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THE SYNTHESIS AND CHARACTERIZATION
OF THERMOTROPIC POLYESTERS WITH
SUBSTITUENTS ON THE MESOGENIC UNITS

A Dissertation Presented
By
QI-FENG ZHOU

Submitted to the Graduate School of
The University of Massachusetts in
Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

February 1983
Polymer Science
and Engineering
QI-FENG ZHOU

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To My Motherland, China,
Who Means Everything to Me
I wish to thank my adviser Professor Robert W. Lenz and my dissertation committee members Professor Edwin L. Thomas, Professor Otto Vogl and Professor J.-I. Jin for their guidance, encouragement and the sympathetic understanding throughout this work.

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Finally, I especially thank my mother, my wife and my lovely daughter for their love, understanding and support.
ABSTRACT

THE SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC POLYESTERS WITH SUBSTITUENTS ON THE MESOGENIC UNITS

September 1982

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The syntheses of a series of new thermotropic liquid crystalline homopolymers, copolymers, and polymer blends, as well as their monomers were discussed. These polymers were prepared from 1,10-decanedienedioic acid dichloride and substituted hydroquinones, and had a general structure as follows:

\[-\left(\text{HOOC} - \text{COO} - \text{OOCCOO} - \text{COO} - \left(\text{CH}_2\right)_n\right)\text{-}X\]

where \(X = (\text{CH}_2)_n - \text{H}; \quad n = 0, 1, 2, 3, \ldots, 10.\)

or \(X = \text{Br}, -\text{CN}, -\text{NO}_2, -\text{OCH}_3.\)
In the copolymers, X was either \(-\text{CN}\) or \(-\text{OCH}_3\) of different ratios.

The structures and the thermotropic properties of these polymers were characterized by inherent viscosity measurements, gel permeation chromatography, \(^{13}\text{C-NMR}\), differential scanning calorimetry, and polarizing microscopy observations.

All of the polymers had fairly low melting temperatures, which were desirable for thermotropic liquid crystalline polymers, and most of them had a mesophase (very likely nematic) above the melting point. As an example, the ethyl-substituted polymer had a melting point of 71°C and an isotropization temperature of 127°C.

The substituent effects on the thermotropic behavior of these polymers were systematically studied in terms of both steric and polar effects. Increasing the size of the substituents resulted in the decrease of the thermal stability of the mesophase, while the higher polarity of the substituents resulted in a higher stability. With some success a theoretical treatment was developed which partly answered the questions which arose from the different behavior of polymers with different
substituents; for example, why the methoxy-substituted polymer was (to the author’s suprise) non-liquid-crystalline.

The copolymerization of monomers with different substituents was found to be a good way to lower the melting point of the polymers. Copolymerization also caused a steady change in the mesophase thermal stability with changing composition of the copolymers.

Observations on the optical microscopy revealed that no phase separation occurred in the mesophases of the blends formed from two different thermotropic polymers. However the liquid crystalline polymers were immiscible with a non-liquid-crystalline polymer, and consequently both phase separations and phase inversions were observed with changing combination of the two components of these blends.
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CHAPTER I

LIQUID CRYSTAL AND LIQUID CRYSTALLINE POLYMERS

As the fourth state of matter, liquid crystals have been attracting a great deal of attention by people who work in various scientific branches. Great rewards have been achieved after the efforts of pioneers. The property of molecular organization in this state is becoming increasingly clear; subclassifications of this state have received sound experimental support; characterization techniques have developed appreciably; theoretical and empirical predictions of liquid crystal formation have resulted in a rush to make and find more new liquid crystalline compounds, while no doubt the industrial and social interest of the applications of liquid crystalline materials has inspired thousands of new compounds.

Liquid Crystals, the Fourth State of Matter

"Liquid crystals" represent a state of matter in which the degree of molecular order, positional and/or orientational, is intermediate between the almost perfect long-range order found in solid crystals and the
statistical long-range disorder in ordinary isotropic amorphous liquids. The term "liquid crystal", although self-contradictory, strongly emphasizes the intermediate property of this unique material state. Obviously another more proper term is "mesophase".

Knowledge of the liquid crystalline state of matter has advanced to the point where we can give it a meaningful classification based especially on microscopy and X-ray examinations. The two major categories of liquid crystals are identified as thermotropic and lyotropic. Thermotropic liquid crystals are obtained on heating certain organic or organometallic compounds, while lyotropic liquid crystals are obtained for solutions of such compounds in appropriate solvents.

Both thermotropic and lyotropic liquid crystals have been further classified depending on the degree and type of molecular orientation. For thermotropic liquid crystals, "smectic", "nematic" and "cholesteric" have been appointed as three subdivisions, and these are presented in Fig.1. In these sketches each bar represents a rod-like molecule or molecular structural unit (mesogenic unit).
Fig. 1. Schematic structure of smectic A, nematic and cholesteric liquid crystals.
As many as eight smectic phases have been identified by Sackmann, Demus, de Vries and others [1-5] using X-ray, microscopy, DSC and miscibility analyses. In contrast to the nematic phase, smectic phases have stratified structures, with the long axes of the rod- or lath-like molecules parallel to each other in the layers. In most smectic phases, the molecules are mobile in two directions and can rotate about one axis. The interlayer attractions are weak compared with the lateral forces between the molecules, and the layers are able to slide over one another relatively easily. Consequently, the smectic phases have fluid properties, but are much more viscous than the other mesophases. Consistent with their higher order, the smectic phase always occurs at lower temperatures.

X-ray diffraction [5-7] has been used to distinguish the interlayer spacings of the characteristic periodic packing of molecular layers in a smectic phase from each other, and from other mesophases. The X-ray diffraction pattern of nonoriented smectic samples (powder pattern) consists essentially of two rings: (1) an inner ring at small Bragg angles that corresponds to the layer spacing and is very well defined, and (2) an outer ring at larger
angles which is characteristic of the lateral distribution of parallel molecules and which generally looks like a liquid diffraction ring. In contrast, the nematic phase is expected to show only a diffuse ring at larger angles. Oriented samples will result in diffracted arcs. The molecular orientation can be achieved by means of mechanical formation or electro-magnetic fields [8].

The characteristic difference of one smectic phase from another is the way the mesogenic molecules are organized within the strata. For example, in smectic A phase, the molecules are normal to the stratum in each layer with their centres irregularly spaced; while a tilted form of smectic A gives rise to the smectic C phase.

As shown in Fig.1, no stratified structure is present in a classic nematic phase. The only structural restriction for this state is that the long axes of the molecules maintain a parallel or nearly parallel arrangement to each other.

It has been suggested that the cholesteric mesophasic is a special case of the nematic structure. This phase is comprised of helical aggregates of molecules. The helical
array arises from a chiral perturbation, usually the presence of a center of optical activity in the molecules that comprise the mesophase. This chiral perturbation minimizes, relative to other arrangements, the energy content of a stacked array in which each molecule is skewed at some average angle with respect to its neighbors above and below. Of course, two such helices, one right-handed and the other left-handed, are possible, but one is of lower energy than the other because of the chiral nature of the perturbation. A nematic structure may also consist of helical aggregates of molecules, but since the two helical forms are of equal energy, there is no net chiral influence [9].

Because of their unique molecular organizations, liquid crystals show a characteristic appearance on a polarizing microscope. Fig. 2. shows three typical textures of low molecular liquid crystals. (a) is a fan-like texture of smectic A phase of TBBA, N,N'-terephthalylidene-bis(4-n-butylaniline), which was obtained by cooling this sample from its nematic state to its smectic A state; (b) is a cholesteric texture of cholesteryl pelargonate; and (c) is the schlieren or threadlike texture of nematic azoxyanisole. The great
Figure 2a. Fan-like texture of smectic A
Magnification: 320X
Figure 2b. Cholesteric texture. Magnification: 320X
Figure 2c. Nematic Schlieren texture
Magnification: 320X
difference in appearance among these textures has been of considerable use for distinguishing these mesophases from one another, it might be mentioned here that from the schlieren texture the term "nematic" was created. The threads result from a change in the preferred molecular alignment in the vicinity of the axis of the thread. Nematic crystals exhibit positive birefringence indicating that the optic axis of the nematic phase coincides with the preferred direction of the long axis of the molecule.

The alignment of molecules within a nematic mesophase is not precisely parallel because of thermal motion. A measurement of the degree of parallel alignment is obtained by a determination of the order parameter, $S$, by means of the following expression for rod-like molecules:

$$S = \frac{1}{2} \left( 3 \cos^2 \theta - 1 \right)$$

where $\theta$ is the angle between the long molecular axis and some external reference, such as the direction of an applied electro-magnetic field, for example. For perfect alignment of molecules parallel to an external reference, $S=1$; for a completely random isotropic phase, $S=0$; and
The unique structure and unique properties of liquid crystals have stimulated extensive efforts to develop applications of these materials. These materials have so far been used, for example, for disposable thermometers, breast tumor detection, aerodynamic testing, digital readout on various instruments, wristwatch faces, electronic microcircuit testing, solvents in nuclear magnetic resonance spectroscopy, stationary phases in gas-liquid chromatography, toys and decorative materials. The number and type of applications for liquid crystals now appear to be limited only by the imagination, so their future must be very bright.

**Molecular Constitution and Liquid Crystalline Properties**

Good liquid crystalline materials have to have good thermal stability of the mesophase which means a wide temperature range in which mesophase maintained. In addition, a low transition temperature from solid to mesophase would be important for an application of this mesophase at lower temperature and for their convenient
characterization. The state of the mesopnase is also important. According to the application either the cholesteric state, or the nematic state, or the smectic state may be desired. Finally the rheological properties and other physico-chemical properties have to be considered, too.

For formation of liquid crystals, some molecular structural prerequisites must be met including a high length-to-width ratio, anisotropy of the cohesive forces between elongated molecules, a suitable magnitude of these forces and rigidity of the molecules. The following are some guidelines regarding the features of molecular structure that favor liquid crystal formation, many of which are common to both nematic and smectic phase formation [10-15]:

1. The molecule is long relative to its diameter, and flat segments such as aromatic rings, favor liquid crystal formation;

2. The molecule has some rigidity along its long axis; double bonds and ring structures enhance rigidity;
3. The molecule may have strong dipoles and/or easily polarizable groups. Liquid crystal formation is favored if both are present and if the strong dipole is along the molecular axis;

4. The molecule may have weak polar groups at its extremities, although this characteristic is less influential than those listed above;

5. Molecular interactions that favor liquid crystal formation are dipole-dipole interactions, ion-dipole interactions, induced interactions and possibly hydrogen bonding;

6. Anisotropy of the cohesive forces between elongated molecules is essential. If intermolecular forces are very weak, the cohesive forces may be inadequate to maintain order in the fluid state. If the intermolecular forces are too strong, however, the melting point may be elevated to such a high temperature that thermal motion will prevent the existence of the ordered mesophase after melting occurs. Therefore for liquid crystal formation it is essential that the cohesive forces operating between elongated molecules are both anisotropic and of appropriate magnitude.
While these structural requirements are not very difficult to satisfy, it is believed that only approximately 5% of all organic compounds exhibit liquid crystalline behavior, but more and more new liquid crystalline compounds are being specifically prepared in laboratories.

The majority of substances that give liquid crystals on heating are aromatic. Aromatic nuclei are polarizable, planar and rigid, and if suitable substituents are correctly positioned in the aromatic rings, elongated molecules are obtained between which reasonably strong intermolecular forces should operate. For benzene nuclei, substituents must occupy para-positions and be of such a kind that they link up at least one other benzene ring which also carries a para-substituent. It is preferable if the central group which joins the rings is itself of a rigid nature, i.e., the two rings and the central group should constitute a lath- or rod-like core of molecule. Central groups usually contain a multiple bond or a system of conjugated double bonds, or involve a ring formed by dimerization of carboxyl groups.
Thus, many compounds which form liquid crystals fall into the general category represented below,

![Chemical structure diagram](image)

The following are some examples of central groups,

-CH=CH-; -(CH=CH)\textsubscript{2} -; -C≡C-; -CH=N-;

-N=N-; -N=N-; -CH=CH-CO-O-; -CH=N-;

-CO-O-; -(CH=CH)\textsubscript{2} -CO-(CH=CH)\textsubscript{2} -; -CH\textsubscript{2}CH\textsubscript{2} -;

-CH=N-N=CH-; -O-CH\textsubscript{2}CH\textsubscript{2}O-;

The common feature of these linkages is their capability to maintain the linearity and proper rigidity of the molecules.

Changes in these central linkages within a series of molecules can result in great differences in thermal stability of the liquid crystalline phases. Van Meter and
Klanderman [16] compared three series of liquid crystal compounds, the para-substituted dibenzoates, para-substituted diphenyl terephthalates and para-substituted phenyl 4-benzoyloxybenzoates. The results are shown in Table 1.
<table>
<thead>
<tr>
<th>R</th>
<th>OCH₃</th>
<th>OC₂H₅</th>
<th>OC₅H₁₁</th>
<th>C₅H₁₁</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>R©COO©OOC©R</td>
<td>213-297</td>
<td>226-287</td>
<td>145-222</td>
<td>123-186</td>
<td>226-246</td>
</tr>
<tr>
<td>R©OOC©COO©R</td>
<td>205-277</td>
<td>216-267</td>
<td>167-213</td>
<td>152-178</td>
<td>195-226</td>
</tr>
</tbody>
</table>

Table 1. Liquid crystalline properties and molecular central linkage symmetry
These three series of compounds are very similar. The only differences within this series is in the orientation between phenylene rings of the two ester linkages, i.e., -CO-0- and -0-OC-; or -0-OC- and -CO-0-; or -CO-0- and -CO-0-. These small differences, as shown in the table, brought great changes in the thermal behavior of these compounds. The dissymmetry brought by the change in the orientation of linkage of phenyl 4-benzoyloxybenzoates caused a substantial reduction in the solid-mesophase transition temperature. This reduction has been explained by the less efficient packing in the crystal lattice of these compounds. However, because the overall length and molecular geometry are quite similar for each set of the three isomeric compounds, the mesophase-to-isotroic state transition (often referred to as the clearing temperatures) of the respective mesophases are similar, and therefore the nematic range of the phenyl 4-benzoyloxybenzoate liquid crystals is extended significantly resulting in a higher thermal stability of the mesophase of this compound.

Replacement of a terminal hydrogen in a molecule by another substituent enhances the potential of the system to form liquid crystals. If the unsubstituted compound
forms liquid crystals, the substituted one will form liquid crystals which are, in the majority of cases, more thermally stable; only for smectic liquid crystals do certain terminal substituents reduce thermal stability. The role of the terminal substitution is not simply to lower the melting point and reveal liquid crystal behavior latent in the parent system. Indeed, terminal substituents usually raise melting points, but they increase liquid crystal thermal stability even more. It is worth noting here again that terminal substitution must not destroy the linearity or coplanarity of the molecule, and must not raise the melting point too much, or it would prevent liquid crystal formation. Thus, a substitution of terminal hydrogen by hydroxy- or amino- groups is usually unfavorable to liquid crystal formation. Such groups are capable of giving polymeric hydrogen bonding which would raise melting points and may also result in a non-parallel arrangement of the molecule [11]. As an example, 6-hydroxy-2-naphtholic acid does not form liquid crystals whereas the 6-methoxy-2-naphthoic acid does [17].

A common pattern of behavior in various homologous series, as in the case of 4-n-alkoxybenzylidene-4'-aminoazobenzenes, is that the lower homologues are
nematics, the middle members exhibit smectic formation followed by a nematic phase, and the long-chain members are purely smectics [18]. Studies on these homologous series have also shown a steady decrease of the mesophase-isotropic phase transition temperatures with increasing length of the substituents.

The influence on liquid crystalline properties of lengthening the terminal substituents is complex. However, two effects may be involved in decreasing the mesophase-to-isotropic transition temperature with lengthening the substituents. The longer the terminal substituents, the more flexible it will be, and by acting as a diluent, these groups would promote the thermal motion of molecules in the mesophase. This motion, in turn, would destabilize the mesophase. In addition, the intermolecular attraction between mesogens would also be reduced because of this dilution. On the other hand, smectic phase formation apparently requires an intermolecular lateral attractions greater than the terminal attractions of the mesogens. This may be satisfied by lengthening the terminal substituents for a weakening of the terminal attraction between the mesogens.
An unsymmetrical replacement on the two ends of a molecule would be expected to lower the melting point. This has been studied extensively by Haut and coworkers [19]. Their compounds had the following structure:

\[
\text{RO}\bigcirc\text{CO-O\bigcirc}0-\text{OC\bigcirc}\text{OR'}
\]

where R and R' were n-alkyl groups with 1 to 8 carbon atoms. Introduction of dissymmetry by using different R and R' produces the expected melting point depression without lowering the N-I transition temperature very much, consequently the nematic state temperature ranges of the unsymmetrically substituted compounds were always greater than those of symmetrically substituted ones with only one or two exceptions when R and R' were so large that they induce very little dissymmetry into the compound.

Lateral substitution on mesogens has also been studied by several groups of people. Two [14] contradictory effects of this substitution must be considered here: either (1) the long molecular axes of adjacent molecules may be forced apart by the substituent thereby reducing the intermolecular forces of attraction,
which is especially detrimental to smectic phase stability; or (2) substitution of a ring hydrogen of mesogens with a group or a halogen atom could increase lateral intermolecular attractions and enhance liquid crystal thermal stability because the molecular polarizability and the molecular dipolarity can be increased by these atoms or groups.

These effects were first systematically studied by Gray and coworkers for low molecular weight liquid crystalline compounds [20-22]. For example, by introducing a range of substituents into the 3'-position of 4'-n-octyloxybiphenyl-4-carboxylic acid, shown below:

\[
\text{C}_8\text{H}_{17}O\begin{array}{c}
\text{X} \\
\end{array}\begin{array}{c}
\text{C} \begin{array}{c}
\text{O} \\
\end{array} \begin{array}{c}
\text{H} \begin{array}{c}
\text{O} \\
\end{array} \begin{array}{c}
\text{C} \\
\end{array} \begin{array}{c}
\text{OC}_8\text{H}_{17} \\
\end{array} \\
\end{array} \begin{array}{c}
\text{X} \\
\end{array}
\end{array}
\]

they obtained interesting results as shown in Table 2.
### Table 2. Liquid crystal transition temperatures for 3'-substituted-4'-n-octyloxy-biphenyl-4-carboxylic acid

<table>
<thead>
<tr>
<th>3'-substituents</th>
<th>S-N</th>
<th>N-I</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>255</td>
<td>264.5</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>254.5</td>
<td>255.5</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>225</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>214</td>
<td>224</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>192.5</td>
<td>214</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>213</td>
<td>237</td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>214*</td>
<td>214*</td>
<td></td>
</tr>
</tbody>
</table>

**Note:**  
S, Smectic phase  
N, Nematic phase  
I, Isotropic phase  
* S-N transition temperature
These results indicate that in every instance, no matter how big and how polar the substituent was, the substitution of $X$ for $H$ on the aromatic rings of the core part of the molecule decreased the thermal stability of both the smectic and nematic states. By plotting the transition temperature against the molecular breadth or diameter (defined as the diameter of the narrowest cylinders through which the dimerized molecules would pass, and assuming flexible parts such as alkyl chains did not interfere), Fig. 3, they found that the N-I temperatures and S-I temperature for $X=NO_2$ fitted a good relationship (nearly a straight line), indicating that nematic thermal stability decreased regularly as the broadening effect or size of the substituent increased, while the polarities of the substituents had little effect. They concluded from this observation that the forces responsible for maintaining nematic state order were dispersion forces which would decrease rapidly with increasing separation of the long molecular axes.

A different situation was observed with the plot of S-N or S-I temperatures for the same system against molecular diameter. Here a steeply falling curve was drawn only through the points for $X=F,Cl,Br$, and $I$. Lying
Figure 3. Plots of transition temperatures vs. molecular diameters for 3'-substituted 4'-n-octyloxybiphenyl-4-carboxylic acid
below this line were points for H and CH₃, and above this was that for X=NO₂. The dipolar effect was no longer unimportant to smectic phase thermal stability. Halogen atoms have similar polarity so that the stability of halogen atom substituted compounds were decided simply by the broadening effect of these atoms, while for X=H or CH₃ a lower thermal stability exists because C-H and C-CH₃ bonds are of much lower dipolarity. Obviously the nitro-substituted compound had a higher thermal stability for the smectic phase because of the much higher dipolarity of the C-NO₂ bond.

On comparing the two curves in figure 3, a greater slope is seen with curve (b), which is the plot of smectic transition temperature against molecular diameter. This result means that the effect of substitution on smectic thermal stability is greater than that on nematic thermal stability when ring-substituent bonds of like dipolarity are involved. A possible explanation for this observation is that the smectic order depends on, in addition to dispersion forces as for the nematic case, dipole-dipole as well as induced interactions, and all these three interactions will decrease rapidly with increasing separation of the long molecular axes.
More detrimental to the smectic phase than to the nematic phase is the lateral substitution. This conclusion may be further demonstrated by a series of 2-substituted \(4,4'\)-di-(p-n-alkoxybenzylideneamino)-biphenyls, as follows:

\[
\text{ROCH=N-CH=NOR}
\]

Here \(X\) may be H, F, Cl, Br, I, Me and NO\(_2\), which differ in both size and dipolarity [23]. Branch and coworkers [23] found that with any of these substituents the decrease in smectic thermal stability, as measured by the decrease of the corresponding transition temperature, was much greater than the decrease in that property for nematic compounds.

In addition, comparison of the 2- or 2'- substituted compounds with those of 3'-substituted 4'-n-alkoxybiphenyl-4-carboxylic acids reveals that substitution at the 2- or 2'-position has a much greater effect than that at the 3'-position on destabilizing the liquid crystalline thermal stability. Steric interactions, in addition to the molecular broadening
effect, can be used to explain these observations. The presence of a 2- or 2'-substituent in the molecules rotates the rings about the 1,1'-bond, so that the aromatic nuclei are no longer coplanar, as they are in the solid state of biphenyl compounds without a 2- or 2'-substituent. Of course the substituent X will broaden the molecule, but it will also increase the molecular thickness because of this rotation.

Similar results were obtained by Arora and coworkers [24]. A number of 1,4-phenylene bis(4'-alkoxybenzoates) and their methyl substituted homologues were studied, as follows:

![Chemical Structure](image)

Within this series, introducing a methyl group into the phenylene ring resulted in a great decrease in both smectic and nematic thermal stabilities. That for the smectics was greater than that for the nematics; e.g., when R=n-C_{12}H_{25}, the transition temperatures from solid to
smectic, smectic to nematic and nematic to isotropic were
80.2°C, 87.8°C and 136.1°C, respectively, for the methyl
substituent; and 109.1, 155.7, and 171.5°C respectively
for the unsubstituted compound. The decrease in melting
temperature was 28.9°, that for the S-N transition was
67.9°, and that for the N-I transition was 25.4°C.
Furthermore, the unsubstituted compounds had both nematic
and smectic phases when the terminal alkoxy group had 8 or
more carbon atoms, while the methyl-substituted compounds
possessed a smectic phase only after the terminal alkoxy
got 12 carbon atoms. Again these observations can be
explained by the broadening effect, but the effect of a
lateral substituent on the molecular geometry cannot be
ignored. When a substituent is on the central ring, its
position being ortho to the ester linkage, the twisting
around the C-O bond will be different because of the
steric factor of the methyl group as compared to the twist
around the C-O bond. This effect may result in an
unsymmetrical twisting in these molecules and thus further
reduce the coplanarity of the molecules, which in turn,
will decrease the polarizability of the laterally
substituted compounds when compared to the unsubstituted
ones.
It is interesting to compare the effect of a single aromatic methyl substituent on the melting point for a few different mesomorphic materials [25]. The results, shown in Table 3, indicate that the addition of a lone methyl group tends to lower the melting point of a nematogenic compound. Unfortunately, the nematic-to-isotropic transition temperature is also lowered by this methylation.
Table 3. Transition Temperatures of Some Low Molecular Liquid Crystals, °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO</td>
<td>C-N</td>
<td>A=H</td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td>231</td>
<td>179</td>
</tr>
<tr>
<td>HexO</td>
<td>C-N</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>N-I</td>
<td>213</td>
</tr>
<tr>
<td>EtO</td>
<td>C-N</td>
<td>209</td>
</tr>
<tr>
<td></td>
<td>N-I</td>
<td>189</td>
</tr>
<tr>
<td>EtO</td>
<td>C-N</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>N-I</td>
<td>330</td>
</tr>
<tr>
<td>EtO</td>
<td>C-N</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>N-I</td>
<td>134</td>
</tr>
</tbody>
</table>

Note: C-N, Crystal to Nematic phase transition; N-I, Nematic to Isotropic phase transition.
Effects of lateral polysubstitution on liquid crystal thermal stabilities have also been studied [25-27]. This topic can be complicated by the number of substituents, the relative location on the mesogens of these groups, as well as other steric and electronic factors. In general, two substituents, one on each side of the mesogen, will increase molecular breadth and decrease liquid crystal thermal stability. This decreases may be twice as great as that for the corresponding monosubstituted one. Table 4 shows this behavior.
Table 4. Examples of Polysubstitutions of Low Molecular Liquid Crystals

<table>
<thead>
<tr>
<th>Compound</th>
<th>A</th>
<th>B</th>
<th>Temperatur °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtO(\text{\text{COO}}\text{\text{COO}}\text{Bu}</td>
<td>H</td>
<td>H</td>
<td>C-N 124</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N-I 231</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>Me</td>
<td>C-N 91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N-I 179</td>
</tr>
<tr>
<td></td>
<td>Me</td>
<td>Me</td>
<td>C-N 122</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N-I 129</td>
</tr>
</tbody>
</table>

Note: C-N, Crystal to Nematic transition; N-I, Nematic to Isotropic transition.

In summary, introducing molecular dissymmetry by lateral substitution of mesogens will depress melting points of materials but it will also depress the thermal stability of the mesophase of these compounds as much or even more. What is needed is a satisfactory starting compound with as wide a mesophase range as possible and the appropriate melting point. The following compound:

\[ \text{RO}\text{\text{COO}}\text{\text{COO}}\text{\text{OOC}}\text{OR} \]
has proved to be a suitable one for this requirement [19], but many others can be recommended also.

Liquid Crystalline Polymers

In the early 1930's, Vorlander [28] mentioned the possibility of preparing liquid crystalline resins and lacquers. Elliott and Ambrose [29] were first able to describe in detail the birefringence of solutions of rigid, helical macromolecules of biological origin, in 1950. A few years later, Flory, in one of his classic papers [30], predicted the phase separation of a polymer solution at a critical concentration for polymers with rigid rod shapes into an isotropic and an anisotropic nematic phase based on statistical treatment using a modified lattice model. He claimed [31] that the random disorder characteristic of the more commonplace synthetic polymers in the amorphous state required a minimum degree of chain flexibility. For chain molecules failing to meet this requirement, an ordered phase or liquid crystalline domain will occur. This theoretical treatment was confirmed by Hermans's experiment [32] with poly(r-benzyl-L-glutamate), which is rod-like in some solutions
because of helix formation. Since the 1970's an increasingly large number of liquid crystalline polymers have been synthesized. The development of "Kevlar" [33-34], the aramide fibers of high strength and very high modulus manufactured by the du Pont Company, has no doubt set a mile-stone for the development of liquid crystalline polymers.

Flory's theory has been extended to the limiting case when no solvent is present. Di Marzio [35] pointed out that for the case of stable lyotropic phases of rigid-rod-like molecules, the solvent molecules can be withdrawn and replaced by flexible polymers. The theory should still be valid, even if the flexible polymers are attached to the ends of rigid rod-like molecules, which results in the creation of thermotropic liquid crystalline polymers with both flexible and rigid segments.

To make thermotropic liquid crystalline polymers, mesogenic or potential mesogenic units can be either (1) "locked into" macromolecules by crosslinking reaction; or (2) grafted onto polymer main chains; or (3) placed along the backbone of the chains. Crosslinked liquid crystalline polymers, side-chain liquid crystalline polymers and main-chain liquid crystalline polymers are
Figure 4. Schematic structures of liquid crystal polymers
thus obtained. These three types are represented in Fig. 4.

Crosslinked liquid crystalline polymers have been reviewed by Shibayev [36] and an early example is that of Herz. In 1963, he succeeded in "locking in" the organization of the 11-sodium styrylundecanoate-water system [37]. Divinyl benzene was used as cross-linking agent, which was essential to insure the stability of the organized phase of the polysoap well beyond the range of temperatures and compositions of thermodynamic stability for this phase. Further investigations by Blumstein [38], Strzelecki [39], Bouligand [40] and others have revealed that a perfect retention of nematic, smectic, and cholesteric organizations of the monomeric phase can be achieved if large amounts of cross-linking agents are added. Nematic phases were locked into cross-linked networks with the monomer acryloyloxybenzylidene-p-bromoaniline, shown below:

\[ \text{CH}_2=\text{CHCOO} \bigcirc \text{CH}=\text{N} \bigcirc \text{Br} \]

Nematic and smectic phases were obtained with polymers derived from monomer bisacryloyloxybenzylidene-
p-diaminobenzene, shown below:

\[ \text{CH}_2=\text{CHCOO} \quad \text{CH}=\text{N} \quad \text{N}=\text{CH} \quad \text{OCCH}=\text{CH}_2 \]

Smectic phases were obtained with polymers derived from the following monomer:

\[ \text{CH}_2=\text{CHCOO} \quad \text{CH}=\text{N} \quad \text{CH}=\text{CHCOOCH}_3 \]

and cholesteric phases were obtained from terpolymers of mono- and di-acrylic Schiff bases and cholesterylacrylate. In all of these instances large amounts of cross-linking agents were required to provide fast and extensive cross-linking and prevent the detrimental chain relaxation of the ordered nascent macromolecules.

i) Side-chain liquid crystalline polymers.

The persistence of mesomorphic order in a polymer is not limited to insoluble and infusible cross-linked networks [41]. A large number of mesomorphic (or potentially mesomorphic) monomers of the type \( \text{H}_2\text{C}=\text{CRR}' \) or \( \text{H}_2\text{C}=\text{CHR} \), have been synthesized. These monomers were divided into five categories by Blumstein according to the type of the side group \( \text{R} \): monomers with long linear hydrocarbon
chains such as olefins, alkyl ethers and esters; derivatives of benzoic acid; Schiff base derivatives; derivatives of steroids; and miscellaneous monomers including biphenyl esters, azoxybenzene derivatives and many others. The monomers are not necessarily mesomorphic, long chain \( \alpha \)-olefins are examples of the non-mesomorphic monomers. The long side groups of the polyolefins crystallize easily. Above the crystalline melting point a large degree of order is still preserved and layered liquid crystalline structures are formed. Plate and Shibayev [42] established the layered ordering structure of these comblike polymers with X-ray and electron diffraction techniques. Two important spacings were observed above the melting points of these polymers. The wide angle spacing of 4.6 to 5.0 Å, which is independent of the length of the side group, was attributed to the distance between side groups. The second spacing was at small angles and increased regularly with the length of the alkyl moiety in the side group. It was attributed to the distance between the strata that confine the macromolecular backbones.
In a side-chain liquid crystalline polymer, important interactions exist between the mesogenic side chains and the flexible main chain: side chains tend to adapt an ordered state, while the main chain, to which the side chains are attached, tends toward a statistical conformation. This situation was realized and carefully described by Finkelmann and coworkers [43].

If the rigid rod-like mesogenic groups are directly coupled to the polymer main chains, the anisotropic ordering of these groups will be prevented by the statistical movement of the main chains. However, this action can be decoupled by introducing a flexible spacer between the main chain and its side group. In this way the side groups are little affected by the motion of main chain, and an ordering among these groups is no longer impossible, Fig.5. [44].

From these considerations a direct conclusion may be drawn that the liquid crystalline behavior of a side-chain liquid crystalline polymer is not decided only by the mesogenic side groups themselves, but the nature of the main chain and flexible spacers are also play a great part in it.
Figure 5. Linkage of the mesogenic side chain to the main chain
Influence of the mesogenic group. Small changes in mesogenic groups may cause a great change in the mesogenic state of polymers. Finkelmann and coworkers [44] studied systematically the influence of mesogenic groups on side-chain liquid crystalline polymers having the following general structure:

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2 - \text{C} \\
\text{COO(CH}_2)_n \text{O} & \text{C}_2 \text{O}_2 \text{COO} \text{R}
\end{align*}
\]

For \( n=2 \), a drastic change occurred with a change of \( R \) from methyl to methoxy; the former exhibited no liquid crystallinity and the latter had a nematic phase. In general, a temperature range broadening of the mesophase was observed when an alkyl substituent was replaced by an alkoxy group, and when the chain length of the substituent was increased. The same correlations were observed in low molecular weight liquid crystals [45]. This result means that after decoupling from the main chain by flexible spacers, the mesogenic groups are free and independent in their own organization.
Other polymers with different main chain structure were also studied. Finkelmann and Rehage [46] synthesized a series of polysiloxanes with mesogenic side groups. They found no mesophases occurred with biphenyl derivatives. However if pendent benzoic acid groups and 4-substituted phenyl esters were linked as mesogenic groups instead of biphenyl moieties, homopolymers which exhibited a liquid crystalline phase at room temperature were obtained. Among these the methoxy substituted one had a nematic state between 288 K and 334 K, while the hexyloxy one was smectic and had a higher clearing temperature. The cyano-substituted one was also smectic at room temperature. The type of the liquid crystalline phase of these polymers was determined by the substituents of the mesogenic moiety.

Para-substituted benzyldiene-p-aminostyrenes present another example. Cyano-substituted monomer results in a polymer with a nematic mesophase [47], while the butoxy monomer makes a smectic polymer [48].

Magagnini and coworkers [49] investigated the liquid crystalline behaviors of polyesters with similar structures, as follows:
None of these monomers exhibits mesomorphism. Among the polymers only poly(p-biphenylacrylate) and poly(p-cyclohexylphenylacrylate) displayed smectic organization. It is difficult to understand the destruction of smectic arrangements of side groups upon inversion of the order of atoms in the ester linkage, from poly(biphenylacrylate) to poly(vinyl-p-phenylbenzoate). However, a replacement of one phenyl ring by a cyclohexane ring could be tolerated by the polymer without collapse of the smectic organization. Replacement of the phenyl ring by an azophenyl group also lead to highly organized polymers. Copolymers of p-biphenylacrylate and p-cyclohexylphenylacrylate had the same type of layered
morphology as the homopolymers [50].

**Influence of polymer main chain and flexible spacers.**

Very few polymers show liquid crystalline behavior when no flexible spacers exist between the mesogenic side groups and the main chain because of the coupled motion of these side groups by the main chain as stated above. However different situations occur if the flexible spacers are present, and the main chain can act as a promoter for side chain organization. A more highly ordered phase is often observed in such polymers than in their monomers. Nematic polymers may be prepared from non-liquid crystalline monomers, and a nematic monomer may result in a smectic polymer. Good examples for this effect of the main chain on stabilizing the mesophases of the side groups may be observed from Finkelmann and Rehage [46], see Table 5. These results show the influence of polysiloxane main chain in promoting the organizational order of side chains. Monomer (a) and (c) have no mesophases, but their polymers show a nematic and a smectic phase, respectively. Nematic monomer (b) forms a polymer with a smectic mesophase at room temperature, while the cholesteric monomer (d) forms a smectic polymer.
Table 5. Phase Transition of the Vinyl Monomers, CH$_2$=CH-R, and the Corresponding Polymers* 

<table>
<thead>
<tr>
<th>R</th>
<th>Transition Temp.°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>monomer</td>
</tr>
<tr>
<td>(a) -CH$_2$OOCOOCH$_3$</td>
<td>k362i</td>
</tr>
<tr>
<td>(b) -CH$_2$OOCOOHex</td>
<td>k334n350i</td>
</tr>
<tr>
<td>(c) -CH$_2$OOCOCN</td>
<td>k376i</td>
</tr>
<tr>
<td>(d) -CH$_2$COO-Chol</td>
<td>k356ch371i</td>
</tr>
</tbody>
</table>

Note: * crystalline n = nematic
s = smectic i = isotropic
g = glassy ch = cholesteric

* -[Si(CH$_3$)$_2$-O]-
 CH$_2$CH$_2$-R
This effect of the main chain may be used to explain the difficulty in making a cholesteric polymer from a chiral monomer [51]. It was found that the cholesteryl ester of the following general structure:

\[
\text{CH}_2=\text{C(\text{CH}_3}\text{)CONH(\text{CH}_2)_n\text{COOC}_7\text{H}_{45}}
\]

always results in a smectic homopolymer. However, the cholesteric structure of the monomer may be locked into the polymer by cross-linking agents [47, 52]. On the other hand, Finkelmann and coworkers [53] were able to obtain cholesteric copolymers from a nematogenic monomer which formed a nematic homopolymer, and a chiral monomer by the "introduced cholesteric" technique.

A series of liquid crystalline polysiloxanes was made by Finkelmann and Rehage [54] to study the optical properties of cholesteric phases of these polymers and thereby to evaluate the mobility of the mesogenic side groups. They found that all of their polymers formed the Grandjean texture spontaneously, which reflected circularly polarized light. In contrast to low molecular weight cholesteric phases, however, there were remarkable
differences in the time needed for the formation of a unique texture. The copolymer with a spacer of six carbon atoms showed the reflection colours immediately after preparation. While one with 3 carbon atoms had to be annealed up to 20 hours before the texture formation. This result shows qualitatively the increasing influence of the polymer main chain upon the orientation of the mesogenic moieties with decreasing length of the flexible spacer. Their quantitative measurements of the helical twisting power (htp) of these induced cholesteric phase have also shown the decoupling effect of flexible spacers. Increasing hindered motions of the mesogenic groups, due to a decreasing length of the flexible spacer, results in an increasing twisting power. The optical properties of the polymers tend towards the optical properties of the corresponding low molecular derivatives with increasing length of the spacer.

ii) Main-chain liquid crystalline polymers.

Mesogens or potential mesogens may be placed directly into polymer main chains. Thus main-chain liquid crystalline polymers can be obtained, as shown in Fig.4. This organization is generally achieved by polycondensation reactions. In contrast, addition polymerization is
extensively used to make side-chain liquid crystalline polymers. Like other kinds of liquid crystals, main-chain polymeric liquid crystals may be classified as lyotropic and thermotropic. Although some polymers have been found to exhibit both lyotropic and thermotropic behaviors, the lyotropic polymers have in most cases amide linkages in the main chains, while the latter type are generally polyesters.

Compared with side-chain polymers in which the mesophase orientation is essentially perpendicular to the main chain, a main-chain liquid crystalline polymer has its main chains aligned along the same direction of the mesophase. In other words, in a perfect mesophase the polymeric molecules are forced to take a parallel alignment by the interactions among the mesogens in the polymer chains. This alignment offers a chance for macromolecules to exhibit their maximum anisotropic properties mechanically, optically, or electrically, and so forth. This situation is, of course, of great interest to us when we realize from theoretical calculation that even the "flexible" polyethylene can exhibit a very, very high elastic modulus of up to 2900g/denier if the molecules are organized such that their molecular axes are
all parallel to each other. As a matter of fact, by spinning aromatic polyamides from the mesophase state Du Pont has been able to make fibers having initial moduli of greater than 1000g/denier, as, for example, in their well known high-strength/high-modulus "Kevlar" fibers [55-56].

After the discovery of "Kevlar" fibers a great deal of effort has been put into searching for polymers which have the high performance of "Kevlar", but which can be formed from the molten state by melt spinning instead of solution spinning as required for "Kevlar". For this purpose the thermotropic main-chain polymers must have suitable melting temperatures, above which stable ordering states can exist without thermal degradation occurring.

The idea of making such a polymer from hydroquinone and terephthalic acid is logical but not successful. The melting temperature of the resulting poly(p-phenylene terephthalate) is so high (467°C) that no liquid crystal phase can possibly form before the decomposition of the polymer.

To lower the melting point the symmetry, rigidity and linearity of the molecules may be lowered. Several approaches have been employed for this purpose: (a) using
unsymmetrical monomers; (b) copolymerizing with some non-linear comonomer units; (c) introducing flexible spacers between two mesogenic units; and (d) using lateral substitution of mesogens or spacers.

In Table 1 is shown the influence of an unsymmetrical linkage in low molecular liquid crystals. The melting points are remarkably depressed by this dissymmetry, but the mesophase-to-isotropic transition is little affected. The situation should be similar with polymeric liquid crystals. But unfortunately the shortage of available published data makes this comparison very difficult. Nevertheless, Lenz and coworkers [57-58] have made two series of polyesters with the following general structures:

\[ -(CH_2)_n-O-\bigcirc-\bigcirc-\bigcirc-OOC-\bigcirc-COO-\bigcirc\bigcirc-0]- \quad (1) \]

\[ -(CH_2)_n-OOC-\bigcirc-OOC-\bigcirc-COO-\bigcirc-COO]- \quad (2) \]

Although in series (2) the mesogenic unit is longer than that in series (1), which is expected to enhance the mesophase stability, the dissymmetric substitution on the two benzene rings in (2) resulted in larger decreases in
both the solid-to-mesophase transition and the mesophase-to-isotropic transition. The results are shown in Table 6.

Table 6. Effect of unsymmetric linkage of the mesogens on the main-chain liquid crystalline polymers

<table>
<thead>
<tr>
<th>Polymer (1)</th>
<th>n=6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p. °C</td>
<td>267</td>
<td>239</td>
<td>245</td>
<td>229</td>
<td>237</td>
</tr>
<tr>
<td>T(i) °C</td>
<td>330</td>
<td>326</td>
<td>278</td>
<td>298</td>
<td>265</td>
</tr>
<tr>
<td>Polymer (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m.p. °C</td>
<td>227</td>
<td>176</td>
<td>165</td>
<td>174</td>
<td>220</td>
</tr>
<tr>
<td>T(i) °C</td>
<td>290</td>
<td>253</td>
<td>220</td>
<td>233</td>
<td>267</td>
</tr>
</tbody>
</table>

A similar observation was made by Blumstein and coworkers for the following polymers [59]:

-\([\text{OOC-}(\text{CH}_2)_n\text{-COO}]-\) \(\text{CH}=\text{CH}\) - , m.p. 203 °C

-\([\text{OOC-}(\text{CH}_2)_n\text{-COO}]-\) \(\text{CH}=\text{N-}\) - , m.p. 152 °C

Both polymers were smectic above their melting points, but a simple change of CH to N, even though the molecular
polarity and the molecular interactions may have been enhanced, depressed the melting point considerably, probably because of the increased dissymmetry in the mesogenic units.

By decreasing the linearity of mesogens through introduction of non-linear comonomers, a decrease should be observed in the melting point as well as in the mesophase thermal stability. For example, Jin and coworkers [60] studied the thermal behaviors of copolyterephthalates of chlorohydroquinone and bisphenol A. They found the melting point was decreased by the inclusion of bisphenol A and only 40% of this non-linear comonomer could be tolerated before liquid crystallinity was lost. Other non-linear comonomers had a similar influence although the liquid crystal organization had different tolerances to different comonomers. Here the stereogeometry of the bisphenol which was copolymerized seemed to be far more important than polar effects imparted by the type of substituent connecting the two phenolic rings in the bisphenols. Larger substituents (as in bisphenol A), which caused more deviation from linearity and coplanarity of the succeeding aromatic rings, could more effectively disrupt the rigid rod-like
structure of the polymers, thus destroying their thermotropic nature.

The effects on liquid crystal properties of flexible spacers have been extensively studied by several groups. Various polymer systems have been used for this purpose and some general conclusions may be drawn from these studies.

The flexible spacers generally used are polymethylene, poly(ethylene oxide) and polysiloxane. The great flexibility of the siloxane chain was expected to greatly depress the melting points of the polymers, but it was also found to reduce the liquid crystallinity drastically [61]. The poly(ethylene oxide) chain is more polar and more flexible than the polymethylene spacer due to the incorporation of oxygen atoms, therefore, it was expected to have a different effect on polymer mesophases from that of polymethylene. However, both Meurisse [62] and Ober [63] found these two spacers had essentially the same effect. With polyesters from di-n-propyl-p-terphenyl-4,4'-carboxylate and either linear aliphatic diols or "ether diols", the effect of -(CH\(_2\))- segments and -(CH\(_2\)CH\(_2\)O)- segments on the mesophase-isotopic liquid transition temperature was nearly identical. The same
conclusion was obtained for polyesters containing triad aromatic ester mesogens, there the oxygen in the -(CH₂CH₂O)- segments appeared to be equivalent stereochemically to a methylene unit.

The length of the spacers is very important in decreasing the transition temperatures. Roviello and Sirigu [64] systematically studied the spacer length effect on polymers. Their first series was an azide phenyl ester which had the following structure:

\[\text{CH}_3\]
\[-\text{[O}\text{-C=N-N=C-}\text{OOC-(CH}_2\text{)}_n\text{-CO]}\]
\[\text{CH}_3\]

It was found with these polymers that the isotropic transition temperature decreased in both even numbered and odd numbered series with increasing carbon atom number \(n\), but the curve drawn for polymers with spacers of even numbers was above for the odd numbers. Therefore, the odd-even effect was observed. The same effect was also observed in two other polymer series [65], there the
Isotropic transition temperatures decreased in an odd-even manner with increasing spacer length. Also in an odd-even fashion the melting temperatures at first decrease and then level out with increasing the length up to about 14 atoms of the spacer.

Another interesting example of showing this odd-even effect was that observed by Ober and coworkers [57]. With their aromatic polyesters they found the melting points as measured by DSC and TOA decreased regularly in a zig-zag fashion as the number of methylene groups increased to 7 or 8, after which it seemed to increase at longer flexible spacer lengths. The polymer with an even number of methylene groups in the spacer had higher melting points than those with odd numbers. The even-odd fashion was again observed with clearing temperatures of these polymers, although with a lower dependence on spacer length than with the melting temperatures. 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.
Others who also studied the spacer length effects and may be mentioned here are Strzelecki and coworkers [66], and Griffin and coworkers [67]. For polymers with different mesogenic groups they were able to obtain similar results by changing the flexible spacer length.

The morphology of polymeric liquid crystals may also be changed by introducing flexible spacers. A textural change from the nematic to the smectic state with increasing length of the spacer was observed by Luyen [66] and Lenz [60]. The situation seems to be similar to the case of low molecular weight liquid crystals. Increasing the length of terminal substituents may cause a series of morphological changes of the molecules from the isotropic melt (without substitution) to nematic (with short substituents), then to nematic and smectic (with intermediate substituents) and finally one or several smectic phases (with even longer substituents). With their liquid crystalline "triad" aromatic polymers, Lenz and coworkers found a nematic phase existed in polymers with a short spacer, while those with seven or more methylene groups had a smectic phase. In Luyen's polymers a nematic phase was observed with those having a flexible spacer of 5 or less carbon atoms, and with increasing
spacer length two mesophases occurred. Finally if the spacer had 10 or 11 atoms, two smectic phases and one nematic phase were obtained. Evidently the longer spacers provided greater independence of organization for the mesogenic units in the polymer chain, so a more ordered mesophase could be formed. However, the spacer chains do not always help the ordering of mesogenic units. If the spacer is too great in length it can dilute the concentration of mesogens to such a content that no mesophase could be organized. Ober [63] found the weight fraction of spacers that could be tolerated by a mesophase was about 0.5.

Copolymerization of two monomers with different length spacers may result in larger effects of lowering transition temperatures. Roviello and Sirigu [68] studied the thermotropic behavior of homo- and co-polyalkanoates of 4,4'-dihydroxy-α, α'-dimethylbenzalazine having the following structure:

\[
-\left[\begin{array}{c}
\text{OCC-(CH}_2\text{)}_n\text{-COO}-
\end{array}\right]
\]

\[
/ \quad / \quad \text{CH}_3 \quad \text{CH}_3
\]
where \( n = 6 \) or 10 for homopolymers, and \( n = 6 \) (25\%), 10 (75\%) or \( n = 6 \) (50\%), 10 (50\%), and \( n = 6 \) (75\%), 10 (25\%) for three copolymers. It was found that while the melting temperature went through a minimum value for the 50/50 composition, the clearing temperature decreased regularly as the content of octanoyl groups decreased. As a consequence, the thermal stability range of the liquid crystal phase was wider for the copolymers than for the homopolymers with a maximum for the 50/50 composition.

The same behavior was observed by changing the combination of two flexible spacers in Blumstein's [69] azoxy-copolymers. The melting temperature had a minimum value at a 50/50 combination, and the clearing temperature decreased steadily with increasing content of the monomer having the longer spacer.

The 50/50 copolymer made by Griffin and Havens [67] had the following structure:

\[
-\left[\text{OC(O-C(CH_2)_x-O-COO-C(CH_2)_y-O(O)}\right]-
\]

In each series of copolymers with \( y = 6, 8, \) or 10 the nematic to isotropic transition temperatures decrease in a
zig-zag fashion with an increasing value of $x$. However, the melting temperature changes have not been discussed.

In summary, flexible spacers play a very important part in forming mesophases. Without any spacer, rigid rod polymers may not be able to maintain ordered mesophases above their very high melting points. However, as Ober [63] stated, the flexible spacer did more than simply allow the mesogenic groups to order into a mesophase by "decoupling" their activities from the rest of the main chain. The flexible spacer, in other words, very much determined the nature of the resulting mesophase. Ober's review offers a consultative discussion of this aspect.

The most important constitutional factor in formation of liquid crystals is, of course, the "core" of the molecules. That is, the "mesogenic units". Just as with low molecular weight liquid crystals, the mesogenic units in a polymer main chain are required to have a certain degree of rigidity, linearity, coplanarity and axial ratio. Factors that depress these properties will depress the thermal stability of the mesophases. Introducing non-linear comonomers is used in order to lower the linearity, and a flexible spacer can be thought as, on the other hand, to shorten the axial ratio of mesogens.
Further examples are shown in Table 7.
Table 7

Examples of Thermotropic Polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tm</th>
<th>Ti</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1), -[OOC(\text{--CH}\cdot\text{--COO-(CH}_2\text{)}\text{)}_6\text{]}-</td>
<td>209</td>
<td>229</td>
<td>[62]</td>
</tr>
<tr>
<td>(2), -[OOC(\text{--CH=CH}\cdot\text{--COO-(CH}_2\text{)}\text{)}_6\text{]}-</td>
<td>238</td>
<td>256</td>
<td>[62]</td>
</tr>
<tr>
<td>(3), -[OOC(\text{--CH}\cdot\text{--COO-(CH}_2\text{)}\text{)}_6\text{]}-</td>
<td>235</td>
<td>255</td>
<td>[62]</td>
</tr>
<tr>
<td>(4), -[OOC(\text{--OOC\text{--O-(CH}_2\text{)}_10\text{]}-</td>
<td>185</td>
<td>212</td>
<td>[67,70]</td>
</tr>
<tr>
<td>(5), -[OOC(\text{--CH=CH}\cdot\text{--COO-(CH}_2\text{)}\text{)}_10\text{]}-</td>
<td>197</td>
<td>200</td>
<td>[62]</td>
</tr>
<tr>
<td>(6), -[OOC(\text{--CH}\cdot\text{--COO-(CH}_2\text{)}\text{)}_10\text{]}-</td>
<td>256</td>
<td>311</td>
<td>[62]</td>
</tr>
<tr>
<td>(7), -[OOC(\text{--OOC\text{--COO-(CH}_2\text{)}_10\text{]}-</td>
<td>237</td>
<td>265</td>
<td>[58]</td>
</tr>
<tr>
<td>(8), -[OOC(\text{--COO\text{--O-(CH}_2\text{)}_10\text{]}-</td>
<td>236</td>
<td>294</td>
<td>[58]</td>
</tr>
<tr>
<td>(9), -[OOC(\text{--COO\text{--O-(CH}_2\text{)}_10\text{]}-</td>
<td>258</td>
<td>374</td>
<td>[71]</td>
</tr>
<tr>
<td>(10), -[OOC(\text{--COO\text{--O-(CH}_2\text{)}_10\text{]}-</td>
<td>224</td>
<td>248</td>
<td>[71]</td>
</tr>
<tr>
<td>(11), -[OOC(\text{--COO\text{--O-(CH}_2\text{)}_10\text{]}-</td>
<td>236</td>
<td>294</td>
<td>[58]</td>
</tr>
<tr>
<td>X=H</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>162</td>
<td>274</td>
<td>[58]</td>
</tr>
<tr>
<td>Cl</td>
<td>157</td>
<td>279</td>
<td>[58]</td>
</tr>
<tr>
<td>Br</td>
<td>146</td>
<td>270</td>
<td>[58]</td>
</tr>
<tr>
<td>Phenyl</td>
<td>151</td>
<td>168</td>
<td>[71]</td>
</tr>
</tbody>
</table>

Note: the temperatures are in °C
Table 7. (cont.)

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Tm</th>
<th>Ti</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12), (-[O\text{COO}O\text{OOC}O(CH_2)_0])-</td>
<td>200</td>
<td>255</td>
<td>[58]</td>
</tr>
<tr>
<td>(13), (=\text{NNO}CH\text{CH}]=</td>
<td>-</td>
<td>-</td>
<td>[72]</td>
</tr>
<tr>
<td>(14), (=\text{NNO}CH\text{CH}]=</td>
<td>-</td>
<td>-</td>
<td>[72]</td>
</tr>
<tr>
<td>(15), (-[O\text{C}N\text{N}C\text{OOC}(CH_2)_n\text{CO}]-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n=6</td>
<td>511</td>
<td>568</td>
<td>[64]</td>
</tr>
<tr>
<td>8</td>
<td>476</td>
<td>529</td>
<td>[64]</td>
</tr>
<tr>
<td>10</td>
<td>479</td>
<td>512</td>
<td>[64]</td>
</tr>
<tr>
<td>(16), (-[\text{CH=CH}\text{OOC}(CH_2)_8\text{COO}]-)</td>
<td>203</td>
<td>-</td>
<td>[59]</td>
</tr>
<tr>
<td>(17), (-[\text{CH=C}\text{OOC}(CH_2)_10\text{COO}]-)</td>
<td>184</td>
<td>218</td>
<td>[73]</td>
</tr>
<tr>
<td>(18), (-[\text{OOC}\text{NNOCOO}(CH_2)_10]-)</td>
<td>198</td>
<td>No</td>
<td>[69]</td>
</tr>
<tr>
<td>(201)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(19), (-[\text{COO}\text{NNOCOO}(CH_2)_10]-)</td>
<td>216</td>
<td>265</td>
<td>[69]</td>
</tr>
<tr>
<td>(20), (-[\text{COO}\text{NNOCOO}(CH_2)_10]-)</td>
<td>118</td>
<td>163</td>
<td>[69]</td>
</tr>
<tr>
<td>(21), (-[\text{COO}\text{NNOCOO}(CH_2)_10]-)</td>
<td>142</td>
<td>165</td>
<td>[69]</td>
</tr>
</tbody>
</table>

Note: The temperatures are in °C.
Polymer 18 in this Table shows again how difficult it is to predict the thermotropic behavior of a polymer from its structure. This polymer has no mesophase after melting. However an inversion of the ester linkage of this polymer results in polymer 19, which exhibits a good nematic range of from 216 to 265°C.

A very interesting aspect that can be seen in Table 7 is the influence of substitution on mesogenic units. Reviewing the results of studies on low molecular weight liquid crystals it is known that substituents act to lower the coplanarity of mesogens and to thicken, and therefore, to shorten the axial ratio of the mesogens. In addition, an ordering arrangement among the mesogens becomes more difficult because the side groups are trying to push the mesogens apart from each other to meet their own steric requirements. However, the increased polar interactions caused by the substitution may be also counted.

The earliest substituted main chain thermotropic liquid crystalline polymers reported in the literature was that of Roviello and Sirigu [64], see Table 7, polymer 15. Here two methyl groups are attached to the mesogenic unit. However, although the authors' initial goals were apparently not to evaluate the substitution effect, no corresponding unsubstituted polymers was reported, so that
a discussion of the substitution effect on this polymer system is impossible. The first published work which was designed to study the substitution effect on lowering the melting temperature of main-chain thermotropic polymers may be that from du Pont [74]. Their polymers were prepared in the melt by transesterification of dicarboxylic acid and diacetates of chloro-, bromo- or methyl-substituted hydroquinones. The use of monosubstituted hydroquinones in random copolymers resulted in a depression of the melting temperatures of these polymers and allowed a melt-spinning process to be carried out on them from their liquid crystalline state. Later, Millaud and coworkers [72] found that the high melting temperature of their aromatic polyazomethine could be lowered by introducing a methyl group onto the phenylene diamine rings, as shown in Table 7, polymers 13 and 14, to help the formation of a thermotropic mesophase.

Other examples listed in Table 7 are 16 and 17 of Blumstein [59] and Sirigu [73]; 19, 20 and 21 of Blumstein and coworkers [69]; and 11 of Lenz and coworkers [58, 71].
A good comparison of substitution effects among different side groups has been that in the work of Lenz. Melting points of these polymers were all depressed by 60-70 degrees by these substitutions. It seems however that the isotropization temperature is less affected unless a large side group, phenyl, is used. Catala and Lenz [75] very recently synthesized a series of alkyl substituted poly(1,4-phenylene terephthalate)s in order to lower the transition temperatures of the parent polymer (m.p. 467°C) and to help correlate the structure with the liquid crystalline behavior of the polymers. By changing the length of the alkyl group on the phenylene ring from hexyl to dodecyl group, they found the melting point and the isotropic transition temperature decreased with increasing side chain length.

Thermotropic polymers with substituents on flexible spacers have been made by Meurisse and coworkers [62], and also by Ober [63]. In Meurisse's terphenyl polymers a replacement of flexible -(CH₂)- or -(CH₂CH₂O)- by branched aliphatic chains -CH₂CX₂CH₂- substantially reduced both the melting and clearing temperatures. This effect was much more pronounced as the substituent size was increased. It seems that similar effects exist for substituents no matter whether the side groups are on the
mesogens or on the spacer. However, it may be questionable to use the unit: \(-\text{CH}_2\text{CX}_2\text{CH}_2\)- as a "flexible" spacer because it is so short. Therefore, the poly(propylene oxide) spacers used by Ober may be a better example. In a real "flexible" spacer, replacement of hydrogen by a methyl group (from a polyethylene oxide to a polypropylene oxide chain) resulted in very little adverse effect on the formation of a mesophase.
Because of their potential importance to both theory and practice, no sooner was the first thermotropic liquid crystalline polymer reported [76] than a great deal of effort was put into research on the preparation of new liquid crystal polymers with desirable properties and to find out the structural parameters which control their properties. In this and the following chapters we will introduce our newly synthesized thermotropic polyesters and discuss the structure-liquid crystalline property relationships basically in terms of substituent effects. Most of our polymers have fairly low melting temperatures and considerable mesophase stability, and it is also possible to obtain a quenched mesophase, very likely a nematic phase, at room temperature for at least one sample, polymer-2. This possibility offers not only convenience for their study, but it also offers a potential state of interest for their applications.
As discussed in chapter I, in order to form liquid crystals, some molecular structural requisites must be met, including: anisotropy of the cohesive forces between elongated molecules, a suitable magnitude of these forces, and the proper rigidity of the molecules [77].

The formation of a liquid crystal requires that the crystal breaks down in stages on heating, because a liquid crystal has a positional and/or an orientational order in between the three dimensional order of crystal and the disorder of an amorphous isotropic liquid. A stage-wise break down of the crystal depends upon a pronounced anisotropy of the cohesive forces which maintain the order in the crystal, and on heating these forces may weaken more readily in certain planes or directions than in others. This anisotropy requires, in turn, the existence of an anisotropy in the geometry of the molecule; that is, the molecules must be elongated and lath-like, or rod-like in shape.

The intermolecular attractions must not, however, be either too strong or too weak. If they are too strong, the melting point of the crystals may be so high that thermal motion prevents the existence of an ordered liquid crystalline phase after melting occurs. If the
intermolecular forces are very weak, on the other hand, it may be impossible to maintain the order in the fluid state even though the melting temperature may be lower.

In chapter I the relationship of molecular constitution and liquid crystalline behavior of low and high molecular weight molecules was discussed with examples. The constitutional aspects were essentially discussed in terms of the mesogenic cores for low molecular weight molecules: the rigidity, linearity, coplanarity, axial ratio, terminal and lateral substitutions, and so on. Studies on low molecular liquid crystalline compounds have offered basic guidance to the studies on high molecular homologues. For the latter, especially for those with mesogens in the main chains, attention has been focussed on how the transition temperatures of rigid-rod polymers can be lowered to some proper region so that their latent thermotropic properties can be revealed and an effective combination of the unique properties of both polymers and liquid crystals may be obtained. Approaches toward this goal have included: (1) the use of asymmetrical monomers; (2) the incorporation of non-linear comonomers; (3) the insertion of flexible spacers between the rigid mesogens; and (4) the
introduction of substituents on the mesogens. Such structural modifications are expected to interfere with the molecular packing in the solid state and thereby decrease the molecular interactions. These interactions would in turn have a great influence on the thermal behaviour of the polymers.

Among the four approaches mentioned in the previous paragraph, the introduction of substituents onto the mesogens has been very interesting but few systematic investigations have been carried out probably because of the great difficulties in introducing on the mesogens suitable substituents. Therefore, the studies described in this and the following chapters represent an approach to the solution of this problem.

A series of polymers with following structures was synthesized:
in which \( X = (\text{CH}_2)_n - \text{H}, \ n = 0, 1, 2, 3, \ldots \)

or \( X = \text{OCH}_3, \ 	ext{Br, CN, NO}_2, \)

The bases for the selection of these structures were:

(a) the mesogenic unit selected had been found to have a good thermal stability in the sense of the temperature range for liquid crystallinity presumably because, with the hydroquinone moiety located in the middle, a good linear and coplanar geometry is obtained \( [78] \) as shown in Fig.6; (b) this unit might be nematogenic \( [79, 19] \) which may be of even higher interest than the smectogenics; (c) with a flexible spacer the polymers will have lower transition temperatures which is desirable for their characterization and potential use \( [60] \); and (d) this unit is versatile for introducing different lateral substituents. By using substituents with different sizes
Fig. 6. Linearity of the polyesters from hydroquinones and 1,10-decane bisterephthaloyl chloride
and / or different polarities and by keeping the other parts of the molecules unchanged it is possible to make an examination of the substituent effects on the liquid crystalline behavior of these polymers.

**Results and Discussion**

i) Polymers and copolymers.

The polyesters were prepared by solution polycondensation reactions of DBTC, 1,10-decane bisterephthaloyl chloride, and the corresponding 2-substituted hydroquinones. Tetrachloroethane and pyridine were used as the reaction solvent and the condensation catalyst, respectively. The resulting polymers and their inherent viscosities are listed in Table 8. Gel permeation chromatography analysis of several of the polymers in THF based on polystyrene standards for calibration, are listed in this table.
### Table 8. Inherent Viscosity and GPC Analysis of Polymers with Substituents on Mesogenic Units

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Substituent</th>
<th>Viscosity</th>
<th>Mw</th>
<th>Mn</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>0.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Methyl</td>
<td>.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ethyl</td>
<td>.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Propyl</td>
<td>.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Butyl</td>
<td>.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pentyl</td>
<td>1.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Hexyl</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Octyl</td>
<td>.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Decyl</td>
<td>.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bromo</td>
<td>.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyano</td>
<td>.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitro</td>
<td>.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methoxy</td>
<td>.63</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**COPOLYMERS**

<table>
<thead>
<tr>
<th>Cyano : Methoxy</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 : 0</td>
<td>0.56</td>
</tr>
<tr>
<td>5 : 5</td>
<td>0.39</td>
</tr>
<tr>
<td>4 : 6</td>
<td>0.27</td>
</tr>
<tr>
<td>2 : 8</td>
<td>0.26</td>
</tr>
<tr>
<td>1 : 9</td>
<td>0.31</td>
</tr>
<tr>
<td>0 : 10</td>
<td>0.63</td>
</tr>
</tbody>
</table>
Copolymers from DBTC and two different hydroquinone monomers with different polar substituents were made by dissolving the two hydroquinones in TCE and reacting the mixture with the diacid chloride, DBTC.

At room temperature these polymers are soluble in halogenic solvents such as chloroform, and tetrachloroethane, with the exception of Polymer-H, the unsubstituted parent polymer of this series, which, however, could be dissolved in p-chlorophenol at a temperature higher than the melting point of this solvent. The polymerization reactions, therefore, were homogeneous (except for the parent polymer), and consequently, the copolymers are presumed to be random.

The structures of the polymers were confirmed by $^{13}$C-NMR spectroscopy, Fig. 7. Elemental analysis were used only for the bromine and nitrogen containing polymers.

In Table 9, 10, and 11 are transition temperatures for the alkyl substituted polymers, the polar group substituted polymers and the copolymers, respectively. For convenience this and the other type of liquid crystalline behavior will be discussed in the followed chapters.
Fig. 7a. $^{13}$C-NMR spectrum of methyl substituted polymer
Fig. 7b. $^{13}$C-NMR spectrum of methoxy substituted polymer
Fig. 7c. $^{13}$C-NMR spectrum of cyano substituted polymer
Table 9. Transition temperatures of polymers with alkyl substituents on mesogenic units

<table>
<thead>
<tr>
<th>No.*</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_g)**</td>
<td>67</td>
<td>44</td>
<td>35</td>
<td>27</td>
<td>35</td>
<td>25</td>
<td>17</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>(T_g***</td>
<td>57</td>
<td>27</td>
<td>24</td>
<td>25</td>
<td>25</td>
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<td>17</td>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>(T_m)</td>
<td>231</td>
<td>154</td>
<td>71</td>
<td>97</td>
<td>75</td>
<td>79</td>
<td>75</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
<td>(T_i)</td>
<td>267</td>
<td>190</td>
<td>127</td>
<td>110</td>
<td>103</td>
<td>94</td>
<td>86</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(T_i-T_m)</td>
<td>36</td>
<td>46</td>
<td>56</td>
<td>13</td>
<td>28</td>
<td>15</td>
<td>11</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Numbers of carbon atoms in the n-alkyl groups of the polymers
** From heating cycle of DSC measurements
*** From cooling cycle of DSC measurements
The temperatures are in °C.
Table 10. Transition temperatures of polymers with polar substituents on mesogenic units

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Tg</th>
<th>Tm</th>
<th>Ti</th>
<th>Ti-Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>44</td>
<td>154</td>
<td>190</td>
<td>36 (°C)</td>
</tr>
<tr>
<td>Ethyl</td>
<td>35</td>
<td>71</td>
<td>127</td>
<td>56</td>
</tr>
<tr>
<td>Bromo</td>
<td>44</td>
<td>140</td>
<td>196</td>
<td>56</td>
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<tr>
<td>Cyano</td>
<td>47</td>
<td>157</td>
<td>219</td>
<td>62</td>
</tr>
<tr>
<td>Nitro</td>
<td>42</td>
<td>161</td>
<td>194</td>
<td>33</td>
</tr>
<tr>
<td>Methoxy</td>
<td>50</td>
<td>158</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 11. Transition temperatures of copolymers from cyano- and methoxy- hydroquinones and DBTC

<table>
<thead>
<tr>
<th>Cyano/methoxy</th>
<th>Tg</th>
<th>Tm</th>
<th>Tm2</th>
<th>Ti</th>
<th>Ti-Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/0</td>
<td>47</td>
<td>157</td>
<td>-</td>
<td>219</td>
<td>62 (°C)</td>
</tr>
<tr>
<td>5/5</td>
<td>42</td>
<td>133</td>
<td>-</td>
<td>177</td>
<td>44</td>
</tr>
<tr>
<td>4/6</td>
<td>45</td>
<td>124</td>
<td>134</td>
<td>165</td>
<td>31</td>
</tr>
<tr>
<td>2/8</td>
<td>37</td>
<td>115</td>
<td>140</td>
<td>157</td>
<td>17</td>
</tr>
<tr>
<td>1/9</td>
<td>39</td>
<td>150</td>
<td>-</td>
<td>154</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>116*</td>
<td>-</td>
<td>-</td>
<td>148*</td>
<td>31</td>
</tr>
<tr>
<td>0/10</td>
<td>50</td>
<td>158</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* From the cooling cycle of DSC thermogram
ii) 1,10-Decane terephtaloyl chloride.

The monomer diacid chloride, DBTC, was prepared by the route shown in Fig. 8. The general procedure used was the same as that reported by Hasslin and coworkers [80]. The elemental analysis results of DBTC and its precursor, DBTA, 1,10-decane terephthalic acid, are given in Table 12.

The infrared spectra of DBTC and its precursors shown in Fig. 9 confirmed the structure change from the diacid to diacid chloride. The O-H stretching vibration of the dimeric acid exhibits a broad band in the 3400 to 2500 cm⁻¹ region (2.94-4.00 μ). This band overlaps the C-H stretching region. The carbonyl frequency of the ester is 1715 cm⁻¹ while that of the acid carbonyl group is at 1690 cm⁻¹, which is much lower than that of the normal monomeric acid (ca 1760 cm⁻¹). The 942 cm⁻¹ broad band is due to O-H out-of-plane bending. In addition to the carbonyl absorption, the characteristic vibrations for the ester groups are found in a region of 1350 to 1050 cm⁻¹ (7.4-9.5 μ). Two strong absorptions appear in this region as a result of the asymmetric and symmetric vibration of the C-O-C group of the ester. The asymmetric band (the higher-frequency band of the two) is stronger
Fig. 8. Preparation of 1,10-Decane Terephthaloyl Chloride
<table>
<thead>
<tr>
<th>Monomers</th>
<th>Yields, %</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBTA*</td>
<td>73</td>
<td>230-32</td>
</tr>
<tr>
<td>DBTC**</td>
<td>90</td>
<td>91-93</td>
</tr>
<tr>
<td>Methyl- hydroquinone</td>
<td>-</td>
<td>127-28</td>
</tr>
<tr>
<td>Ethyl-</td>
<td>57</td>
<td>107-09</td>
</tr>
<tr>
<td>Propyl-</td>
<td>34</td>
<td>89-90</td>
</tr>
<tr>
<td>Butyl-</td>
<td>31</td>
<td>85-87</td>
</tr>
<tr>
<td>Pentyl-</td>
<td>47</td>
<td>85-86</td>
</tr>
<tr>
<td>Hexyl-</td>
<td>36</td>
<td>84-85</td>
</tr>
<tr>
<td>Octyl-</td>
<td>47</td>
<td>95-96</td>
</tr>
<tr>
<td>Decyl-</td>
<td>46</td>
<td>103-04</td>
</tr>
<tr>
<td>Bromo- hydroquinone</td>
<td>-</td>
<td>110-11</td>
</tr>
<tr>
<td>Cyano-</td>
<td>75</td>
<td>170-73</td>
</tr>
<tr>
<td>Nitro-</td>
<td>9</td>
<td>131-33</td>
</tr>
<tr>
<td>Methoxy-</td>
<td>67</td>
<td>87-89</td>
</tr>
</tbody>
</table>

* 1,10-Decane terephthalic acid
** 1,10-Decane terephthaloyl chloride
<table>
<thead>
<tr>
<th>Monomers</th>
<th>Asked %</th>
<th>Found %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>DBTA</td>
<td>66.37</td>
<td>6.43</td>
</tr>
<tr>
<td>DBTC</td>
<td>61.54</td>
<td>5.56 Cl: 13.96</td>
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<tr>
<td>Hydroquinones</td>
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<td></td>
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<tr>
<td>Ethyl-</td>
<td>69.48</td>
<td>7.30</td>
</tr>
<tr>
<td>Propyl-</td>
<td>70.96</td>
<td>8.36</td>
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<tr>
<td>Butyl-</td>
<td>72.29</td>
<td>8.49</td>
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<tr>
<td>Pentyl-</td>
<td>73.22</td>
<td>8.95</td>
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<tr>
<td>Hexyl-</td>
<td>74.19</td>
<td>9.34</td>
</tr>
<tr>
<td>Octyl-</td>
<td>75.63</td>
<td>9.97</td>
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<tr>
<td>Decyl-</td>
<td>76.75</td>
<td>10.47</td>
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<tr>
<td>Cyano-</td>
<td>62.22 N: 10.37</td>
<td>62.41 N: 10.44</td>
</tr>
<tr>
<td>Nitro-</td>
<td>46.45 N: 9.03</td>
<td>46.42 N: 8.87</td>
</tr>
<tr>
<td>Methoxy-</td>
<td>60.00</td>
<td>5.71</td>
</tr>
</tbody>
</table>
Fig. 9a. IR spectrum of DBTA, the precursor of DBTC
Fig. 9b. IR spectrum of DBTC
than the carbonyl stretching frequency and is quite broad. This band is quite characteristic of the ester functional group.

Substitution of a chlorine atom on the carbon atom of the carbonyl group of the acid results in a shift of the carbonyl stretching absorption to a higher frequency. Besides the normal ester carbonyl group absorption, two aroyl chloride absorption bands are seen in the spectrum. The higher frequency band at 1778 cm$^{-1}$ is due to the normal carbonyl stretching vibration, whereas the lower-frequency absorption may be interpreted as being due to conjugative interaction of the aromatic ring with the carbon-oxygen band.

iii) Alkylhydroquinones.

Hydroquinone and methylhydroquinone are commercially available, recrystallizations of these monomers were carried out in toluene.

The other alkylhydroquinones were prepared by the reductive alkylation of benzoquinone with the corresponding trialkyborane [81, 82], as follows:
The preparation of the appropriate trialkylborane was carried out according to published procedures of Brown and coworkers [83], by the hydroboration of alkenes:

\[ 3 \text{CH}_2=\text{CHR}' + (\text{BH}_3) \rightarrow \text{B(CH}_2\text{CH}_2\text{R}')_3 \]

Diborane was generated externally from the reaction of NaBH with BF$_3$-OEt$_2$ in a solvent, diglyme, at room temperature. This reaction has to be controlled by slowly adding into the BF$_3$-OEt$_2$-diglyme solution the NaBH$_4$ solution in diglyme because the reaction is very fast. NaBH$_4$ also reacts with moisture very fast so that the solvent must be very dry before being used. Diborane generation seemed to be the key step to obtain a high yield of the final alkylhydroquinones, involving a high purity of NaBH$_4$, dryness of solvent, and a controlled
reaction rate, which was also required by the next reaction, the hydroboration of alkenes.

Externally generated diborane gas was introduced into the olefin solution in THF. A 25-50% excess of olefin was used to ensure complete conversion to the trialkylborane. The reaction was carried out at ambient temperature. A vigorous stirring was necessary to disperse the diborane gas within the solution. For lower member of the olefins, from C_2 to C_4, because they are gaseous, their well mixing with diborane gas was so important that, if it did not occur, little product was obtained. Therefore these two gaseous compounds should be mixed before being introduced into the ether solvent. After stopping the introducing of diborane, an additional period of about 30 minutes of introducing the gaseous olefin introducing may be necessary to ensure trialkylborane formation. The trialkylborane formed was used in next step reaction without being separated out from the reaction mixture.

The reaction of trialkylboranes with benzoquinone is essentially instantaneous at ambient temperatures and strongly exothermic. 1,4-Benzoquinone, dissolved in THF, was added to the trialkylborane solution instead of the
inverse addition in order to minimize the possible oxidation of the reaction product by benzoquinone. The reaction mixture was then steam distilled to remove solvent, boronic and borinic acids and unused reagents. On cooling, the alkylhydroquinone separated as a crystalline mass in the steam distillation flask. The product was then separated and recrystallized in toluene and/or petroleum. The characterization data for the prepared alkylhydroquinones are collected in Table 12. Also included in Table 12 are the yields of these products based on the starting material sodium borohydride. These results are for the overall yields of three reactions: the diborane generation, hydroboration of the olefin, and the reductive alkylation of benzoquinone, Fig. 10.

IR and NMR spectra of these monomers further confirmed their structures. For a comparison, Fig. 11 shows the IR spectra of hydroquinone and one of the alkylhydroquinones. $^1$H-NMR spectra of these alkylhydroquinones are relatively simple. They are composed of four or five kinds of proton resonance peaks including a triplet at a chemical shift of about 2.50 for the $\alpha$-CH$_2$ protons, and another triplet but at higher field for the methyl protons. The other methylene protons
Alkylhydroquinones

\[
\begin{align*}
\text{NaBH}_4 + \text{BF}_3 & \rightarrow (\text{BH}_3)_2 \\
\text{CH}_2=\text{CHR}' + (\text{BH}_3)_2 & \rightarrow \text{R}_3\text{B} \\
\text{O} &= \text{O} + \text{R}_3\text{B} & \rightarrow \text{HO} \boxed{\text{OH}} \\
\end{align*}
\]

Methoxyhydroquinone

\[
\begin{align*}
\text{HO} \boxed{\text{CHO}} & \rightarrow \text{OH}^{-} & \text{H}^{+} \rightarrow \text{HO} \boxed{\text{OH}} \\
\end{align*}
\]

Cyanohydroquinone

\[
\begin{align*}
\text{CH}_3\text{O} \boxed{\text{OCOCH}_3} & \rightarrow \text{CuCN} \rightarrow \text{CN} \\
\end{align*}
\]

Nitrohydroquinone

\[
\begin{align*}
\text{HO} \boxed{\text{NO}_2} & \rightarrow 0 - 20^\circ\text{C} \rightarrow \text{K}_2\text{S}_2\text{O}_8 \rightarrow \text{KOH} \rightarrow \text{H}^{+} \rightarrow \text{HO} \boxed{\text{NO}_2} \\
\end{align*}
\]

Fig. 10. Synthesis of Substituted Hydroquinones
Fig. 11a. IR spectrum of hydroquinone
Fig. 11b. IR spectrum of ethylhydroquinone
Table 13. Chemical shifts of protons of substituted hydroquinones

<table>
<thead>
<tr>
<th>Substituents</th>
<th>OH</th>
<th>Ring-H</th>
<th>Ring-CH</th>
<th>-(CH₂)⁻</th>
<th>-CH₃</th>
<th>OCH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>7.62</td>
<td>6.76</td>
<td></td>
<td></td>
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<tr>
<td>Methyl</td>
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<td>2.17</td>
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<td>Ethyl</td>
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<td>6.62</td>
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<td>Propyl</td>
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<tr>
<td>Butyl</td>
<td>7.40</td>
<td>6.59</td>
<td>2.53</td>
<td>1.44</td>
<td>0.89</td>
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<td>Pentyl</td>
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<td>6.58</td>
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<td>1.40</td>
<td>0.87</td>
<td></td>
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<td>Hexyl</td>
<td>7.40</td>
<td>6.57</td>
<td>2.50</td>
<td>1.35</td>
<td>0.87</td>
<td></td>
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<tr>
<td>Octyl</td>
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<td>0.83</td>
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<td>1.33</td>
<td>0.85</td>
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<td>Bromo</td>
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<td></td>
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<td>8.78</td>
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<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>7.25</td>
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<td></td>
</tr>
<tr>
<td>Methoxy</td>
<td>7.64</td>
<td>6.40</td>
<td></td>
<td></td>
<td></td>
<td>3.80</td>
</tr>
</tbody>
</table>
Fig. 12. NMR-$^1$H spectrum of ethylhydroquinone
Solvent: Acetone-$d_6$
form a multiplet around a shift of 1.40. Two phenolic hydroxy protons give two peaks at about $\delta = 7.40$. These results are collected in Table 13. As an example, Fig. 12 shows the $^1$H-NMR spectrum of ethylhydroquinone.

iv) Cyanohydroquinone.

Following the procedure of Wallenfels and coworkers [84], this monomer was prepared by the following reactions:

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{CuCN} \\
\text{Br} & \quad \text{H}_3\text{CO} \\
\text{OCH}_3 & \quad \text{CN} \\
\text{AlBr}_3 & \quad \text{HO} \\
\text{OH} & \quad \text{CN}
\end{align*}
\]

The substitution reaction yield was 44%, which is similar to that reported by Wallenfels, who used 1-iodo-2,5-dimethoxybenzene as the starting material. Yield and the characterization results for this monomer are collected in Table 12. Chemical shifts from $^1$H-NMR
analysis of the cyanohydroquinone are shown in Table 13. Because of the strong electron-withdrawing effect of the cyano group, the ring protons and hydroxy protons are all shifted remarkably to the lower field, while those of alkylhydroquinone shifted towards higher field as can be seen in Table 13. Fig.13 is the \(^1H\)-NMR of cyanohydroquinone.

Fig.14 is the infrared spectrum of this monomer. In addition to the broad O-H stretching band at about 3250 cm\(^{-1}\) and other aromatic C-H and C-O absorptions, a characteristic C≡N stretching band at 2230 cm\(^{-1}\) exists. In general, monomeric aliphatic nitriles exhibit a C≡N stretching vibration near 2245 cm\(^{-1}\) (4.45 \(\mu\)). When conjugated with unsaturated linkage including aromatic nuclei, the band is shifted to lower frequencies, 2230 to 2210 cm\(^{-1}\) (4.48 to 4.53 \(\mu\)), and the intensity of the absorption band is increased.

v) Nitrohydroquinone.

This monomer was made by oxidation of o-nitrophenol. The procedure as shown below, follows Baker and Brown [85], as well as that of Fouest and Petrow [86]:
Fig. 13. NMR-\textsuperscript{H} spectrum of cyanohydroquinone
Solvent: Acetone-d\textsubscript{6}
Fig. 14. IR spectrum of cyanohydroquinone
The main side reaction is the formation of 3-nitrocatechol which would be harmful to the liquid crystal formation of these polyesters, if it reacted as a comonomer because its participation in the repeating units would destroy the linearity and coplanarity of the units. Hence, the separation of nitrohydroquinone from 3-nitrocatechol was very important. This separation may be based on the different boiling points or the different solubilities of these two phenols. Extracting with boiling light petroleum ether proved to be a suitable method because nitrocatechol had a higher solubility possibly because of differences in the melting points of the two compounds, 86 and 133 °C, respectively, for nitrocatechol and nitrohydroquinone.

Besides the melting point, the color may be an additional criterion of product certification. Nitrocatechol is yellow, while the nitrohydroquinone is a red crystal. The product yields and the characterization
Fig. 15. NMR-H$^1$ spectrum of nitrohydroquinone
Solvent: Acetone-d$_6$
results for this monomer are listed in Table 12. Fig. 15 is the 'H-NMR of this monomer from which can be seen the strong electron-withdrawing effect of nitro group on the protons.

The infrared spectrum of nitrohydroquinone is shown in Fig. 16. Two absorptions at 1525 and 1335 cm\(^{-1}\) are believed to be for NO\(_2\) stretching vibrations.

vi) Methoxyhydroquinone.

Methoxyhydroquinone was synthesized by the well known Dakin reaction [87], as follows:

\[
\text{HO}_2\text{C} = \text{CHO} \rightarrow \text{HO}_2\text{C} \text{OH}
\]

Results of this preparation are included in Table 12.

The H-NMR spectrum of this monomer is shown in Fig. 17. A shift of the ring-protons to higher field means that the methoxy group is an electron-donating group. The comparison of the chemical shifts for this monomer with that of the other hydroquinones is made in Table 13.
Fig. 17. NMR-H\textsuperscript{1} spectrum of methoxyhydroquinone
Solvent: Acetone-d\textsubscript{6}
Fig. 18a. IR spectrum of methoxyhydroquinone.
Fig. 18b. IR spectrum of vanillin
Fig. 18-(a) and 18-(b) are the IR spectra of this monomer and its precursor, vanillin. The essential difference between these two spectra is the absorption of the carbonyl group at 1675 cm⁻¹, which is not present in the spectrum of the monomer. In addition, a much stronger O-H absorption at 940 cm⁻¹ for this monomer further proved the conversion. In general, since the mass of the oxygen and the strength of the C-O bonds are quite similar to the corresponding carbon-carbon system, it is not unexpected to find a close similarity in band positions between the C-C and the C-O absorptions. However, since the change in dipole is much larger for the C-O vibration, the intensity of the ether absorption band is considerably greater. The determination of the presence of absence of the ether linkage from infrared spectral studies is a difficult task. Nevertheless, the C-O-C asymmetric stretching absorption is observed in the 1275 to 1200 cm⁻¹ region when this linkage is conjugated with an aromatic group, while the symmetric stretching vibration absorbs in the region of 1075 to 1020 cm⁻¹, and this absorption is weaker than the asymmetric stretching vibration absorption. In our spectra two bands at 1238 and 1027 cm⁻¹ are related to the asymmetric and symmetric stretching vibrations. In addition, the methyl group absorptions are also seen in
Experimental

Elemental analyses were performed by the Micro-analysis Laboratory of the University of Massachusetts.

Melting points were measured on a Fisher-Johns type hot stage.

A No.150 Ubbelohde viscometer was used for inherent viscosity measurements of the polymers. With one exception, all the measurements were at 40 °C and at a concentration of 0.5 g/dl in tetrachloroethane. The polymer made from DBTC and hydroquinone had little solubility in TCE, so that p-chlorophenol was employed for this purpose, the temperature of measurement was 50 °C in this special case.

GPC measurements were made on a Waters type instrument. The molecular weight and its distribution were calculated by computer based on polystyrene standards.
A Perkin-Elmer DSC-II was used to examine the thermal properties, including the melting points, liquid crystal-isotropic phase transition temperatures, and the enthalpy and entropy changes during these transitions.

A Varian S-60T $^1$H-NMR was used to obtain the H-NMR spectra of monomers. Acetone-d was used as the solvent and TMS as the internal standard.

IR spectra were made on a Pekin-Elmer IR-203 instrument.

$^{13}$C-NMR spectra of the polymers were obtained on an FT-20 machine. Deuterated chloroform was used as solvent and TMS as the internal standard.

1) Preparation of DBTC.

The monomer 1,10-decane terephthaloyl chloride was prepared by the route shown in Fig.8, which included six reaction steps to prepare the following compounds:

(1). Dibenzyl terephthalate. Terephthaloyl chloride (50 g, 0.25 mole) was dissolved in 250 ml of absolute THF, and benzyl alcohol (61.4 ml, 0.55 mole) was dissolved in 50 ml of pyridine. The acid chloride solution was added dropwise to the alcohol solution with mechanical stirring.
The mixture was stirred overnight at room temperature, then about half of the THF was removed by distillation. The residue was poured into 750 ml Na₂CO₃-ice water. The white crystals were filtered off and washed with dilute HCl and then with water. Recrystallization was carried out in ethanol. (yield 95%, m.p. = 97°C)

(2). Monobenzyl terephthalic acid. Dibenzy1 terephthalate (40 g) was dissolved in 120 ml benzyl alcohol at 55°C. 6.5 g KOH was dissolved in 90 ml benzyl alcohol and cooled to about 30°C. The basic solution was added dropwise to the dibenzyl ester solution within about 1 hour. The temperature increased to about 60°C due to the exothermic heat of reaction. This temperature was maintained for another 1 hour. The mixture was then cooled with an ice bath to about 5°C, and about 80 ml toluene was added. The product was filtered off and washed twice with toluene and dried for several hours at 120°C under vacuum.

The dry product was dissolved in excess water, filtered to remove the unreacted dibenzyl ester. The solution was titrated with 0.1 N HCl to a pH of 5.3. Mechanical stirring was necessary during this time because a large amount of precipitate came out. The pH was set at
5.25, the product was kept overnight at 0°C, then filtered and dried. The solid was dissolved in an equimolar Na$_2$CO$_3$ solution, and the insolubles were filtered. The titration was repeated and the final product was washed thoroughly with water. The product was dried and recrystallized in toluene (yield 67%, m.p. = 180°C).

(3). Monobenzyl terephthaloyl chloride. The halogenation reagent, thionyl chloride, was purified as follows. 16 ml Triphenyl phosphite was added into 100 ml of SOCl$_2$(tech. grade), stirred for several hours and then fractionated (b.p. of SOCl$_2$, 76°C; 210°C/1 mmHg of triphenyl phosphite).

A dry flask with stopper was weighed before being used. The reagents (monobenzyl ester of terephthalate, 20 g; SOCl$_2$, 75 ml; and three drops of DMF) were mixed in the flask and refluxed for about one hour. The excess SOCl$_2$ was removed by vacuum distillation. When the product was partially dried, absolute toluene was added and distilled again (an aspirator was used first, then a vacuum pump at ice bath temperature) to remove all of the SOCl$_2$ and the toluene. (yield 86%, m.p. = 28°C)
(4). Dibenzyl 1,10-decane bisterephthalate. 21.4 g Monobenzyl terephthaloyl chloride was mixed with 20 ml pyridine (dry) and 40 ml dioxane (dry), and the mixture was heated to dissolve the acid chloride. A solution of 6.1 g 1,10-decanediol in 140 ml of dried dioxane was added. The mixture was refluxed for 2 hours. Cooled and the pyridine-HCl salt was filtered, the filtrate was poured into a large quantity of water. The product was filtered, washed with water, dried and then recrystallized in a mixed solvent of 1:1 petroleum and toluene, (yield, 87%; m.p. 110-111°C; C, 74.08%, H, 6.42%; asked C, 73.85%, H, 6.46%)

(5). 1,10-Decane bisterephthalic acid. At room temperature 12.5 g dibenzyl 1,10-decane bisterephthalate was dissolved in 125 ml trifluoroacetic acid. 14.5 ml HBr (in acetic acid, 30-32% HBr) was added dropwise into this solution. The reaction was continued for 3 hours. The reaction mixture was poured into icy water to precipitate the acid formed, which was then filtered, washed with water, dried and recrystallized in a 1:1 mixture of toluene and dioxane. (yield, 73%; m.p. = 230-232 °C; C, 66.36%, H, 6.59%; asked C, 66.37%, H, 6.43%)
1,10-Decane bisterephthaloyl chloride. 1,10-Decane bisterephthalic acid (41 g) was dissolved in excess SOCl₂ (130 ml) and 1/2 ml of DMF was added. The mixture was refluxed for 3 hours. A water aspirator was used to take off the excess SOCl₂ (a liquid nitrogen trap was used). Then some toluene was added, the mixture was aspirated again to a partially dry state, then a vacuum pump was used to complete the solvent removal. The product was washed with petroleum ether and dried. Recrystallization was from n-heptane. (yield, 90%; m.p.=91-93°C; C, 61.65%, H, 5.54%, Cl, 13.77%; asked C, 61.54%, H, 5.56%, Cl, 13.96%)

ii) Preparation of alkylhydroquinones.

Fig.19 is a sketch of the experimental equipment used for this purpose. The equipment is essentially the same as that suggested by Zweifel and Brown [88], except that in between the two flasks another passway was inserted, which was designed for cases when a gaseous olefin was used. The gaseous olefin and the generated diborane were mixed in the tube before they were introduced into the solvent in the left flask.
In general, 75 ml of 1 M sodium borohydride in diglyme was put in the dropping funnel. Into the right flask 23.4 g (0.165 mole, 65% excess) of boron trifluoride etherate was placed and in the left flask was placed 0.45 mole (50% excess) of olefin in THF. The system was protected by a N₂ atmosphere. Magnetic stirrers were used for both flasks. An ambient temperature or an ice-bath temperature was used. The NaBH₄ solution was dropped into the BF₃-ether-diglyme solution, and the diborane generated was introduced into the olefin solution in the left flask. After completion of the sodium borohydride addition, the trialkylborane solution in the left flask was allowed to stand overnight at room temperature.

To the alkylborane-THF solution, 0.08 mole of benzoquinone dissolved in THF was added dropwise. This reaction was instantaneous and heat was evolved. Following the addition, the reaction mixture was maintained at the reflux temperature for 30 min. The reaction mixture was then steam distilled to remove the solvent, boronic and borinic acids and unused reagents. On cooling, the alkylhydroquinone separated as a crystalline mass in the flask. The product was separated by filtration and air-dried. Recrystallization was from
Fig. 19. Preparation of Alkylhydroquinones
petroleum ether for higher members or from petroluem/toluene for lower members in this series. Results of these preparations are collected in Table 12.

iii) Cyanohydroquinone.

(1). 2-Cyanohydroquinone dimethyl ether. Into a 250 ml 3-necked flask equipped with stirrer and reflux condenser, 50 g of 1-bromo-2,5-dimethoxybenzene, 20 g of cuprous cyanide and 100 ml dry dimethyl formamide were introduced. This mixture was stirred overnight at reflux temperature. Subsequently the hot reaction mixture was filtered and the filtrate was poured into a solution of 150 g FeCl₃ in 150 ml water and 50 ml HCl. The mixture was left untouched for 3 hours at a temperature of 70 °C. During this time some HCN was formed. After this the mixture was filtered and the residue was extracted with water until the filtrate was completely clear. The product was twice recrystallized from glacial acetic acid (200 ml) under the addition of active carbon (m.p. = 80-81 °C, yield, 44%).

(2). 2-Cyanohydroquinone. 15 g 2-Cyanohydroquinone dimethyl ether was dissolved in 450 ml absolute toluene. 600 ml of a 10% solution of AlBr₃ in absolute toluene was
added into this solution and the mixture was heated to reflux for 14 hours with thorough stirring. The temperature of the oil bath was 100°C. After 30 min. a yellow precipitate separated and increased in amount. After the completion of this demethylation, the flask contents were poured into 1 liter of ice water, and the toluene solution was separated from the water solution. The water phase was strongly acidified and was extracted with ether. The ether solution was dried and evaporated. The remaining product was a yellow crystalline compound, which was sublimed in high vacuum at a temperature of 140°C. Recrystallization was from toluene / acetonitrile. (m.p.=170-173°C; yield, 75%)

iv) Nitrohydroquinone.

The o-nitrophenol (39 g) was dissolved in a 10% NaOH (56 g NaOH) solution and oxidized by a slow addition during about 3 hours of a saturated aqueous solution of potassium persulfate (75.7 g). Throughout the addition the mixture was continually stirred. The temperature was not allowed to above 20°C. After standing overnight, the solution was acidified to congo-red. Filtered if necessary, and extracted twice with ethyl acetate. The aqueous layer was treated with excess of HCl, heated on the water bath for
half an hour, cooled and extracted with ether. The extracts were then dried, and the residue was extracted with boiling light petroleum (60-80°C, d.p.) to remove the 3-nitrocatechol. The residue was distilled to obtain the final product (red, m.p. = 132-133°C; b.p. = 95-120°C/0.5 mm). The results are listed in Table 12. (yield, 9%)

v) Methoxyhydroquinone.
Vanillin (36 g) was dissolved in 360 ml of 2 N KOH solution with N₂ passing through for about 10 min. The solution was cooled in an ice-bath. 270 ml of an ice-cooled 3% H₂O₂ solution was added into the vanillin solution. The colour changed from yellow to wine red or brown. 15 Minutes later the reaction was brought to room temperature and held there for another 30 min., then it was acidified with 2 N HCl, extracted with ether, washed with water, with sodium bisulfite solution (Na₂S₂O₅) and with water, respectively, and finally dried over anhydrous Na₂SO₄. After removal of the ether, a deep brown pasty was obtained. Recrystallization was from a mixture of 1:1 toluene/skelly-C (three times). (yield, 67%; m.p. = 87-89 °C)
Polymerizations.

The homo- and copolymers were prepared by solution polycondensation reaction of 1,10-decane bisterephthaloyl chloride (DBTC) and the hydroquinones, Fig. 20.

As an example, DBTC (% mmole) dissolved in 20 ml dry 1,1,2,2-tetrachloroethane (TCE) was added dropwise to a solution of bromohydroquinone (% mmole) in 20 ml TCE and 6 ml of dry pyridine under a nitrogen atmosphere with magnetic stirring. The mixture was stirred for 20-24 hours at room temperature, after which the polymer was precipitated into 400 ml of acetone with stirring. The product was filtered and thoroughly washed with acetone, water, and acetone, then dried at room temperature under vacuum. The characterization results are given in Table 8-11.
Fig. 20. Polymerization of DBTC and hydroquinones.
CHAPTER III
ALKYL SUBSTITUTED POLYMERS

Introduction

The synthesis of substituted polymers from 1,10-decane bisterephthaloyl chloride and substituted hydroquinones were discussed in the previous chapter. These polymers may be divided into two groups according to the type of substituent on the hydroquinone ring, one with n-alkyl groups of similar polarity but various sizes for studying the steric effect of substituents on mainchain thermotropic liquid crystalline polymers, and another group having polar substituents including halogen atoms (Br), cyano-, nitro-, methoxy- and alkyl groups as well. These substituents have different electro-negativity or polar constants and have been incorporated into the polymer to study the polar effects of such substituents. In addition to these two groups of homopolymers, copolymers were made from 1,10-decane bisterephthaloyl chloride and two hydroquinones (cyanohydroquinone and methoxyhydroquinone) with substituents of different polarity. These copolymers were prepared in order to
study the substitution effect from another point of view as well as the effect of copolymerization on transition temperatures. Another aspect of substitution effects can be observed by preparing polymer blends. Blends were prepared to investigate the miscibility of two liquid crystals polymers and also of a liquid crystal and a non-liquid crystal polymer mixture.

For ease of discussion, the two homopolymer series mentioned above, copolymers and blends will be considered in different chapters. In this chapter, attention will be focused on only the alkyl-substituted polymers.

Studies of low molecular liquid crystals have revealed that a lateral substituent on a mesogenic unit can have two principle effects [14]: (1) the substituents can force closely positioned mesogenic units apart from each other because of their space requirements; and (2) the opposite effect can occur in that a change from a ring-H bond to a ring-X bond with the substituent can increase the molecular polarizability and possibly also the molecular dipolarity. The former would lower the packing efficiency of the molecules in both the solid and liquid crystalline states, thereby reducing the intermolecular attraction forces and lowering the thermal
stability of both the crystalline and liquid crystalline states. The latter effect would increase the lateral intermolecular attraction forces, thereby enhancing the crystalline and liquid crystalline thermal stabilities. These two opposing aspects have made it very difficult in previous studies to evaluate the two effects separately. It is, therefore, desirable to have substituents with different sizes but similar polarity, or vice versa.

The most systematic research in this area to date has been that of Catala and Lenz [75]. Using alkylhydroquinones as the bisphenol monomers, they were able to make a series of substituted poly(1,4-phenylene terephthalate)s containing alkyl group with between 6 to 12 carbon atoms. They found that the melting points of these polymers were very much depressed by the substitution and that mesophases were observed in a temperature range above the melting points. However, because of the very high rigidity of the main chains in these polymers, the melting temperatures were still too high for complete characterization of the polymers.
Incorporating flexible spacers into the main chains of polymers has proved to be another very effective approach to lowering transition temperatures of rigid polymers. Therefore, introducing both flexible spacers and substituents into the same polymer can result in an even greater effect on lowering transition temperatures. These investigations have also been carried out by Lenz and coworkers [58,71] who prepared the triad aromatic polyester with 1,10-decylen spacers. As shown in Table 7, this polymer, polymer 11, has a melting temperature of 236°C. By introducing a substituent onto the mesogens of this polymer they obtained a series of polymers having fairly low melting points at around 150°C.

Only a few other polymers with substituents have been synthesized; see Table 7, polymers 14,17, and 20,21. The substituents used were limited to halogen atoms and to a few alkyl groups (methyl and C-6 to C-12 alkyls). More extensive and more systematic studies are, therefore, necessary in order to understand the effect that substitution has on thermotropic mainchain polymers.
Results and Discussion

Solution properties.

In Table 8, are inherent viscosities and molecular weights of a series of alkyl-substituted polyesters in which the alkyl groups used were linear and had from 1 to 6, 8 or 10 carbon atoms. The solubilities of these polymers have all been increased by the presence of the substituents, and all of these alkyl-substituted polymers are soluble in tetrachloroethane (TCE) at room temperature. In contrast, the unsubstituted polymer does not dissolve in TCE even at elevated temperatures. However, the unsubstituted polymer is soluble in para-chlorophenol at 50°C. This solubility makes it possible to measure the viscosity of a dilute solution of this polymer. Inherent viscosities of these polymers were measured at concentrations of about 0.5 g/dl. All of the polymers had intermediate molecular weights. A number average molecular weight of about 24,000 was determined by GPC on the sample dissolved in THF for the pentyl-substituted polymer which had the highest inherent viscosity of 1.02. This molecular weight corresponds to a degree of polymerization of about 40. Because of the good solubility in TCE of the substituted polymers it should
not be very difficult to obtain polymers with even higher molecular weights.

The structure of these polymers has been confirmed by $^{13}$C NMR spectroscopy. In Fig. 7 is the spectrum of the methylsubstituted polymer in CDCl$_3$ solvent. The chemical shifts of the carbon atoms at different positions in the molecules of this polymer are assigned as follows:

<table>
<thead>
<tr>
<th>Carbon atoms</th>
<th>Chemical shifts (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_3$</td>
<td>16.43</td>
</tr>
<tr>
<td>-(CH$_2$)$_n$-</td>
<td>26.01, 28.68, 29.24, 29.43</td>
</tr>
<tr>
<td>-(O-CH$_2$)$_n$-</td>
<td>65.70</td>
</tr>
<tr>
<td>Phenylene</td>
<td>120.02, 122.88, 124.09</td>
</tr>
<tr>
<td></td>
<td>129.75, 130.12, 131.82</td>
</tr>
<tr>
<td></td>
<td>132.04, 133.13, 135.04</td>
</tr>
<tr>
<td></td>
<td>148.87</td>
</tr>
<tr>
<td>-(CO)$_n$-</td>
<td>164.00, 164.34, 165.71</td>
</tr>
</tbody>
</table>
Thermal analysis.

The transition temperature data collected in Table 9 were determined by DSC analysis. Fig. 21 contains the DSC thermograms of one of these alkyl-substituted polymers, polymer-2, where 2 represents to the number of carbon atoms in the substituent. The solid curve in Fig. 21 is for the first heating cycle at a rate of 10 degrees per minute, and the dotted curve is for first cooling cycle at the same rate. From the heating curve two endothermic peaks can be seen, one fairly sharp with a peak temperature of 71 °C, and the other quite broad with a maximum temperature at about 127 °C.

In addition to these two endothermic peaks there is also a step change of heat capacity at about 35 °C in Fig. 21. This temperature is considered to be that of a glass transition. This step change can also be seen on the cooling cycle for the same sample, although it is positioned at a temperature about 10 degrees lower. This temperature may be too high to be considered that of a glass transition from the empirical rule governing most of the common polymers for which the glass transition temperatures generally occur at a ratio of 0.5-0.7 to the melting temperatures on the Kelvin scale. However, we are
Fig. 21. First heating and first cooling curve on DSC of polymer-2, the ethyl-substituted polyester.
not dealing with a normal polymer here. We are apparently dealing with polymers which have unusual morphologies. In our polymers some unusual molecular segment ordering, arising from the mesophase formation, may be present even in the amorphous state. This ordering could result in a higher activation energy of segmental motion and consequently a higher glass transition temperature.

The glass transition temperatures for all of the alkyl-substituted polymers are collected in Table 9. Data in the first row are from the DSC heating cycles, and those in second row are from cooling cycles. The glass transition temperatures are also plotted in Fig.22 against the number of carbon atoms in the substituents. The different Tg values obtained from heating and cooling of same polymer sample are probably due to different thermal histories of the sample and from the different approaching directions to Tg during heating and cooling.

However, there are decreasing trends of Tg in both curves in Fig.22, with increasing side group length. The substituent causes a large decrease in glass transition temperature of the parent polymer. Tg can be further decreased by increasing the length of alkyl groups. This observation may be explained by the free volume theory,
Figure 22. Plot of Tg values of polymers vs. numbers of carbon atoms in the substituents
which says that the molecules need a certain amount of vacant space in the solid state before segmental motions can start. Substitution has lowered the molecular packing efficiency in the solid state and, therefore, more vacant spaces are left. As a result, the molecular segments can find enough space at lower temperatures. On the other hand, the substitution has also lowered the molecular ordering in the solid state when the side groups force apart the mesogenic units. Consequently a lower activation energy and a lower Tg are observed. If this explanation is of some value one may expect a normal Tg behavior when the substituents are so large that no molecular ordering can occur and a totally disorganized amorphous solid state is formed. Indeed when an alkyl group has 8 or 10 carbon atoms the polymer has a Tg/Tm relationship close to that of common polymers, and these two polymers were also found to be non-liquid crystalline.

Solid-to-mesophase transitions of polymers.

The endothermic peak at 71°C, Fig.21, is for the melting transition, but a corresponding crystallization exothermic peak is not seen in the cooling cycle probably because of the slow crystallization of this polymer.
The introduction of alkyl groups lowers the molecular symmetry and molecular interactions, and as a result the potential for crystallization is reduced in these polymers. On the other hand, the melting temperatures of these polymers were greatly decreased by substitution while Tg values were lowered a smaller extent. These effects on the polymer in Fig. 21 result in a Tm which is so close (only ca 36 degrees) to the Tg that the crystallization is even more difficult for kinetic reasons.

This interpretation is proven reasonable by the experimental results. Heats of fusion of alkyl substituted and unsubstituted polymers are shown in Table 14. What we see in this table is that the unsubstituted and methyl-substituted polymers have melting enthalpies of 4.1 and 4.5 Kcal/mol respectively. By increasing the length of the alkyl group from 2 to 6 carbon atoms, the enthalpy is very much decreased to a value of about 1.0 to 2.0 Kcal/mol. By further increasing the alkyl length to 8 or 10 carbon atoms, an enthalpy of 4.0 or 3.9 Kcal/mol is obtained. These results suggest the higher potential for crystallization of polymers with either long or very short substituents, the octyl-, decyl-, methyl- and
non-substituted polymers, and the much lower crystallization potential of those polymers with substituents of intermediate length. This result is indeed the case as observed by DSC measurements.
Table 14. Enthalpy and Entropy Changes at Phase Transitions of Polymers with Alkyl Substituents on the Mesogenic Units

<table>
<thead>
<tr>
<th>No.</th>
<th>$\Delta H_1$</th>
<th>$\Delta S_1$</th>
<th>$\Delta H_m$</th>
<th>$\Delta S_m$</th>
<th>$\Delta H_i$</th>
<th>$\Delta S_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5</td>
<td>3.2</td>
<td>4.1</td>
<td>8.1</td>
<td>0.89</td>
<td>1.7</td>
</tr>
<tr>
<td>1</td>
<td>0.55</td>
<td>1.4</td>
<td>4.5</td>
<td>10.0</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1.9</td>
<td>5.5</td>
<td>1.7</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>0.43</td>
<td>1.3</td>
<td>0.87</td>
<td>2.3</td>
<td>2.8</td>
<td>7.3</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>3.4</td>
<td>1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>4.3</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>6.1</td>
<td>1.4</td>
<td>3.9</td>
</tr>
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<td>7</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
<td>11.0</td>
<td>-</td>
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<td>9</td>
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<tr>
<td>10</td>
<td>0.63</td>
<td>2.0</td>
<td>3.9</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: The unit of enthalpies is in Kcal/mol. of repeat units of polymer chains; that of entropies is in cal/mol.°K.

* Carbon atom numbers in n-alkyl substituents.
By DSC analysis all of these polymers show a melting endotherm on their first heating cycle from the powder sample, and these temperatures are also recorded in Table 9. The cooling cycles of these polymers may be divided into two groups; those that show an exothermic crystallization peak, and those that do not show such a peak at the same cooling rate of 10 degrees/min. In the first group are those polymers that have melting enthalpies of about 4 Kcal/mol, the octyl-, decyl-, methyl- and non-substituted polymers, while the other polymers with lower melting enthalpies belong to the second group. However, the high enthalpy of the methyl-substituted polymer is questionable, and it may be explained as being caused by an increase of molecular polarizability by introduction of a methyl group which is small and does not inhibit the crystallization process. Alternatively, the high melt enthalpy may be simply a result of the higher crystallinity resulting from kinetic reasons. This polymer has a melting temperature of 154 °C which is 110 degrees above the glass transition.

All the alkyl substituted polymers were obtained after precipitation from solution and then dried under vacuum. The presence of solvent most likely made them
crystallize more easily during precipitation and during drying. This suggestion explains why the first heating cycle on DSC of these polymers all show crystallinity and a melting peak. Annealing has also been used to demonstrate the slow crystallization process of these alkyl polymers.

As seen in Fig. 21, the starting powder sample of this polymer shows two endotherms on the first heating curve: one peak due to melting, and another due to the mesophase to isotropic liquid transition. However, during the cooling of this polymer from its isotropic melt at a rate of 10 degrees/min it shows no corresponding exothermic crystallization peak. This result has been explained in a previous paragraph as being due to the low potential of crystallization, that is, it is explained thermodynamically. No matter how small the potential is, it does have a potential to crystallize.

If we put the cooled sample for a period of time at a suitable temperature somewhere above Tg and below Tm, the sample crystallizes and shows a melting endotherm on DSC when it is heated again. The annealing results are shown in Fig. 23, where curve A is that of the first heating cycle of the initial sample. The isotropic melt was
Fig. 23. DSC of Polymer-2, Ethyl-substituted Polyester

B: After cooled and annealed at 325°K for 12 hrs.
C: After cooled and annealed at 330°K for 40 hrs
   at 325°K for 3 hrs and at 320°K for 3 hrs.
A: First heating curve from the powder product
cooled at a rate of 10 degrees/min to 325°K (52 °C) which is 17 degrees above Tg and 19 degrees below Tm. This temperature was maintained for 12 hours and the sample was then heated at a rate of 10 degrees/min. This treatment produced curve B. When the annealing condition was changed to 40 hours at 330°K, followed by 3 hours at 325°K and then 3 hours at 320°K, curve C was obtained. For curves A, B, and C the heating rate was the same, but for C, a higher sensitivity of recorder was used such that the size difference of these peaks may not be meaningful.

Curves B and C prove that this polymer was semicrystalline but that the crystallization process was slow. Annealing under the proper conditions may increase the crystallinity and therefore, the melting peak on the DSC curves may be recovered even though the peaks have moved to temperatures of a few degrees higher than that of initial powder sample. These observations are probably the result of crystalline multiplicity and fewer crystalline defects of the annealed samples.

Similar results were obtained with other polymers. For example, with polymer-4, the butyl-substituted polymer. The initial powder sample which was obtained by precipitation from solution and then washed and dried in
vacuum showed, one Tg at 35°C, a melting endotherm at 75°C and the endotherm at 103°C of the mesophase to isotropic melt transition. When the polymer was cooled from its isotropic melt to a temperature of about 0°C at 10 degrees/min, the DSC thermogram showed only one exotherm corresponding to the isotropic to mesophase transition and a step heat capacity change of Tg. When this solid was heated again from 0°C at the same rate, the DSC curve showed only one endotherm at 103°C due to a mesophase to isotropic melt transition and a Tg. The melting peak was lost obviously because there was not a crystallization process. So the cooled solid was either amorphous or a quenched liquid crystalline solid. This amorphous property is also shown by a steeper heat capacity change at Tg of this sample than that of the initial powder because the powder sample is semicrystalline and has a smaller percentage of an amorphous or non-crystalline portion and consequently a smaller change of heat capacity at Tg. However, the "lost" melting peak can be recovered by annealing the cooled sample or simply by a very slow cooling process from its melt. A sample treated like this has two endothermic peaks on its DSC heating curve although the melting peak has been moved to 84°C and is a few degrees higher than that of the powder sample.
Fig. 24 collects the DSC results for initial powder samples of alkyl substituted polymers. The number on each thermogram is the number of carbon atoms in the substituents of the polymer. Some of these thermograms show more than two peaks. The quantitative interpretation of individual peaks is more difficult especially when the two peaks are so closely located. However, microscopy and other observations may help in the solution of this problem.

Multiple peaks are not unique to this polymer series. Many other polyesters show more than one melting endotherm, as does, for example, that of Meurisse [61] and coworkers.

In our polymer system the molecular structure is complicated by mesogenic rigid segments and flexible spacers as well as alkyl side groups. Therefore, it is possible to form more than one kind of crystalline state. The different type of crystalline structures are also expected to require different activation energies for crystallization and to have different crystallization rates. The thermal history must affect the DSC results of the samples.
Fig. 24. First heating curves on DSC of substituted polyesters. Rate: 10 degrees per minute. Number on each curve is the carbon atom number in the substituents on each polymer.
Consequently it is not unreasonable to find an irregular change of melting temperature with changing alkyl group length in these polymers, as shown in Table 9 and in Fig.25. Nevertheless there is a trend in the melting points of these polymers. By replacing a hydrogen atom with a methyl group a remarkable decrease in melting point, from 231 to 154 °C, occurs. This temperature further decreases in an approximately odd-even zig-zag fashion when the alkyl group changes from methyl to hexyl. Among these polymers the lowest melting temperature is the 71°C of the ethyl-substituted polymer. While further increasing the length of side groups, the melting point seems to increase slightly and then level out. Probably a further increase of the side alkyl group beyond 8 carbon atoms does not produce more steric effects that interfere with the molecular packing in the solid state, while the internal plasticization effect of the long alkyl groups can enhance the crystallization process.

Mesophase-to-isotropic melt transition.

Most of these polymers have a mesophase, and DSC, stir opalescence and polarizing microscope observations have been used to confirm the presence of the mesophases.
Figure 25. Plot of \( T_i \) and \( T_m \) of the alkyl substituted polymers vs. numbers of carbon atoms in alkyl groups.
The peak temperature on the DSC curve is assigned as the transition temperature. However, in most cases the mesophase to isotropic melt transition peak is very broad, as shown in Fig. 21 for the ethyl-polymer. As often happens in nematic system of low or high molecular weight molecules, the transition is very reproducible in the heating and cooling cycles by DSC analysis. This behaviour is the outstanding difference from the melting or glass transitions on which the thermal history has remarkable influence as discussed in previous section.

The mesophase to isotropic melting transition, or more simply, the isotropization temperatures of alkyl substituted polymers are also included in Table 9. The data are all from DSC measurements, which usually give somewhat higher temperatures than those obtained from microscopy observations. These temperature are assigned as Ti, the isotropization temperature.

Data in Table 9 are also plotted in Fig. 25 against the number of carbon atoms in the alkyl group. Introducing a methyl group on the mesogenic unit caused a big depression of the isotropization temperature. Ti of the parent polymer is 267°C, and that of the polymer with the methyl group substituent is 190°C. This depression
happens to have the same value (77 degrees) as that of the melting point caused by the same substituent. Therefore these two polymers have exactly the same temperature region of the mesophase, 36 degrees.

A change of methyl to ethyl group caused another big depression of Ti just as occurred with the melting point. However, this depression is 20 degrees smaller than that of Tm. This difference gave this polymer a broad mesophase range of 56 degrees which happens to be the largest in this series.

After the ethyl group, Ti decreases slowly and steadily with increasing substituent length, and eventually it arrives at a point where the melting point is even higher, that is, a liquid crystalline mesophase is no longer observed, which is the case of polymers with octyl- or decyl-substitutions. These two polymers have appear to be non-liquid crystalline by DSC and polarizing microscopic observations. Under the polarizing microscope these two polymers showed no birefringence in their initial powder or the melt state.
Enthalpies ($\Delta H_i$) and entropies ($\Delta S_i$) of the clearing transition of these thermotropic polymers are included in Table 14. As in the case of the $H_m$ values, the $H_i$ values were determined from the areas under the transition peaks using an indium sample for their calibrations. The peak areas are measured by a planimeter.

The $\Delta H_i$ obtained for these polymers have values of about 1-2 Kcal/mol. These values are not influenced by the thermal history of the polymers. But they do, of course, reflect the degree of molecular order and intermolecular attraction in the mesophase as well as in the isotropic phase. Because all of these mesophases are found to be very likely nematic by polarizing microscopic observations, a similar degree of molecular ordering in the mesophases of these samples may be expected. Therefore, the degree of molecular disorder in the isotropic liquid state must be responsible for the $H_i$ values. Intermolecular attractions in the nematic state as well as in the isotropic liquid state may have less responsibility for the variation of $H_i$ values since all these alkyl groups have similar polarizability and polarity.
The degree of disorder in the isotropic liquid state is represented by $S_i$. This quantity as shown in Table 14, increased rapidly at first with increasing substituent size, arrived at a maximum for the propyl-substituted polymer, and then decreased again. This observation may be partially explained by the steric effects of alkyl groups.

In an isotropic solution the steric effects of alkyl groups may be evaluated in terms of Taft's steric parameter, which is defined as

$$E = \log \left( \frac{K}{K_0} \right)$$

where $K$ is the reaction rate constant of a certain reference reaction, with $K_0$ for the methyl-substituted compound and $K$ for compounds with other substituents. In Table 15, are the $E$ values of hydrogen and some alkyl groups [89,90], as well as $\Delta S_i, \Delta H_i$ values of the substituted polymers:
<table>
<thead>
<tr>
<th>R</th>
<th>E of R</th>
<th>Polymers</th>
<th>ΔSi</th>
<th>ΔHi</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>+1.12</td>
<td></td>
<td>1.7</td>
<td>.89</td>
</tr>
<tr>
<td>CH₃</td>
<td>0</td>
<td></td>
<td>3.6</td>
<td>1.7</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>-0.08</td>
<td></td>
<td>4.2</td>
<td>1.7</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>-0.31</td>
<td></td>
<td>7.3</td>
<td>2.8</td>
</tr>
<tr>
<td>n-C₄H₉</td>
<td>-0.31</td>
<td></td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>-0.31</td>
<td></td>
<td>2.8</td>
<td>1.0</td>
</tr>
<tr>
<td>n-C₆H₁₃</td>
<td>---</td>
<td></td>
<td>3.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

ΔH: Kcal/mol
ΔS: cal/mol.°K
A comparison of the data in Table 15 offers some interesting information. The steric parameter, \( E \), decreases with alkyl-substituent length. The greatest changes occur on going from hydrogen to the methyl group, and from ethyl to the propyl group. A further increase of the alkyl group length seems to result in little additional steric effects. The change of \( E \) from the methyl to ethyl is not as large as expected. The steric hindrance of the alkyl groups, of course, results in higher degrees of disorder of the units in the isotropic liquid state. Therefore, a higher value of the entropy change occurred during the transition. As a matter of fact, \( Si \) increased with a substituent change from hydrogen to the propyl group. Corresponding to the change of \( E \), \( Si \) had steep changes when the substituent changes from \( H \) to methyl, and from ethyl to the propyl group. The change from methyl to ethyl has a much smaller value, and as in the case of steric parameters. The propyl substituted polymer had a maximum value of \( ^4Si \).

However, the almost constant value of the steric parameters of the propyl, butyl and pentyl groups cannot explain the steep decrease of \( ^4Si \) from propyl-polymer to butyl-polymer. Some other factors have to take this into
account. The steric parameters may have different values in polymer melts than those obtained for solutions.

In order to have a better understanding of this question, it would be very desirable to study the thermodynamic properties of some model compounds. Unfortunately such model compounds have not yet been reported. Nevertheless, a series of substituted low molecular weight liquid crystalline compounds having the following structures have been made by Dewar and Griffin [91],

\[
\begin{align*}
H_3C\text{O} & (\text{COO})_n\text{OOC} \quad (\text{OCH}_3_x) \\
\text{X} & 
\end{align*}
\]

where \( X = \text{H, F, Cl, Br, I and CH}_3 \). These compounds are similar in structure to the mesogenic units in our polymers. A discussion of the thermodynamic behaviour of these compounds may be helpful to the further understanding of substitution effects on mesophase thermal stabilities. Table 16 contains the results obtained by these authors.
Table 16. Effect of lateral substituents on thermodynamic parameters for N-I transitions

<table>
<thead>
<tr>
<th>compounds</th>
<th>Ti</th>
<th>ΔHi</th>
<th>ΔSi</th>
<th>R(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = H</td>
<td>301.0</td>
<td>.408</td>
<td>.711</td>
<td>1.2</td>
</tr>
<tr>
<td>F</td>
<td>278.5</td>
<td>.404</td>
<td>.732</td>
<td>1.35</td>
</tr>
<tr>
<td>Cl</td>
<td>252.4</td>
<td>.463</td>
<td>.881</td>
<td>1.8</td>
</tr>
<tr>
<td>Br</td>
<td>241.1</td>
<td>.487</td>
<td>.947</td>
<td>1.95</td>
</tr>
<tr>
<td>I</td>
<td>222.9</td>
<td>.493</td>
<td>.994</td>
<td>2.15</td>
</tr>
<tr>
<td>CH₃</td>
<td>252.1</td>
<td>.529</td>
<td>1.01</td>
<td>2.0</td>
</tr>
</tbody>
</table>

R = Van Der Walls radius of ortho substituent
As expected, every substituent lowers the mesophase (nematic) to isotropic transition temperature. And among the halogen derivatives, a steady decrease in Ti occurs with increasing size of the halogen. However, this result is not due to a decrease in $\Delta H$ in the series but to a steady increase in $\Delta S$. Indeed, $\Delta H$ shows a small but significant and uniform increase with increased size of the substituent. Introduction of a methyl substituent also leads to a large decrease in the isotropization temperature, again as a result of a large increase in S. These results are very similar to those of our substituted polymeric liquid crystals. In both cases Ti decreased steadily with increased size of the substituent. This decrease is a result of the increased entropy, but not of an enthalpy decrease.

The increase of entropy has been explained by Dewar and Griffin as the result of an "Interlocking" of substituents on different molecules. This interlocking should hinder motions parallel to their long axes in the nematic state and consequently the entropy of the nematic phase is reduced. However, as discussed above the increase of the entropy of the isotropic liquid phase caused by steric effects may be another part of the
answer, or some other factors which we do not know yet may have played a more important part in determining the thermodynamic properties of the mesophases.

Morphological aspect of polymers.

The polarizing microscope has been used to observe the liquid crystalline textures of these polymers. This technique has the advantage of convenience.

For this investigation, a Leitz microscope (Model-Ortholux) equipped with cross-polarizers and a Mettler FP-2 model hot-stage was used. The initial magnification was 320X. During the observations the sample was put between two cover glasses.

Fig. 26 (a)-(c), are photomicrographs of the mesophases of several polymers in this series.

Photomicrograph (a) was taken at 253°C while heating the powder sample of the unsubstituted polymer which has a Tm at 231°C and a Ti at 267°C by DSC measurement. This texture seems to be more complicated than that observed in most cases of low molecular weight liquid crystals. Polymer melts have much higher viscosities which make perfect mesophase organization and thin melt film preparation more difficult. Thus better ordering texture
Figure 26a. Photomicrograph of the unsubstituted polymer, taken at 253°C during heating
Magnification: 320X
Figure 26b. Photomicrograph of the unsubstituted polymer, taken at 239°C during cooling
Magnification: 320X
Figure 26c. Photomicrograph of the ethyl-polymer, taken at 78°C. Magnification: 320X
would be expected if the sample is cooled down from its less viscous isotropic melt to the mesophase, instead of being heated from its highly viscous solid state to the mesophase. This result has been found to be true in our observations, and photograph (b) is a good example. This photograph is of the same sample but was taken at 239°C when the isotropic liquid was cooled down to this point. Here a typical nematic schlieren texture is observed, which shows both two and four dark brushes starting from point-like disclinations.

The alkyl-substitution has no dramatic influence on the texture of the mesophase of this polymer. All of the polymers with 1 to 6 carbon atom alkyl groups show nematic Schlieren textures under a crossed polarizing microscope. Fig 26 (c) represents this behavior.

This effect is a logical result of the polymer series under discussion. The unsubstituted polymer of this series discussed above has only a nematic mesophase; substitution in the mesogenic groups of this polymer by an alkyl group, which is weakly polar but bulky, in no case favors formation of a more highly ordered mesophase. As a matter of fact a lateral substituent on the middle position of a mesogen of low molecular weight usually
results in a mesophase of the lowest degree of order, that is the nematic, as in the case of Dubois [92], and of Van Meter [16].

In summary, alkyl-substitution has a remarkable effect on depressing the polymer melting point as well as the mesophase thermal stability. By incorporating alkyl substituents onto the mesogenic units of polymers with flexible spacers several thermotropic liquid crystalline polyesters with fairly low melting points were obtained. Polymers with alkyl substituents longer than 8 carbon atoms were found to be non-liquid crystalline. Thermodynamic properties of these polymers have been discussed basically in terms of steric effects. By crossed polarizing microscopic observations these liquid crystalline polymers, including the unsubstituted one, were found to be nematic.
CHAPTER IV
POLYMERS WITH POLAR SUBSTITUENTS

Introduction

Substitution effects may be considered from two aspects: either steric or electronic. The former arises from a space requirement of the substituents. While the latter is due to the molecular electro-magnetic field disturbances caused by substitution. These two effects are universal in organic chemistry and have been studied extensively. Studies have advanced so much that it is now possible to evaluate the substitution effects by certain quantitative parameters, for instance, Taft's steric parameters and Taft's polar constants. Therefore, it is a challenge to study these effects on the mesophase properties of liquid crystalline materials.

In chapter III, the steric effects of alkyl substituents on the properties of thermotropic polyesters were discussed. Where normal-alkyl groups with different carbon atoms were assumed to have a similar polarity. A steady decrease in the mesophase thermal stability with
increasing alkyl group size (in this case, length) was found as shown in Fig. 25. Because the enthalpy of mesophase-to-isotropic melt transition of the polymer is increased by the substitution, the decrease of this transition temperature may not be due to an enthalpy factor, and instead an entropy increase in the isotropic melt is considered responsible.

Suitable intermolecular attractions between mesogens are essential for the formation of a mesophase. Certain changes in properties of the mesophase would, therefore, be expected if polar substituents are introduced into the mesogenic units.

Substitution of a hydrogen atom in mesogens by other atoms or chemical groups will cause changes in molecular polarity, polarizability, dipole moment, and so on, and, consequently, will have an extensive influence on molecular interactions. The magnitude of this influence will vary, of course, vary with different substituents. Alkyl groups, for example, can be considered one kind of polar group although the polarity is small.
In order to study the polar effects of substituents on the liquid crystalline behavior of thermotropic polymers it is necessary to introduce into the mesogens different groups or atoms with different polarities. The most ideal system for this study would be to use those groups having similar sizes but different polarities. However, this suggestion is unrealistic because no two groups have the same size and different polarities. Nevertheless, the study of the steric effects of substituents may be helpful in finding a solution to this problem. For example, it has been found (chapter III) that the mesophase-to-isotropic phase transition temperature decreases with increasing size of alkyl groups. Thus the clearing temperature of a polymer having substituents which are larger than the methy1 group but smaller than the ethyl group, must be some value in between the clearing temperatures of the methy1- and ethyl-substituted polymers. Assuming there are no polar effects. Any deviation from this value must be, therefore, from the polar effects or some other factors.

In this chapter the changes of thermotropic behavior caused by some polar groups will be specifically discussed. The groups studied are the methy1, bromo,
cyano, nitro, methoxy, as well as the ethyl groups. The sizes of these groups are compared in terms of molecular diameters of mesogenic units in these polymers:

Following Gray [21, 22], the diameter (or the breadth) of the mesogenic units is defined as the diameter of the narrowest cylinders through which the molecules would pass assuming that the flexible parts in the molecules do not interfere. Table 17 collects the results of the calculations of the diameters, the bond lengths, angles and van der waals radii used in the calculations are also listed in the table.
Table 17. Molecular Diameters of X-substituted Mesogenic Units of the Polymers

<table>
<thead>
<tr>
<th>bond length</th>
<th>bond angle</th>
<th>radii</th>
<th>diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>ring</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-ring</td>
<td>1.07</td>
<td>H</td>
<td>1.20</td>
</tr>
<tr>
<td>H₂C-ring</td>
<td>1.46</td>
<td>Me</td>
<td>2.0</td>
</tr>
<tr>
<td>Br-ring</td>
<td>1.80</td>
<td>Br</td>
<td>1.95</td>
</tr>
<tr>
<td>O₂N-ring</td>
<td>1.46</td>
<td>O</td>
<td>1.40</td>
</tr>
<tr>
<td>CN-ring</td>
<td>1.46</td>
<td>N</td>
<td>1.50</td>
</tr>
<tr>
<td>MeO-ring</td>
<td>1.44</td>
<td>Me</td>
<td>2.0</td>
</tr>
<tr>
<td>H₅C₂-ring</td>
<td>1.46</td>
<td>Me</td>
<td>2.0</td>
</tr>
</tbody>
</table>
From the data in table 17 it is seen that all of the polar groups, Br, CN, NO₂, and methoxy, are larger than the methyl but smaller than the ethyl group.

The polarities of these substituents may be evaluated by Taft's polar constants, [93] which are shown in Table 18.

Table 18. Taft's Polar Constants of Some Substituents

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>+3.9</td>
</tr>
<tr>
<td>CN</td>
<td>+3.7</td>
</tr>
<tr>
<td>Br</td>
<td>+2.8</td>
</tr>
<tr>
<td>OMe</td>
<td>+1.5</td>
</tr>
<tr>
<td>H</td>
<td>+0.49</td>
</tr>
<tr>
<td>Me</td>
<td>0.00</td>
</tr>
<tr>
<td>Et</td>
<td>-0.10</td>
</tr>
</tbody>
</table>
Results and Discussion

The preparations of these polymers has been discussed in chapter II. They are all soluble in tetrachloroethane, TCE, so that the polymerization systems are homogeneous. Inherent viscosities of these polymers measured in TCE at 40°C at a concentration of about 0.5 g/dl are included in Table 8, chapter II. The nitro-substituted polymer has the lowest viscosity of 0.29. This value could be increased by better control of the reaction conditions.

The polymers with bromo-, nitro-, cyano-, and methoxy-substituents were only slightly soluble in THF, therefore the GPC measurements were not performed (the bromo-polymer dissolved in warm THF).

The structures of these polymers were confirmed by $^13$C-NMR spectroscopy studies. For example, Fig. 7a is the spectrum of the methoxy substituted polymer. The characteristic feature of this spectrum is the absorption of the carbon atoms of methoxy groups, which have a chemical shift at 56.15 ppm.
The thermal behavior of these polymers was studied by differential scanning calorimetry using a Perkin Elmer DSC-II instrument. Some of these results are shown in Fig. 27, 28, 29, and 30 for methyl-, cyano-, nitro-, and methoxy-substituted polymers, respectively. The transition temperatures of these polymers, obtained as the peak temperatures of their DSC first heating curves, are collected in Table 10.

**Glass transition of the polymers.**

The glass transition temperatures of these substituted polymers, as shown in Table 10, are all significantly lower than that of their parent polymer. The substituents used cover a broad range of polar constants, from -0.10 for the ethyl group to +3.9 for the nitro group, Table 10. Therefore, the following conclusion can be drawn for the substitution effect on the glass transition temperatures of the thermotropic polymer system being studied: the introduction of a substituent, no matter how large (at least up to the decyl group) and how polar it is, will depress the glass transition temperature of the polymer. However, the degree of this depression seems to be a function of both the size and the polarity of the substituents.
Fig. 27. DSC results of methyl-substituted polymer. 10°C/min. A: first heating; B: cooling; C: second heating curve.
Fig. 28. DSC curves of cyano-substituted polyester.
A: first heating curve;   B: first cooling curve;
C: second heating curve;  D: second cooling curve.
Rate of heating and cooling: 10 degrees per minute.
Fig. 29. DSC of nitro-substituted polyester, 10°C/min.
A: heating; and B: cooling curve.
Fig. 30. DSC curves of first heating and cooling of methoxy-substituted polyester
Rate: 10 degrees per minute
The size, or the steric effect of the substituents on $T_g$ was discussed in chapter III, where it was shown that the $T_g$ values of normal-alkyl substituted polymers decreased steadily with increasing length of the alkyl group. This result is similar to that for some other polymer systems, for example, that of Vogl and coworkers [94] who found that in the study on polyterephthalates of 2,3-disubstituted-1,4-butanediols long normal alkyl-groups decreased the $T_g$ of the polymers.

The size of the substituent is not the only factor that influences the $T_g$ of a polymer. As shown in Table 17, the Br, CN, NO$_2$, and OMe substituents are all larger than the methyl group. If only the steric effect was influential, the polymer with any of these substituents should have a $T_g$ lower than that of the methyl-substituted polymer, but such is not the case. As a matter of fact the $T_g$ values of these polymer are all similar to, or ever higher than that of the methyl-polymer. Polar substituents can enhance the molecular interaction and consequently it is reasonable to expect that they can impart a higher activation energy for the motion of molecular segments, and thus a higher $T_g$. 
Tg, as measured by DSC, is not a thermodynamic equilibrium transition, but it depends very much on the thermal history of the sample. In addition, the crystallinity of the sample as well as molecular weight and molecular weight distribution will also influence the Tg values of the polymers. Therefore, the real situation must be more complicated.

Solid-to-mesophase transition of the polymers.

As shown in figures 27-30, all of these polymers have a melting endotherm in their DSC thermograms. The endothermic peak temperatures of melting are collected in Table 10. For the sake of comparison the transition temperatures of the ethyl-substituted polymer are also shown in the table.

The melting points of all of these substituted polymers are much lower than that of their parent polymer, which is 231°C, while those of the substituteu polymers are all at temperatures near 150°C. This depression in the melting point must be from the steric effect of the substituents. As shown in Table 18, the non-alkyl groups are all more polar than the hydrogen atom, the increased polarity is expected to enhance molecular interactions. All of the substitutions have significantly increased
molecular diameters, as shown in Table 17, the molecular packing efficiency is decreased and this effect would cause lower the melting point. Therefore, in our thermotropic polyester system the melting point can be depressed by a substituent on the mesogenic unit. And it must be concluded that the steric effect is the controlling factor and that the polarity of the substituent has little effect on the melting point.

Nevertheless, the polarity of the substituents does indeed influence to some degree the melting point of the polymer. This effect is shown in Table 10. As discussed, the bromo, cyano, nitro and methoxy groups are expected to have lower melting points than that of methyl-polymer from the viewpoint of steric effects because all these groups are larger than the methyl group. The bromo-polymer does have a lower melting point, but the others have melting points either similar to, or even higher than, that of methyl-polymer, and the most-polar-substituted polymer, the nitro-polymer, has the highest melting temperature. The polymer with methoxy groups on the mesogenic group has about the same molecular breadth as that of the ethyl-substituted polymer, as shown in Table 17, 8.9 and 9.0 Å, respectively, but the melting point (158°C) of the
former is much higher than that (71°C) of the latter.

This complicated situation is also shown by the enthalpies and entropies during the melting of these polymers (Table 19).

Table 19. Enthalpy and Entropy Changes at Phase Transitions of Polymers with Polar Substitutions on the Mesogenic units

<table>
<thead>
<tr>
<th>Substituents</th>
<th>$\Delta H_m$</th>
<th>$\Delta S_m$</th>
<th>$\Delta H_i$</th>
<th>$\Delta S_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4.1</td>
<td>8.1</td>
<td>0.89</td>
<td>1.7</td>
</tr>
<tr>
<td>Methyl</td>
<td>4.5</td>
<td>10.0</td>
<td>1.7</td>
<td>3.6</td>
</tr>
<tr>
<td>Bromo</td>
<td>3.7</td>
<td>8.9</td>
<td>1.1</td>
<td>2.4</td>
</tr>
<tr>
<td>Nitro</td>
<td>4.1</td>
<td>9.4</td>
<td>0.76</td>
<td>1.6</td>
</tr>
<tr>
<td>Cyano</td>
<td>2.8</td>
<td>6.5</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td>Methoxy</td>
<td>1.9</td>
<td>4.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethyl</td>
<td>1.9</td>
<td>5.5</td>
<td>1.7</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Note: $\Delta H's$ in Kcal/mole; $\Delta S's$ in Cal/mol.$^\circ$K

Another noticeable phenomenon of these polymers may be seen on their DSC cooling curves. Unlike the less-polar alkyl-substituted polymers (with the exception of the methyl-polymer), these polymers crystallize much more easily. In the DSC cooling thermograms of these polymers there is an exothermic crystallization peak, although a supercooling of about 30-40 degrees was observed under the experimental conditions used (cooling
rate, 10°C/min.), Thermodynamically the crystallization enthalpies of these polymers were higher than those of the less-polar alkyl-substituted polymers. Kinetically, the wide temperature difference between the Tg's and the Tm's of these polymers offers a chance for these polymers to crystallize at a temperature rather higher than the Tg of the polymers. Therefore, for these polymers it is not necessary to anneal them in order to recover their crystallinity after the melting.

Mesophase-to-isotropic melt transition of the polymers.

The mesophase to isotropic melt transition temperatures (the clearing or isotropization temperatures), Tc, recorded in Table 10 are the peak temperatures of DSC endotherms for the transitions of these polymers.

From these data, two significant phenomena can be observed: (1) the methoxy-substituted polymer does not exhibit a mesophase, therefore, no isotropization temperature exists; (2) the isotropization temperature of the bromo-, cyano-, and nitro-substituted polymers are higher than that of the methyl-substituted polymer, even though the methyl group is smaller than these atom or groups.
To interpret these two observations the substitution effects must again be considered, both the steric and polar effects. From the viewpoint of steric effects, we may predict the order of isotropization temperatures of these polymers, assuming no polar effects are involved. Let us assume that there is a linear decrease of the isotropization temperature of polymers with increasing molecular breadth or diameter from 7.8 Å of the methyl-substituted polymer to 9.0 Å of the ethyl-polymer. This assumption may be considered reasonable if the results obtained in chapter III for the alkyl-polymers are considered, and therefore the Ti values of the polymers being studied may be predicted by simple calculations with the results shown below in Table 20.
The predicted isotropization temperatures of these polymers are all much lower than the experimental values. Therefore, these values must be corrected by other parameters. All of the substituents investigated are rather polar, and this property is expected to enhance the molecular interactions and, therefore, increase the mesophase thermal stability of the polymers.

Among these polymers the cyano-polymer has the highest Ti (219°C), which deviates considerably from the predicted value (163°C). This polymer has a relatively high molecular weight (inherent viscosity, 0.56), and, therefore, we may assume that this polymer has reached its limiting Ti (some authors have found the isotropization temperature of a thermotropic polymer increases with...
increasing molecular weight up to about an $M(n)$ of 6000-7000, and the transition temperature is unaffected by a further increase in the molecular weight [69, 10u]), consequently, we may assume that the highest contribution of the polar effect is made by the cyano-group because it increases the transition temperature by 56°C ($= 219 - 163$).

If the contribution of the polarity of the polar substituents to the transition temperature is also a linear function of the polarity, the isotropization temperatures of these substituted polymers may again be predicted. Table 21 shows the results of this prediction.

Table 21. Prediction of Isotropization Temperatures of Polar-substituted Polymers from Both Steric and Polar effects

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Polar Constant</th>
<th>$T_i^*$</th>
<th>$T_i^{**}$</th>
<th>$T_i^{***}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>0.0</td>
<td>190</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>Bromo</td>
<td>2.8</td>
<td>174</td>
<td>196</td>
<td>21b</td>
</tr>
<tr>
<td>Nitro</td>
<td>3.9</td>
<td>163</td>
<td>194</td>
<td>221</td>
</tr>
<tr>
<td>Cyano</td>
<td>3.7</td>
<td>163</td>
<td>219</td>
<td>219</td>
</tr>
<tr>
<td>Methoxy</td>
<td>1.5</td>
<td>132</td>
<td>158(Tm)</td>
<td>155</td>
</tr>
<tr>
<td>Ethyl</td>
<td>-0.10</td>
<td>127</td>
<td>127</td>
<td>129</td>
</tr>
</tbody>
</table>

* Predicted from steric effects
** Found experimentally
*** Predicted from both steric and polar effects

These calculations were based upon an empirical equation as
follows:

\[ Ti = Ti(0) - a(D - D_0) + b\sigma \] (1)

where \( Ti(0) \) is the Ti of the reference polymer, here it is that of the methyl-substituted polymer. The selection of this polymer is based on the fact that the methyl group has a Taft polar constant of 0. In the equation, \( D \) is the molecular diameter of the substituted polymer and \( \sigma \) is the Taft's polar constant of the substituent. \( a \) and \( b \) are coefficients.

This prediction is rather successful in this particular polymer series. The predicted Ti of the methoxy-substituted polymer is 155°C, which is even lower than the melting point of this polymer, consequently a mesophase cannot exist above the melting.

Copolymers of DBTC and both the cyano- and methoxy-hydroquinones, which will be discussed in chapter V, offer a very good confirmation of this prediction: The isotropization temperature of the copolymers decreased steadily with increasing content of the methoxyhydroquinone, as shown in Table 11. At a content of 90% methoxyhydroquinone, the Ti of this copolymer is 154°C. Consequently, from the trend of Ti, it is expected
that Ti must be a few degrees lower than 154 °C if the content of this monomer is further increased to 100%. The Ti of the homopolymer from methoxyhydroquinone and DBTC must have a value in the range of 150 to 154°C. This value is very close to the predicted one.

The methoxy-substituted polymer was therefore, expected to be monotropic. On a Fisher-John's microscope this sample melted at about 160°C, but no stir opalescence was observed. However, it did exhibit stir opalescence when its melt was cooled down to a temperature range of about 160-145 °C before it solidified. A similar phenomenon was observed on a polarizing microscope: during cooling this sample displayed strong birefringence in a small temperature range just before its solidification. These observations could be evidence for the expected monotropic behavior of this polymer. The DSC studies on this sample also suggested a possible transition from the isotropic melt to a mesophase of this polymer: as shown in Fig. 30, on the cooling thermogram there was a crystallization exothermic peak; on the higher temperature side of this peak was a shoulder which was probably the result of the liquid-crystallization. However, in order to support these observations further
investigations are required.

The highest Ti's which the polymers may have can also be predicted. The differences between the experimental values and the predicted ones of the bromo- and nitro-substituted polymers may occur because of the low molecular weights of these polymers. Their inherent viscosities are 0.33 and 0.29, respectively. If this is the reason then either an increase of molecular weight of these polymers should bring the observed Ti values up towards the predicted values or the proposed theoretical treatment must be modified.

For the sake of clarity the results of the experimentally determined and the predicted values of Ti are plotted in Fig. 31.

The proposed treatment may also be examined by other polar-substituted polymer systems with reasonably high molecular weights. Unfortunately at present time such systems are not available.

Morphology observations.

These polymers have been studied under a crossed polarizing microscope with a magnification of 320X.
Figure 31. Comparison of the predicted and the experimentally found isotropization temperatures of the polymers.
Except for the methoxy-substituted polymer, all the others show melt birefringence in the temperature range between melting the point and the isotropization temperature. The photomicrographs obtained are shown in Fig. 32. (a) is that of the bromo-polymer; (b) is that of the cyano-polymer; and (c1) and (c2) are those of the nitro-polymer.

Thread-like textures were observed for these polymers, as shown in Fig.32 (c1) of the nitro-substituted polymer. However, for the same polymer at the same temperature a more complicated structure was observed in the thinner film region (along the edge of the melt film), as shown in Fig.32 (c2). Those of bromo- and cyano-substituted polymers are also not as the typical thread-like textures usually observed for low molecular nematic liquid crystalline compounds. Therefore the type of liquid crystalline phases which exist in these samples have not yet been determined, however texture identification may be made by X-ray analysis. The parent polymer of these polymers has a nematic mesophase, as shown in Fig.26(b). The structure of the mesophase may be changed by introducing a strong polar group into the mesogenic units. Such groups have enhanced the molecular
Figure 32a. Photomicrograph of the bromo-polymer, taken at 178 °C. Magnification: 320X
Figure 32b. Photomicrograph of the cyano-polymer, taken at 173°C. Magnification: 320X
Figure 32-c1. Photomicrograph of the nitro-polymer; -c2. Photomicrograph of the same polymer. taken at 170°C, magnification: 320X
interactions of the mesogens a great deal, so that a highly ordered mesophase may be expected for these polymers.

Two of these polymers, the cyano- and the bromo-substituted ones, have been investigated for the possibility of orientation in an electromagnetic field while in the liquid crystal state by Stein and coworkers in this University. The cyano-polymer was found to be too viscous to have any orientation under the field, while the bromo-polymer which had a lower inherent viscosity of 0.33 showed strong orientation along the field direction.
CHAPTER V
COPOLYMERS FROM THE REACTION OF DBTC WITH CYANO- AND METHOXY-HYDROQUINONES

Introduction

It is well known that copolymerization may affect both the glass transition and melting temperatures of polymers. Block and graft copolymers usually exhibit the two individual glass transition temperatures of their constituent parts provided that the molecular weights are high enough and the solubility parameters are different enough for the constituent parts to separate into different phases. In most cases the Tg values of random and alternating copolymers are intermediate between those of the two components, and some empirical relationships may be followed. In cases, for example, the random copolymer of styrene and methyl methacrylate, a plot of the glass transition temperature as a function of composition contains a minimum at a certain composition of th copolymer [95].
The crystallization and fusion of copolymers have been reviewed by Mandelkern [96]. For random copolymers the incorporation of the comonomer units decreases the regularity of the molecular chains, and, therefore, a lower packing efficiency and lower crystallinity are obtained. This effect has been described both theoretically and experimentally. In the case when the two components are crystallizable, the melting point decreases with increasing the amount of the comonomer to a minimum point and then increases steadily. There is generally also an intermediate range of compositions at which crystallinity is absent. Various copolyesters and copolyamides have been studied as examples of this effect [97, 98, 99].

The same behavior has been observed for thermotropic liquid crystalline polymers capable of crystallizing. For example, Roviello and Sirigu [68] found that their copolyalkanoates of 4,4'-dihydroxy, 'dimethylbenzalazine had lower melting points than the homopolymers, the minimum melting point was that of the copolymer having a 50/50 composition of the two comonomers. Although the copolymerization was also found to have a detrimental effect on the thermal stability of the mesophases, the
stable mesophase range was wider for the copolymers than for the homopolymers with a maximum for the 50/50 composition.

No reports have been found in the literature of thermotropic copolymers with different substituents on the mesogenic units. This chapter is dedicated to filling that gap. A series of copolymers have been synthesized which have the following structure:

\[
-\left[\text{OOC} \underset{\text{CN/OMe}}{\text{COO}} \underset{\text{OOC}}{\text{COO}} - \left(\text{CH}_2\right)_{10}^{-}\right]-
\]

As discussed in chapter IV, the cyano-substituted homopolymer is thermotropic and has a wide temperature range of mesophase stability from 157-219°C. In contrast, the methoxy-substituted homopolymer is non-liquid crystalline. However, as predicted in chapter IV, the methoxy-polymer may exhibit a mesophase if its melting temperature is depressed to some point below its predicted Ti (155 °C), see Table 21. Because the melting point of the methoxy-homopolymer is 158°C, which is not very much higher than the predicted value of Ti, it is reasonable to expect a mesophase of this polymer by incorporating into
it a small amount of the comonomer, the cyanonhydroquinone, as long as this incorporation can result in a few degrees depression in the melting temperature of this polymer.

It was most fortunate in our study that this expectation came true. By incorporating 10% of the cyanonhydroquinone monomer a copolymer was obtained which had a melting point of 150°C and a peak temperature for the mesophase-to-isotropic melt transition at 154°C, when examined during the heating cycle; while a temperature range of stable mesophase behavior of 31 degrees, from 148-116°C, was observed on cooling from its isotropic melt at a rate of 10°C/min. This result also indicates that the theoretical treatment made in chapter IV is meaningful.

Results and Discussion

The cyano-/methoxy-copolymers were prepared by solution polycodensations of DBTC with cyano- and methoxy-hydroquinones. Inherent viscosities of these copolymers are collected in Table 8.
the solubility of these copolymers is a function of their composition. For example, in THF the solubility decreases with increasing the percentage of the cyanohydroquinone fraction. But TCE is a good solvent for all composition of the copolymers.

In Table 11 are collected the transition temperatures of these copolymers. These data were all determined on a Perkin-Elmer DSC-II instrument at heating and cooling rates of 10 °C/min. \( T_m \) and \( T_i \) were taken as the endothermic peak temperatures of the corresponding transitions. In Table 22 are the corresponding transition enthalpy and entropy changes of the copolymers.

The 1/9 cyano-/methoxy- copolymer.

The DSC thermogram of this copolymer is shown in Fig.33. During the first heating cycle of the powder product a broad peak was resulted, curve A. The peak temperature was taken as the melting temperature, which was 150°C. A shoulder at the peak at 154°C is believed to be the isotropization temperature. This assignment was made after analysed the total DSC results of both the heating and cooling cycles, as shown in Fig.33. During cooling the liquid-crystallization and crystallization
Table 22. Enthalpy and entropy changes at phase transitions of copolymers from cyano- and methoxy- hydroquinones and DBTC

<table>
<thead>
<tr>
<th>Cyano/methoxy</th>
<th>ΔHm</th>
<th>ΔSm</th>
<th>ΔHm2</th>
<th>ΔSm2</th>
<th>ΔHi</th>
<th>ΔSi</th>
</tr>
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<tbody>
<tr>
<td>0/10</td>
<td>1.9</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1/9*</td>
<td>2.1</td>
<td>5.3</td>
<td></td>
<td></td>
<td>1.3</td>
<td>3.1</td>
</tr>
<tr>
<td>2/8</td>
<td>1.2</td>
<td>3.1</td>
<td>1.9</td>
<td>4.6</td>
<td>.77</td>
<td>1.8</td>
</tr>
<tr>
<td>4/6</td>
<td>3.1</td>
<td>7.7</td>
<td>.28</td>
<td>.69</td>
<td>.80</td>
<td>1.8</td>
</tr>
<tr>
<td>5/5</td>
<td>2.9</td>
<td>7.2</td>
<td></td>
<td></td>
<td>1.2</td>
<td>2.8</td>
</tr>
<tr>
<td>10/0</td>
<td>2.8</td>
<td>6.5</td>
<td></td>
<td></td>
<td>1.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

* For this copolymer the results were obtained from its cooling cycle on DSC.

Unit for ΔH is Kcal/mol.
for ΔS is cal/mol.K.
Fig. 33. DSC of copolymer 1/9 (cyano/methoxyhydroquinone).

A: first heating curve from the powder product; B: first cooling;
C: second heating; D: second cooling; and E: third heating curve.
were well distinguishable by the DSC, because the degree of supercooling of liquid-crystallization was usually much smaller than that of the crystallization. If the cooled sample was heated again, curve C was obtained. Although this thermogram was again not well defined, there must be a peak which correlates with the liquid-crystallization peak on the cooling thermogram of this sample. The peak at 154°C was assigned to the isotropization temperature, Ti.

Polarizing microscopy observations proved the presence of a mesophase of this polymer. Fig.37 is a photomicrograph of this copolymer which was taken at a temperature of few degrees higher than the isotropization peak temperature in the DSC thermogram. A Schlieren texture is observed in this photograph which suggests the presence of a nematic phase.

The 2/8 cyano-/methoxy- copolymer.

Fig.34 contains the DSC thermogram of this copolymer. The first heating cycle, A, showed at least three endotherms at 115, 140, and 157°C, respectively. The last one at 157 °C was assigned as the isotropization temperature.
Fig. 34. DSC of copolymer 2/8 (cyano/methoxyhydroquinone)
A: first heating; B: first cooling; and C: second heating curve
Fig. 35. DSC of copolymer 4/6 (cyano/methoxyhydroquinone)
A: first heating; B: first cooling; and C: second heating curve
Fig. 36. DSC of copolymer 5/5 (cyano/methoxyhydroquinone).
A: first heating, B: first cooling, C: second heating curve.
Figure 37. Photomicrograph of 1/9 copolymer, taken at 160°C, magnification: 320X
Difficulties arose when trying to interpret the other two endothermic peaks. They might be thought of as two melting transitions of the sample when the cooling and second heating DSC cycle were also considered. However, this interpretation became questionable when the sample was observed on the polarizing microscope. The sample was found to melt at about 115 °C and a highly intense birefringence was observed after that. Fig. 38 contains the photomicrograph of the sample, taken at 128 °C when the sample was found to be a free flowing melt.

Another phase transition was observed if the sample was further heated to the second DSC peak temperature. A nucleation process of the sample was observed at about 135 °C when the original clear melt changed to a turbid. This nucleation phenomenon is recorded in Fig. 39. This photomicrograph was taken at 139 °C during the first heating cycle of this sample. Above this temperature the sample was a clear melt again and the texture is shown by Fig. 40.
The 4/6 cyano-/methoxy- copolymer.

The DSC thermogram of this sample is shown in Fig.35. These curves are very similar in shape to those of 2/8 copolymer shown in Fig.34. Three endothermic peaks at 124, 134, and 165 °C were observed on the first heating cycle. The 165 °C peak was assigned with no doubt to the isotropization temperature of this copolymer. The other two are recorded as Tm1 and Tm2 with some uncertainty.

Fig.41-43 containes the photomicrographes of this copolymer taken at temperatures above Tm2 and below T1. Fig.41 was taken at 147 °C when the sample was first heated to this temperature. This photograph shows a very nice circular thread-like texture. A "cobble" texture was obtained if the sample was cooled down from its isotropic melt. Fig 42 shows this cobble texture, which was recorded at 155 °C when the sample was cooled to this point. On further cooling to 146 °C the cobble texture changed a little to that shown in Fig.43.
Figure 38. Photomicrograph of 2/8 copolymer, at 128°C, magnification: 320X
Figure 39. Photomicrograph of 2/8 copolymer, at 139°C, magnification: 320X
Figure 40. Photomicrograph of 2/8 copolymer, at 141°C, magnification: 320X
The 5/5 cyano-/methoxy- copolymer.

Fig. 36 contains the DSC results of this copolymer. Unlike the other copolymers, the 5/5 copolymer has the expected DSC thermograms with two endotherms in the heating cycle and two exotherms in the cooling cycle. The endotherm at the lower temperature in the thermogram is for the solid-mesophase transition, the other at a higher temperature is for the mesophase-isotropic melt transition.

The mesophase texture of this copolymer was shown in Fig. 44. The photomicrograph was taken at 151°C on the polarizing microscope. Neither typical nematic Schlieren or typical smectic textures were observed for this copolymer. The type of mesophase formed by this polymer must be determined by other techniques.

Copolymerization and properties of the copolymers.

As shown in Table 11, the glass transition temperatures of the copolymers were all lower than that of the two homopolymers. A non-linear change of Tg with composition was observed.
Figure 41. Photomicrograph of 4/6 copolymer, taken at 147°C during heating, 320X
Figure 42. Photomicrograph of 4/6 copolymer, at 155 °C during cooling, 320X
Figure 43. Photomicrograph of 4/6 copolymer, at 146°C during cooling, 320X
Figure 44. Photomicrograph of 5/5 copolymer, at 151°C, 320X
The melting temperature of the copolymer was found to be a function of the copolymer composition. With increasing content of the minor comonomer, the melting point of the copolymers decreased, passed through a minimum, and then increased. The lowest melting point was that of the 50/50 copolymer (133°C), which was about 15 degrees below that of the two homopolymers.

The isotropization temperature of the copolymers changed steadily with changing copolymer composition. Presence of the cyanohydroquinone units favored a higher thermal stability of the mesophase, while the introduction of methoxyhydroquinone units decreased the isotropization temperature of the copolymers. Because the influence of the copolymerization was larger on $T_i$ than that on $T_m$ of the copolymers, the temperature range of the stable mesophase was also narrowed by copolymerization.

As mentioned in chapter IV, the methoxy-substituted polymer was non-liquid crystalline. The predicted isotropization temperature of this polymer was 155 °C, which was three degrees lower than the melting point of this polymer. Therefore, the methoxy-substituted homopolymer was not able to form a stable mesophase after it melted. However, it was concluded that the potential
of forming a mesophase of this polymer might be realized if its melting point was depressed by certain methods. The results of the copolymerizations as shown in Table 11, supported this prediction.

According the decreasing tendency of the isotropization temperature with increasing methoxyhydroquinone content of the copolymers, the Ti of the methoxy-substituted homopolymer can be predicted to be near 154°C (Ti of the 1/9 copolymer). By introducing only 10% of the cyanohydroquinone moiety into the polymer, the melting point was depressed to 150°C, which was lower than the predicted isotropization temperature, and indeed a mesophase was formed by this copolymer on melting.

In summary, the following conclusion can be made: MANY OF THE APPARENTLY "NON-LIQUID CRYSTALLINE" ROD-LIKE POLYMERS HAVE A POTENTIAL OF FORMING LIQUID CRYSTALLINE PHASES, AND THIS POTENTIAL MAY BE REALIZED BY A CONSIDERABLE DEPRESSION OF THEIR MELTING POINTS.
CHAPTER VI
LIQUID CRYSTALLINE POLYMER BLENDS

Introduction

The properties of mixed materials depend very much on the miscibility of the components. A perfect molecular mixture would behave as a new material which has, for example, a single melting point differing from that of its two components. This mixture would be a true solution. On the other extremity, if the two components are totally immiscible, the two components will form their own phases individually and these phases would behave more or less independently of each other.

In general, the addition of low molecular weight soluble compounds to crystalline polymers results in a melting point depression. The melting point depression in this case can be determined by the expression:

\[
\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_2}{\Delta H_2 V_1} \left\{ (1 - \phi_2) - \chi_{12}(1 - \phi_2) \right\}
\]

where \( \phi \) is the interaction parameter, \( T_m \) the experimental melting point, \( T_m^0 \) the equilibrium melting point, \( \Delta H \) the
heat of fusion of the 100% crystalline polymer per mole of repeating units, \( V_1 \) the molar volume of diluent, \( V_2 \) the molar volume of polymer repeat unit, and the volume fraction of crystalline polymer.

If the diluent is another polymer instead of a low molecular compound, the equation may be written as follows, according to Nishi and Wang [101]:

\[
\frac{1}{T_m} - \frac{1}{T_m^*} = \left( -\frac{RV_2}{\Delta H_f^r V_1} \right) \chi_{12}(1-\phi_2)^2
\]

This equation indicates that a negative will yield a melting point depression as observed experimentally. With a positive interaction parameter, the theory predicts that a melting point elevation would result. However, a positive will most probably result in phase separation because of the unfavorable thermodynamic situation for high molecular weight polymer mixtures.

Just as with the melting points, the liquid crystal transition temperatures of mesogens may be lowered by the presence of foreign substances. When a mesogen is mixed with another mesogen or a non-mesogen, the solid-mesophase, mesophase-mesophase and mesophase-amorphous liquid transition temperatures may be depressed. The degree of this depression will depend upon the concentration of the
added component in the mixture.

Dave and Vora have reviewed the influence of molecular structure and composition on the type of the liquid crystals formed by mixtures of low molecular non-amphiphilic compounds [102].

Arnold and Sackmann [103] have examined the miscibility of liquid crystal phases. They reported that the nematic phases of two different compounds are completely miscible and form a homogeneous nematic liquid crystalline phase. The smectic phases of two different compounds are likewise miscible, forming a homogeneous smectic mesomorphic phase. However a smectic phase of one compound and a nematic phase of another compound, being distinct phases, are not miscible. On the other hand, a non-mesogenic compound may be miscible with either a smectogenic or a nematogenic compound and form a mesophase [104, 105]. The liquid crystalline transition temperatures are usually decreased by the mixing, but some exceptions exist[104]. For example, the plot of the transition temperatures for the smectic phase to the isotropic liquid phase against the mole% of smectogen for the physical mixture of ethyl p-azoxybenzoate and p-nitrobenzylidene-p-phenetidine exhibits a maximum. In
this case the mesophase-to-amorphous transition temperatures within a certain composition range are higher than that of the pure smectogenic compound.

The behavior of mixing of two mesophasic components has been used in the characterization of high molecular liquid crystalline phases [67, 10b]. Usually because of the high viscosity of polymers, as well as their broad molecular weight distributions and the coexistence of crystalline and amorphous phases, a positive identification of the polymeric mesophase may be difficult, that is, the mesophase textures of polymers as observed on a polarizing microscope may be not as well defined as for low molecular weight compounds. X-ray patterns may be of help for identifying the smectic mesophase. They are, however, often too diffuse to be used for unoriented nematic or cholesteric phases. The miscibility test of polymers with identified low molecular liquid crystals has offered another auxiliary method, which is very convenient and is becoming increasingly used for mesophase identifications, although the applicability of this test is not yet firmly established.
However, the mixing behavior of one thermotropic polymer with another thermotropic or with a non-liquid-crystalline polymer has received little attention. In this chapter two types of polymeric blends are discussed: (1) blends of two thermotropic polymers; and (2) blends of one thermotropic and one non-liquid-crystalline polymers. The morphology and the phase transitions of these two types of blends will be considered separately.

Results and Discussion

i) 1/1 Blends of two substituted mesogenic polymers.

The polymers were comixed in solution as follows: 1/1 mixtures (by weight) of the two polymers were dissolved in tetrachloroethane solvent. The solution was precipitated into a large quantity of acetone with stirring, and filtered out, washed with acetone, and dried under vacuum at room temperature. The blends were all characterized by DSC, as shown in Figures, 45–47, a heating and cooling rate of 10°C/min.
Fig. 47. DSC of polymer blend-2 (1:1 bromo-methyl-substituted polymers): first heating curve of the powder product
A: first heating curve
B: first cooling curve
Fig. 46. DSC of polymer blend-3 (1:1 cyano- : methyl-substituted polymer). A: first heating; and B: first cooling curve
Fig. 47. DSC of polymer blend-4 (1:1 nitro-, methyl-substituted polymer). A: first heating; and B: first cooling curve.
The DSC thermograms of the blend from the bromo- and methyl-substituted polymers showed two melting peaks, at 138 and 151°C, in the heating cycle, corresponding to those of the two components of the blend. These temperatures were each two degrees lower than those of the corresponding pure homopolymers (140 and 154 °C, respectively). This result indicates the presence of polymorphism in the solid state of this blend. However, the mesophases of these two polymers seemed to have better miscibility because only one broad isotropization endotherm was seen in the DSC thermogram, and this endotherm was similar in shape to that for the methyl-substituted polymer alone(Fig.27). As expected, the isotropization peak temperature of the blend was lower than that of one of the components but higher than the other.

Similar result was observed for the blend of the cyano- and methyl-substituted polymers. In this case one melting peak with a shoulder was observed in the DSC heating cycle at 154 and 158 °C, respectively. These temperatures were essentially identical to, or even a bit higher than, those of the two separate components.
Unlike the two blends first described, that from the nitro- and methyl-substituted polymers showed only one melting peak in the DSC heating cycle at 154°C.

A comparison of the results for these three different blends suggests that the results may be related to the increased polarities of the side groups in the series: Br, CN, NO₂.

No phase separation was found in the mesophase of these blends by observation on the polarizing microscope. In Fig.48 is a photomicrograph of the blend of the nitro- and methyl-polymers taken at 164°C. This observation might be an evidence of the same type of mesophase of these two homopolymers.

The thermodynamic parameters of these blends are collected in Table 23. A decrease in the isotropization temperatures of the blends compared to the homopolymers is readily seen from the data in this table.
Figure 48. Photomicrograph of blend of 1:1 methyl and cyano substituted polymers, taken at 164°C, magnification: 320X
Table 23. Transition properties of 1:1 blends with methyl-substituted polymer

<table>
<thead>
<tr>
<th>Substituents in the polymers</th>
<th>Methyl</th>
<th>Bromo</th>
<th>Cyano</th>
<th>Nitro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tm, °C</td>
<td>(154)</td>
<td>137,151(140)</td>
<td>154;158(157)</td>
<td>154(161)</td>
</tr>
<tr>
<td>Ti, °C</td>
<td>(190)</td>
<td>192(196)</td>
<td>204(219)</td>
<td>194(194)</td>
</tr>
<tr>
<td>Ti-Tm</td>
<td>(36)</td>
<td>41(56)</td>
<td>46(62)</td>
<td>40(33)</td>
</tr>
<tr>
<td>Δ Hm, Kcal/mol.</td>
<td>(4.5)</td>
<td>4.3(3.7)</td>
<td>3.3(2.8)</td>
<td>3.8(4.1)</td>
</tr>
<tr>
<td>Δ Sm, cal/mol°K.</td>
<td>(10)</td>
<td>10(8.9)</td>
<td>7.6(6.5)</td>
<td>8.9(9.4)</td>
</tr>
<tr>
<td>Δ Hi, Kcal/mol.</td>
<td>(1.7)</td>
<td>1.2(1.1)</td>
<td>1.2(1.1)</td>
<td>.70(.76)</td>
</tr>
<tr>
<td>Δ Si, cal/mol°K.</td>
<td>(3.6)</td>
<td>2.5(2.4)</td>
<td>2.5(2.2)</td>
<td>1.5(1.6)</td>
</tr>
</tbody>
</table>

Note: dates in the parentheses are that of the corresponding homopolymers.
ii). Blends of one mesogenic and one non-liquid-crystalline polymer.

This group of blends was made from the cyano-substituted polymer, which was mesogenic, and the non-liquid-crystalline methoxy-substituted polymer. The procedure for mixing was the same as described in the previous section for the preparation of blends of two liquid crystalline polymers. The blends were all characterized by DSC and with a polarizing microscope.

Figures 49-51 are DSC thermogram of three of the blends. Because the two components of the blends have melting temperatures very close to each other (158 and 157 °C, respectively) the melting endotherms of the blends are usually composed of a peak and a shoulder on the peak. In the cooling thermograms all of the blends show two crystallization exotherms because the two components have different recrystallization temperatures; in other words, the degrees of supercooling of the two polymer melts are different. The peak and its shoulder-temperatures for each blend in the DSC heating cycle are collected in Table 24, in which the temperatures of the shoulders are put in the parentheses. As shown in this table, the melting points of the blends are the same or only slightly higher
than those of the two separate components.
Fig. 49. DSC of blend-C (80% of methoxy-, 20% of cyano-substituted polyesters). A, first heating; B, first cooling; C, second heating curve. Rate: 10°C/min.
Fig. 50. DSC of blend-E (60% of methoxy- and 40% of cyano-substituted polyesters). Rate: 10°C per minute. A: first heating; B: first cooling; C: second heating curve.
Fig. 51. DSC of blend-\( G \) (30\% of methoxy-\( G \) 70\% of cyano-substituted polymers), A: first heating, B: cooling curve.
Table 24. Transition Temperatures of Methoxy-/cyano-substituted Polymer Blends

<table>
<thead>
<tr>
<th>Blend</th>
<th>Methoxy %</th>
<th>Tm1</th>
<th>Tm2</th>
<th>Ti, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>158</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>158</td>
<td>(163)</td>
<td>?</td>
</tr>
<tr>
<td>C</td>
<td>80</td>
<td>159</td>
<td>(163)</td>
<td>221</td>
</tr>
<tr>
<td>D</td>
<td>70</td>
<td>160</td>
<td>(163)</td>
<td>221</td>
</tr>
<tr>
<td>E</td>
<td>60</td>
<td>160</td>
<td>163</td>
<td>221</td>
</tr>
<tr>
<td>F</td>
<td>50</td>
<td>(160)</td>
<td>163</td>
<td>220</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>(160)</td>
<td>164</td>
<td>220</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>157</td>
<td>-</td>
<td>219</td>
</tr>
</tbody>
</table>

Note: Data in the parentheses are the shoulder temperatures on the DSC melting endotherms.
Table 25 collects the enthalpy and entropy changes of the phase transitions of these blends. A significant increase in the enthalpy of melting was observed for the blends. This increase is probably a result of the change of the interfacial and the surface energy during the melting process. Mahr [107] and Wu [108] have discussed the relationship of the interfacial and the surface tensions with the heat of the fusion of the polymers.

Observations made with the use of a polarizing microscope have shown the occurrence of phase separation in the temperature range between the melting and clearing points of these blends. Two phases were observed for all of the blends of all compositions. The methoxy-substituted homopolymer was non-liquid crystalline and only an isotropic phase was observed above the melting point. Addition of the cyano-substituted polymer to this polymer resulted in the formation of a mesophase of the cyano-polymer separated by a continuous isotropic phase of the methoxy-polymer, as shown by Fig.52 for the blend containing 30% of the cyano-polymer. On further increasing the amount of the liquid crystalline polymer, a phase inversion was observed. A photomicrograph of the 60/40 blend of the methoxy- and cyano polymers is shown in
Fig. 53. In this case the mesophase is the continuous phase and the non-mesophase is the discontinuous phase.
Table 25. Enthalpy and entropy changes at phase transitions of blends of methoxy- and cyano-substituted polymers

<table>
<thead>
<tr>
<th>Blends</th>
<th>Cyano-%</th>
<th>$\Delta H_m$ (cal/g)</th>
<th>$\Delta H_i$ (cal/g)</th>
<th>$\Delta H_i$ (cal/g of Cyano-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>20</td>
<td>6.4</td>
<td>0.53</td>
<td>2.7</td>
</tr>
<tr>
<td>D</td>
<td>30</td>
<td>6.8</td>
<td>0.61</td>
<td>2.0</td>
</tr>
<tr>
<td>E</td>
<td>40</td>
<td>6.2</td>
<td>0.94</td>
<td>2.3</td>
</tr>
<tr>
<td>F</td>
<td>50</td>
<td>5.7</td>
<td>1.2</td>
<td>2.5</td>
</tr>
<tr>
<td>G</td>
<td>70</td>
<td>5.2</td>
<td>1.7</td>
<td>2.5</td>
</tr>
<tr>
<td>H</td>
<td>100</td>
<td>4.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Figure 52. Photomicrograph of blend of 70/30 methoxy and cyano substituted polymers, taken at 190°C, magnification: 320X
Figure 53. Photomicrograph of blend of 60/40 methoxy and cyano substituted polymers, taken at 186°C, magnification: 320X
CHAPTER VII
SUMMARY AND SUGGESTIONS FOR FUTURE WORK

Substitution Effects on the Liquid Crystalline Polymers

Introduction of substituents into the mesogenic units of liquid crystalline compounds can extensively influence the properties of these compounds. The most important aspect of the liquid crystalline properties is, of course, the thermal stability of the mesophase. In other words, a wide temperature range of a stable liquid crystalline state is desirable. Other aspects may include the morphology and the rheological properties of the mesophase. The study described in the previous chapters is dedicated to the substitution effects on the thermal stability and the morphology of the mesophase of the polymers.

After this study, the following conclusions may be obtained:
When substituents are introduced into the mesogenic units of the polymers a depression of the melting temperature of the polymers will take place, no matter how large and how polar the substituents are. This effect is shown in both Table 9 and Table 10. In this polymer series a minimum depression of 70°C in the melting point was caused by the nitro group which has the highest polarity among the substituents, while the largest depression (160°C) was caused by the ethyl group. The steric effects of the substituents are considered to be responsible for the depression of the melting points of the polymers. In the solid state the molecular packing efficiency is lowered by the substituents and consequently there is a lower degree of crystallinity and a higher degree of the defects in the crystals.

A similar influence of the substituents is also observed on the glass transition temperature of the polymers. These results are shown in Table 9. A decrease in Tg of at least 23 degrees was caused by every linear alkyl substituent. This observation may be explained by the free volume theory, which says that the molecules need a certain amount of vacant space in the solid state before the segmental motions can start. Substitution has lowered
the molecular packing efficiency in the solid state and, therefore, more vacant space is left. As a result, the molecular segments can find enough space for starting the motion at lower temperatures.

(2). Similar to the cases of low molecular weight liquid crystals [14], substitution on the mesogenic units of liquid crystalline polymers would result in depression in the thermal stability of the mesophase. The isotropization temperature of all of the substituted polymers are all significantly lower than that of the unsubstituted polymer. These results are shown in Table 9 and 10.

(3). The deviation of the substituted polymers in the isotropization temperature from that of the unsubstituted polymer depends on both the steric and the polar effects of the substituents. The steric effect is detrimental to mesophase formation by pushing apart the mesogens from each other; on the other hand the polar effect is good for stabilizing the mesophase, because the molecular interactions between the mesogenic units are enhanced. An attempt was made in this study to predict the isotropization temperatures of the substituted polymers using the steric and polar parameters of the
substituents. A comparison of the predicted and the experimentally found values of the isotropization temperatures of the polymers is made in table 21.

(4). Copolymerization of monomers with different substituents will decrease both the melting and the isotropization temperatures, as shown in Table 11. The 50/50 copolymer has the lowest melting point, and a steady change in the isotropization temperature with the composition of the blends was observed.

(5). In our polymer series, the liquid crystalline polymers are found to be miscible with each other in their mesophase, while phase separation was observed in both the mesophase and the solid phase if a liquid crystalline polymer is mixed with a non-liquid crystalline polymer. These are shown in Figures 48, 52 and 53.

Suggestions for Future Work

A series of liquid crystalline polymers and copolymers were synthesized in this study. Most of these products were found to have fairly low melting
temperatures and a wide temperature range of the mesophase. These properties are desirable for their characterization and their practical applications. However, further investigations have to be done before the polymers can possibly be used. These investigations may include: the rheological properties; the molecular orientation of the mesophase under an electromagnetic field; the relaxation phenomenon of the molecules after an external electromagnetic field or a stress field is taken away; the miscibility of the liquid crystalline and non-liquid crystalline polymers and the morphology of the blends; and so on.

Introduction of substituents into the mesogenic units is found to be effective in depressing the melting points of the polymers. Among the various substituents the smaller alkyl groups, such as the ethyl and the n-butyl groups, are very effective in lowering the melting temperatures of the polymers, and a wide temperature range of the stable mesophase is maintained. These and the other substituents may be, therefore, introduced into other rigid rod-like polymers to produce thermotropic polymers which have a melting point low enough for the characterization and application of these polymers.
Finally, a theoretical treatment was made in this study to evaluate quantitatively the substitution effects on the isotropization temperatures of the thermotropic polymers. In order to support or to modify this treatment it is necessary to synthesize some other series of polymers having substituents on the mesogenic units, and having reasonably high molecular weights.
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