schlieren texture of polymer II-6 shown in Figure 17a). This texture shows the brushes generating from point defects that are characteristic of the nematic mesophase.

Figure 17b) shows the appearance of the mesophase as it nucleated in spherical droplets from the isotropic melt, which appears black in this photograph. At the left of the figure can be seen the fully developed nematic mesophase.

The appearance of the smectic state was much different than that of the nematic state, and some idea of these differences can be seen in the remaining photomicrographs that appear in Figure 17. The blocky texture of the polymer with nonane diol spacer was typical of the appearance of the smectic mesophase and resembled the smectic C mesophase of several low molecular weight and polymeric compounds reported in the literature. (67)

On the other hand both the polymers with spacers consisting of
Figure 17. Photomicrographs of the mesophase of several polymers with triad mesogenic groups and polymethylene spacers. Magnification equals 360x.

a) Polymer with hexamethylene spacer at 257°C nucleating from the isotropic melt. (above)

b) Polymer with hexamethylene spacer at 250°C showing the Schlieren texture. (below)
Figure 17. (cont'd)

c) Polymer with nonamethylene spacer at 175°C showing the blocky texture resembling the smectic C mesophase of low molecular weight liquid crystals.

d) Polymer with decamethylene spacer at 219°C showing a fan-shaped texture typical of the smectic A mesophase.

Magnification of both photographs equals 360x.
Figure 17. (cont'd)

e) Polymer with dodecamethylene spacer at 230°C demonstrating the effect of orientation produced by shearing the cover-glass, and also showing the focal-conic texture.

Magnification equals 360x.
10 and 12 methylene groups showed a distinct focal-conic texture more representative of the smectic A mesophase. The crosses that appeared in this texture were due to the layered structure of this mesophase and occurred when the layers were attached to the upper and lower surfaces, thereby forming sections of cones. A much clearer description of this structure can be found in Hartshornes's book on the microscopy of liquid crystals.(26)

Another method conventionally used to characterize liquid crystalline materials is X-ray diffraction. Low molecular weight LC compounds must be studied in the melt, often under the influence of a magnetic or electrical field in order to orient the melt.(25) Thermotropic polymers often crystallize slowly enough that the mesomorphic order can be maintained at low temperatures by quenching-in of the mesophase for X-ray studies, but the triad polymers crystallized sufficiently quickly that study of the mesophase could be carried out only in the melt.

The triad polymers were capable of forming either the smectic or nematic mesophases according to texture observations. As explained in Chapter I, the nematic polymers would be expected to generate an X-ray diffraction pattern of only a diffuse ring at 4-5 Å. Several of the polymers were studied, and indeed this spacing was found to be present for polymers II-6 to II-12 as shown in Table 5, for which the ring dimensions can be found for these polymers. The distances in the 4-5 Å range represent the interchain spacing, and this value is quite normal for both monomeric and polymeric LC
Table 5. Repeat distances of the mesophases determined by X-ray diffraction.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>d, Å</th>
<th>D, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-9</td>
<td>4.8</td>
<td>28</td>
</tr>
<tr>
<td>II-10</td>
<td>4.9</td>
<td>31</td>
</tr>
<tr>
<td>II-12</td>
<td>4.5</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 6. Properties of polyesters of various molecular weights with aromatic triad mesogenic units and a decamethylene spacer.

<table>
<thead>
<tr>
<th>[η] (dl/g)</th>
<th>T_m (°C)</th>
<th>T_i (°C)</th>
<th>ΔT (°C)</th>
<th>ΔH_m (kcal/mol)</th>
<th>ΔH_i (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.176</td>
<td>197</td>
<td>230</td>
<td>33</td>
<td>3.82</td>
<td>1.82</td>
</tr>
<tr>
<td>.243</td>
<td>189</td>
<td>227</td>
<td>38</td>
<td>2.07</td>
<td>1.37</td>
</tr>
<tr>
<td>.335</td>
<td>220</td>
<td>267</td>
<td>47</td>
<td>3.25</td>
<td>2.00</td>
</tr>
<tr>
<td>.471</td>
<td>217</td>
<td>266</td>
<td>49</td>
<td>2.76</td>
<td>1.82</td>
</tr>
</tbody>
</table>
The larger dimension listed for the polymers with 9 to 12 methylene units in the spacer is the size of the structural repeat unit of the layers found in the smectic mesophase. The mesogenic unit itself is only about 20 Å, so the extra separation is due to the flexible spacer. Assuming that the spacer is in an extended chain conformation, then the polymer chains might not be perpendicular to the layers, since the extended spacer more than accounts for the extra distance of the repeat length. While the extension of the chain is often assumed, the spacers might also be partly folded or coiled so that folding of the chain would be another possible explanation for the size of the layers.

The solid polymers showed a considerably larger number of clearly defined spacings, because they were semi-crystalline solids. Wide angle X-ray diffraction patterns revealed rings in the 3.0 Å to 6.0 Å range for all of these polymers which was probably associated with the interchain spacings of the crystal repeat units. Upon melting, these spacings gave way to the rings just discussed which is a demonstration of the decreased order present in the mesophase with respect to the solid as would be expected for the LC state.

**Transition temperatures versus spacer length.** The melting points of the polymers as measured by DSC and TOA decreased regularly in a zig-zag fashion as the number of methylene groups (n) increased to 7 or 8, after which the melting temperatures seemed to increase at longer flexible spacer lengths. As commonly observed, the polymers with an even number of methylene groups in the spacer had
higher melting points than those with odd numbers of methylene groups as shown in Figure 18, in which transition temperatures are plotted as a function of spacer length.

Theoretical attempts have been made to explain the even-odd behavior of liquid crystalline compounds. These explanations, which have generally dealt with low molecular weight compounds having alkyl terminal groups, were based on consideration of either the changes of the mesogenic dipole\(^ {98,99}\) or conformation alternations.\(^ {100,101}\) These differences were attributed to both the increased length of the spacer and to passing from an odd to an even number of methylene groups in the spacer. The increase in \(T_i\) with the polymer using a decamethylene spacer, after \(T_i\) had decreased in an even-odd fashion could be due to a change in the conformation of the spacer. It would be expected to exist in the extended trans conformation of the polymethylene spacer in the mesophase, but with longer spacers, could change to a conformation with one or more gauche units, which would be less energetically favorable, but would stabilize the structure of the mesophase.\(^ {100}\)

An interesting feature of the plot of transition temperature versus spacer length is the lower dependence of the clearing temperature \((T_i)\) on spacer length than the melting temperature. As a result, the polymers with spacers having odd number of methylene groups not only had lower melting temperatures than polymers with even-numbered spacers but also had wider temperature ranges of mesophase stability.
Figure 18. Plot of transition temperature vs. the degree of polymerization of the poly(methylene) spacer in polymers with main-chain mesogenic triad units.
Another effect on increasing flexible spacer length was the change from polymers having a nematic mesophase to those having a smectic mesophase. The polymers with spacers going from as few as two methylene groups to those having as many as six methylene units produced textures under the polarizing microscope that showed the characteristic features of the nematic state. In contrast to this group of polymers, those polymers with seven or more methylene groups had the appearance of the smectic mesophase in the liquid crystalline melt. Evidently, the longer spacers provided greater independence of organization for the mesogenic units in the polymer chain, so more ordered smectic structures could be formed.

As a result of the moderate molecular weights of these polymers, the samples studied may have been in a molecular weight range where transition temperatures are sensitive to slight changes in molecular weight. The possibility also existed that the crystalline and liquid crystalline behavior of these polymers was affected by molecular weight. For this reason, several polymers of different inherent viscosities but identical chemical compositions were prepared by slight variation of reaction conditions. Generally, more dilute reaction mixtures gave lower molecular weight polymers. The properties of these polymers are listed in Table 6.

In all cases, the general features of the melting and clearing endotherms of the samples in this series were the same. The properties that changed were the actual temperatures of transition, and as might be predicted, those polymers with lower inherent viscosities,
had lower transition temperatures. This relationship again shows the marked dependence that the properties of liquid crystalline polymers have on molecular weight. Observation with the polarizing microscope showed that the polymers all exhibited textures characteristic of the smectic state. What is important to note then, is that the basic mesophase structures of these compounds did not change, so that it must be the actual structure of the polymers that determines the mesophase organization and not the molecular weight.

Several types of polymers have been reported which were prepared in a homologous series using a single mesogenic unit and different lengths of polymethylene flexible spacer. Generally, the series have been incomplete so that reliable comparison of the results are difficult. The melting temperature of the different polymers seemed to be determined by mesogen type, but discussion of the effect of the mesogenic unit will be limited to Chapter VI. The general features of the relationship of transition temperature to flexible spacer length were the same for all homologous series of polymers. Basically, each series showed a decrease in the transition temperatures as spacer length increased and an even-odd relationship in the melting temperature.

The homologous series prepared by Roviello and Sirigu (polymers 1 to 5 of Table 2) consisted of one group with a stilbene mesogenic unit connected by an \( \alpha,\omega \)-dicarboxylic acid with different numbers of methylene groups, and another group with a benzalidene mesogen connected in a similar fashion.\(^{(14,102)}\)
The first series of polymers exhibited no remarkable changes in the mesophase structure as the length of the flexible spacer increased. Therefore one can conclude that when considering only polymers with the stilbene mesogenic unit, as the spacer length is increased, the transition temperature is decreased. However, the lack of any examples of polymers with odd-numbered spacers prevented the observation of an even-odd effect. Several of the polymers, some of which possessed smectic mesophases, were found to be monotropic, and most possessed polymorphism in the solid and liquid crystalline states.\(^{14}\)

The phenomenon of polymers that form nematic phases with short spacers changing to polymers that form smectic mesophases when longer spacers are used has been observed by Strzelecki and co-workers.\(^{104}\) The mesogenic group used by them is listed in Table 2 as polymer 19, and is the same mesogenic unit studied by Noel\(^^{67}\) and by Jin.\(^^{85}\) However, there are differences in the liquid crystalline behavior between the various polymers in the three laboratories. The Strzelecki polymers all reportedly had nematic mesophases, but those with spacers longer than 5 methylene groups possessed an additional smectic mesophase. It should be noted, however, that neither the polymer of Jin with a spacer of 10 methylene groups, nor the polymer reported by Noel with a spacer of 6 methylene groups, had reported transitions equal to those in reference \(^{104}\). This discrepancy highlights the difficulties that different synthetic procedures can cause when comparing supposedly identical compounds.
Lenz and coworkers also studied a polyester with a triad mesogenic unit quite similar to the mesogenic group of the subject polymers of this chapter (see polymer 31 in Table 2) which was also similar to the triad mesogenic unit of the polymers discussed in the previous paragraph. The number of methylene groups was increased from 5 to 10, and with this increase an even-odd decrease of the melting transition occurred. Those polymers with odd-numbered spacers had lower melting points and larger ranges of mesophase stability than the neighboring polymers with even-numbered spacer.

Griffin, in contrast, used a mesogenic dyad consisting of the oxybenzoate and hydroquinone residues (polymer 35, Table 2) and complicated the structure-property relationships by using mixtures of polymethylene spacers. However, when one flexible spacer was kept constant and the other one varied by increasing its length then this series of polymers showed a nearly perfect even-odd decrease for both the melting and clearing transitions. All polymers were found to form nematic mesophases, as might be expected because of both the lower persistence length of the dyad mesogen when compared to the triad types and to the mixing of the flexible spacer lengths, which would produce a polymer with a lower inherent structural order.

In general then, all homologous series of mesophase-forming polymers showed the trend of reduced melting and clearing temperature with increased spacer length. All polymer types showed even-odd effects, and several showed changes in the particular mesophase formed
as spacer length was increased, with smectic mesophases being formed preferentially at higher spacer sizes. The individual properties of each system was highly dependent on the mesogenic group used so that the particular melting points and mesophases formed were a function of that polymer series only. The basic trends observed for all of these series of polymers were in good agreement with those of the triad polymers. Therefore, the behavior of the triad series seem to be typical of liquid crystalline polymers with flexible spacers and mesogenic groups in the main chain.

**Thermodynamic properties versus spacer length.** The availability of several homologous series of thermotropic polymers allowed a study of the role that additional methylene units can play in the melting and mesophase transitions. The heats and entropies of the transition for several series of low molecular weight liquid crystals have been considered, and it was shown that along with the even-odd relationship associated with the increased alkyl end group lengths, an increase in the entropy of clearing was found to occur with each additional methylene group.

Generally, for low molecular weight LC compounds, a value for the change of entropy at the nematic to isotropic transition ($\Delta S_{N-I}$) of about 0.4 cal/mol-K was found. Until 6 or more carbon atoms are present in the alkyl end group, the mesophase was usually nematic, and a small, steady increase of the entropy of clearing was observed. With sufficiently long end groups the compounds in the series begin to show increases in the entropy of clearing, which can be related
to the development of the ability of these compounds to form the smectic state. It was usually at this point that the effect of the added methylene groups could be easily identified, and the value for the entropy of clearing was increased by 0.15 cal/mol-K for each methylene group added if the dialkoxyphenyl nitrone series was considered. Other examples of low molecular weight LC compounds showed increments of as much as 0.5 cal/mol-K for every methylene group added above six carbons. These values were, however, an average, and there was considerable scatter in these examples.\(^{106}\)

For polymers, such a clear relationship is not always observed. Polymers generally have a distribution of molecular weights, and so the entropy per monomer repeat unit must be considered. Another factor that can influence such behavior is the effect of hindered packing in the chain structure. For example, virtually no polymer shows total crystallinity in the solid state, hence it would be likely that no polymer can contribute completely to the liquid crystalline state. In other words, not all of the polymer molecule may be free to become ordered into a mesophase structure, which should be reflected in the thermodynamic data. Conversely, if a value for the clearing transition of the perfect structure was known, then the degree of liquid crystallinity could be calculated, but at present this is not possible.

The thermodynamic data calculated for the triad polymers that are reported in this chapter have been listed in Table 7, in which both the heats and entropies of the melting and clearing transitions
Table 7. Thermodynamic properties of polyesters with poly(methylene)
spacers based on triad ester mesogens.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Spacer Length</th>
<th>$T_m$ (oC)</th>
<th>$\Delta H_m$ (Kcal/mol)</th>
<th>$\Delta S_m$ (cal/mol K)</th>
<th>$T_i$ (oC)</th>
<th>$\Delta H_i$ (Kcal/mol)</th>
<th>$\Delta S_i$ (cal/mol K)</th>
<th>$\Delta T$ (oC)</th>
</tr>
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<tbody>
<tr>
<td>II- 2</td>
<td>2</td>
<td>342</td>
<td>1.68</td>
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<td>365</td>
<td>-</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>II- 3</td>
<td>3</td>
<td>243</td>
<td>1.81</td>
<td>3.5</td>
<td>315</td>
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<td>-</td>
<td>75</td>
</tr>
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<td>345</td>
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<td>-</td>
<td>60</td>
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<td>II- 5</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>267</td>
<td>1.50</td>
<td>2.7</td>
<td>-</td>
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<td>II- 6</td>
<td>6</td>
<td>227</td>
<td>2.10</td>
<td>3.9</td>
<td>275</td>
<td>0.54</td>
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<td>48</td>
</tr>
<tr>
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<td>7</td>
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<td>63</td>
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<td>3.25</td>
<td>6.6</td>
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<td>2.00</td>
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<td>7.8</td>
<td>245</td>
<td>1.85</td>
<td>3.6</td>
<td>33</td>
</tr>
</tbody>
</table>
are given. Standard methods for calculating the heats of transition were employed. Assuming that the peak maxima were the correct transition temperatures, and that both melting and clearing were equilibrium processes (which they most certainly were not), the entropies of transition may be calculated using the relationship:

\[ \Delta G = 0 = \Delta H - T \Delta S \]  

(II-1)

All measurements were made at heating rates of 10°C/min so that kinetic effects would be minimized at least for comparison within the series.

As the table shows, no thermodynamic data could be calculated for either the clearing transitions of polymers II-2 to II-4, which decomposed upon reaching the isotropic state, or for the melt transition of polymer II-5, which showed no reproducible melt endotherm. Unlike other polymers in the series, the polymer with the pentamethylene spacer showed crystallinity only as the untreated precipitate, and even though it showed a reproducible clearing transition, it needed to be annealed to recover any melt transition after one heating cycle.

The heats of melting were between 1.5-2.5 Kcal/mol for the polymers with lower spacer sizes and began to increase upon reaching spacer lengths of about 9 methylene groups. The entropy of melting, in contrast, showed a fairly steady increase over the entire range of spacer lengths. In contrast, the entropy of melting of the low molecular weight model compound (see Table 8 below) was much higher
at 20 cal/mol-K. These data indicate that the crystallinity of the polymers was fairly low, if the model compound can be regarded as similar to a repeat unit. The polymer molar heats and entropies of clearing were still lower than those of melting, as would be expected from reports dealing with both polymeric and monomeric liquid crystals. \( ^{(73,107,83)} \)

Table 8. Transitions of LC Model Compound:

<table>
<thead>
<tr>
<th>Transition Type</th>
<th>Temperature ( ^o )C</th>
<th>( \Delta H ) kcal/mol</th>
<th>( \Delta S ) cal/mol-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>K - S</td>
<td>196</td>
<td>9.75</td>
<td>20.8</td>
</tr>
<tr>
<td>S - N</td>
<td>207</td>
<td>0.27</td>
<td>0.56</td>
</tr>
<tr>
<td>N - I</td>
<td>241</td>
<td>0.15</td>
<td>0.50</td>
</tr>
</tbody>
</table>

a. Abbreviations: K-crystalline, S-smectic, N-nematic, I-isotropic

As already mentioned, monomeric liquid crystals often show a steady increase in the entropy of clearing, until an alkyl end-group length of about 6 carbon atoms is reached, then large increases in the entropy of clearing occur. If an end group can be equated to one-half the polymeric spacer length, then a sudden increase in the entropy of clearing might be expected when twelve methylene groups
were present in the spacer. Unfortunately, the thermodynamic properties of no series of polymers has yet been reported that had more than 12 methylene groups, and no sudden change in the entropy of clearing was observed in the triad polymers reported here, although there are still interesting trends in this triad series.

As observed in previous investigations of polyesters,(85) the values of $\Delta S_i$ generally increased with $n$ even though $T_i$ steadily decreased (discounting even-odd effects). Haller and coworkers, in their study of a homologous series of aldonitrones, made a similar observation that $\Delta S_i$ increased smoothly with added methylene groups.(105) The increase of $\Delta S_i$ with longer spacers indicates that, for polymer molecules with larger polymethylene spacers, the conformations of these chains and the arrangement of the mesogenic group were increasingly more ordered for the mesophase relative to the isotropic state.

By considering only the data listed in Table 7 for the entropy of clearing of the polymers with even-numbered spacers, a fairly steady increase can be observed. A value of an increase of approximately 0.5 cal/mol-K can be found for each additional methylene unit. That the polymers with shorter odd-numbered spacers do not fit this simple curve shows the even-odd effect obtained when studying such materials, and is also typical of the data for many of the polymeric liquid crystalline systems.(83) Even though many low molecular weight LC compounds do show an even-odd effect in the entropy of clearing, a similar effect in polymers has not been
reported before.

Comparison of the polymers in this series to the model compound first made by Dewar (recall Table 8) shows that all polymers have a value for the entropy of clearing that is much higher than the 0.4 cal/mol-K reported for the model. Therefore, besides showing lower crystallinity than the model, the polymers also showed a much more ordered mesophase if equal degrees of order can be assumed for the isotropic states.

The only low molecular weight compounds that showed such high rates of increase of the entropy of clearing (0.5 cal/mol-K) and values of $\Delta S_i$ greater than 0.5 cal/mol-K are those that form a smectic mesophase. The fact that the polymers do have values of $\Delta S_i$ that match these conditions would be indirect evidence that the triad polymers with a polymethylene spacer have smectic mesophases. Unfortunately, most thermotropic polymers that form nematic states also have values of $\Delta S_i$ in this range, so other evidence must be relied upon such as the polarizing microscope and X-ray observations previously discussed in this chapter.
CHAPTER III
STRUCTURALLY ORDERED THERMOTROPIC POLYESTERS
WITH SPACERS OF GLYCOLETHERS

Introduction

A great deal of research has now been devoted to understanding the effects that different mesogenic units have on influencing polymers which contain both flexible spacers and mesogenic groups in the main chain.\(^{(14-20)}\) However, only recently has work begun on studying the effect on such systems by altering the structure of the flexible spacer.\(^{(15,18,67,93)}\)

The spacer first studied, for which the greater part of information available is reported, has been the polymethylene unit. Chain lengths have been limited to between two and twenty methylene groups, because of the availability of the appropriate diols and diacids. Researchers have now turned to studying the effect of different types of spacers, such as polyalkylene oxides, or of substitution of the flexible spacer on mesophase behavior.

Meurisse and coworkers studied the effect of using \(2,2'\)-disubstituted propanediol spacers in a polymer chain containing a terphenyl mesogenic group.\(^{(18)}\) By adding alkyl substituents, for example, they were able to produce polymers with both reduced transition temperatures and altered mesophase stability relative to other
polymers with the same mesogenic group. The ethyl group presumably acted to separate the polymer chains more efficiently than the methyl groups, and as a consequence a lower melting transition temperature was observed with the former.

The simple addition of a substituent to an even-numbered methylene chain can produce a spacer with asymmetric center. Several polymers of this type have been prepared and studied in both their racemic and optically active forms. The presence of a substituent tends to lower the transition temperature, and when chiral sites are present in a nematic mesophase-forming polymers, a cholesteric mesophase is formed. (15,76,108)

Several examples of polymers using this approach have been reported in recent publications, each one of which used essentially a methyl adipic acid spacer with various nematogenic groups. The presence of a chiral site can induce a twist in the orientation of the nematic layers and impart to the polymer the physical and optical properties of a cholesteric mesophase as discussed in Chapter I. While this characteristic behavior has been observed before in low molecular weight compounds, its development in main-chain polymers will provide possible new applications for mesophase forming polymeric materials.

Another approach has been to simply change the type of flexible spacer used, and in this regard, instead of a polymethylene chain, a polysiloxane (87,59) or a poly(alkylene oxide) (18,88,93) chain has been used. Both of these spacers have had the effect of greatly
modifying the transition temperatures as well as changing the major features of the liquid crystalline melt. The work by Lenz and co-workers(87) and Ringsdorf and coworkers(59) using polysiloxanes was briefly outlined in the introductory chapter.

The use of poly(ethylene glycol) as a spacer group is a logical extension of the work already performed with polymethylene residues. The former is more polar and while structurally similar to the latter, the former has also been described as being more flexible due to the reduced steric hindrance around the oxygen atom.

Besides increasing the flexibility of the spacer and its expected reduction of the transition temperatures, another possible advantage of incorporating oxygen atoms in the spacer would be their ability to interact more strongly with extremely polar molecules such as water. Both of these aspects would be useful characteristics for polymers prepared for applications involving hemocompatible membranes.(109) While some of the polymers discussed in Chapter II possess the correct thermal properties for membrane formation, they would probably not have the permeability to water needed for this application. In order to provide a membrane having these properties, a series of polymers was prepared that employed the mesogenic group used in the previous chapter in conjunction with several oligomers of poly(ethylene oxide) as flexible spacers to form the structure shown below:

\[
\begin{array}{c}
\text{R} \equiv \text{H, Me} \\
\end{array}
\]
The spacers used included oligomers that were either essentially monodisperse and those that had a distribution of molecular weights which ranged from 200 to 1000.

A methyl group added to the ethylene glycol group (that is, propylene glycol) creates an asymmetric center. The presence of a methyl group in the spacer would be expected to lower the transition temperatures of a polymer and if an optically active glycol were used then a cholesteric mesophase might result. To explore the first possibility another series of polymers with the structure shown above was prepared with propylene glycol and poly(propylene glycol) oligomers as flexible spacers using the same mesogenic triad discussed in Chapter II. This section of the dissertation reports the preparation and properties of the triad polymers made with poly(alkylene oxide) spacers.

Polymer sample designations used in this chapter for this series were PE, for those containing PEO units (R = H), and PP for those containing PPO units (R = CH₃). This designation is followed by a number indicating the degree of polymerization of the unit and also a D if the unit is an oligomer fraction containing a distribution of units rather than a single molecular species.

**Experimental**

*Monomer and polymer preparation.* All glycol monomers were azeotropically distilled with benzene to remove absorbed water, dried under vacuum and stored under dry nitrogen. All solvents were
dried by distillation and storage over molecular sieves.

i) Benzyl 4-hydroxybenzoate, I. To a solution of 60 g (0.43 mol) of 4-hydroxybenzoic acid in 600 ml of 95% ethanol was added a solution of 48.4 ml (0.42 mol) of benzyl chloride in 530 ml of 1N NaOH. The reaction mixture was stirred for one half hour at room temperature and refluxed for 2h; then 600 ml of solvent were distilled off, and the product formed an oil which crystallized on cooling. The crystals were separated from the mother liquids, washed with dilute HCl, filtered and dried. Recrystallization from 60% ethanol gave I as white needles. (112) Yield 55%; mp 107-108°C.

ii) Bis(4-carbobenzoxyphenyl)terephthalate, II. 17.3 g (72 mmol) of I, 7.3 g (36 mmol) of terephthaloyl chloride and 150 ml of dry pyridine were stirred under nitrogen at 70°C for one hour. The reaction mixture was allowed to cool, then poured into 600 ml of stirred 2N HCl. After filtering, the white precipitate was stirred in NaHCO₃ solution, filtered and washed consecutively in water, dilute HCl, and water; then it was stirred in 95% ethanol, left overnight and filtered. A white powder (mp 179-181°C) was obtained in 60% yield. The IR spectrum of this compound is shown in Figure 29a).

Anal. calcd. for C₃₅H₂₅O₈: C, 73.7; H, 4.3. Found: C, 74.0; H, 4.6. IR(KBr): 3060 (weak), 1735 (C=O), 1720 (C=O), 1600, 1500, 1455, 1435, 1410, 1380, 1270, 1215, 1160, 1120, 1070, 1015, 885, 755, 715, 690. ¹H-NMR(CDCl₃) δ 8.25-8.02 (m, 4, terephthalate & 2,6-oxybenzoate), 7.58-7.10 (m, 7, 3, 5-oxybenzoate and aromatic
iii) **Bis(4-carboxyphenyl)terephthalate, III.** 9.8 g (17 mmol) of the benzyl-blocked diacid II were dissolved in 150 ml of trifluoroacetic acid and allowed to stir for 10 min; then 5 ml of 33% HBr in acetic acid were added and allowed to stir for 4h. A precipitate formed after approximately 15 min, and stirring became more difficult. The reaction was stopped by the addition of acetone. The product was then filtered, washed with acetone, and dried under vacuum. (110) Yield was 95%, and the compound decomposed above 348°C. The IR spectrum of the diacid is shown in Figure 29b).

Anal. calcd. for C_{22}H_{14}O_8: C, 65.0; H, 3.5. Found: C, 64.9; H, 3.7. IR(KBr): 2800 (very broad), 1740 (C=O), 1690 (C=O), 1605, 1505, 1430, 1410, 1270, 1200, 1165, 1070, 1020, 880, 760, 715.

^1_H-NMR (d_6-DMSO) δ 8.58 (s, 2, tereph.), 8.31 (d, 1, 2, 6-oxybenzoate), 7.79 (d, 1, 3, 5-oxybenzoate).

The model compound listed in Table 8 was prepared according to the procedure used by Dewar and Goldberg. (95)

iv) **Polymerizations.** In a typical polymerization, 2.00 g (5.9 mmol) of the diacid III were refluxed for one hour in 40 ml of SOCl_2 in the presence of catalytic amounts of DMF. The unreacted SOCl_2 was removed under vacuum, toluene added and also removed to force off remaining traces of SOCl_2, the product IV was dissolved in 1,2-dichloroethane at 60°C, and the solution transferred into an appropriate flask. After cooling, 1.14 g (5.9 mmol) of tetraethylene glycol were added under nitrogen atmosphere along with 5 ml of dry...
pyridine. The resulting mixture was heated at 60°C and stirred for one hour. Once in solution, the reagents were stirred for an additional 15h at room temperature. The polymeric products were purified in the case of samples containing PEO with DP_n ≤ 9 and PPO spacers by precipitation in 50-80% aqueous acetone. The product was filtered, dried, then broken up and stirred in dilute HCl, 5% NaHCO_3, 5% HCl, and finally water. The polymeric products containing PEO with DP_n > 9 were dried to yield an oil, washed by stirring in dilute HCl, NaHCO_3 solution, dilute HCl, and water. The samples of PE1 and PE2 were prepared according to the procedure used in Chapter II.

**Polymer Characterization.** Viscosity measurements were carried out at 25.0°C in either trifluoroacetic acid or 1,2-dichloroethane solutions by using a Desreux-Bischoff dilution viscometer. IR spectra were recorded on a Perkin-Elmer IR-238 spectrophotometer on KBr discs. ^1H-NMR spectra were recorded in TFA solution at 37°C, using tetramethylsilane as an internal standard, on a Varian T-60 spectrometer. Calorimetric analyses were carried out on a Perkin-Elmer DSC-2 apparatus at a heating and cooling rate of 10°C/min under dry nitrogen flow. Indium standards were used for temperature calibration and enthalpy change evaluation as in Chapter II. Thermal-optical analysis (TOA) measurements were performed on an American Optical Microstar polarizing microscope, suitably equipped with a Mettler FP-52 programmable heating stage and a photometer. Texture photographs and observations were made with a Leitz Ortholux polarizing microscope and the same model hot stage.
Results and Discussion

Monomer and polymer synthesis. Initially, it was planned to follow the synthetic route which was used in Chapter II for the preparation of the previous polymers with linear alkylene spacers,\(^{(96)}\) and the polymers with ethylene glycol and diethylene glycol spacers were prepared in this manner. However, for polymers with longer ethylene and propylene oxide spacers, the bisphenol monomers needed for the step-growth polymerization reaction could not be isolated in high purity. For this reason a new synthetic route was developed in which a mesogen-type monomer was first synthesized and then reacted with the diol oligomer to give polymer, as outlined in Figure 19.

Figure 19. Synthesis of triad polyesters with poly(alkylene oxide) flexible spacers.

\[
\begin{align*}
\text{I} & : \text{CH}_2\text{Cl} + \text{HOC-OC-OH} \xrightarrow{\text{NaOH}} \text{CH}_2\text{OC-OC-OH} \\
\text{II} & : \text{HOC-OC-OC-OC-CO-COH} \xrightarrow{\text{TFA/HBr}} \text{Bz-OC-OC-OC-CO-Bz} \\
\text{III} & : \text{SOCl}_2 \xrightarrow{\text{HOC-OC-OC-OC-CO-COH}} \text{SOCl}_2 \\
\text{IV} & : \text{ClC-OC-CO-CO-CCl} \xrightarrow{\text{R-OC-OC-OC-CO-CCl}} \text{POLYMER} \\
\text{V} & : \text{HO(CH}_2\text{O)}_\text{nH} \xrightarrow{\text{R}} \text{POLYMER}
\end{align*}
\]

This reaction gave a polymer with the same well-defined mesogen as obtained before,\(^{(96)}\) when the mesogenic unit was formed during the polymerization reaction.

The addition and removal of benzyl blocking groups shown in the equations above has been previously reported in the literature,\(^{(110)}\)
and the synthesis of the blocked mesogenic unit is analogous to that used for the preparation of model compounds with thermotropic properties.\textsuperscript{(95)} Table 9 lists the yields and properties of these intermediates. As shown in the equation above, the polymers of this series were prepared by reaction of the diacid chloride (IV) with the diol oligomer in 1,2-dichloroethane (DCE) at 60°C with excess pyridine as the acid acceptor. Such temperatures were necessary to completely dissolve the diacid chloride. While this monomer was never isolated and purified, spectroscopic observations indicated that the product was indeed the desired acid chloride but little was known about the purities of these monomers and only relatively low molecular weight polymers were formed. None of the polymers prepared in this manner precipitated from the polymerization mixture even after cooling to room temperature. It is interesting to note that none of the starting materials themselves are liquid crystalline, nor are any of the intermediates.

**Polymer properties.** The physical properties of these polymers were characterized for their thermal properties by differential scanning calorimetry (DSC), by use of a hot stage on a polarizing microscope, and by thermal optical analysis (TOA), as well as by qualitative observation of stir opalescence. Some properties of the polymers synthesized are reported in Table 10.

Glycols or glycolethers of well defined structures were used for the preparation of polymers PE1-PE4 and PPI, whereas oligomers with a distribution of units having a rather narrow degree of dispersion
Table 9. Properties of Monomer Intermediates

\[
\begin{array}{cccc}
\text{R} & \text{Yield} & \text{T}_m & \text{Recryst. Solvent} \\
& (\%) & ^\circ\text{C} & \\
\text{-CH}_2- & 60 & 179-181 & \text{EtOAc} \\
\text{H} & 95 & d 348 & \text{DMSO/H}_2\text{O} \\
\end{array}
\]
Table 10. Synthesis and properties of a series of polyesters containing triad aromatic ester mesogens and flexible spacers of different compositions and lengths.

<table>
<thead>
<tr>
<th>Polymer(^a)</th>
<th>Flexible spacer</th>
<th>Yield (%)</th>
<th>PEO(or PPO)(^b) (wt-%)</th>
<th>([\eta]) c</th>
<th>(T_m) (^d) (°C)</th>
<th>(T_p) (^d) (°C)</th>
<th>(T_i) (^d) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td></td>
<td>1.0</td>
<td>80.0</td>
<td>13.8</td>
<td>0.18</td>
<td>342</td>
<td>-</td>
</tr>
<tr>
<td>PE2</td>
<td></td>
<td>2.0</td>
<td>78.1</td>
<td>20.5</td>
<td>0.23</td>
<td>185</td>
<td>222</td>
</tr>
<tr>
<td>PE2Cl</td>
<td></td>
<td>2.0(Cl)</td>
<td>80.2</td>
<td>17.8</td>
<td>0.24</td>
<td>185</td>
<td>-</td>
</tr>
<tr>
<td>PE3</td>
<td></td>
<td>3.0</td>
<td>57.1</td>
<td>28.4</td>
<td>0.25</td>
<td>180</td>
<td>203</td>
</tr>
<tr>
<td>PE4</td>
<td>PEO</td>
<td>4.0</td>
<td>100</td>
<td>34.6</td>
<td>0.21</td>
<td>121</td>
<td>211</td>
</tr>
<tr>
<td>PE4D</td>
<td></td>
<td>4.1</td>
<td>76.8</td>
<td>34.7</td>
<td>0.28(^e)</td>
<td>103</td>
<td>158</td>
</tr>
<tr>
<td>PE8D</td>
<td></td>
<td>8.7</td>
<td>15.3</td>
<td>51.6</td>
<td>0.26(^e)</td>
<td>102</td>
<td>-</td>
</tr>
<tr>
<td>PE13D</td>
<td></td>
<td>13.2</td>
<td>60.0</td>
<td>61.7</td>
<td>0.12(^e)</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td>PE22D</td>
<td></td>
<td>22.3</td>
<td>10.4</td>
<td>72.8</td>
<td>0.11(^e)</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>PP1</td>
<td></td>
<td>1.0</td>
<td>28.9</td>
<td>16.5</td>
<td>0.12</td>
<td>262(^f)</td>
<td>-</td>
</tr>
<tr>
<td>PP6D</td>
<td>PPO</td>
<td>6.6</td>
<td>21.0</td>
<td>51.6</td>
<td>0.08</td>
<td>181(^f)</td>
<td>-</td>
</tr>
<tr>
<td>PP20D</td>
<td></td>
<td>20.3</td>
<td>17.5</td>
<td>76.3</td>
<td>nd(^g)</td>
<td>188(^f)</td>
<td>-</td>
</tr>
</tbody>
</table>

\(a\) Symbols for polymers are explained in the text of the introduction. \(b\) By NMR spectroscopy. \(c\) In trifluoroacetic acid, at 25°C. \(d\) Peak maximum in the DSC endotherm. \(e\) In dichloroethane, at 25°C. \(f\) Flow temperature by microscopy. \(g\) Insoluble.
were employed in all of the other cases. Fairly high yields of linear polymeric products, soluble in chlorinated solvents or p-chlorophenol, were obtained in almost all reactions. The polymers had chemical compositions corresponding to the starting feed mixtures and were characterized by intrinsic viscosities in the range of 0.1-0.3. Better results were obtained from this standpoint in the synthesis of polymers containing the PEO residues.

The chemical composition of the PEO polymers could be determined by NMR spectroscopy using TFA as solvent under ambient conditions. The characteristic features of this series of polymers are shown in the proton NMR spectrum in Figure 20. Integration of the polymer spectra leads to values for polymer compositions equal to that of the monomer mixture within experimental error. No spectra of polymers with PPO spacers were possible because at the concentrations needed to obtain a high resolution spectrum a gel formed. However, this problem did not occur in the case of the PPO polymers at concentrations needed for solution viscosity measurements.

Generally speaking, the PEO polymers were fusible and characterized by fairly sharp melting transitions, $T_m$, depending on the content and length of the flexible spacers. In most cases the formation of a mesophase could be directly observed under the polarizing microscope, and the corresponding clearing (or isotropization) temperature $T_i$, for this phase are given in Table 10. It was also possible to detect in some cases within the mesophase a temperature $T_p$, at which a liquid crystal-to-liquid crystal transition occurred.
Figure 20. 60 MHz $^1$H-NMR of the polymer containing triad mesogenic units and PEO 200 as flexible spacer in the main chain.
The properties of the polymers with the PPO spacers are not so easily summarized, but yields and intrinsic viscosities were somewhat lower than those with the corresponding PEO samples. In two cases, these polymers possessed a mesophase that was not clearly definable by DSC or microscopy, as discussed below.

Several polymers have been prepared by others that allow direct comparison of the effect of changing the polymethylene spacer to a poly(ethylene glycol), PEO, spacer of comparable length. These main chain, liquid crystal polymers were synthesized with the mesogenic units \((18, 88, 93)\) shown below:

\[
\text{In these studies, the PEO spacers included the dimer, trimer and tetramer of ethylene glycol, and no effort was made to determine either the effect of spacer molecular weight distribution or the mole fraction of spacer that caused the loss of liquid crystallinity.}
\]

The polymers of Roviello and Sirigu, structures d and e above, were found to have melting and clearing temperatures that decreased with increasing spacer size, and these transitions were only slightly lower if a PEO spacer were used instead of a polymethylene spacer of approximately the same length.\(^{(93)}\) The temperature range of the
mesophase also decreased with increased spacer size. Both types of spacers produced nematic mesophases while the polymers with diethylene glycol were also claimed to produce a monotropic smectic mesophase that could be frozen in. The heats of clearing of their polymers with the PEO spacers had enthalpies of clearing which were only 10% of those of the comparable polymers with a polymethylene spacer.

Koide and coworkers produced polymers, structures b and c, with mesogenic groups of the azo- and azoxybenzene types. These polymers contained the same aromatic segments as those which Blumstein prepared for his study of mesophase forming polymers with alkyl flexible spacers. Both series of polymers followed the trend of increased spacer length giving reduced melting and clearing temperatures as well as a reduced mesophase temperature range as a function of increased spacer length. These workers observed LC phases by DSC for the azo polymers with tri- and tetraethylene glycol spacers, but they mentioned that no LC textures were observed which is a partial contradiction. The azoxy- polymers were claimed to have a focal-conic texture, which is usually associated with a smectic mesophase.

A very interesting finding by Koide was the appearance of an apparent crystalline X-ray diffraction pattern for the LC phase of polymers with the azoxy mesogenic group and PEO spacers. The only major difference between its appearance and the appearance of the diffraction pattern of the solid was the lower intensity of certain peaks. This observation suggested that the crystalline molecular
arrangement in the solid state was retained even in the mesophase. No other explanation was put forward, however, and no low angle X-ray diffraction studies were made which might clarify the structure of the melt.

The final series of polymers, structure a, with PEO spacers was that synthesized by Fayolle using a terphenyl mesogenic group and subsequently studied by Monnerie and coworkers. From their work, they concluded that the effect of polymethylene PEO segments of the same length on the mesophase-isotropic transition was about the same, and, therefore, the oxygen atom was considered to be stereochemically equivalent to the methylene unit.

The mesophases of the polymers with PEO spacers, as well as the polymers studied by Monnerie and coworkers, with the equivalent polymethylene spacers, were smectic according to microscopic characterization. The thermal properties of the polymers with the two different spacer were roughly equivalent, and, for example, the entropy of clearing for all the polymers was between 1.0 and 3.0 cal/mole-K. Also present in the series was a polymer with a spacer obtained from the decamer of ethylene glycol. It was also said to be mesophase forming, but of a much less well-defined nature. No polymer with a comparable polymethylene spacer was prepared.

Melting and clearing temperatures of PEO polymers. In the present work, transition temperatures were determined by both TOA and DSC, and examples of these results are given in Figures 21 and 22 for polymer PE4 and PE8D, respectively. All polymers studied showed
supercooling of the melting endotherm but not of the mesophase transition. This result appears to be a common feature of liquid crystalline polymers.  

Interestingly, in Figure 21 there are two liquid crystal transitions detectable by TOA and by DSC in the polymer containing the tetraethylene glycol spacer, PE4. Similarly, the presence of two transition peaks within the liquid crystal temperature range was also observed for polymers having spacers obtained from diethylene glycol, PE2, triethylene glycol, PE3, and tetraethylene glycol oligomer, PE4D and in each case, the melting peak obtained was more intense and showed some structuring during the heating cycle. These general features were observed for polymers PE2 through PE4D in Table 10, but the degree of liquid crystallinity diminished, as judged by the intensity of birefringence on attaining a spacer length based on an oligomer $\overline{DP}_n$ of 9 (Figure 22) and disappeared with a spacer length based on an oligomer $\overline{DP}_n$ of 13 (PE13D). Typical of polymers with a spacer of $\overline{DP}_n > 10$, polymers PE13D and PE22D, showed only very faint birefringence on crystallization and no mesophase behavior. Comparison of the results for polymers with the pure tetraethylene glycol and the oligomer, PEO 400, spacers, indicates that for the latter case: (1) the intensity of birefringence was greatly reduced, (2) there was apparently only one mesophase, and (3) the clearing temperature range was much broader. However, it should be noted that these TOA measurements are only qualitative because care was not taken to ensure the same sample thickness in
the observation area.

From the data in Table 10, a decrease in melting temperature is clearly seen in going from polymer PE1 to PE22D (excluding PE2C1). That is, as has been observed for other main chain liquid crystal polymers, the greater the spacer length the lower the melt transition. In the present polymer series, a change from ethylene glycol, PE1, to tetraethylene glycol, PE4, resulted in a sharp decrease in the melting temperature, and for PEO spacers with average molecular weights of 200 and above, the melting temperature was close to 100°C or even lower.

The clearing temperature, while also decreasing with increasing spacer length did not show the same sharp drop as the melting temperature, but rather decreased much more gradually. In fact, by comparing the results for well-defined PEO spacers with alkyl spacers having the same number of atoms in the main chain, it appears that the melting and clearing temperatures are approximately the same when the same mesogen is used. Similar observations have been made by Meurisse and coworkers(18) on polyesters containing terphenyl mesogenic units and glycolethers as spacers.

In Figure 23 are plotted transition ranges as a function of spacer length or degree of polymerization, n, showing that the increased chain length had the greatest effect on the melt transition at short spacer lengths. The eventual disappearance of liquid crystalline properties is explainable by the fact that the amount of mesogenic units as a fraction of the whole became insufficient to
Figure 21. Thermal-optical analysis (TOA) and differential scanning calorimetry (DSC) of the triad polymer with a spacer of tetraethylene glycol. a) Heating and b) cooling cycles.
Figure 22. Thermal-optical analysis (TOA) and differential scanning calorimetry (DSC) of the triad polymer with a PEO 400 flexible spacer. a) Heating and b) cooling cycles.
Figure 23. Plot of transition temperature vs. the degree of polymerization of the PEO flexible spacer.
induce enough order in the system to produce a mesophase.

Another feature observed in this series was the difference between polymers using spacers of a well-defined composition compared to those containing a distribution of oligomers. An example of the latter type is the polymer with PEO 200 spacer P4E4D, which exhibited both a lower $T_m$ and a reduced liquid crystal range when compared with the tetraethylene glycol-based polymer (P4E4) which showed a much different thermal response for approximately the same molecular weight spacer. This result may be due to an incompatibility of spacer blocks of different sizes analogous to polyesters containing ethylene glycol and polymethylene glycols in a random distribution\[21, 96\]. In this earlier case the presence of two spacers produced a glassy polymer, but did not greatly effect the clearing transition.

Model compounds. As a part of this study of polymers based on a specific triad aromatic ester mesogenic unit, the behavior of the analogous low molecular weight model compound was also evaluated. The model compound, in Table 8, was previously synthesized by Dewar and Goldberg,\[95\] but only its mesophase behavior was reported.

Our investigations revealed that this compound possessed two liquid crystal phases instead of one as reported by those workers. The transition temperatures and heats of fusion of these transitions are given in Table 8, and observations with the polarizing microscope confirm the existence of more than one mesophase, so it is not surprising that the polymers with PEO spacers also show two
distinct mesophases.

The presence of substituents in the mesogenic unit is known to lower the transition temperatures of low molecular weight liquid crystal compounds.\(^{111}\) To investigate the analogous effect in mesogenic polymers, a polymer containing the diethylene glycol spacer was prepared in which the oxybenzoate residues of the triad mesogens were substituted with a chlorine atom in the 3-position. Its properties are reported as polymer PE2Cl in Table 10. The DSC thermogram of this polymer contained two endothermic peaks; the lower at 147°C may have been from some type of crystal-crystal transition, but the endotherm at 185°C was the melting transition. No clearing transition was observed, so the presence of the chlorine substituent resulted in the loss of the mesophase.

This observation was not surprising because, in a compositionally similar polymer,\(^{70}\) we detected not only a lowering of the expected transition temperature but a large decrease in the mesophase range. That polymer, however, had two symmetrically placed substituents on the mesogenic unit which apparently served to separate the units in the liquid crystalline melt but did not destroy the nematic structure. On another structurally similar mesogenic unit with a single substituent in the central aromatic ring, the only effect of its presence was to lower the melting temperature without affecting the mesophase stability. These results demonstrate the sensitivity that mesogens have to slight changes in structure.

Melting and clearing temperatures of PPO polymers. The PPO spacer
was studied because the asymmetry of the unit in this spacer caused by the pendent methyl group ought to impart different properties to these polymers. In fact, the behaviors of the PPO and PEO spacer polymers were quite different as shown by thermal and optical measurements. Of the three polymers synthesized, those with spacers based upon either 1,2-propanediol or PPO 400, polymers PP1 and PP6D, respectively, were definitely liquid crystalline, as judged by their optical behavior and stir opalescence, while polymer PP20D, the polymer with the PPO 1200 spacer, was not thermotropic. However, neither of the former showed any detectable melt endotherm by DSC, and so the temperatures reported for the melting points in Table 10 were based on flow temperatures observed optically. No visual clearing could be seen, and these polymers showed no thermal transitions below decomposition. However, a \( T_g \) of 87°C was detectable for PP1 while no transition above -70°C was detected for PP6D. Values of 20-30°C for polymers PE3 and PE4 with PEO spacers were found.

The presence of an asymmetric center in PPO was expected to hinder crystallization but it apparently did not adversely affect the formation of a mesophase. Also, as happened for polymers using PEO spacers, a \( \bar{D}_P \) of approximately 10 was the limit to mesophase forming behavior for polymers with PPO spacers, but because of the limited number of polymers prepared, the exact influence of their diol length on the disappearance of their mesophase remains unknown.

**Thermodynamic properties.** The thermodynamic properties of the PEO polymers as obtained from their DSC thermograms are tabulated in
Table 11. For all of these polymers, the melt transition enthalpy was determined, and for all polymeric liquid crystals except PEI and PE8D, the clearing enthalpy was also measured. From these values and the temperatures of transition (taken here as the maximum of the endotherm), the entropies of clearing were found to be much less than those of melting. This result suggests that the mesophase is much less ordered than the crystalline solid, as would be expected for a nematic mesophase. Compared to analogous polymers with polymethylene spacers, there is also a much lower heat of transition for both PEO polymers.

Values of $\Delta H_m$ of about 1.5-3.0 kcal/mol are common, in general, for liquid crystal polymers, as are the values of $\Delta S_m$ which were obtained in the present study. However, the enthalpies and entropies of the mesophase clearing transitions from 0.79 to 0.10 kcal/mol for the former, and from 1.6 to 0.2 cal/mol$^0$-K for the latter, are noticeably lower than those for comparable polymers with a polymethylene spacer,$^{(96)}$ indicating a smaller change in the degree of order for the clearing transitions of the PEO polymers. The range of values is, however, quite close to the values of $\Delta S_i$ for the model compound, (Table 8), and supercooling of the model compound melt transition was also observed.

Of interest also are the higher values of $\Delta H_m$ for PE2C1 and PE22D, both non-liquid crystalline polymers. In the case of PE2C1 (the chlorine substituted DEG polymer), the higher value represents a greater ability of this polymer to crystallize under the same
Table 11. Thermodynamic properties of polyesters of glycol and glycolethers based on triad ester mesogens.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>n</th>
<th>(T_m^a)</th>
<th>(\Delta H_m)</th>
<th>(\Delta S_m)</th>
<th>(T_p^a)</th>
<th>(\Delta H_p)</th>
<th>(\Delta S_p)</th>
<th>(T_i^a)</th>
<th>(\Delta H_i)</th>
<th>(\Delta S_i)</th>
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<td>cal/mol(^{0})K</td>
<td>oC</td>
<td>Kcal/mol</td>
<td>cal/mol(^{0})K</td>
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<td>342</td>
<td>1.68</td>
<td>2.7</td>
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<td>-</td>
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<td>3.22</td>
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<td>91</td>
<td>2.77</td>
<td>7.6</td>
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<tr>
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<td>22.3</td>
<td>85</td>
<td>12.4</td>
<td>47.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>

\(a\) Peak maximum position in the DSC endotherm.
conditions compared to the unsubstituted polymer which could be responsible for the absence of a mesophase. For polymer PE22D, the polymer with PEO 1000 spacer, the $\Delta H_m$ value approached that of PEO itself, which is not unexpected considering that the polymer contains 73 weight percent PEO.

Texture observations. All samples were observed for their texture in the liquid crystal phase by use of a polarizing microscope equipped with a hot stage. The transition temperatures determined by DSC and TOA were in agreement with those observed by microscopy. The magnification of all photomicrographs is 360 x, and the scale markers in all figures shown are 20 $\mu$m.

Polymers that were not liquid crystalline showed very faint birefringence in the solid state but not in the isotropic melt. Photographs of several polymers exhibiting mesophases are reproduced in Figures 24 to 28. The texture of the polymer with the 1,2-propanediol spacer (PP1) is shown in Figure 24. The texture observed was that of a nematic phase, and was similar to that of the polymer with the PPO 400 spacer (PP6D). No change in appearance was detected upon cooling either polymer to room temperature.

The thermotropic polymers with the PEO spacers were quite different in appearance and behavior. Initially, the mesophase nucleated upon cooling from the isotropic melt state in spheres, which after further cooling coalesced to form large domains as shown in Figure 25a). Polymers PE2, PE3, and PE4 then became
Figure 24. Polymer with triad mesogenic group and 1,2-propanediol spacer at 252°C showing nematic mesophase. Magnification equals 360x.
Figure 25. Photomicrographs of polymer PE4 in the mesophase.

a) Polymer PE4 cooled from the isotropic melt showing the mesophase at 172°C. (above)

b) Polymer PE4 showing the mesophase at 148°C with homeotropic regions which appear black. (below)

Magnification of a) and b) equals 360x.
Figure 26. Photomicrographs of polymer PE4 in the liquid crystalline state.

a) Polymer PE4 in the mesophase immediately after shearing between glass plates at 164°C. (above)

b) Polymer PE4 after relaxing for 5 minutes from the time of shearing, still at 164°C. (below)

Magnification of a) and b) equals 360x.
Figure 27. Polymer PE2 at 246°C showing the presence of two liquid crystalline phases. (above)

Figure 28. Polymer PE8D at 212°C showing weak birefringence especially in areas subjected to some melt flow. (below)

Magnification of both figures equals 360x.
homeotropic at a temperature which corresponded to the temperature $T_p$ listed in Table 10. Figure 25b) shows the observed texture of sample PE4 in which the dark regions are formed by the homeotropic zones. The onset of homeotropism corresponds to both the reduction in intensity of transmitted light in the TOA plot and the endotherm in the DSC thermogram of PE4, both of which are shown in Figure 21.

Homeotropic regions appear black because the polymer chains are aligned in the same direction as the incident light beam. The bright regions are due to polymer oriented at some finite angle to the polarized incident beam, so when the sample is sheared, the homeotropic regions become extremely birefringent.

A particularly interesting texture was achieved by shearing sample PE4 at 164°C which caused the sample to have a texture resembling crystalline lamellae, Figure 26. In the relaxed state, the sample had a texture that appeared filamentous, and as shown in Figure 26b) the sample still retained the effects of shearing.

Polymer PE2 shows a typical texture in Figure 27 upon heating at 246°C, which is indicative of a change between mesophases. Shearing of PE2 just above $T_m$ gave a texture similar to those of both PE3 and PE4 under the same conditions.

Samples PE4D and PE8D both contained lower molecular weight PEO spacers with broad distributions. Polymer PE4D showed a similar appearance to polymers PE3 and PE4 at nucleation and also showed some homeotropic texture upon further cooling. The mesophase of this polymer was found to exhibit nematic characteristics such as Schlieren
texture in the higher temperature region, while a poorly definable change appeared at $T_p$. Polymer PE8D was observed to produce a much weaker birefringent mesophase above the melting temperature as shown in Figure 28. Birefringence was observed to be brighter in areas of melt flow presumably due to some shear orientation.

While these observations of polymeric textures strongly indicate the type of liquid crystalline state present, additional characterization studies now in progress should provide more definitive information which will be necessary to fully characterize these mesophases.
Figure 29. Infrared spectra of a) bis(4-carbobenzoxyphenyl)terephthalate (R=benzyl), and b) bis(4-carboxyphenyl)terephthalate (R=H).
CHAPTER IV
DYAD THERMOTROPIC POLYESTERS WITH
MESOGENIC ELEMENTS AND FLEXIBLE SPACERS
IN THE MAIN CHAIN

Introduction

In the previous chapters, a mesogenic group based on an aromatic ester triad was studied. It consisted of a terephthalate residue flanked by two oxybenzoate groups, and this triad was shown to induce liquid crystallinity in both low molecular weight and polymeric materials. This triad mesogenic group was also a possible source of the thermotropic behavior of the polymers produced by melt-transesterification of PET with p-acetoxybenzoic acid in our laboratories, as discussed in Chapter V. Consideration of the content of oxybenzoate group incorporated into the polyester made it equally likely that the aromatic ester dyad of the polymer structure shown below was responsible for the mesophase forming behavior of the polymers prepared from copolymerization of PET and p-ABA.

The dyad, which will be defined as a mesogenic group composed of two phenyl rings linked by an ester group is, like the triad, known to form low molecular weight LC compounds when there are alkyl end...
groups attached to the mesogenic unit.\(^{(114)}\)

Always present as one of our goals of preparing thermotropic polyesters was the possible use of such polymers in biocompatible membranes with frozen-in liquid crystalline properties. For this application polymers with moderate melting temperatures (\(\leq 200^\circ\text{C}\)) are needed and can be prepared with long spacers as shown in Chapters II and III, but another approach is in the reduction of the size of the mesogenic group.

There is basis in both theory and experiment for using this technique to modify the behavior of the mesophases formed by liquid crystalline polymers. In his early theory on liquid crystals, Flory showed that depending on the concentration density, rod-like molecules should form two phases, an isotropic one and a liquid crystalline one.\(^{(115)}\) An important property of these rods was their length-to-diameter ratio, that is, their persistence length. Most theories that have appeared subsequently have also been based on the rigid-rod concept, but some investigators additionally considered the effect of dipolarity as in the Maier-Saupe theory,\(^{(116)}\) and as in the Marcelja modification\(^{(117)}\) the latter of which also considered the effect of flexible end-groups.

The greater the length of a rod relative to its diameter, the more likely it is to form a mesophase. Of course, in practice if a rigid-rod molecule is sufficiently long, the compound will have an extremely high melting point (eg. hexaphenyl). Most useful mesogenic groups, from the viewpoint of lower transition temperatures, are
composed of two or more aromatic rings connected by a semi-rigid group such as an ester group or an azoxy group as shown in Figure 6, Chapter I. These mesogenic linking groups, like most others, are conjugated with the rings and hence show a type of resonance stabilization leading to increased rigidity. The conjugation increases the stiffness of the mesogenic group and so increases its length-to-width ratio thereby promoting liquid crystallinity.

In practice, decreasing the length of the mesogenic group has had two effects on a liquid crystalline compound. The first effect is that the overall rigidity of the compound is reduced so that transition temperatures are typically lower and the range of mesophase stability is reduced. The second effect is that the decrease in lateral interactions favors formation of the nematic state in preference to the smectic mesophase. Of course, if a chiral site is present, the reduced length of the mesogenic unit favors formation of a cholesteric mesophase rather than a twisted smectic.

This chapter reports the work undertaken to modify polymer mesophase behavior by reducing the size of the mesogenic unit from the triad to the dyad. Also studied were effects that different flexible spacers and dyad placement in the main chain had on the liquid crystalline properties of these polymers.

Experimental

Synthesis of polymers with alternating dyads.

i) Dibenzyl terephthalate, III. Terephthaloyl chloride (II)
(50 g, 0.25 mol) was dissolved in 250 ml of absolute THF and 61.4 ml (0.55 mol) of benzyl alcohol (I) were mixed with 50 ml of dry pyridine. The acid chloride solution was added dropwise to the alcohol under mechanical stirring. After the reaction was run overnight at room temperature, half of the THF was removed by distillation and the residue was poured into 750 ml of a Na₂CO₃-ice water mixture. The white precipitate was washed, after filtration, with dilute HCl, water, and the product was crystallized from 95% ethanol to give the dibenzyl ester, III in 95% yield (mp = 98°C). (129)

ii) Monobenzyl terephthalate, IV. To a solution of 20 g (0.058 mol) of III in 450 ml benzyl alcohol was added solution of 3.2 g (0.058 mol) of potassium hydroxide in 45 ml of benzyl alcohol over a period of 45 minutes. The temperature of the exothermic reaction rose to 60°C and was maintained at that temperature by cooling with a water-bath. The temperature of the reaction mixture was reduced, and the reaction mixture was filtered. The solid product was washed with toluene and dried under vacuum at 120°C. The salt was purified by first dissolving it in excess water, filtering, and then titrating the solution with 0.1N HCl to pH 5.3. After half an hour, the pH of the solution was adjusted to 5.25, and the solution left overnight at 0°C. The isolated product was filtered, washed and dried. Finally, it was recrystallized from toluene. Yield was 65%, and the melting temperature 176°C. (110, 129)

iii) α,ω-Bis(benzyl terephthaloyloxy) polymethylene, VI. The acid chloride of monobenzyl terephthalate (V) was prepared by
refluxing the acid (IV) for one hour in a 3 to 1 (v/w) excess of thionyl chloride with DMF as catalyst. After removal of the thionyl chloride, by vacuum distillation, dry toluene was added under N₂ atmosphere. The toluene was removed to drive off the final traces of thionyl chloride, and 21.6 g (0.078 mol) of the acid chloride (V) was dissolved in 250 ml of dry dioxane. A solution of the diol (4.09 g, 0.035 mol of 1,6-hexanediol, for example), excess pyridine, and dioxane (50 ml) were added dropwise with stirring. After addition, the mixture was refluxed for 4-5 hours, the product cooled, and mixed into 1 l of dilute hydrochloric acid. The precipitate was washed with water after filtration, stirred in an aqueous sodium carbonate solution, filtered again, washed with water and dried. Finally the product was recrystallized in 80% ethanol. The yield, recrystallization solvent and melting point of the bisbenzyl esters are compiled in Table 12a. Some spectral data is listed below for the product compounds, and the initial number refers to the number of methylene groups in the spacer.

2: IR(KBr): 2980 (w), 1720 (C=O), 1690 (C=O), 1410, 1340, 1270 (broad), 1210, 1120, 1100, 720, 690. \(^1\)H-NMR(TFA) \(\delta\) 8.35 (s, 2, tereph.), 7.50 (s, 2.5, benzyl), 5.6 (s, 1, CH₂), 5.0 (s, 1, CH₂ glycol).

6: IR(KBr): 2960 (w), 1730 (C=O), 1410, 1275 (broad), 1120, 1100, 1025, 730, 690. \(^1\)H-NMR(d6-DMSO) \(\delta\) 8.35 (s, 2, tereph.), 7.55 (s, 2.5, benzyl), 2.65 (s, 1, CH₂), 4.65 (t, 1, CH₂), 1.8 (m, 2, CH₂ chain).

10: Anal. calcd, for C₃₃H₃₆O₈(Monobenzyl ester): C, 70.7; H, 6.5. Found: 3, 70.8; H, 6.5. IR(KBr): 2920, 2850, 1720 (C=O), 1590,
Table 12a) Precursors of polymers with alternating dyads

\[
\begin{array}{|c|c|c|c|c|}
\hline
R & \text{Spacer Length} & \text{Yield} (\%) & T_m \degree \text{C} & \text{Recryst. Solvent} \\
\hline
\text{CH}_2^- & 2 & 65 & 129 & \text{Pet. Ether/Toluene} \\
" & 6 & 80 & 107 & \text{EtOH} \\
H & 2 & 60 & \text{Decomp.} & \text{Dioxane} \\
" & 6 & 80 & 242 & \text{Diox./EtOH (1/3)} \\
" & 10 & 85 & 214 & \text{EtOH} \\
\hline
\end{array}
\]

Table 12b) Precursors of polymers with random dyads

\[
\begin{array}{|c|c|c|c|}
\hline
R & T_m \degree \text{C} & \text{Yield} (\%) & \text{Recryst. Solvent} \\
\hline
\text{CH}_2^- & 94 & 86 & \text{EtOAC} \\
H & 314 & 50 & \text{HOAc/H}_2\text{O} \\
\hline
\end{array}
\]
1415, 1276 (broad), 1120, 1020, 870, 730, 690, 600. $^1$H-NMR (TFA) δ 8.35 (s, 4, tereph.), 7.7 (s, 2.5, benzyl), 5.5 (s, 1, CH$_2$), 4.35 (t, 2, CH$_2$), 1.4 (m, 4, CH$_2$ chain).

iv) α,ω-Bis(terephthaloyloxy) polymethylene, VII. The benzyl groups of VI were removed by dissolving the benzyl ester in a ten-fold (w/v) excess of trifluoroacetic acid, and one part (volume) of 33% hydrobromic acid in acetic acid (Fluka) was added. The mixture was stirred for four hours at room temperature, and the reaction product was precipitated by addition of acetone. The yields melting points and recrystallization solvents of the diacids are shown in Table 12a). (110)

2: IR(KBr): 2800 (very broad, acid OH), 1720 (C=O), 1690 (C=O), 1575, 1505, 1425, 1250 (broad), 1130, 1105, 1015, 930, 880, 800, 730. $^1$H-NMR(d$_6$-DMSO) δ 8.15 (s, 2, tereph.), 4.65 (s, 1, CH$_2$).

6: Anal. calcd. for C$_{22}$H$_{22}$O$_8$: C, 63.5; H, 5.8. Found: C, 63.4; H, 5.8. IR(KBr): 2900 (very broad), 1720 (C=O), 1690 (C=O), 1580, 1515, 1430, 1280 (broad), 1130, 1110, 1020, 950, 880, 800, 730. $^1$H-NMR(d$_6$-DMSO) δ 8.15 (s, 2, tereph.), 4.4 (t, 1, CH$_2$), 1.6 (m, 2, CH$_2$ chain).

10: Anal. calcd. for C$_{26}$H$_{30}$O$_8$: C, 66.4; H, 6.4. Found: C, 65.3; H, 5.8. IR(KBr): 2900 (very broad, acid OH), 1715 (C=O), 1690 (C=O), 1580, 1510, 1480, 1430, 1410, 1280 (broad), 1130, 1100, 1020, 950, 875, 795, 730. $^1$H-NMR(d$_6$-DMSO) δ 8.2 (s, 2, tereph.), 4.2 (t, 1, CH$_2$), 1.35 (s, 4, CH$_2$ chain). IR in Appendix.

v) Polymers with alternating dyads, IX. The diacid (VII) was
converted to the bis(acid chloride) monomer in the manner described above for the acid chloride of the monobenzyl terephthalate. The acid chloride was dissolved in approximately 50 ml of 1,1,2,2-tetrachloroethane, and to the acid chloride solution was added an equimolar quantity of the diphenol (VIII) having the same spacer as the diacid. This diphenol was the same one as that used in the preparation of the triad polymers, and the synthesis of these compounds are reported in Chapter II of this thesis. Pyridine (5 ml) was added as proton acceptor, and the reaction mixture was then stirred for 24-48 hours. At the end of this period, the polymerization product was precipitated with acetone, filtered, and stirred first with dilute hydrochloric acid then with dilute sodium carbonate in the manner described in Chapter II for the polymer preparation. After drying at 50°C in a vacuum oven for two days, the polymers were characterized.

Synthesis of polymers with random dyads.

i) Benzyl 4-Hydroxy benzoate, XII. The procedure employed in the preparation of this compound is the same as that used in Chapter III.

ii) Bisbenzyl ester of 4-carboxy phenyl terephthalate, XIII. Monobenzyl terephthaloyl chloride (V) (15.5 g, 48 mmol) was added to a solution of 15 g (66 mmol) of benzyl 4-hydroxybenzoate (XII) in 200 ml of dry pyridine. The mixture was maintained at 60°C for 4 hours, stirred at ambient temperature for 2 days, and poured into
Figure 30. Synthesis of the polymers with alternating mesogenic dyads and flexible spacers in the main chain. \((n = 2, 6, 10)\)
600 ml of 2N HCl. The precipitate was filtered, dried and crystal-
ized in 95% ethanol. Yield was 64.8%, and the melting point was
98-100°C. Other properties appear in Table 12b).

Anal calcd. for C_{29}H_{22}O_{6}: C, 74.7; H, 4.7. Found: C, 74.4;
H, 4.8. IR(KBr): 3060(weak), 1740(C=O), 1720(C=O), 1605,
1500, 1450, 1410, 1380, 1370, 1260, 1205, 1160, 1105, 1065,
1015, 760, 730, 715, 695. $^1$H-NMR(CDCl$_3$) δ 8.40-8.05(m,3,
tereph. and 2.6-oxybenzoate), 7.65-7.20(m,6,aromatic benzyl and
3,5-oxybenzoate), 5.39(s,2,CH$_2$).

iii) (4-Carboxyphenyl) terephthalate, XIV. The benzyl blocked
diacid,(XIII) (10 g) was dissolved in 150 ml of trifluoroacetic
acid. Then 10 ml of a 33% solution of HBr in acetic acid were added
and allowed to react at room temperature for 4 hours with stirring.
A precipitate formed after about 15 minutes, and stirring became more
difficult. The reaction was then stopped by the addition of acetone
and the product was filtered, washed with acetone and dried under
vacuum at 50°C. Some benzyl groups were observed by NMR, so the
procedure was repeated. Yield was 79% and the product decomposed
above 310°C. Other properties are listed in Table 12b).

Anal. calcd. for C_{15}H_{10}O_{6}: C,62.9; H, 3.6. Found: C, 63.2;
H, 3.9. IR(KBr): 2900(very broad), 1745, 1690(C=O), 1500,
1425, 1270, 1205, 1175, 1070, 1020, 760, 720. $^1$H-NMR(d$_6$-DMSO)
δ 8.45-7.90(m,3,tereph. and 2,6-oxybenzoate), 7.36(d,1,
3,5-oxybenzoate). IR spectrum is located in the Appendix.

iv) Polymers with random dyads, XV. In a typical polymerization,
Figure 31. Synthesis of polymers with randomly placed mesogenic dyads and flexible spacers in the main chain.
1.84 g (0.00643 mol) of the diacid (XIV) was refluxed for one hour in 15 ml of thionyl chloride with a catalytic amount of DMF, the excess thionyl chloride was removed under vacuum, toluene was added and removed, and the resulting product was dissolved in 1,2-dichloroethane at 60°C. The solution was then transferred to the appropriate container under nitrogen atmosphere, and after cooling, 0.96 g (0.00643 mol) of the appropriate diol in 5 ml of dry pyridine were added to the acid chloride. The mixture was heated at 60°C for one hour, cooled to room temperature without precipitation, and the contents were stirred for 15 more hours. The reaction was terminated by removal of the solvent under vacuum, and by washing the resulting oil with dilute aqueous HCl, 5% aqueous NaHCO₃, dilute HCl and water. The resulting solid product was washed with acetone several times and dried under vacuum at 50°C.

Characterization of polymers. The polymers were characterized by differential scanning calorimetry (DSC), thermal optical analysis (TOA), and polarized-light microscopy. The methods used were exactly the same as those described in Chapters II and III of this thesis where the triad polymers were studied. The inherent viscosities were measured at 45°C with solution of 0.5 g of polymer in 100 ml of p-chlorophenol with a Cannon-Ubbelohde viscometer.

Results and Discussion

As in the case of the triad polymers, there were essentially
two ways to prepare polymers incorporating only the dyad mesogenic group into the main chain. The first method used a diphenol previously prepared during the synthesis of the triad polymers of Chapter II, and this diphenol was reacted with a diacid chloride having a built-in alkyl spacer. The polymerization outlined in Figure 30, was performed under mild conditions in solution to avoid any rearrangement caused by high temperature.

Another route, similar in nature to the one used in Chapter III, was also employed for preparation of dyad polymers. A major difference in the two methods for dyad polymer preparation was due to the asymmetry of the central ester linkage in the mesogenic group, so polymers prepared by the first method had a strictly alternating, head-to-head, tail-to-tail placement of the mesogenic dyad. Polymers prepared by the route shown in Figure 31 instead had a random placement of the dyad in the chain, and while this is only a small structural change, it might be expected to have an observable effect on the mesophase properties of these polymers.

1) Polymers with alternating dyads.

a) Monomers. The diphenols used were those prepared in the synthesis of the triad polymers reported in Chapter II. The diacids and diacid chlorides were similar to those prepared by Wegner and coworkers in their study of poly(butylene terephthalate). The properties of the diacids and their precursors are listed in Table 12a) and include the recrystallization solvents and melting temperatures of these materials.
The spectral characteristics of the monomeric materials were studied and are included in the experimental section. The diacid chloride compounds were not isolated but were assumed to be completely converted from the diacid, because NMR and IR measurements showed the presence of the acid chloride functionality.

b) Polymers and properties. The properties of the polymers containing the alternating dyad are listed in Table 13. Only three samples were prepared, and each contained only a single spacer length. In the table are also listed the inherent viscosity values, and the transition temperatures. The values of inherent viscosity were determined in p-Chl phenol at 45°C and were in the range of 0.13 to 0.30 d1/g. Such values were about the same as other polymers reported in the other chapters of this thesis. The 1H-NMR spectra of polymers IV-6A and IV-10A in TFA showed that they were of the correct composition. The polymer with the ethylene glycol spacer, IV-2A, was soluble only in p-chlorophenol and so no NMR spectrum was measured.

The transition temperatures of these polymers are also listed in the table. The reported transitions will be commented upon individually since the behavior of the series is difficult to generalize because of its brief nature. The first polymer, with ethylene glycol spacer, had a weak reproducible melt endotherm and no observable clearing by DSC. Only in the initial heating cycle was a sharp melt transition observed, and the temperature at which this melting occurred is the value listed in the table. However, a Tg
Table 13. Properties of polymers with polymethylene spacers and an alternating placement of the mesogenic dyads.

```
\[
\begin{array}{cccccc}
\text{Polymer} & n & \text{Yield} & [\eta] & T_m & T_i & \Delta T \\
\text{(dl/g)} & (\degree C) & (\degree C) & (\degree C) \\
\hline
\text{IV-2A} & 2 & 47 & .13 & 235 & 285 & 50 \\
\text{IV-6A} & 6 & 89 & .30 & \text{heat} 205 & - & - \\
\text{IV-10A} & 10 & 42 & .13 & 124 & - & 0 \\
\end{array}
\]
```
could be observed at $132^\circ$C, which was quite similar to the value reported for poly(ethylene terephthalate). The high $T_g$ and the short flexible spacer probably made crystallization difficult from the point of view of crystallization kinetics. This slow rate of crystallization was similar to PET itself, and like PET, the endotherm associated with the melt transition could be increased with annealing.

The polymer with a hexamethylene spacer, on the other hand, had much more reproducible thermal properties, but a lower range of mesophase stability. The polymer was also monotropic, because the mesophase was accessible only from the isotropic melt. Once in the solid state, the polymer could be returned to the mesophase only by melting and then cooling. Figure 32 illustrates the thermal and optical properties of polymer IV-6A.

The final polymer prepared in this manner was that made from the alternating dyad, and the decamethylene spacer, polymer IV-10A. Unlike the other two polymers which formed mesophases, polymer IV-10A was not liquid crystalline, but had a very sharp melting endotherm on heating, and upon cooling exhibited a sharp exotherm, as shown in Figure 33. An interesting feature of this polymer was the dual peak nature of the melt transition. This second minor peak was not a clearing transition that could be confirmed by polarized light microscopy, so it may simply have been a crystalline modification produced during the heating cycle of the DSC run.

Certain conclusions about this series of dyad polymers can be
Figure 32. Thermograms from differential scanning calorimeter (DSC) analysis and thermal-optical analysis (TOA) of the polymer with alternating dyads and hexamethylene spacer. a) heating, b) cooling.
Figure 33. Heating (a) and cooling (b) cycles by TOA and DSC of the alternating dyad polymer V - 10A.
made even when its limited scope is considered. Comparison of these polymers with their analogues in the triad series is especially fruitful. Like every other series of mesophase forming polymers, the polymers with dyad mesogens arranged in an alternating fashion follow the relationship of decreased melting temperature with increased spacer size. An even-odd relationship in this series would be also probable, but could not be demonstrated because all spacers have even numbers of methylene groups.

The use of a smaller mesogenic group in the polymers with dyad mesogenic groups reduced both the melting temperature \( T_m \) and the range of mesophase stability \( \Delta T \), both of which are listed in Table 13. For example the melting temperature of the dyad polymer with ethylene glycol spacer was 100°C lower than that of the triad polymer. The range of mesophase stability was also greater for the dyad, because the liquid crystalline range was not reduced by decomposition as it was in the case of the polymer with a triad mesogenic group.

Similar reductions in the transition temperatures of the other two polymers also occurred, but a wider range of mesophase stability was observed for the polymers with triad mesogenic groups. Probably the most surprising aspect of these comparisons was the disappearance of a mesophase in the polymers with the decamethylene spacer. Instead of increasing the independence of the aromatic groups, as occurred with the triad polymer, and allowing them to order into a smectic mesophase, the decamethylene spacer acted to disrupt or to
dilute the mesophase forming capabilities of the dyad mesogen. Referring back to the case of the mesophase in the triad polymers with PEO spacer reported in Chapter III, it should be recalled that loss of mesophase forming ability occurred at a composition of approximately 50 weight-% flexible spacer. This amount of spacer was essentially the amount present in the dyad polymers, so the disappearance of the mesophase was not entirely surprising.

By changing the ester group linking the spacer to the dyad or triad mesogenic unit into an ether, the triad polymers prepared by Strzelecki (104) and the dyad series of polymers prepared by Strzelecki (75) and Griffin (83) would be obtained. Coincidentally, these dyad polymers also showed the head-to-head, tail-to-tail sequence of aromatic ester dyads. The spacers involved in Griffin's dyad polymers were made of 6, 8, and 10 methylene groups. Both the ether dyad and ether triad polymers followed the expected transition temperature-spacer length relationship but both series had much higher transition temperatures than the analogous ester dyad or ester triad series. Values of transition temperatures for both series of ether-linked polymers were taken from the literature and reported in Table 14. The transition temperatures show that polymers with ether dyad mesogens formed mesophases that are of lower thermal stability than the comparable polymers with ether triads. These dyad polymers also had lower transition temperatures than the comparable triad polymers, so as a result, similar conclusions can be drawn about the effect of the mesogenic unit by comparison of both
of the ether series of polymers reported in the literature, or by comparison of series of ester dyad and ester triad polymers reported here.

The differences between the dyad and triad mesogenic groups can probably be largely attributed to the greater persistence length imparted to the polymer by the triad mesogenic unit, since any dipolar interactions would be different by only one carbonyl function. The longer length to diameter ratio of the triad creates a polymer of higher stiffness, and so mesophases of polymers with triad mesogenic groups are less likely to be disturbed by spacers than are mesophases formed by polymers with a dyad mesogen. A further reduction in the size of the mesogenic group would lead to polymers such as PET which show no liquid crystalline properties at all in the melt. The reader is referred to the concluding chapter of this thesis for discussion of the effects of various mesogenic groups on polymers with main-chain flexible spacers.

Several conclusions can be drawn from the comparison of these four series of mesophase forming polymers:

a) Polymers containing an ester group connecting the spacer to the mesogenic unit have lower transition temperatures and shorter ranges of mesophase stability than those with an ether group linking the spacer to the mesogenic group.

b) Polymers with mesogenic dyads have transition temperatures and mesophase ranges reduced with respect to polymers with analogous mesogenic triads.
Table 14. Transition Temperatures of Polymers with Dyad and Triad Mesogenic Units Linked to Flexible Spacers by Ether Groups (75, 104)

![Chemical Structures]

<table>
<thead>
<tr>
<th>Transition:</th>
<th>K</th>
<th>S₁</th>
<th>S₂</th>
<th>N</th>
<th>I</th>
<th>K → N</th>
<th>N → I</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=4</td>
<td></td>
<td>305</td>
<td>380</td>
<td></td>
<td></td>
<td>210</td>
<td>300</td>
</tr>
<tr>
<td>n=5</td>
<td></td>
<td>275</td>
<td>315</td>
<td></td>
<td></td>
<td>165</td>
<td>230</td>
</tr>
<tr>
<td>n=6</td>
<td></td>
<td>220</td>
<td>280</td>
<td>380</td>
<td></td>
<td>220</td>
<td>245</td>
</tr>
<tr>
<td>n=8</td>
<td></td>
<td>240</td>
<td>300</td>
<td>350</td>
<td></td>
<td>175</td>
<td>230</td>
</tr>
<tr>
<td>n=9</td>
<td></td>
<td>220</td>
<td>250</td>
<td>305</td>
<td></td>
<td>160</td>
<td>200</td>
</tr>
<tr>
<td>n=10</td>
<td>105</td>
<td>215</td>
<td>225</td>
<td>270</td>
<td></td>
<td>185</td>
<td>212*</td>
</tr>
</tbody>
</table>

* reference (72)
c) Polymers with the mesogenic triad combined with longer flexible spacers can form smectic mesophases, whereas polymers with a mesogenic dyad either form only nematic mesophases or show no liquid crystallinity according to the results obtained to date.

2) Polymers with random dyads.

   a) Monomers. The synthesis of the polymers with a random dyad placement in the main chain was performed using the methods outlined in the experimental section. The properties of the diacid monomer and its blocked precursor are given in Table 12b. The infrared spectrum of the blocked monomer showed the absence of any acid functionality, and the presence of three carbonyl peaks at 1740, 1720, and 1710 cm\(^{-1}\) due to the three esters. After removal of the benzyl groups, the compound showed a carboxylic acid band at 2900 cm\(^{-1}\), and a broad carbonyl peak at 1745 cm\(^{-1}\) for the two acid groups and at 1690 cm\(^{-1}\) for the central ester. The NMR spectra confirmed these changes, and also showed that, for complete removal of the benzyl groups, the reaction needed to be performed a second time. After purification of the acid, it was then converted to the acid chloride and used directly in a polymerization reaction with a dried diol.

   b) Polymers and properties. In this series of dyad polymers, only two examples were synthesized, one having a decamethylene spacer, and the other having a triethylene glycol spacer. The flexible spacers were chosen for incorporation into a dyad polymer because of their ability to form smectic mesophases when used as spacers in the triad polymers. As already explained, these dyad polymers
differed from the other dyad polymers both in the synthetic method used, and in the way that the dyad was arranged in the chain. Any differences in the mesophases of two polymers with the same composition could, therefore, be attributed to either of the above reasons.

Both of the polymers listed in Table 15 formed mesophases when cooled from the isotropic melt. Characterization by polarized light microscopy showed that both polymers formed nematic mesophases, and DSC and TOA studies also presented some interesting results. In the case of the dyad polymer with triethylene glycol spacer, Figure 34, after an initially sharp melting peak on the first heating cycle, an enantiotropic mesophase was formed. Upon cooling, a very weak crystallization peak occurred, and a Tg at 0°C could also be observed. However, on the next heating cycle, while the birefringence of the sample did increase upon formation of the mesophase and finally drop to zero as the polymer reached the clearing temperature, only a weak melt endotherm could be observed. This weak endotherm was reproducible over several heating and cooling runs, so it would seem that this polymer had difficulty in crystallizing at the cooling rate used once it had melted. This low crystallinity is very reminiscent of the polymer with the ethylene spacer reported for the other dyad series. Another mechanism is probably at work in the case of the polymer with triethylene glycol spacer, because it was noted that triad polymers with PEO spacers always showed reduced heats of melting with respect to polymers with polymethylene spacers of comparable
Table 15. Properties of polyesters containing mesogenic aromatic dyads randomly placed in the main chain.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>Diol Content&lt;sup&gt;a&lt;/sup&gt; mol%</th>
<th>[η]&lt;sup&gt;b&lt;/sup&gt; (dl/g)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV- TR</td>
<td>46.0</td>
<td>48</td>
<td>0.09</td>
<td>63</td>
<td>86</td>
</tr>
<tr>
<td>IV-10R</td>
<td>98.7</td>
<td>47</td>
<td>0.17</td>
<td>heat 140</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cool 100</td>
<td>133</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by NMR.  
<sup>b</sup> In DCE at 25°C.  
<sup>c</sup> Peak maximum position in the DSC endotherm.  
<sup>d</sup> Spacer of triethylene glycol.
Figure 34. Thermograms from differential scanning calorimetry (DSC) and thermal-optical analysis (TOA) of the polymer with a randomly placed mesogenic dyad and a triethylene glycol spacer. Both the heating (a) and cooling (b) cycles are shown. Curve 1 is the first cycle and curve 2 is the second heating run.
Figure 34

\[ \text{Temperature (°C)} \]

- DSC
- TOA
chain length. While the two polymers do have similar thermal characteristics, the disappearance of the melt endotherm was probably caused by different factors.

The polymer with a decamethylene spacer, and a randomly oriented mesogenic dyad was found to form a monotropic mesophase. The formation of a mesophase would be unexpected in view of the results obtained for the compositionally identical polymer with a mesogenic dyad oriented in an alternating fashion. This latter polymer, as reported in the preceding section was not liquid crystalline.

Before going on to describe possible reasons for the differences in the behavior of the two dyad polymers with decamethylene spacer, a brief description of the monotropic mesophase properties of polymer IV-10R shown in Figure 35 would be useful. As explained, this polymer melts upon heating and goes directly to the isotropic melt at 135°C. Upon cooling a mesophase forms at 133°C that is stable provided the temperature is not lower than 102°C or raised above 133°C. If it is lowered below 102°C, then the polymer crystallizes, and a mesophase can be achieved only by reheating the sample to the isotropic melt and recolling to the liquid crystalline state.

The two dyad polymers with decamethylene spacers were studied using both 13C and 1H-NMR methods with TFA as solvent at ambient temperature. Proton NMR showed that the spectra and composition of the two polymers were essentially identical. There did, however, seem to be a fine structure in the aromatic region (δ ~ 7.0-8.0) of the polymer with the alternating dyad, see Figure 36a) and b).
Figure 35. TOA and DSC of the dyad polymer with a decamethylene flexible spacer and randomly arranged mesogenic unit. a) Heating and b) cooling cycles.
Figure 36. 60 MHz $^1$H-NMR spectra of the polyesters with a decamethylene spacer and mesogenic dyads in a) alternating order and b) randomly arranged.
Proton NMR also showed small amounts of the benzyl group in the random dyad polymers. By $^{13}$C-NMR larger differences could be observed, again in the aromatic region of the spectrum at ~130 ppm, as shown in Figure 37a) and b). Consideration of the spectrum of the triad polymer with decamethylene spacer and the synthetic methods used suggest that the major differences in structure are due to the presence of oxybenzoate end groups in the case of the alternating dyad polymer. This conclusion was supported by the presence of a peak at 117.3 ppm which was also present in the triad polymers made with the diphenol but not present in the polymers made with the preformed mesogenic dyad and triads.

Low molecular weight compounds without alkyl terminal groups are generally not liquid crystalline; however, both of these polymers with dyad mesogenic groups and decamethylene spacer possessed moderately high molecular weights thereby reducing chain end effects. As shown before in the study of triad polymers of different molecular weights, the essential mesophase behavior was the same regardless of synthetic method used or molecular weight obtained. The only differences were shifts in transition temperatures associated with changing polymer molecular weights as measured by inherent viscosity. It is unlikely therefore that differences in endgroups play the only role in the determination of whether or not the polymers showed liquid crystallinity.

Another important difference which could be expected to influence the liquid crystallinity would be the already described alternating
Figure 37(a). $^{13}C$-NMR of the polymer with mesogenic dyads arranged in an alternating fashion and a decamethylene spacer. $x = \text{solvent peak (TFA)}$.
Figure 37b. $^{13}$C-NMR of the polymer with the mesogenic unit arranged in a random sense and a decamethylene flexible spacer. $\times$ = solvent peak (IPA)
versus random placement of the dyads. There were great structural similarities between the two polymers because only the orientation of the central ester group in the dyad had been altered. It is not surprising, therefore, that the melting temperatures of the polymers were nearly identical.

This change in the orientation of the central ester of the dyad seems to have had a great effect on the heat of melting because the alternating dyad produces a polymer with a much larger endotherm. The heat of melting was greater than the combined heats of transition of the polymer with the random dyad. The irregularity of placement of the central ester seemed to reduce crystallinity under a given set of conditions without adversely affecting the mesophase order. The antagonism between higher crystallinity and lower mesophase stability has been observed before with the triad polymers with diethylene glycol spacer, polymer PE2 and PE2Cl. Changing the direction of an ester link in a mesogenic group has also been shown to affect the mesophase stability of low molecular weight and polymeric liquid crystalline compounds. (69)

Several conclusions can be drawn from the polymers synthesized with a randomly directed mesogenic dyad besides those already made concerning polymers with alternating dyads:

a) The dyad mesogenic group is much poorer at producing the more structurally ordered smectic mesophases because in no case was a smectic mesophase formed, yet triethylene glycol and decamethylene flexible spacers when used in polymers with triad
mesogenic groups did produce smectic mesophases.

b) The position of the central ester link of the dyad is very important in determining mesophase behavior, and its importance is very likely due to changes in the dipole moment of the polymer chain and the subsequent changes in solid and mesophase chain-chain interactions. Other factors such as the structural differences observed by $^{13}$C-NMR made this conclusion tentative so more work will be needed to confirm this observation.
CHAPTER V
POLYESTERS CONTAINING MESOGENIC UNITS
PRODUCED BY MELT TRANSESTERIFICATION

Introduction

This chapter discusses the initial work performed in our laboratory to incorporate flexible spacers into polymers containing main-chain mesogenic groups. The synthetic methods used were based upon those employed by Jackson and Kuhfuss(4) to prepare a thermotropic polymer with mesogenic groups and flexible spacers in the main chain. Research in this area was initiated in the laboratory of Profesor Lenz from his discovery and continued interest in crystallization-induced reactions (CIR)(71) but the studies reported here deal with the synthesis and characterization of polyesters with liquid crystalline properties intended for use in biocompatible membranes. This polymer system was chosen because of its good mechanical properties and liquid crystallinity making it suitable for membrane applications.

The synthesis of these polymers required first the preparation of polymers of poly(ethylene terephthalate) or its homologues and then a second reaction with p-acetoxy benzoic acid as shown in Figure 38 to form the liquid crystalline polymer.

The amount of oxybenzoate units incorporated depended on the
Figure 38. The synthesis of homopolymers and copolymers of poly(alkylene terephthalate) and their copolymerization with p-acetoxybenzoic acid.
reaction conditions and the initial reaction mixture concentrations. As the amount of oxybenzoate unit increased, the polymer changed from one that was quite like PET to one resembling poly(oxybenzoate). Optimum properties have been found for polymers containing 40-80% oxybenzoate units, and within this range, the best mechanical properties were found for samples with 60% oxybenzoate unit but solubility of the polymers was at the same time reduced.\(^{(4)}\)

An increase in the oxybenzoate content of the polymer chain led to only slight changes in the melting temperature which decreased from 245°C to 226°C while increasing from 1 to 40 mole-% oxybenzoate group. The PET crystalline fraction disappeared conti-

nously with increased oxybenzoate concentrations, and this decrease could be followed by X-ray diffraction. An interesting observation was made in the melt viscosity studies of the various polymer compositions. The polymer melt viscosity at 275°C increased until a polymer composition of 30 mole-% oxybenzoate unit was reached but above this composition the viscosity decreased, and at 60-70 mole-% oxybenzoate unit, it increased again. This viscosity decrease indirectly confirmed the liquid crystallinity, because nematic mesophases are known to be of lower viscosity than the isotropic melt which may be related to their improved shear orientation in the liquid crystalline state. The formation of the mesophase in turn leads to high orientation during processing and therefore better mechanical properties in samples produced from the nematic state.

The characteristics of the polymers were of course controlled
by the distribution of comonomers in the polymer chain. NMR studies showed that there was a random distribution of oxybenzoate units in the copolymer, and gel permeation chromatography (GPC) studies showed that the polymer possessed a normal molecular weight distribution indicating that reaction kinetics should give a random copolymer.\(^{(119)}\)

In subsequent research in this area, Feichtinger showed that there were between 2 and 3 adjacent aromatic units needed for liquid crystallinity,\(^{(70)}\) and if CIR was allowed to take place, then the aromatic units tended to segregate, and a microblock copolymer was formed. This structure was reflected in changes in the melting and clearing temperatures as well as the formation of an insoluble second phase which had a high content of p-oxybenzoate units. From structure studies of the two fractions it was shown that sequences of more than 4 aromatic units caused insolubility. The possible structures capable of creating a liquid crystalline melt are shown in Figure 39.

One means of lowering transition temperatures and of improving the solubility of a polymer is by the addition of substituents along the chain. Several substituents have been studied by Feichtinger giving substituted polymers which were characterized by NMR, DSC, X-ray diffraction, and SALS.\(^{(71)}\) The substituents were either methoxy or chloro groups in the 3-, or 3,5-positions, and led to substituted copolymers which had melting endotherms which were either very broad and weak or diminished with respect to the unsubstituted products. The presence of substituents raised the transition
Figure 39. Possible mesogenic structures formed during the melt transesterification reaction.

\[ T = \text{terephthalate} \]
\[ H = \text{oxybenzoate} \]
temperatures of the oxybenzoate homopolymers presumably due to hindered rotation in the chain, and this temperature increase occurred for both mono- and disubstituted materials. This surprising result made it necessary to use another approach for the lowering of transition temperatures without adversely affecting the liquid crystallinity of the polymeric materials.

An alternative method of adjusting the transition temperatures of main chain polymers is by the addition of an element of dissymmetry to the chain itself. B.P. Griffin has termed two approaches to temperature adjustment, as the use of "frustrated chain packing" and "non-linear (rigid) links".\(^{(13)}\) The former refers to any mechanism that preserves the linearity and chain stiffness but hinders proper crystal or liquid crystal packing. The latter concerns the addition of non-linear groups to the chain to reduce the effective persistence length of the molecule. Examples of several types of polymers based on the oxybenzoate-terephthalate system are shown in Table 15a. Of course, these additional components both lower the transition temperatures and act to disrupt liquid crystallinity, so at sufficiently high levels of insertion they can eliminate liquid crystalline behavior altogether.

As reported in the first four chapters, it is possible to modify transition temperatures by changing the chain length of the flexible spacer. This method has been used for various liquid crystalline and crystalline polymers,\(^{(119,14)}\) and this approach was adopted in this chapter. In the method employed for polymer preparation, in
Table 15a. Mesophase-forming polyesters with oxybenzoate units in the main chain.

<table>
<thead>
<tr>
<th>Mesogenic structure</th>
<th>Spacer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical structure 1" /></td>
<td>(-\overset{\circ}{\text{C}}-(\overset{\circ}{\text{CH}}_2)_n\overset{\circ}{\text{C}}-) (n=5-12)</td>
<td>103</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical structure 2" /></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical structure 3" /></td>
<td>NONE</td>
<td>69</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical structure 4" /></td>
<td></td>
<td>69</td>
</tr>
<tr>
<td><img src="image5" alt="Chemical structure 5" /></td>
<td></td>
<td>69</td>
</tr>
<tr>
<td><img src="image6" alt="Chemical structure 6" /></td>
<td></td>
<td>13</td>
</tr>
</tbody>
</table>
contrast to the techniques used in earlier chapters the flexible spacer was first introduced into the poly(alkylene terephthalate) prepolymer. These prepolymer were then reacted in the manner of Jackson and Kuhfuss to produce a liquid crystalline polymer with various aliphatic spacers.

There are of course many routes available for the preparation of PET and these related polymers, but the route most often used is that of the transesterification of dimethyl terephthalate. This same technique shown in Figure 38 can be used for the preparation of the homologues of PET, and even copolymers with different alkyl diols or poly(ethylene oxide) glycols can be made. Therefore, the method of melt transesterification would be expected to allow the introduction of any single type or mixture of diols into the final liquid crystalline polymer.

The introduction of different diols would be important from the standpoint of both the final properties of the polymers and the desired application of these polymers for use in dialysis membranes. Longer alkyl spacers are known to decrease the mechanical properties of a given polymer somewhat, but it is also important to have a polymer that can be processed in a useful temperature range. The inclusion of polyethylene glycols would allow greater permeability to water and ought therefore to be important for membrane use. It was for these reasons that we pursued the goal of the addition of various alkyl diols and diethylene glycol spacers into the polymer main chain, and while this method was not entirely successful, it did
suggest the alternative methods that have been described in detail in the previous chapters.

Experimental

Monomer preparation.

i) p-Acetoxybenzoic acid. Acetic anhydride (25.5 g) was used to dissolve p-hydroxybenzoic acid (13.8 g, 0.10 mol), and this mixture was heated to 60°C. One or two drops of concentrated sulfuric acid was added, and the heat removed. The product then crystallized from solution, and was then recrystallized from benzene. Yield was almost quantitative, and the melting point was 187°C.

ii) Dimethyl terephthalate. The compound supplied by the Eastman Chemical Co. was recrystallized in absolute ethanol, and dried in a vacuum oven at 40°C.

iii) Diols and solvents. Diols (Aldrich) were dried by refluxing with sodium metal and distilling under vacuum. Non-halogenated solvents were dried in the same manner, and were obtained from the UMASS chemistry stockroom. Halogenated solvents were used only for extraction purposes and therefore were used as obtained from the supplier.

Polymer preparation.

\[ \left\{ \begin{array}{c}
\left[ \begin{array}{c}
\text{C} \\
0
\end{array} \right] \\
\left[ \begin{array}{c}
0 \\
\text{CO} - \text{CH}_2 - \text{O} \\
0
\end{array} \right]
\end{array} \right\} 
\]

i) Terephthalate Homopolymers (A). Polymers of type A were
prepared by melt-phase transesterification using dimethyl terephthalate and an excess of the desired diol in the presence of titanium tetraisopropoxide or a calcium oxide/antimonium oxide catalyst mixture.

In a typical experiment, 19.8 g (0.102 mole) of recrystallized dimethyl terephthalate (DMT), 31.9 mg (0.207 mmole) of calcium acetate (0.10% solution in water) and 7.5 mg (0.026 mmole) of antimony tri-oxide (0.05% solution in water) were placed in a reaction vessel. After the removal of traces of water by repeated evacuation and purging with dry nitrogen, the appropriate diol (0.105 mol) was added. The reagent mixture was then subjected to the following heating cycle: 200°C(3 hours), 220°C(0.5 hours) and 270°C(0.2 hours). The reaction began as soon as the contents of the flask were molten. Methanol was collected in a liquid nitrogen trap and used to evaluate the course of the reaction. For the final reaction stage, a vacuum was slowly applied over a period of 0.2-0.3 hours at 270°C to reduce the pressure to 0.2-0.5 mmHg. These conditions were maintained an additional 5 hours.

After cooling under nitrogen, the reaction product was removed from the reaction vessel and the product was purified by dissolving it in trifuoroacetic acid or chloroform and then reprecipitated in excess methanol.

When a titanium catalyst was used, it was added to the reaction mixture preheated to 170°C, and shorter reaction times were adopted (2 hours at each of 200°C and 270°C). In all cases the products were
white powders and yields were greater than 90% with respect to DMT.

\[
\left(\begin{array}{c}
\text{C} - \text{O} - \text{C} - \text{O} - \text{CH}_2\text{CH}_2\text{O}
\end{array}\right)\]

\[
\left(\begin{array}{c}
\text{C} - \text{O} - \text{C} - \text{O} - (\text{CH}_2\text{CH}_2\text{O})_m
\end{array}\right)
\]

ii) Terephthalate Copolymer (B). A second series of polymers was prepared using a similar procedure, and these copolymers were composed of polyterephthalates based on ethylene glycol and different \(\alpha,\omega\)-polymethylene diols or diethylene glycol with the following structures.

The procedure employed for the preparation of the copolymers was very much like that used for the homopolymers except that an equimolar mixture of the diols was used in place of the single diol. As an example of the synthetic route used, the following method is given.

\[
\left(\begin{array}{c}
\text{C} - \text{O} - \text{C} - \text{O} - \text{CH}_2\text{CH}_2\text{O}
\end{array}\right)\]

\[
\left(\begin{array}{c}
\text{C} - \text{O} - \text{C} - \text{O} - (\text{CH}_2\text{CH}_2\text{O})_m
\end{array}\right)\]

\[
\left(\begin{array}{c}
\text{C} - \text{O}
\end{array}\right)
\]

iii) Transesterification with p-Acetoxy benzoic acid. Before reaction, the terephthalate homopolymers (A) and copolymers (B) were ground with a mechanical grinder in the presence of dry-ice, and passed through a series of wire-mesh sieves to produce a 20-40 mesh powder.

The polymers of series A, and the copolymers of series B were reacted in catalyst-free conditions at 270-280°C with an equimolar amount of p-acetoxy benzoic acid based upon the terephthalate moiety content. The copolymers of series B were also reacted with p-acetoxy benzoic acid with 30 mole-% of the latter component. In all cases,
the reactions were carried out under magnetic stirring in a 100 ml flatbottomed cylindrical flask equipped with two ground glass fittings located at the top of the apparatus for the nitrogen inlet and the condensate outlet which was attached to a liquid nitrogen trap.

In a typical experiment, 12.0 g (62.5 mmole) of poly(ethylene terephthalate) (20-40 mesh powder) and 11.3 g (62.5 mmole) of p-acetoxy benzoic acid were mixed to produce a homogeneous powder. After evacuating and purging the container with nitrogen at least three times, the contents were kept at 110°C at reduced pressure (0.1-0.05 mmHg) for 30 minutes. The container was then placed in a fused-salt bath that was preheated to 275°C, and the reaction mixture was maintained at that temperature under nitrogen gas for a half hour. Stirring of the reaction was continued throughout this time. A vacuum of 0.1-0.5 mmHg was applied at the end of this period, and the vacuum was maintained for 4 hours.

The resulting products possessed high melt viscosities, in all cases were opaque, light tan in color, and were characterized by strong adherence to the glass. They were removed from the reactor by heating overnight in trifluoroacetic acid (TFA) at reflux temperature. Two fractions of product were obtained, one being soluble and the other insoluble in TFA. The soluble fraction was isolated by precipitation in methanol while the insoluble fraction was simply suspended in methanol and stirred. For the example reported above, the total yield was 69.2%, and the soluble portion was 74.0% of the total.
Characterization. The resulting polymers were studied by proton and $^{13}$C-NMR, and the former was used to determine the amount of incorporation of the oxybenzoate residue in the polymer chain. The solvent used was TFA with 1% TMS as internal reference. Viscosity measurements were performed in a 40/60 weight ratio tetrachloroethane/phenol solution at 25°C. The measurements of transition temperatures and heats of transition were performed with DSC, and microscopic studies were performed on a polarizing microscope with a variable temperature hot stage. All instruments and methods used can be found listed in Chapter II.

The infrared spectra of the copolymers were studied by coworkers at the University of Pisa and were recorded on a Perkin-Elmer 180 Infrared Spectrophotometer with samples that were thin films cast by slow evaporation of the polymer solution on KBr discs. The temperature was controlled on a home-built heating accessory with a heating range going from room temperature to 350°C. The entire spectrum was recorded at each temperature, and then the temperature was raised in a step-wise fashion for each subsequent measurement.

Results and Discussion

Polymer Preparation.

The polymers of series V-A were prepared by the standard melt transesterification method reported by Smith and coworkers,$^{(120)}$ and some of the properties of this series are listed in Table 16.
Table 16. Properties of Polymers and Copolymers with Single Diol Spacers

\[
\begin{array}{cccccc}
\text{Polymer} & \text{Diol} & T_m & [\eta]^a & \text{Polymer} & \text{Yield} \\
\text{n} & (^0\text{C}) & (\text{dl/g}) & & (\%) & \\
V-1A & 2 & 275 & 0.39 & V-6A & 69.2 \\
V-2A & 3 & 234 & 0.56 & V-7A & 73.8 \\
V-3A & 4 & 227 & 0.34 & V-8A & 100.0 \\
V-4A & 6 & 157 & 0.55 & V-9A & 67.4 \\
V-5A & \text{DEG} & 89 & 0.76 & V-10A & 78.3 \\
\end{array}
\]

\begin{array}{cccccc}
\text{Soluble Fraction} & & & & & \\
\% \text{ of Total} & \text{Oxybenzoate} & T_m & [\eta]^a \\
\text{mole-\%} & (^0\text{C}) & (\text{dl/g}) & \\
74.0 & 57.5 & 237 & 0.28 \\
77.5 & 15.9 & 214 & 0.50 \\
57.1 & <1 & 227 & 0.32 \\
75.0 & 6.5 & 139 & 0.51 \\
\end{array}

^a Intrinsic viscosities measured in phenol/tetrachloroethane (60/40 w/v) at 25.0^0\text{C}. DEG denotes diethylene glycol.
The intrinsic viscosities of the polymers were in the range of 0.35-0.95, and the polymers were of sufficiently high molecular weight to be used in the reaction with p-acetoxy benzoic acid (p-ABA). The diols used gave polymers having a wide range of melting temperatures and one of them, diethylene glycol, introduced an oxygen atom into the diol chain.

A study of the composition of these polymers using a 90 MHz proton NMR showed the anticipated spectral features. The diols in the polymer chains gave peaks at both 4.8 ppm and 1.8 ppm except for poly(ethylene terephthalate), PET, which showed only the former peak and the terephthalic acid residue showed a peak at 8.3 ppm. A sample spectrum of the polymer with hexamethylene diol is included in Figure 40. Integration of the NMR spectra showed the expected composition of 50 mole-% terephthalic acid and 50 mole-% diol.

The second reaction, termed "melt-blending" by the inventors, involved the mixing of the reactants at elevated temperatures. As soon as the reagents were mixed, an apparent decrease in the viscosity of the reacting material occurred as would be expected for chain cleavage during the incorporation of p-ABA units. After application of the vacuum however, a white sublimate appeared which was identified spectroscopically as p-hydroxybenzoic acid (p-HBA). For all starting polymers except PET, products were recovered that were determined to be the completely unconverted starting material or a product containing a very small amount of oxybenzoate units. Characteristics of the recovered polymers are shown in Table 16.
Figure 40. 90 MHz $^1$H-NMR of (a) poly(hexamethylene terephthalate), and (b) its copolymer with poly(ethylene terephthalate).
In these cases the p-ABA was almost totally converted into the corresponding insoluble and infusible homopolymer, so a physical mixture of the two polymers was obtained. These results seem to indicate that the transesterification reaction occurred by a concerted mechanism and was strongly affected by the polarity of the C-O bond in the polymer involved in the ester interchange. (21) This mechanism could be similar in nature to that of the thermal degradation of PET where an intermediate ring structure is formed. (71)

Due to the success of the addition of the oxybenzoylation reaction with PET, it was decided to attempt this reaction with copolymers of PET and the diols used in the terephthalate homopolymers. Reaction conditions used were identical to those employed previously, and the resulting product was a statistical copolymer of the two diols. The polymers of series V-B are listed in Table 17 along with some of their properties. The relative quantities of the two diols could be measured easily by NMR, and were found to be essentially related to the starting concentrations of the diols. However, the diol of greatest abundance was usually the less volatile one giving effectively the same results as obtained by Smith with copolymers of ethylene glycol/propylene glycol and ethylene glycol/1,4-butane diol. (120) The NMR spectrum of copolymer V-5C is displayed in Figure 41 showing the presence of both diols in approximately equal proportions.

Copolymers. In contrast to the results obtained using the terephthalate homopolymers, the oxybenzoylation reaction occurred readily
Table 17. Properties of Terephthalate Polymers Prepared with Ethylene Glycol and a Second Diol

\[
\begin{align*}
\text{Polymer} & \quad m & \quad \text{Co-diol} & \quad \text{Melting Range} & \quad \Delta H_f & \quad [n] \\
V-1B & 3 & 44 & 137-182 & 8.2 & 0.42 \\
V-2B & 4 & 50 & 165-187 & 8.6 & 0.29 \\
V-3B & 6 & 64 & 100-122 & 5.6 & 0.76 \\
V-4B & \text{DEG} & 58 & 65-83 & 0.9 & 0.61 \\
\end{align*}
\]

DEG - diethylene glycol used as co-diol
Figure 41. 90 MHz $^1$H-NMR of the copolyester of poly(hexamethylene-co-ethylene terephthalate) and p-acetoxybenzoic acid, V-5C.
for the series of statistical copolymers of terephthalic acid and
different poly(methylene) or diethylene glycols. In most cases,
with reaction mixtures containing up to 50 mole-% oxybenzoate units,
the reaction product was completely soluble in either trifluoro-
acetic acid or in halogenated solvents as shown in Table 18. Intrin-
sic viscosities of the resulting polymers, series V-C, were somewhat
lower than the starting copolymers.

The copolymerization reaction of p-ABA with the terephthalate
copolymers was performed using 30 mole-% and 50 mole-% p-ABA in the
reaction mixture based upon the average molar concentration of repeat
units in the starting terephthalate polymer. The composition of the
products showed that the amount of oxybenzoate units incorporated in
the copolymer was somewhat less than the starting feed mixture, again
due to the sublimation of some p-HBA out of the reacting system.
Presumably, it was the presence of ethylene glycol in the polymer
chain that allowed the addition of oxybenzoate unit to the copolymer.
Unfortunately, there were no direct methods for determining the exact
location of structural units in the polymer.

The oxybenzoylation reaction of the starting terephthalate co-
polymers led in all cases to marked changes in the appearance and
transition temperatures of the DSC melting endotherms of the resulting
products. A considerable broadening of the melt endotherm occurred
in the product DSC, and this was accompanied by the appearance of
several apparent transitions within the melting peak. Figure 42 shows
the appearance of the DSC for starting polymer V-2B, and the copolymer
Table 18. Properties of Soluble Fraction of Product of Melt-Blending Reaction

\[ \text{Polymer} \quad m \quad \text{Yield (\%)} \quad \text{TFA Soluble Fraction (\%)} \quad \text{Oxybenzoate (mole-\%)} \quad \text{Melting Range (\degree C)} \quad \Delta H_f \quad [\eta] \\
V-1C* \quad 3 \quad 66.4 \quad 73.2 \quad 12.5 \quad 137-175 \quad 5.0 \quad 0.35 \\
V-2C \quad 3 \quad 59.7 \quad 83.3 \quad 7.7 \quad 137-177 \quad 6.6 \quad 0.38 \\
V-3C* \quad 4 \quad 73.0 \quad 100 \quad 41.5 \quad 137-189 \quad 4.8 \quad 0.16 \\
V-4C \quad 4 \quad 85.0 \quad 100 \quad 21.9 \quad 127-187 \quad 7.5 \quad 0.30 \\
V-5C* \quad 6 \quad 60.0 \quad 77.8 \quad 31.0 \quad 94-143 \quad 6.0 \quad 0.27 \\
V-6C \quad 6 \quad 72.1 \quad 100 \quad 20.0 \quad 98-139 \quad 8.0 \quad 0.35 \\
V-7C* \quad \text{DEG} \quad 78.9 \quad 76.9 \quad 54.2 \quad 58-77 \quad 0.3 \quad 0.19 \\
V-8C \quad \text{DEG} \quad 59.0 \quad 100 \quad 17.5 \quad 67-90 \quad 1.8 \quad 0.25 \\

* starting ratio was 50 mole-% p-ABA: 50 mole-% terephthalate repeat unit; remaining products had a starting reaction ratio of 30 mole-% p-ABA: 70 mole-% terephthalate repeat unit
Figure 42. Thermogram by differential scanning calorimetry of copolymers V-3C (----), V-4C (-----) and V-2B (-----).
(V-4C) with oxybenzoate units. Such structuring of the transition was very reproducible and has been known to occur in polyesters where simultaneous melting and crystallization leads to the multi-peak shape.

All of the samples that were prepared and contained more than 30 mole-% oxybenzoate unit showed very weak birefringence at temperatures up to 80°C above the melting range. However, only one sample showed anything vaguely resembling a clearing temperature on the DSC. This was polymer V-3C which contained the highest amount of oxybenzoate incorporated into any of the copolymers. Figure 43 shows optical micrographs of these samples in the melt, and here the relatively weak birefringence can be seen. These figures exhibit points of birefringence which presumably corresponded to small regions of liquid crystallinity in an isotropic melt. While no definite texture and hence no mesophase structure could be assigned to these photomicrographs, the mesophase was probably nematic. Polymers with poorly defined structure have been generally found to be of the nematic class.

Only the compounds containing a substantial amount of oxybenzoate units produced a change in the transition temperature of the starting copolymers. Theory predicts this temperature lowering for polymers with compatible copolymer elements in the chain, but the broadness of the new transition suggests that several structures are possibly contributing to the exotherm, and so for example a "microblock" copolymer with mesogenic dyads or triads might actually
Figure 43. Photomicrograph of polymer V-3C at a temperature of 200°C in the melt, and a magnification of 360x.
be widening the transition range.

The copolymers discussed in Chapter II showed the effect that using two flexible spacers can have on suppressing the crystallinity of the sample, without seriously impairing the ability to form a mesophase. The presence of two spacers did produce a nematic mesophase rather than allowing the organization of the mesogenic units necessary to produce a smectic state. These triad polymers however possessed a single type of mesogenic group in the main chain which was not the case for the copolymers with incorporated oxybenzoate units listed in Table 18.

It is also interesting to compare the series of terephthalate polymers (polymer V-1A to V-4A) with the triad polymers of Table 4. By replacing the terephthalate moiety with the triad mesogen, the melting temperature was substantially increased by as much as 100°C, and above that there was also a mesophase region. The increased persistence length and increased dipole of the triad could account for both observations. Again considering the terephthalate polymers, if comparison is made with polymers discussed in Chapter IV one observed that the melting temperature of the dyad polymer with ethylene glycol spacer was lower than the analogous terephthalate polymer and showed no difference in the melting temperature of either polymer with hexamethylene spacer. It is not surprising then that the product of the melt transesterification with any of these possible mesogenic structures showed such broad transition ranges.
The fact that only small domains appeared to be liquid crystalline, suggests that these polymers are really microblock copolymers composed of sections of the starting copolymer and sections of the inserted oxybenzoate groups. Lenz and coworkers have shown by NMR analysis that between two and three adjacent aromatic groups are necessary for liquid crystallinity, and that more than four form an insoluble crystalline phase.\(^{(70)}\)

These possible mesogenic groups were those shown in Figure 39 of the introduction, and two of them are the mesogens used in the polymers of the previous chapters where they were shown to produce liquid crystalline polymers. However, in those polymers the mesogenic units were regularly distributed in the chain with a single type of mesogenic group, and here the low oxybenzoate (OB) levels generated a block nature in the copolymers.

**Infrared Spectroscopy.** Analysis of the hexamethylene copolymers V-5C and V-6C by infrared spectroscopy over a range of temperatures from room temperature to the clearing temperature showed that there were noticeable differences throughout most of the spectral region.\(^{(121)}\) This work, performed by coworkers at the University of Pisa, indicated that both the positions of several bands and their intensities showed changes with heating and the most marked of these changes occurred in the absorptions at 1335 cm\(^{-1}\) in the methylene wagging and twisting region, and 415 and 395 cm\(^{-1}\) in the skeleton vibration spectral region. As shown in Figure 44a) the percent
Figure 44. Variation of IR optical density ratio with temperature for various copolymers. (a) deals with polymer V-6C. Reproduced from reference 121.
transmission of these bands, after comparison with a suitable reference band, could be plotted as a function of the temperature. A substantial decrease in the transmitted light intensity occurred over the temperature range detected by DSC analysis that was associated with the melt transition and therefore indicated that this method was very sensitive to the measurement of phase changes in the copolymers under investigation. After being cooled to room temperature, the once-melted samples displayed their original spectra with essentially no change in relative intensities, which indicated that the observed differences in the spectra were due to conformational changes in the polymer and not due to any degradation phenomena.

For two of the specimens studied, V-5C and V-6C, the infrared analysis seemed to be sensitive to some type of transition within the melting range which could be assigned to a solid-solid transition (at 80°C) which was not revealed by DSC analysis. This difference might be attributable to the dynamic nature of the DSC analysis, and the static method of IR measurement. On the other hand, in the copolymer series with both hexamethylene and ethylene glycol flexible spacers, the transmitted light ratio, \( \frac{D_{1335}}{D_{1020}} \) of the copolymer with the higher OB content, V-5C with 30 mole-% OB, was unaffected over a fairly broad temperature range below the melting point (25-80°C), see Figure 44b). Under the same conditions, the ratio for the V-5C copolymer containing 20 mole-% OB units decreased continuously from room temperature to the melting point, indicating the existence of
a very broad phase transition in this copolymer. These observations support the concept of an irregular, blocky structure for the copolymer which was formed by a crystallization induced reorganization during insertion of the oxybenzoyl units, since an additional transition was observed at higher OB content.

As discussed in Chapter I, infrared spectroscopy has been used to study the transition phenomena in various liquid crystal systems. The most useful results occur when the alkyl end groups of low MW liquid crystals are considered, and the observed change is due to their different degrees of motion. This is the one of the few groups that shows changes on passing through the transition from the nematic to isotropic phase, and the changes are due to differences in the chain conformation which are believed to be a significant component of the entropy change at the phase transition. The change in intensity observed with these polymers was similarly associated with the alkyl spacer; however, no clearing transition was detected for the polymers, and this occurred despite the fact that the presence of the oxybenzoate group was detected in this band at a lower temperature than the melting temperature, see Figure 44b).

Shibaev, in his study of liquid crystalline polymers by infrared spectroscopy,\(^{(62)}\) investigated a polymer (21, Table 1) containing a side-chain mesogenic dyad. This dyad was very similar in structure to the dyads that can be expected in the polymers studied in the same manner in this chapter. A large change in the absorbance of the methylene wagging band was observed at the melting temperature, along
with other changes in the spectrum associated with the aromatic group, and two ester linkages. This polymer, while having a very stable mesophase up to 160°C, showed no significant change in the spectrum upon clearing. This polymer was reported to form a smectic mesophase, and the fact that no clearing is observed by IR indicates that there are potential difficulties with this technique. Therefore, it is not surprising that no clearing transition was observed for polymers V-5C and V-6C when a nematic to isotropic transition was involved since this is a transition with an even smaller change in structure than the smectic to isotropic transition.

NMR Spectroscopy. These two copolymers were also studied by $^{13}$C-NMR to get some indication of the possible sequences of the aromatic components in the polymer chain. The presence of more than one diol did not greatly affect the chemical shift of the aromatic components, and it would be expected from such low insertion levels of oxybenzoate that the average aromatic sequence length was that of the dyad. Calculations could not be made using the method of Feichtinger,(71) because of uncertainties of exact peak assignment in the copolymer. Therefore, no aromatic sequence length was determined due to the fact that several species of oxybenzoate groups were present which complicated the spectra in the aromatic region especially.

Figure 45 shows a $^{13}$C-NMR spectrum of copolyester V-5C with hexamethylene and ethylene glycol spacers. It is instructive to compare
Figure 45. $^{13}$C-NMR of the polyester prepared from poly(hexamethylene-co-ethylene terephthalate) and p-acetoxybenzoic acid using TMS reference. $x = \text{solvent peak (TFA)}$
this spectrum with that of the related triad and dyad polymers with poly(methylene) spacers which are shown in Figures 46a) and b) respectively. The symmetry of the triad unit was evident from the lower number of peaks that were present in the spectrum, but such symmetry was not evident in the case of the dyad where its disymmetry generated more types of carbons and this spectrum is much closer to that of the copolymer produced by transesterification, indicating that the dyad is likely the prevalent mesogenic unit.
Figure 46a). $^{13}$C-NMR of the polymer with a triad mesogenic unit and a tetramethylene flexible spacer. $x =$ solvent peak (TFA)
Figure 46b. $^{13}$C-NMR of the polymer with mesogenic dyads arranged in an alternating sense and a hexamethylene spacer. $x =$ solvent peak (TFA)
CHAPTER VI

THE EFFECTS OF MESOGENIC UNITS AND FLEXIBLE SPACERS
ON POLYMERIC MESOPHASES

Introduction

There are many ways of modifying the liquid crystalline properties of a mesophase-forming compound, and these techniques can be used whether the mesogen is of low or high molecular weight. Many of the methods available for the modification of the behavior of liquid crystalline polymers have been used in the work reported in this dissertation and include: i) changing the length and type of the flexible spacer, ii) altering the size and type of mesogenic unit employed, and iii) addition of substituents to the mesogenic unit and/or flexible spacer.

In each of the previous chapters, a specific series of polymers was discussed in which the spacer length was changed, but only one mesogenic group was studied in each section. As a result, the effects of changes of the spacer on liquid crystallinity have been thoroughly described, but the differences between liquid crystalline polymers that have identical spacers and different mesogenic groups have not been fully detailed. Part of this concluding chapter will, therefore, be devoted to a comparison of those polymers prepared in the course of these studies having
decamethylene spacers, but different mesogenic groups.

There are in fact quite a large number of liquid crystalline polymers having the decamethylene spacer in the main chain, but no effort has yet been made to generalize the influence that mesogenic units have on the mesophase properties of these polymers. These units seem to exhibit the same relationships between each other in polymers as they do in low molecular weight compounds.

The final section of this chapter discusses the possible directions that future work can take in the area of liquid crystalline polymers. The study of polymeric materials possessing mesophases formed by well-defined elements in the polymer chain is a recent development in the field of polymer science. As a result, more work is needed in the area of polymer characterization because much of the literature on the subject has not yet bridged the gap between the purely theoretical and the work that is essentially the synthesis of new liquid crystalline polymers.

**Liquid Crystalline Polymers with**

**Decamethylene Spacers in the Main Chain**

Four examples of polymers with decamethylene spacers but with different mesogenic elements were reported in this dissertation. Some of the properties of these polymers, which are listed in Table 19, show the surprising differences between these polyester. The polymers with triad ester mesogenic groups possessed
higher solution viscosities than did the dyad polymers, and as a result the polymers with the dyad mesogens may be in the range where transition temperatures are affected by molecular weight. However, as was shown in Chapter II, the structure of the mesophase is much more a function of the chemical structure than the molecular weight of the compound.

The polymer with the unsubstituted triad mesogenic group possessed the highest melting and clearing temperatures of the series, but the addition of chlorine substituents to the mesogenic unit caused a drastic change in mesophase behavior. A drop of approximately 70°C occurred in the melting temperature as well as a change from an enantiotropic, smectic mesophase for the non-chlorinated polymer to a monotropic, nematic mesophase for the substituted polyester. The range of mesophase stability of the latter was also reduced with respect to the former.

The reduction in melting temperature was expected, but such a large change in mesophase behavior could not be anticipated. Monotropism is usually associated with mesogenic groups that are only weakly mesophase forming, yet few structural changes were made by adding chlorine. There are several explanations for this behavior, based either on polar effects or on steric crowding. In the former case, the presence of the chlorine group would act to change the polarity of the mesogenic group in such a way that it reduced the lateral dipole interactions of the polymer with neighboring mesogenic groups. This diminished interaction would lead in
Table 19. Properties of thermotropic polyesters with a decamethylene flexible spacer.

![Chemical Structure](image)

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<td>T&lt;sub&gt;i&lt;/sub&gt;</td>
<td>ΔH&lt;sub&gt;m&lt;/sub&gt;</td>
<td>ΔH&lt;sub&gt;c&lt;/sub&gt;</td>
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<td></td>
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<td>(%)</td>
<td>(d1/g)</td>
<td>°C</td>
<td>°C</td>
<td>Kcal/mol</td>
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<td>124</td>
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</table>
turn to weak mesophase ordering, and thus the observed behavior could result.

Alternatively, the chlorine substituent could act to force apart the mesogenic groups and thus sterically hinder the ordering in the mesophase. This possibility is usually more likely to occur than changes in the dipolarity of the mesogen. However, the third possibility, that the structure of the mesogenic group is distorted, is an even more likely possibility. The presence of the chlorine substituents act to hinder formation of a long rigid structure by interfering with the adjacent ester linkage. The ability of substituents when placed on aromatic groups to force the adoption of non-planar arrangements is well known for biphenyl mesogenic group caused by twisting about one of the bonds. In the biphenyl systems, the steric changes led to reduced thermal stabilities of the mesophase, and with some substituents, the loss of the smectic mesophase.

In effect, the addition of chlorine to the triad mesogenic group reduced its mesophase-forming properties and made them comparable to those of the dyad group. The dyad aromatic mesogenic unit also had weaker mesophase-forming properties than the triad because of its lower length-to-diameter ratio. As a result the dyad was not as "rigid" in the sense that its persistence length was not as great as the triad. The absence of an additional ester link in the dyad also acted to produce a mesogenic group of lower dipolarity than the triad, and hence the lateral interactions
leading to smectic mesophase formation were reduced, and in fact sufficiently weakened that monotropism was exhibited in the case of the polymer with a random orientation of the dyads.

An alternating order of the mesogenic dyad used in conjunction with the decamethylene spacer, however, gave a polyester showing no mesophase as was described in Chapter IV. This observation indicates that there are other factors besides the length and dipolarity of the mesogenic units that can influence mesophase formation.

In order to compare these mesogenic groups to others reported in the literature, a list has been made of reported polymers containing decamethylene flexible spacers. These polymers are listed in Table 20 showing their structure, the size of the mesogenic group, and the polymeric transition temperatures where known. These polymers follow the general trend of increased length of the mesogenic unit leading to increased transition temperatures. Exceptions to this rule are observed when mesogenic groups with differences in their rigidity, and therefore, differences in their persistence lengths are compared. For example, a comparison of biphenyl with the longer, less rigid stilbene unit, show that the short, rigid biphenyl has a higher transition temperature. Compounds with a greater persistence length have, of course, both the tendency to have higher transition temperatures as well as the tendency to form the smectic mesophase.

The polymers with dyad and triad ester mesogenic groups fit
Table 20. Various LC polymers with decamethylene spacers and mesogenic groups in the main chain.

<table>
<thead>
<tr>
<th>Mesogenic Group</th>
<th>Size (Å)</th>
<th>Linking Group</th>
<th>Transition Temp. (°C)</th>
<th>Reference</th>
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<td>ether</td>
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<td>ester</td>
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<td>40</td>
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<td>&quot;</td>
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<td>&quot;</td>
<td>N 203 I</td>
<td>40</td>
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<td>&quot;</td>
<td>N 240 I</td>
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<tr>
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<td>K 197 S 200 I</td>
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<td>&quot;</td>
<td>K 256 S 311 I</td>
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<td>ether</td>
<td>K 237 N 265 I</td>
<td>85</td>
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</tbody>
</table>
very well with the trends found for the polymers listed in Table 20. The dyad group with a length of 13 Å possessed a nematic mesophase, whereas the triad mesogenic unit with a length of 18 Å had a smectic mesophase. Direct comparison of the dyad and triad ester mesogenic units with the ether mesogenic units (the first and last listed in Table 20 respectively), show the unpredictable effect of adding the carbonyl moieties. In the dyad mesogenic group when compared to the ether dyad, the presence of the esters lowers the transition temperature in the random case and destroys mesophase behavior in the alternating case. On the other hand, when compared to the ether triads the presence of the esters does not affect transition temperatures, but enhances lateral interactions enough to create a smectic mesophase with a thermal stability comparable to the terphenyl mesogenic group.

Effects of Flexible Spacers on Mesophase Behavior

The research results reported in the previous chapters demonstrated quite conclusively that the flexible spacer played an active role in the determination of the mesophase properties. Briefly summarized, increased spacer length favored reduced transition temperatures and when the spacer was sufficiently long, a smectic mesophase could result. This statement is really an oversimplification, because different spacers gave different types of mesophases, and the change in mesophase type occurred despite the
fact that spacers of approximately the same size were used with the same mesogenic group.

It is obvious, therefore, that the flexible spacer did more than simply allow the mesogenic groups to order into a mesophase by "decoupling" their activities somewhat from the rest of the main chain. The flexible spacer, in other words, very much determined the nature of the resulting mesophase, which can be seen by comparing the properties of the triad polymers with either decamethylene or tetraethylene glycol flexible spacers. The spacers were of the same approximate length, yet the presence of oxygen in the spacer in the latter produced a polymer with very different properties with respect to the former.

This behavior suggests that there is no finite division between a flexible spacer and a mesogenic unit so that in fact the parts of the molecule that connect the two components probably have properties of both spacer and mesogenic group. Also, addressed in this study was how much spacer could be added before the liquid crystalline properties of a polymer were lost. It appeared that at approximately 50 weight-% spacer, the polymer could no longer form a mesophase, so here again the effect of the spacer on mesophase properties could be seen. No real conclusion could be drawn about how the extended spacer eliminated the mesophase-forming properties of the mesogenic unit.
Future Work

The possible techniques that can be used to modify the mesophase properties have been explored in this dissertation research program using oxybenzoate-terephthalate mesogenic groups. These methods can be used with any type of liquid crystalline polymer, so the research need not have been performed only on the studied mesogenic groups. Many questions remain unanswered, however; for example, what is the role that the spacer plays in the mesophase formation, and what are the effects that various spacers can have with different mesogenic groups? The questions can be further studied by preparation and characterization of polymers with different spacer types and mesogenic units.

Another study that could be performed with existing polymers would be to examine the properties of blends of liquid crystalline polymers with non-liquid crystalline materials. Combinations of mesophase-forming compounds and either polymeric or low molecular weight compounds have retained liquid crystallinity up to a substantial amount of non-liquid crystal component.\(^{131}\)

The nature of the mesophases of the reported polymers has been established by microscopic observation, and in several cases, by X-ray diffraction studies of the molten polymer. The availability of an accurate heating cell for the Wahrus camera will allow further study of several of the polymers reported here and will give more information about the structure of the polymer in the
liquid crystalline state.

Addition of thermotropic polymers to other polymers would be expected to induce the liquid crystalline state if added in the proper amounts. This technique, if successful, could take small amounts of expensive liquid crystalline polymers and blend them with readily available commodity polymers to upgrade properties.

Another area that could be explored might be the formation of block copolymers of liquid crystalline and non-liquid crystalline components. Thermotropic polymers are themselves block copolymers on the microscale when flexible spacers are used. The suggested polymers would therefore consist of blocks of several repeat units, or even AB or ABA-type copolymers. Liquid crystal polymers of the type reported in this dissertation are made by condensation methods, so in order to prepare these block copolymers the same methods would need to be used for the mesophase-forming segments. By proper addition of functional groups, however, other blocks could be used, such as polystyrene segments functionalized with hydroxy or carboxylic acid terminal groups.

Methods of characterizing these new compounds would be by the methods usually used with liquid crystalline polymers, which include microscopy, thermal methods and scattering techniques. Addition of low molecular weight components that could act to label the mesophase would allow study of the melt by fluorescence and ESR. Preparation of deuterated compounds could also be used to answer the question of chain-folding in the liquid crystalline melt, and possib-
ly whether the spacer is extended or coiled in the mesophase by studying these compounds with neutron scattering methods.

Liquid crystalline polymers are recent developments in the study of polymer science, and many additions to the understanding of this "fourth state of matter" are still possible. This thesis is, therefore, a report of the work undertaken in the early stages of this area of polymer science and should be followed by much new exciting research.


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Figure 47. IR spectrum of 4-carboxyphenyl terephthalate.
Figure 48. IR spectrum of bis(terephthaloylox)decane.