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## Synthesis and characterization of thermotropic liquid crystalline polyesters for use in molecular composites/

Sridevi Narayan-Sarathy  
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SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC  
LIQUID CRYSTALLINE POLYESTERS FOR USE  
IN MOLECULAR COMPOSITES

A Dissertation Presented

by

SRIDEVI NARAYAN-SARATHY

Submitted to the Graduate School of the  
University of Massachusetts Amherst in partial fulfillment  
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1995

Polymer Science & Engineering

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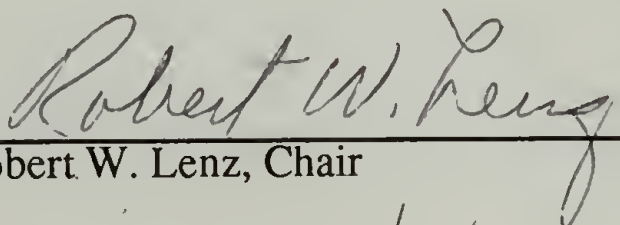
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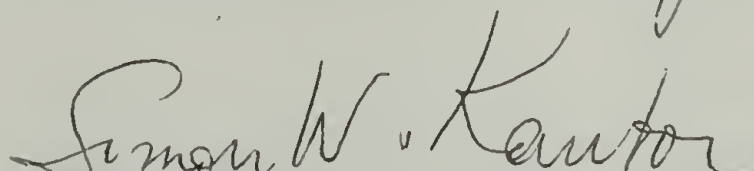
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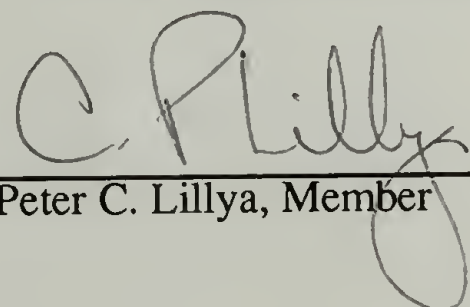
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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC  
LIQUID CRYSTALLINE POLYESTERS FOR USE  
IN MOLECULAR COMPOSITES

FEBRUARY 1995

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A molecular composite can be defined as a system where one polymer reinforces another at a molecular level to give enhanced properties. This concept could be applied to the enhancement of mechanical properties of flexible coil polymers like PET. Molecular level reinforcement of PET with rigid polymers could be achieved by increasing the flexibility of the latter in an effort to increase the entropic mixing and by selection of the rod-like and coil molecule, with specific interactions to increase enthalpy of mixing. Thermotropic liquid crystalline polyesters (LCP) were chosen for the rigid counterpart in our research as these materials exhibit orientation in the direction of draw resulting in unusually high strengths and moduli of the fibers in the draw direction. Also they exhibit lower melt-viscosity values at higher temperatures consequently lowering the processing temperatures of their blends compared to PET. Thus they function as processing-aids in addition to being reinforcing agents.

This dissertation work has involved the synthesis of thermotropic liquid crystalline polyesters containing various oxyethylene substituted hydroquinones. The

hydroquinone monomers were synthesized, which were then polymerized with terephthaloyl chloride by a solution state polycondensation method. Random and block copolymers containing the mesogenic segments and flexible PET / PBT segments were also synthesized and studied as these LCPs are expected to be miscible with PET by the interaction of the isotropic segments in the melt state. The systems investigated include poly ( 2-butoxyethoxy-1,4-phenylene terephthalate ) [PBEHT], poly ( 2-ethoxy-1,4-phenylene terephthalate ) [PEHT] and the random and block copolymers containing PEHT and PET / PBT segments. Some copolymers containing poly ( 1,4-phenylene terephthalate ) and PET / PBT segments were also investigated.

The polymers were mainly characterized by viscometry, thermogravimetry, DSC, NMR and optical microscopy. Especially in the case of the copolymer systems, extensive NMR analysis was done to get both the composition and sequence distribution. Structure-property relationships were drawn from copolymers with varying ratios of the rigid and flexible block sizes. Optimization of reaction conditions like solvent, acid-acceptor, temperature and time, to get high molecular weight polymers formed an important aspect of the research work. Rheological studies were done to study the role of the LCPs as processing-aids in the blends.

The presence of the flexible pendant group brings down the transition temperatures of the LCP to the processing temperature range of PET. The PBEHT system was found to be a good processing-aid for PET. The high molecular weight PEHT/BT copolymers obtained by conducting polymerization at high temperatures yielded thin films of good strength and mechanical integrity. The processing parameters of the blends of these polyesters with PET have to be optimized to draw conclusions about the reinforcing ability of the LCPs.



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## CHAPTER 1

### INTRODUCTION

A liquid crystal or mesomorphic substance can be defined as a state of matter which has liquid like fluidity and yet possesses anisotropy in certain properties. Polymeric materials exhibit mesomorphic behavior when the degree of order either in the solution or melt is intermediate between the almost perfect long range order observed in solid crystals and the statistical order present in isotropic liquids or gases.<sup>1,2</sup> Thus in a liquid crystalline polymer (LCP), the chains are sufficiently rigid to remain mutually aligned in the liquid phase although a long range positional order is absent.

Liquid crystalline polymers are high performance materials having versatile applications owing to their unique morphological behavior with respect to solvent or with respect to heating and cooling. High tensile strength fibers become possible through the preparation and subsequent spinning of anisotropic solutions of polyesters and polyamides.<sup>3-6</sup> These materials are characterized by very low melt-viscosity and long relaxation times with high molecular alignment. This property may be exploited for the development of high modulus materials.<sup>7,8</sup> Highly oriented polymeric films with the homeotropic orientation of mesogenic groups can be prepared and applied in opto-electronics.<sup>9</sup> A unique combination of properties like good solvent resistance, high continuous use temperature, excellent solder resistance, low thermal expansion, excellent barrier properties and low water absorption makes them available for a variety of applications in modern technology.<sup>10</sup> Molding



compounds exhibit low melt viscosity, long flow, and short cycles with little shrinkage and warpage because of polymer alignment and are ideal for tight tolerant molding of intricate, thin - walled parts.<sup>11</sup>

Polymer systems which possess liquid crystalline properties can be divided into 3 groups :

- 1 ) Lyotropic ( in solution )
- 2 ) Thermotropic ( in melt )
- 3 ) Amphotropic ( both in melt and in solution )

#### Lyotropic LCP systems

In the lyotropic mesophase state which is formed by dissolving a material in certain solvents, the molecular complexes are arranged in the solvent medium and exhibit lamellar, spherical or cylindrical mesomorphic states. The state of lyotropic liquid crystallinity is primarily achieved by change in solvent content. Liquid crystalline phases are not observed in the melt for lyotropic LCPs, primarily because the melting points of these materials are so high that they degrade before they melt. The criteria for the formation of nematic instead of an isotropic phase are :

- 1 ) Polymer concentration is above a critical value beyond which randomness of orientation is no longer possible.<sup>12</sup>
- 2 ) Polymer molecular weight is above a critical high value.
- 3 ) Temperature is below a critical value.

In general, the critical concentration is a function of the temperature, molecular weight and molecular weight distribution, chain rigidity and the solvent applied. A typical phase diagram for these lyotropic polymers shows the anisotropic

regions at higher polymer and solvent concentrations and an isotropic phase at lower polymer concentrations. In some systems, a narrow biphasic region may be found in which the mesomorphic and isotropic phases co-exist.

In the range below the critical concentration, the viscosity of the solution increases with increasing concentration, but at the critical concentration this viscosity reaches a maximum and with the onset of mesophase formation it drops rapidly to a minimum. As the concentration is further increased, the viscosity rises again until the point of solidification.<sup>13</sup> This change is shown in Fig ( 1.1 ) for a solution of poly ( p - benzamide ) in dimethyl acetate containing 4 wt % lithium chloride.<sup>22</sup>

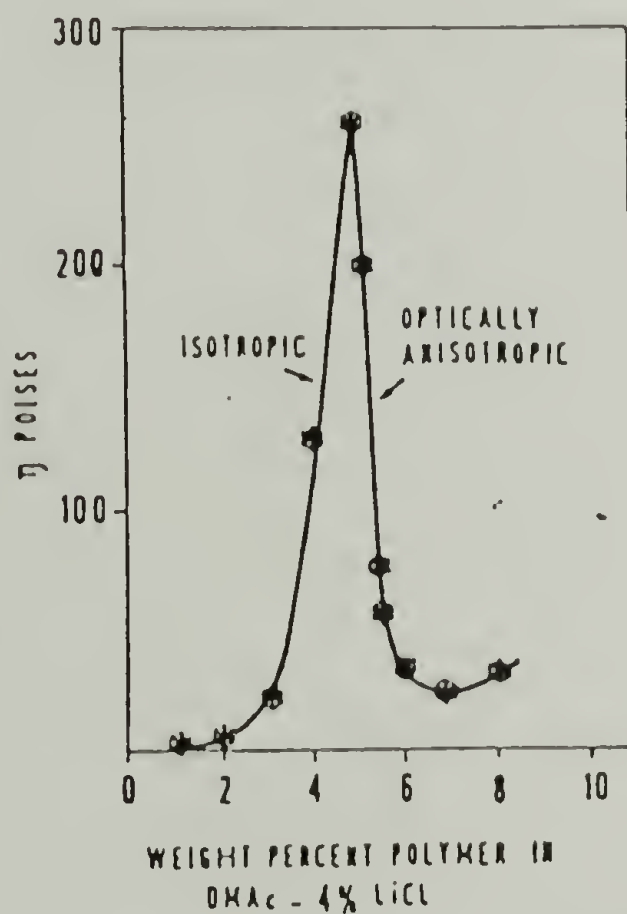


Fig. 1.1: Critical concentration for PBA

Two mechanisms can lead to the formation of a nematic phase in a liquid solution. The first mechanism is based on the Onsager or Flory type of approach which predicts the following:<sup>14,15</sup>

- 1 ) At a certain concentration the molecular asymmetry alone is sufficient to create an ordered phase without any attractive interactions. Solution of hard, asymmetric particles should separate into two phases above a threshold concentration ( $v^*$ ) which depends on the axial ratio of the particles. By the Flory relationship

$$v^* = 8 / x ( 1 - 2 / x ) \text{ where } x = \text{axial ratio.}$$

- 2 ) Critical concentration is bridged by a phase concentration.
- 3 ) Polydispersity broadens biphasic gap.
- 4 ) Nematic phase totally excludes coil while the reverse is not true.
- 5 ) Semi - flexible LCPs may be treated according to the classical Kuhn model chain where the persistence length is used to determine an effective axial ratio for the particles.<sup>16</sup>

The alternative mechanism is based on the Maier - Saupe mean field theory and shows that a stable mesophase is formed by an anisotropic potential.<sup>17,18</sup> The combination of a worm - like chain model and the Maier - Saupe approach has also been suggested by Jahnig<sup>19</sup> and is developed further by Ten Bosch et al<sup>20</sup> as well as by Warner and co-workers.<sup>21</sup>

The rheological behavior of these lyotropic systems is quite complex. Temperature, concentration and molecular weight dependencies of the viscosity - shear - rate behavior of these solutions have been examined in detail<sup>23-26</sup> and the master curve for viscosity is found to be divisible into three regions ----



yielding region at lower shear - rate, Newtonian region at intermediate shear - rate and shear thinning region at higher shear - rate.<sup>27</sup>

The most prominent physical characteristics of the lyotropic polymers are the tensile and thermal properties of fibers made from these polymers. The fibers are typically characterized by high tensile strength, a low elongation at break and high modulus.<sup>28</sup>

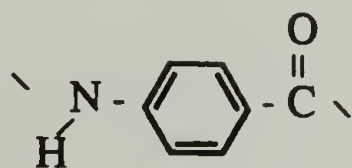
Lyotropic behavior was first recognized in the case of poly (  $\Gamma$  - benzyl - L - glutamate )<sup>29</sup>. Polymers that have gained technical importance are the para - aromatic polyamides or aramids<sup>30,31</sup>, the heterocyclic rigid - rod polymers<sup>28</sup> and the aromatic polyamide - hydrazide. The structures of the important polymers are illustrated in Fig. 1.2. Liquid crystalline polyethers<sup>32</sup>, poly (diacetylenes)<sup>33</sup> and cellulose are the other candidates for high performance yarn preparation<sup>34</sup>.

### Thermotropic LCP systems

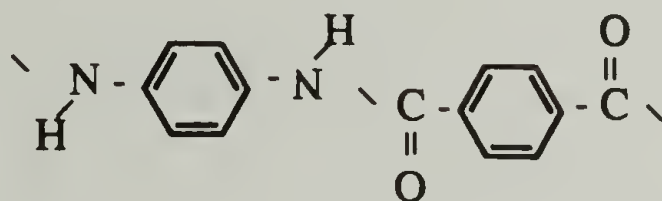
The melting point of rigid polymers can be depressed by introducing a degree of flexibility into the polymer chain, such as with structures that provide a kink or swivel to the chain or with flexible spacer groups that separate the rigid chain segments. In that case, the critical concentration for forming a liquid crystalline phase is high usually requiring bulk polymer, and anisotropic melts are obtained. These materials are thermotropic.<sup>35</sup>

The different types of links possible in thermotropic LCPs are schematically represented in Fig. 1.3.<sup>1</sup>

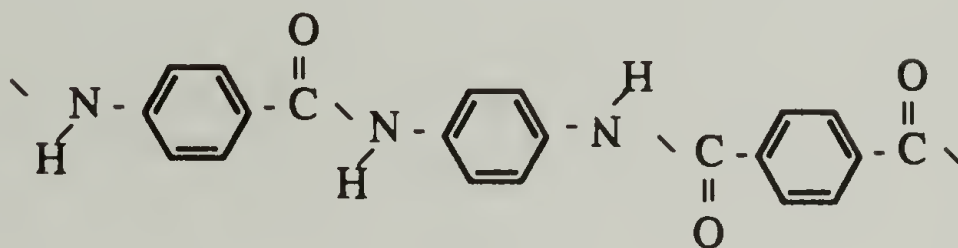
Poly - p - benzamide [ PpBA ]



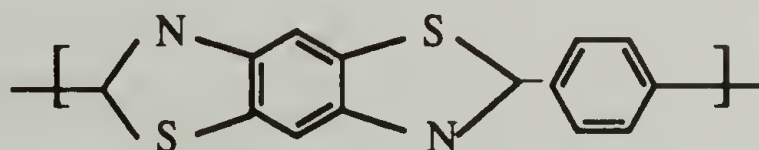
Poly ( p - phenylene terephthalamide [ PpPTA ]



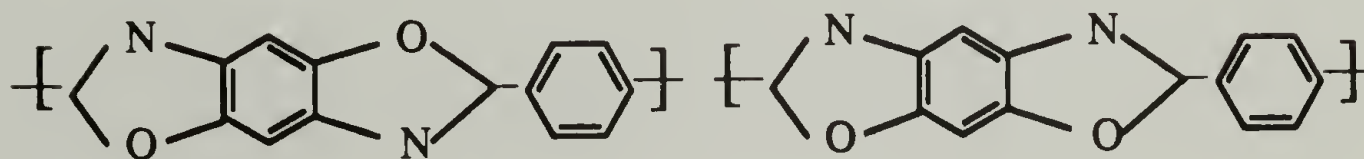
PpBAT



Poly ( benzothiazole ) [ PBT ]



Poly ( benzoxazole ) [ PBO ]



trans PBO

Cis PBO

Fig 1.2: Lyotropic liquid crystalline polymers

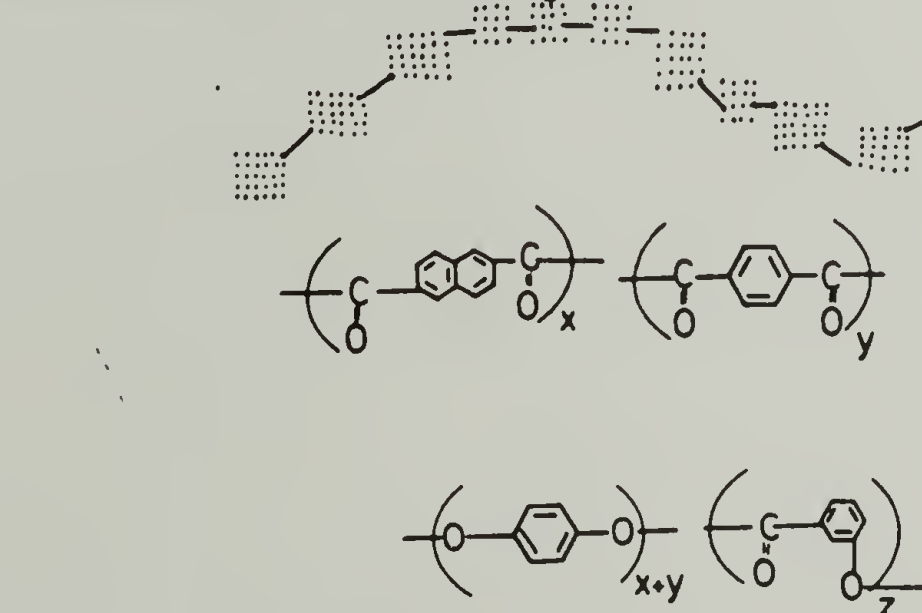
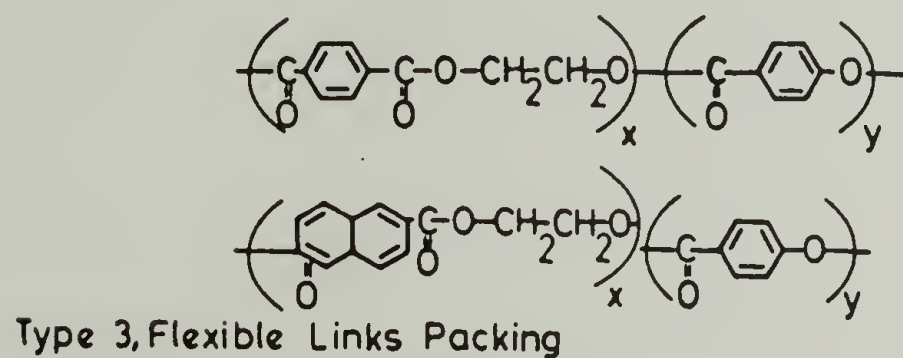
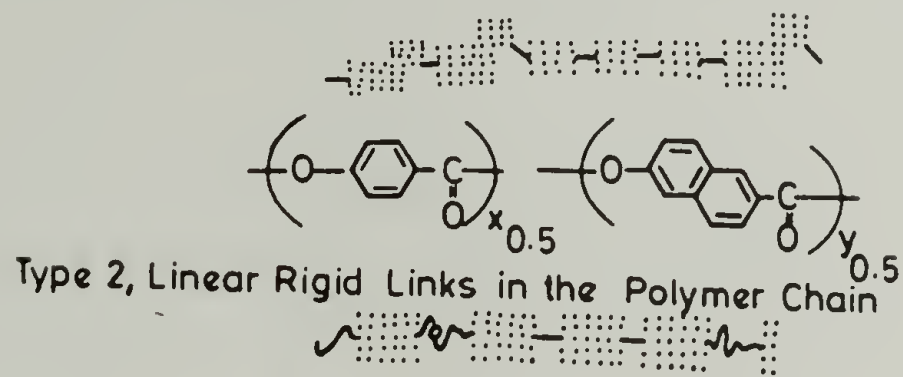
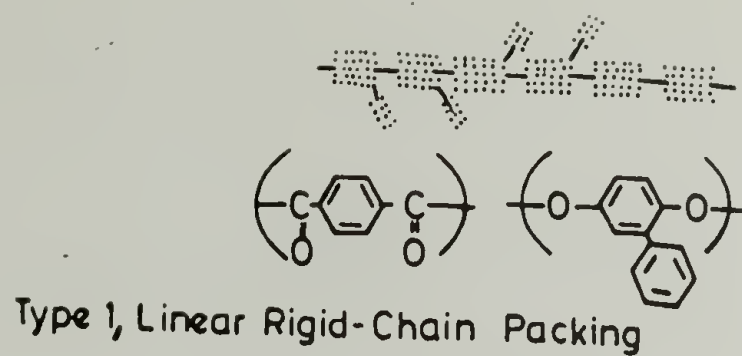


Fig. 1.3 : Possible types of links in thermotropic liquid crystalline polymers



- Type 1 - Linear rigid chain packing refers to any mechanism maintaining essential linearity and regular correlation.
- Type 2 - Flexible links crystallize only at low temperatures, well below those of the aromatic sequence, and this tends to weaken overall chain cohesion in the melt.<sup>36</sup>
- Type 3 - The polymers in this category generally make extended close - packing and crystallization difficult.<sup>37-39</sup>

The transitions of the macromolecular, thermotropic liquid crystals are governed by temperature, pressure and deformation. Molecular level orientational order can best be achieved which are rods, laths or discs. According to Born, permanent dipoles are responsible for the LC behavior while Maier and Saupe hold that the anisotropic dispersion forces are responsible. Onsager took into account the steric interactions or the hard-core repulsions in postulating the theory for the liquid crystalline behavior.

There are three possible ways of obtaining thermotropic polymers having liquid crystalline properties :

- 1 ) Introduction of the mesogenic groups into a polymer back-bone leads to main chain LCPs.<sup>36,37,40</sup>
- 2 ) Attaching the mesogenic groups directly to a polymer back-bone or through some flexible aliphatic chains leads to side - chain LCPs.<sup>41-45</sup>
- 3 ) By the blending of low molecular weight, optically active molecules into the polymer ( i.e. ) inducing liquid crystallinity as a whole.

In general, the different thermotropic liquid crystalline polymer architectures can be represented as in Fig. 1.4.<sup>35</sup>

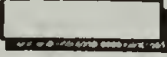




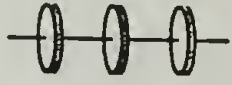




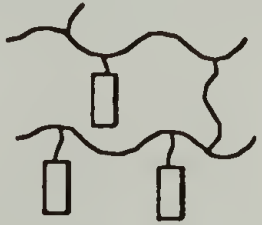
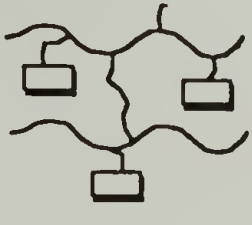
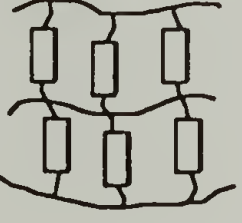
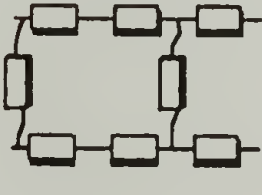
	 Rod-like mesogenic group		 Disc-like mesogenic group	
LC main chain polymer				
LC side chain polymer				
LC side chain elastomer				
LC thermoset				

Fig. 1.4 : Thermotropic LC polymer architectures

## Main chain liquid crystalline polymers

Different models can be considered for the preparation of LC main chain polymers. The mesogenic monomer can be directly connected within the polymer chain. The resulting rigid, rod-like polymer can be described by the molecular axial ratio, which is directly proportional to the degree of polymerization. The chemical constitution of the mesogenic group and their substituents strongly affect the LC behavior too.

If the mesogenic groups are connected via a flexible spacer, the main chain becomes semi-flexible. The back-bone can be described as a chain of freely-joined rods which have the axial ratio of the original mesogenic unit. The axial ratio determines the phase stability of the liquid crystalline polymer. In general, the incorporation of flexible spacers in the main chain results in at least one of the three following effects :

- 1 ) Increased reduction in the transition temperatures with increased spacer length because of decoupling of the intramolecular interactions among the mesogens in the polymer chain.
- 2 ) An odd - even relationship for the transition temperatures in which the melting and clearing temperatures of polymers with an even number of atoms in the spacer generally are higher than those for the polymers with odd - numbered spacers.
- 3 ) Formation of smectic phases, which are rare with shorter chains but become fairly common with longer chains.

The mesogenic group must consist of at least two aromatic ( or cycloaliphatic) rings connected in the para positions by a short rigid link which maintains the linear alignments of the aromatic rings. The linking groups used in LC polymer systems have included imino, azo, azoxy, ester and trans - vinylene



groups, and a direct link between aromatic rings may also be used such as in biphenyl and terphenyl units. The flexible spacers in the main chain, thermotropic LCPs include polymethylene, poly (ethylene oxide) and poly (siloxane) segments. The flexible spacer plays a very important role in determining not only the transition temperature but also the type of mesophase. A thorough list of main chain LCPs is given in the review published by Lenz and coworkers.<sup>52</sup> A few representative polymers with the corresponding references are listed in Table. 1.1.

### Side chain liquid crystalline polymers

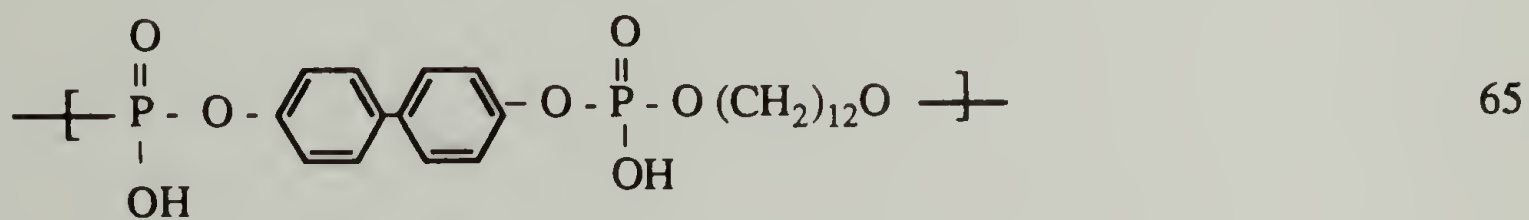
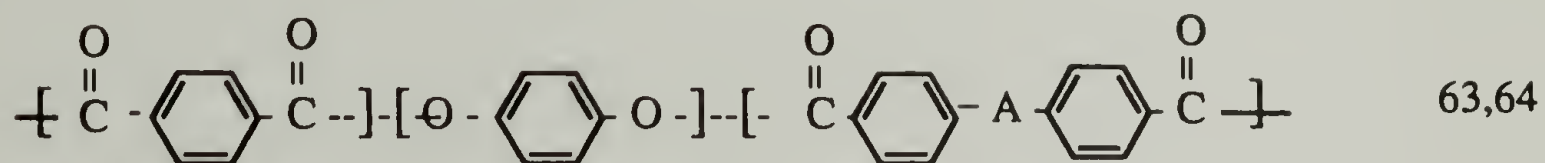
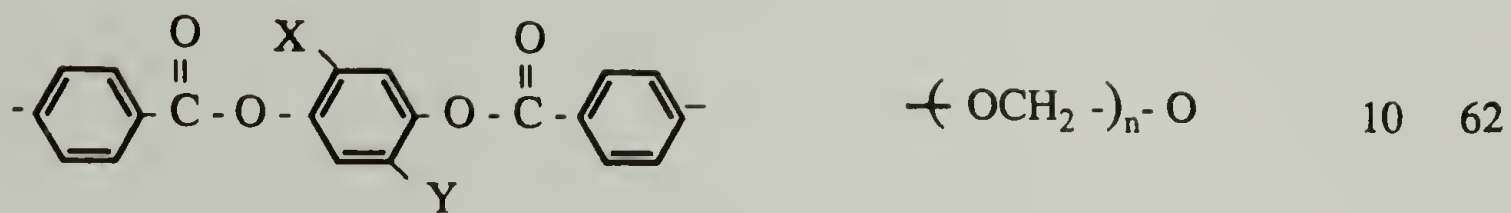
These are liquid crystalline polymers containing the mesogenic groups pendant to a flexible polymer chain. As the mesogenic group has higher mobility in the side - chain, the polymer chain is less restricted in its motions and can respond more quickly to applied fields than main - chain LCPs. The mesogen can be linked to the main - chain via a flexible spacer or without a flexible spacer. If the rigid mesogenic side - chains are directly attached to the polymer back - bone, motions of the polymer segments and the mesogenic groups are directly coupled. In such a case, at temperatures above glass transition, the polymer chains tend to adopt a statistical chain conformation that hinders anisotropic orientation of the mesogenic side - chains. On the other hand, the flexible spacer decouples the motions of the side - chain and the main chain and alleviates this steric hindrance. Variation of the spacer length should clearly influence the LC order of the side - chain. All positional

Table. 1.1 : Main chain liquid crystalline polymers

<u>Mesogenic spacer</u>	<u>Flexible spacer</u>	<u>n</u>	<u>Ref.</u>
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ + \text{O} - \text{C}_6\text{H}_4 - \text{O} - \text{C} - \text{C}_6\text{H}_4 - \text{C} + \\ \quad \quad \quad   \\ \quad \quad \quad \text{C}_6\text{H}_5 \end{array}$	-	-	53
$\begin{array}{c} \text{O} \\ \parallel \\ + \text{O} - \text{C}_6\text{H}_4 - \text{C} - \text{O} - \text{C}_{10}\text{H}_8 - \text{C} + \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{O} \end{array}$	-	-	54
$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ - \text{C}_6\text{H}_4 - \text{C} - \text{N} = \text{N} - \text{C} - \text{C}_6\text{H}_4 - \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$- \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - (-\text{CH}_2-)_{\text{n}} - \overset{\text{O}}{\parallel}{\text{C}} - \text{O} -$	8,10,12	55,56
$- \text{C}_6\text{H}_4 - \text{CH} = \text{N} - \text{C}_6\text{H}_4 -$	$- \text{O} - \overset{\text{O}}{\parallel}{\text{C}} - (-\text{CH}_2-)_{\text{n}} - \overset{\text{O}}{\parallel}{\text{C}} - \text{O} -$	10	57
$\begin{array}{c} \text{O} \\ \parallel \\ - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{N} = \text{N} - \text{CH}_2 - \text{C}_6\text{H}_4 - \\ \quad \quad \quad \downarrow \\ \quad \quad \quad \text{O} \end{array}$	$- \overset{\text{O}}{\parallel}{\text{C}} - \text{O} - (-\text{CH}_2\text{CH}_2\text{O}-)_{\text{n}} - \overset{\text{O}}{\parallel}{\text{C}} -$	2,3,4	58
$- \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 -$	$- \overset{\text{O}}{\parallel}{\text{C}} - \text{O} - (-\text{CH}_2-)_{\text{n}} - \text{O} - \overset{\text{O}}{\parallel}{\text{C}} -$	2,4,5,6,10	59
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ - \text{C}_6\text{H}_4 - \text{C} - \text{O} - \text{C}_6\text{H}_4 - \text{O} - \text{C} - \text{C}_6\text{H}_4 - \end{array}$	$\left( \text{OCH}_2\text{CH}_2\text{O} \right)_{\text{n}}$	4	60

continued next page

Table 1.1 continued



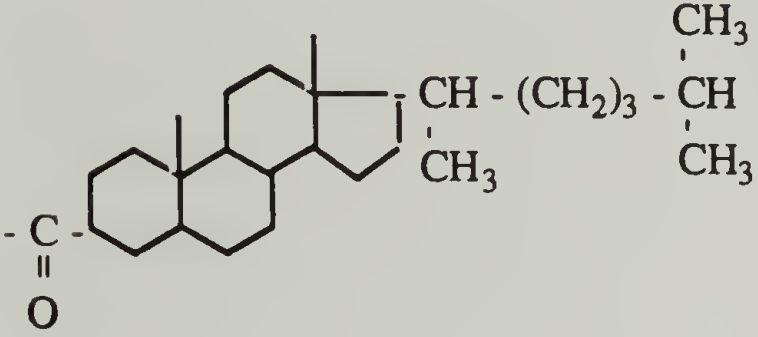


mobility of the mesogen is based on the conformational motion of the flexible spacer and back - bone. With short chains and proper back - bone geometry, a unique crystal encompassing back - bone and side - chain is possible. As the length of the flexible spacer increases, the side - chain can crystallize independent of the back - bone chain and the LC polymers are similar in behavior to low molecular weight liquid crystals. Appearance of the mesophases depends on the specific combination of steric and polar characteristics of the main and side chains.

Recently, an excellent book<sup>66</sup> has been published which describes the scope that side - chain liquid crystalline polymers offer for molecular engineering, including the realization of new mesomorphic series and the detailed texture behavior of these states. Synthetic approaches involve either the formation of polymer from monomers containing the mesogenic groups already present or, alternatively, the attachment of mesogenic groups to a preformed polymer chain. A number of side - chain LCPs have been synthesized by attaching mesogenic groups to methacrylate, acrylate, siloxane and poly (phosphazene) chains.<sup>67,68</sup> Other than conventional mesogenic groups, introduction of crown ethers or the use of half disk and half rod - like mesogenic cores has resulted in very novel LCPs. Discotic mesogenic groups have also been attached to polymer chains.<sup>69</sup> Even ionic linkages have been employed to connect mesogenic cores to a polymer back-bone.<sup>70</sup>

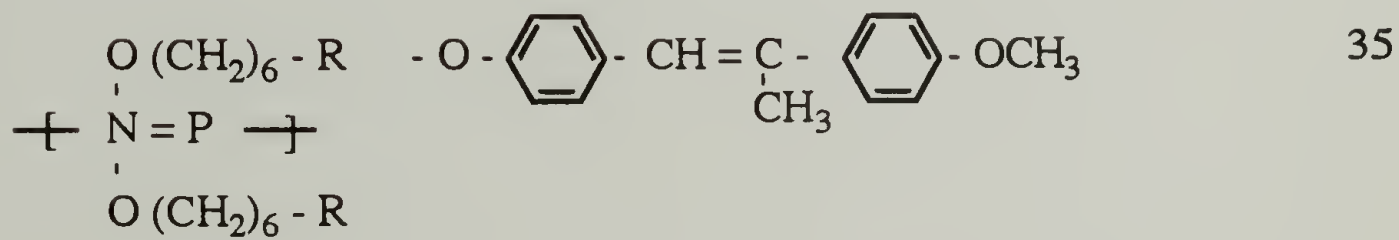
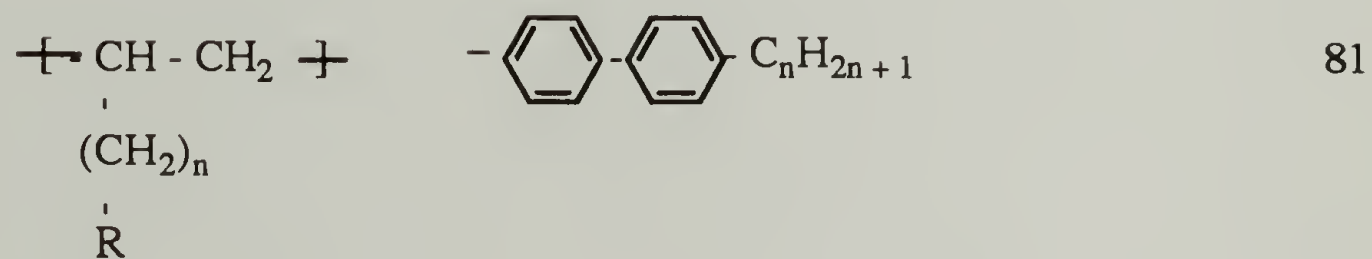
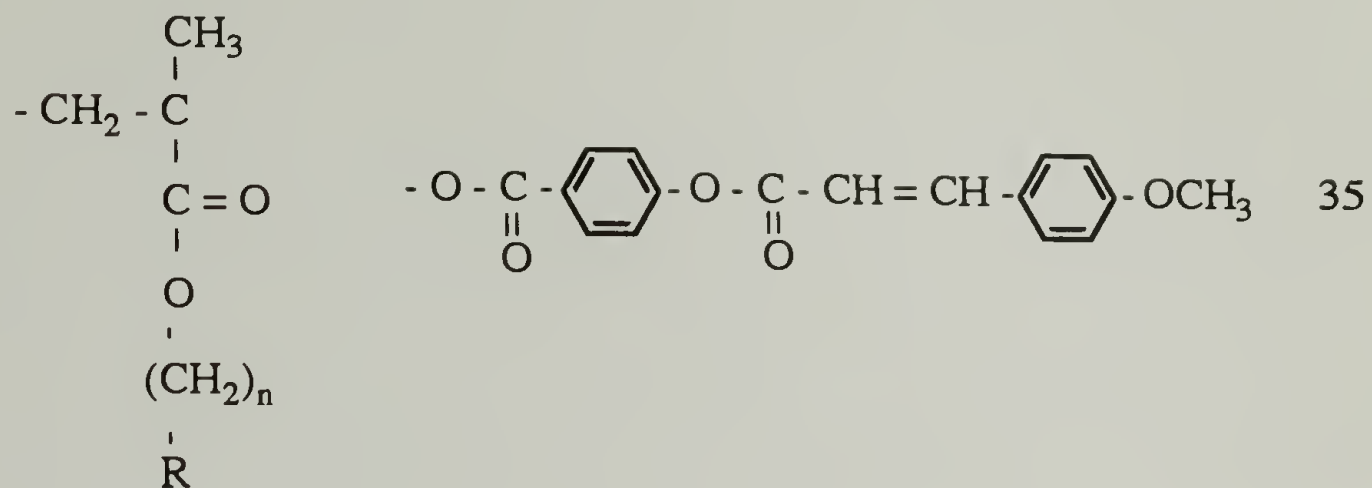
Many detailed reviews have appeared on the synthesis and characterization of side - chain LCPs and the mesophases they form.<sup>71-76</sup> Some representative side - chain LCPs are listed in Table. 1.2.

Table. 1.2 : Side chain liquid crystalline polymers

Backbone	R = Mesogen	Ref.
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{CH}_2 - \text{C} \\    \\  \text{C} = \text{O} \\    \\  \text{NH} - (\text{CH}_2)_n \text{R}  \end{array}  $	$  \begin{array}{c}  \text{O} \qquad \qquad \text{O} \\     \qquad \qquad    \\  -\text{C} - \text{O} - \text{C}_6\text{H}_4 - \text{O} - \text{C} - \text{C}_6\text{H}_4 - \text{OC}_6\text{H}_{13}  \end{array}  $	77
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{CH}_2 - \text{C} \\    \\  \text{C} = \text{O} \\    \\  \text{NH} - (\text{CH}_2)_n \text{R}  \end{array}  $		78
$  \begin{array}{c}  \text{CH}_3 \\    \\  \text{---} \text{Si} \text{---} \text{O} \text{---} \\    \\  (\text{CH}_2)_n \\    \\  \text{R}  \end{array}  $	$  \begin{array}{c}  \text{O} \\     \\  -\text{C} - \text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_{13}  \end{array}  $	79
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{CH}_2 - \text{C} \\    \\  \text{C} = \text{O} \\    \\  \text{O} \\    \\  (\text{CH}_2)_n \\    \\  \text{R}  \end{array}  $	$  -\text{O} - \text{C}_6\text{H}_4 - \text{C}_6\text{H}_4 - \text{CN}  $	80

continued next page

Table 1.2 continued





### LC Elastomers<sup>46,47</sup>

Elastomeric LC networks have the potential for translating mechanical deformation into optical or electric changes and hence applications such as wave-guides & piezoelectric materials are possible.

### LC Thermosets<sup>48-51</sup>

Nematic LC phases were identified in rigid rod molecules end-capped with conventional cross-linking groups such as Maleimide. Thermally induced polymerization occurred in the nematic phase region and resulted in retention of the nematic texture in the final cross-linked solid giving a LC thermoset. These are useful as high performance composite matrix materials.

### Amphotropic LCP systems

Thermotropic liquid crystalline polymers can also exhibit liquid crystallinity in solution provided a suitable solvent can be found in which the polymer can be made to dissolve to concentrations above a critical concentration at a particular molecular weight and temperature. It is possible to obtain LC organizations of both modified hydroxyethyl cellulose derivative<sup>82,83</sup> and poly(isocyanates)<sup>84</sup> not only lyotropically but also thermotropically. Block copolyesters based on trans-1,4-cyclohexyleneoxy, trans-1,4-cyclohexylene carbonyl and terephthaloyl units of variable compositions form nematic LCP phases in o-chlorophenol solutions.<sup>8</sup>

### Molecular arrangements in LC polymers

Four main types of liquid crystalline polymers can be distinguished on the basis of their molecular layers arrangement. Structural differentiation of these phases is related to the packing aspect and dimensionality of the translational organization of the molecules.

## Nematic LCPs

Nematic LCPs are distinguished by a unique director ( optic axis ) in the fluid which is established by the parallelism of the long axes of molecules. There is no translational order in this nominally uniaxial fluid. In nematic phases, chain ends ( defects ) are randomly distributed in the ordered fluid. A schematic representation of the nematic phase is given in Fig. 1.5 ( a ).<sup>2</sup>

The direction of the long molecular axes of the mesogen in a LCP is known as director axis  $n$ . The alignment of the mesogens within a nematic mesophase is not precisely parallel because of thermal motion and an order parameter,  $S$ , characterizes the degree of parallel alignment. It is defined as

$$S = 1/2 ( 3 \cos^2 \theta - 1 )$$

where  $\theta$  = Average angle between individual molecular axis and the director  $n$ .

For random isotropic phase,  $S = 0$

perfect alignment,  $S = 1$

perpendicular alignment  $S = 1/2$

A variation of this molecular arrangement is the cybotactic nematic phase where a bundle of the mesogenic moieties is arranged in a strata in which the plane of the layer is tilted with respect to the mesogen.<sup>86-87</sup> 'Board-like' molecules would result when the rotation about the longitudinal axis is prevented as in the case of side-chain LCPs or by lateral attachment of substituents in main-chain LCPs.

Macroscopically biaxial nematic phase would be formed as a result of the long range orientational order developed by the short molecular axis in such polymers.<sup>88-90</sup>

Threaded Schlieren texture observed by optical microscopy is typical of nematics. This may be the origin of the name of the phase as 'nematos' which means 'threadlike' in Greek.

### Smectic LCPs

Chain parallelism characterizes the smectic phase but translational order is also present in the form of long - range stratification normal to the chain - axes. The molecules are arranged in an ordered or disordered manner in layers and their centers of gravity can move in two dimensions on the smectic plane. A schematic representation of the smectic phase is given in Fig. 1.5 ( b ).<sup>2</sup> This leads to various polymorphic modifications within limits of the smectic type of mesophase. The molecules of the repeating units are arranged in both a parallel and lateral order, often showing highly structured and generally fan - shaped pattern, called a 'focal conic' texture under the microscope. Table. 1.3 shows the division of smectic systems into

- a ) Smectic phases with very little correlation of structures between layers.
- b ) Phases with extensive inter-layer correlations.

Subdivisions depend upon the tilt and packaging of mesogens within the layers.

### Cholesteric LCPs

Cholesteric LCPs are similar to nematics in organization, with the additional feature of a cumulative twist between molecules, giving rise to a helical type structure. This is a result of the asymmetry of intermolecular forces. A schematic representation of the phase is given in Fig. 1.6.<sup>2</sup> There is a long range orientational order of the long axis of the mesogenic molecules characterized by the director  $D$ . The cholesteric phase with an optical axis,  $h$ , is characterized by the pitch ' $P$ ' where



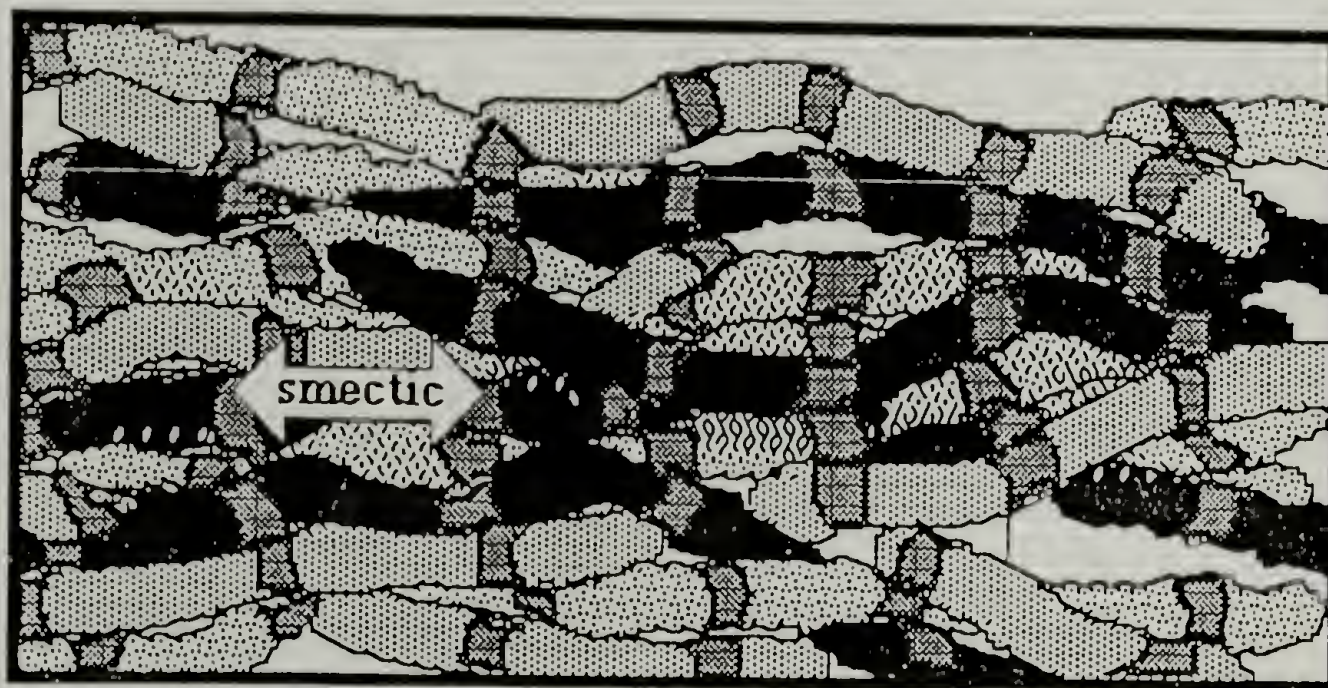
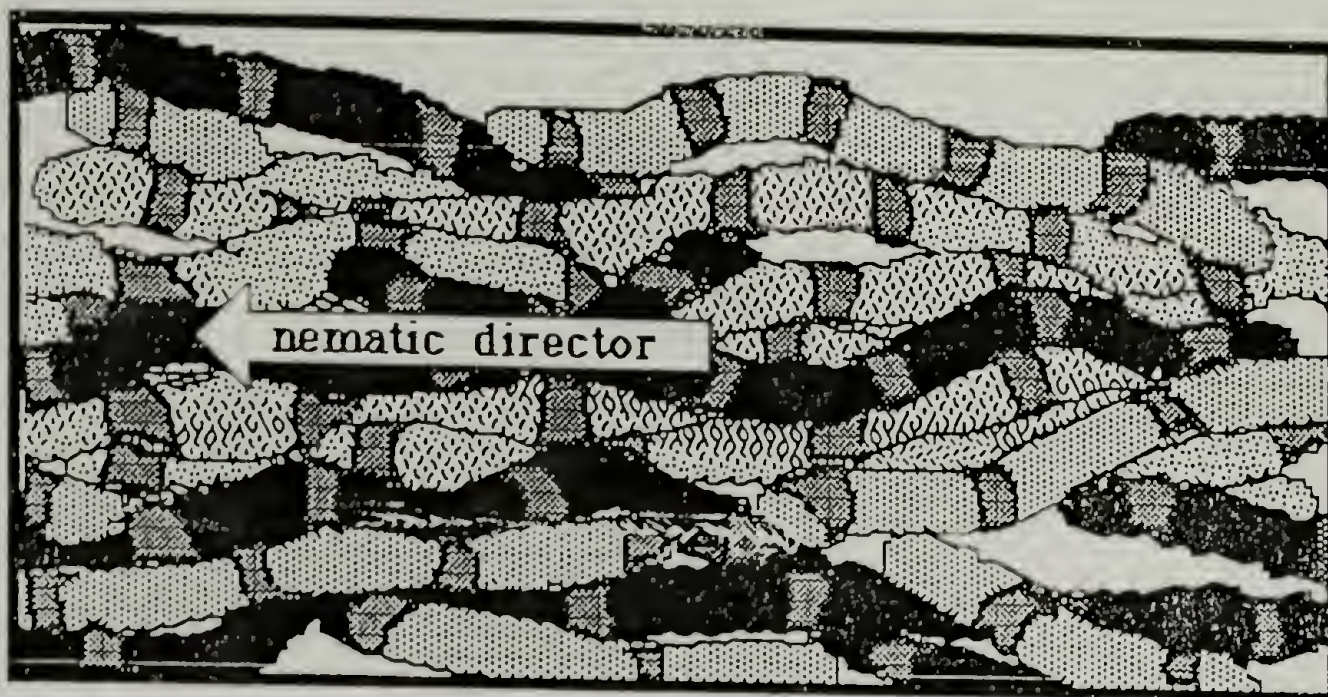


Fig. 1.5 : Schematic representation of the nematic and smectic mesophases



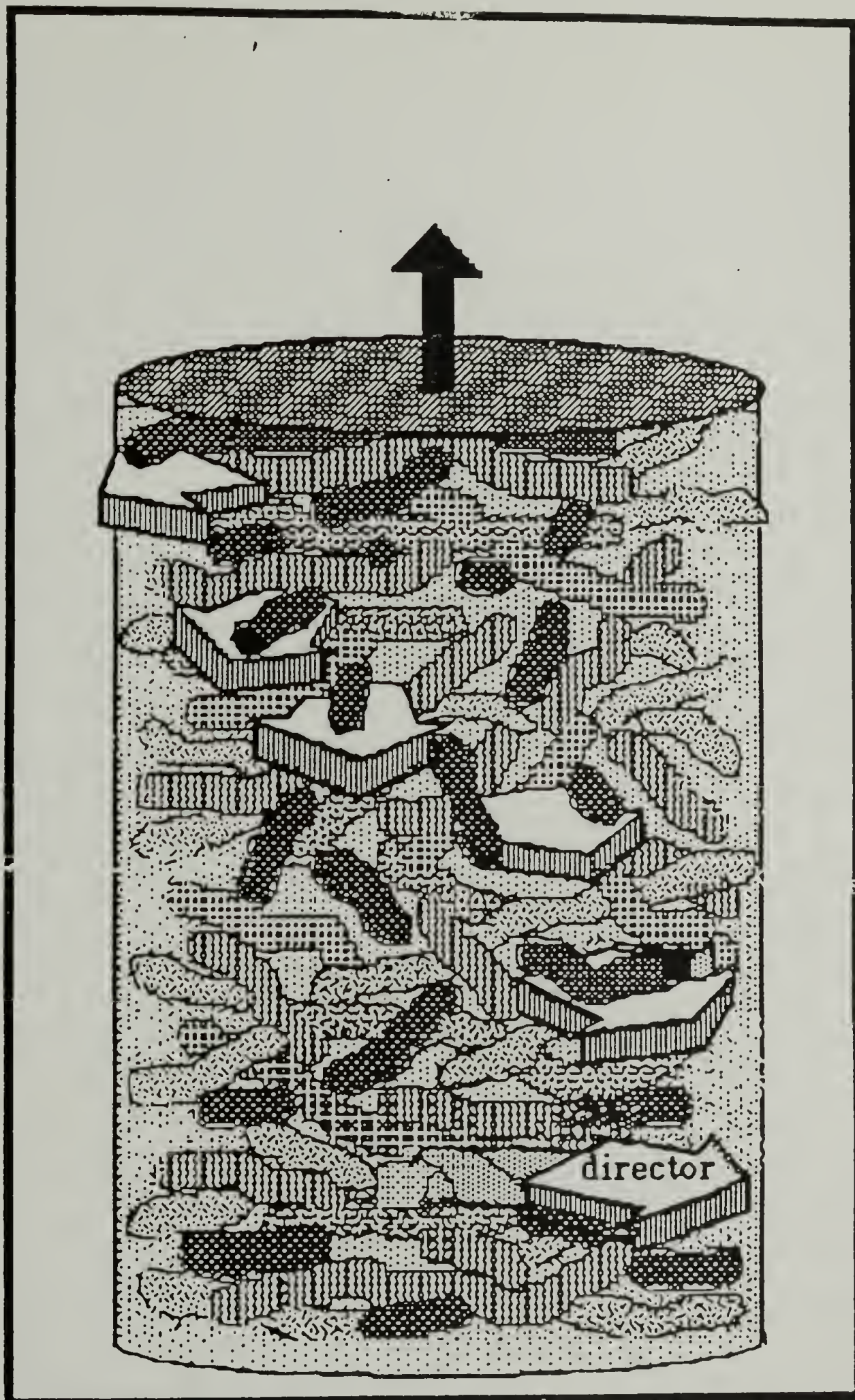


Fig. 1.6 : Schematic representation of the cholesteric mesophase

$$P = 2 \Pi r_{ab} / \Theta$$

$\Theta$  = Twist angle

$r_{ab}$  = Distance of molecules perpendicular to the director

The periodicity of the helical structure leads to spectacular color effects. This phase is usually formed by a nematic mesogen that is optically active in some manner.<sup>91</sup>

Table. 1.3 : Division of smectic systems

( a )			( b )		
Type	Lamellar order	Tilt	Type	Lamellar order	Tilt
SA	None	No	SB	Yes	No
SB	Yes	No	SE	Yes	No
SC	None	Yes	SG, SG'	Yes	Yes
SF	Yes	Yes	SH, SH'	Yes	Yes
SI	Yes	Yes			

### Discotic LCPs

In this system, disc - shaped mesogens form partially ordered mesophases in which they are organized in vertical stacks. Two types of discotic phases have been identified :

- 1 ) Columnar mesophase : Columns are packed together to form a two - dimensional crystal - like array. Within the column, the positions of the mesogens may have short or long range order.
- 2 ) Nematic phase : Characterized by a single order parameter which is associated with the tendency of the disc to align parallel.



### Molecular composite

A molecular composite may be defined as a system where one polymer reinforces another at a molecular level to give enhanced properties. This concept could be applied to the enhancement of the mechanical properties of flexible coil polymers like PET. The coil polymers could be blended with rigid polymers or more specifically LCPs to get molecular level reinforcement. This could be achieved

- a) by increasing the flexibility of the rigid - rod polymer in an effort to increase the entropic mixing.

- b) by grafting the flexible chains on to the backbone of the rigid - rod.

- c) by selection of rod - like and coil molecules with specific interactions to increase enthalpy of mixing

- d) by controlling the kinetics of aggregation.

Appreciation for the initial theoretical development for molecular composites can be attributed to Flory's evaluation of binary / ternary systems consisting of single polymer rigid rods.<sup>16</sup> The evaluation predicted that a critical region will exist wherein there is a single isotropic phase consisting of rods randomly distributed in the coils. By controlling the kinetics of phase separation, materials possessing high level of specific interactions should be obtainable. This is predicted from an extension of a classical composite principle.

The concept of molecular composites was first described by Takayanagi's study<sup>92</sup> of aramid / nylon systems, along with Helminiak and coworkers<sup>93</sup> who developed improved methods of processing these "molecular composites". These systems involving lyotropic LCPs require exotic and highly corrosive solvents for processing. A more desirable situation would be a melt processable LCP which could be incorporated into the conventional processing technology of

thermoplastics<sup>94</sup>. An ideal molecular composite is one where the dispersion of the rigid molecules in the matrix of flexible molecules proceeds until the interfacial surface energy is balanced with the aggregation energy of rigid molecules. When there is an aggregation of the semi-rigid molecules in domains larger than one would consider for molecular composites, the blends are referred to as "in-situ" composites.<sup>95-99</sup>

#### Dissertation prospectus summary

The fundamental focus of this research project is in relation to the 'Molecular Composite Project' funded by AKZO Corporation. The main objective of the entire project has been the development of novel thermotropic liquid crystalline polyesters and polyamides to be blended with the commercial AKZO resins; PET, PBT, Nylon for the enhancement of mechanical and rheological properties of the latter. Blends of novel TLCPs with the commercial polymer at low TLCP content (5 - 30 %) were then evaluated as potential "molecular composites" or "in-situ composites". As mentioned before, one could get enhanced mixing between polymer pairs at the interface by increasing the flexibility of the rigid-rod polymer and selecting the rod-like and coil molecules with specific interactions, say H-bonding.

The main objective was to design and synthesize thermotropic LCPs which are compatible with commercial PET. This involved the synthesis and characterization of novel nematic LCPs with functionalities that could specifically interact with PET, and were liquid crystalline during the processing of PET. Thermotropic LCPs containing substituted hydroquinones have been known for quite sometime now. Of these, the oxyethylene substituted hydroquinones were particularly attractive with respect to molecular composite preparation. The presence



of the flexible pendant group brings down the transition temperatures of the LCP to the processing temperature range of PET, thus preventing the entropy driven demixing of the two in a blend. Also electrostatic / dipolar interactions between the ether group of the pendant and the carbonyl group of PET was expected to result in a molecular level mixing of the two components in a blend.

A second approach for improving the compatibility of the rigid - rod and flexible components in a blend involved the synthesis of random and block copolymers containing the mesogenic segments and flexible PET / PBT blocks. This could result in novel thermotropic liquid crystalline polyesters which are miscible with the semi - crystalline polymers by interaction of the isotropic segments in the melt state.

Once the synthesis parameters for a particular system were optimized, the research prospectus then focused on the complete characterization of the polymers by DSC, Viscometry, NMR, Optical microscopy and other techniques. Thermal and optical characterization of solution blended sample and the rheological study of some melt blended samples were also undertaken.

The following will outline the objectives of the next three core chapters for the dissertation. The objective of Chapter 2 is to present the preparation and characterization of novel TLCP containing 2 - butoxyethanol substituted hydroquinone in the mesogen. The rheological studies of the blends of LCP with PET is also included. The objective of Chapter 3 is to present the synthesis and characterization of random and block copolymers containing 2 - ethoxyhydroquinone in the mesogen. Structure - property relationships for the copolymers derived from various analytical techniques is also described. Finally, the objective of Chapter 4 is to present the

preparation and characterization of random and block copolymers containing unsubstituted hydroquinone in the mesogen.

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## CHAPTER 2

### SYNTHESIS AND CHARACTERIZATION OF PBEHT SYSTEM

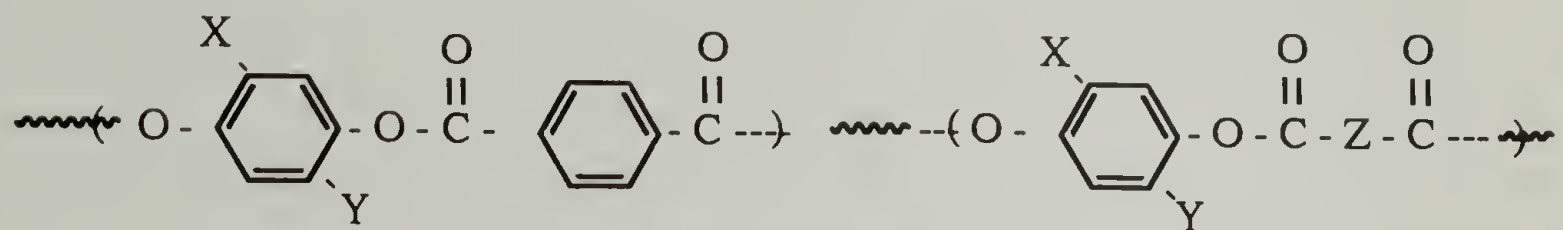
#### Introduction

In the past, many aromatic polyesters with rigid back - bones have been examined for their thermotropic liquid crystalline properties. It is well known that phenyl groups strongly favor a LC phase because of their proclivity to stack on top of each other. Poly ( p - phenylene terephthalate ) which is a representative polyester has a glass transition around  $267^{\circ}\text{C}$  and decomposes before it melts and hence a proper characterization of the mesophase is not possible.<sup>1</sup> In order to lower these transition temperatures without destroying thermotropic behavior, one of the approaches that have been adopted is the use of asymmetrically substituted hydroquinones and terephthalic acids.

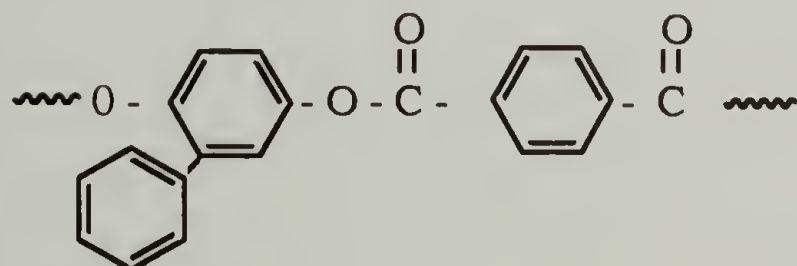
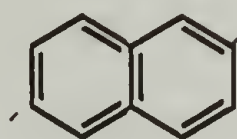
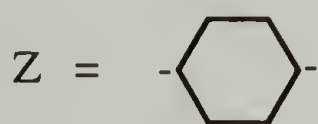
In this regard, one of the earliest patents in this area was assigned to ICI in 1965.<sup>2</sup> Somewhat later, a series of patents assigned to DuPont and Eastman Kodak focused on the thermotropic behavior of various aromatic polyesters based on substituted hydroquinones and many different aromatic or cycloaliphatic diacids as listed in Table. 2.1. The synthesis and characterization of other chloro and methyl substituted hydroquinone containing polymers was later published by Lenz et al.<sup>8</sup> The structure - property relationships in a series of thermotropic poly (2 - n - alkyl - 1,4 - phenylene terephthalate) were studied by the same group.<sup>9</sup> The physical properties of these polymers are listed in Table. 2.2 :



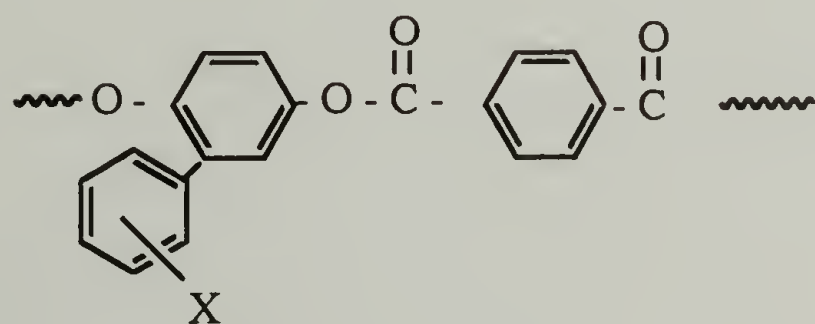
Table . 2.1 : Thermotropic aromatic LCPS based on substituted hydroquinone



X AND Y = - H, - Cl, - Br, - CH<sub>3</sub> (3, 4, 5)



(6)



(7)

Table. 2.2 : Properties of poly (2 - n - alkyl - 1,4 - phenylene terephthalate)

n- Alkyl substituent	$\eta_{\text{inherent}}$ (dL/g)	$T_m$ ( $^{\circ}\text{C}$ )	Isotropization temperature $T_i$ ( $^{\circ}\text{C}$ )	$\Delta T$ ( $^{\circ}\text{C}$ )
Hexyl	0.52	277	323	46
Heptyl	0.48	257	302	45
Octyl	0.47	257	307	50
Nonyl	0.32	237	291	54
Decyl	0.30	217	237	20
Undecyl	0.37	228	292	64
Dodecyl	0.25	217	277	60

It can be seen that the transition temperatures are almost independent of the pendant size, but are molecular weight dependent.<sup>10</sup> An unequivocal nematic texture was observed for each polymer at a temperature approaching nematic to isotropization transition.<sup>11</sup> The decyl substituted hydroquinone polymer was synthesized in the lab again and was confirmed to exhibit homeotropism at high temperatures. Very interesting patterns, where the polymer seemed to be aligned in the flow direction, were obtained on cooling. Previously, these observations were explained as patterns corresponding to a William's domain like phenomenon, but a more correct theory has been proposed by Kleman et al recently.<sup>12</sup> Krigbaum and co-workers also concluded that halogen, alkyl or phenyl substituents on one or both of the aromatic rings result in the lowering of transition temperatures as well as the degree of crystallinity.<sup>13</sup>

Subsequently, the effect of alkoxy substituents in the hydroquinone ring was studied.<sup>14</sup> The properties of the polymer are listed in Table. 2.3 :

Table. 2.3 : Properties of poly (2 - n - alkoxy - 1,4 - phenylene terephthalate)

n- Alkoxy substituent	$\eta_{\text{inherent}}$ (dL/g)	$T_m$ ( $^{\circ}\text{C}$ )	$T_{\text{cooling}}$ ( $^{\circ}\text{C}$ )
Methoxy	1.13	275	200
Ethoxy	1.57	250	174
Ethoxy-methoxy	1.27	210	231
Ethoxy-ethoxy	1.46	207	250
Ethoxy-ethoxy- methoxy	1.26	190	-
Ethoxy-ethoxy- ethoxy	1.25	194	222

An exponential decrease in the melting temperature with increase in the length of the substituent was observed. This was expected as the flexible alkoxy chain was believed to hinder the molecular packing in the polymer due to increased interaction among the substituents and the substituent and the main chain.

For the 'molecular composite project' sponsored by AKZO, new polymers had to be synthesized which could be used as components in molecular composites with flexible coil PET. This concept required that the LCP exhibit partial miscibility

with the isotropic polymer matrix in either the melt or the solid state.<sup>15-17</sup> Even if the LCP is just compatible and forms a reinforcing dispersion within the matrix of the flexible coil polymer, there should be significant improvements to the mechanical properties.<sup>18-19</sup> Hence the thermotropic LCPs containing the oxyethylene substituents were chosen for the study as poly (ethylene oxide) is known to be miscible with many polyester systems. Also, the oxyethylene ether is expected to exhibit electrostatic / dipolar interactions with the ester linkage of the coil polymer.

Ashok Tendolkar synthesized the triethoxy substituted hydroquinone and made a series of random copolyesters containing the monomer, ethylene glycol and terephthaloyl chloride.<sup>20</sup> A summary of the properties of the six copolyesters is given in Table. 2.4. From the properties of the blends of the 60 : 40 copolyester with poly (butylene terephthalate) [ PBT ], it was concluded that there was a good dispersion of LCP within the isotropic matrix and also a fair improvement in strength and modulus of the blends over pure PBT.<sup>21</sup>

But initial results from the work with the system showed that the polymer exhibited thermal instability. This was attributed to the large number of ether groups in the pendant moiety and hence it was decided to choose a system with the minimum number of ether groups but a sufficiently long alkyl chain to manipulate the transition temperatures in the same range as before. Hence 2 - butoxy ethanol substituted hydroquinone polymer system ( Fig. 2.1 ) was chosen for study. Later on it was shown that the thermal instability was due to the presence of the trace amounts of terephthalic acid which was present with the copolymers!



Table. 2.4 : Properties of poly (2 - triethoxy - 1,4 - phenylene terephthalate)

Polymer composition (PTEHT : PET)	$\eta_{\text{inherent}}$ (dL/g)	$T_m$ ( $^{\circ}\text{C}$ )	$T_{\text{lc-lc}^{**}}$ ( $^{\circ}\text{C}$ )	Texture
100 : 0	2.14	212	257	Nematic
80 : 20	0.87	192	242	Nematic
60 : 40	0.65	162	254	Nematic
40 : 60	0.49	162	227	Nematic
20 : 80	0.47	212	-	Biphasic
0 : 100	0.48	256	-	Crystalline

The objective of this chapter is to describe the synthesis and characterization of 2 - butoxyethoxyhydroquinone and the corresponding homopolymer [ PBEHT ] with terephthaloyl chloride ( Fig. 2.1 ). The thermal and morphological characterization of the polymer by cross - polarized optical microscopy and DSC is described. The rheological characterization of the PBEHT blends with PET is also discussed.

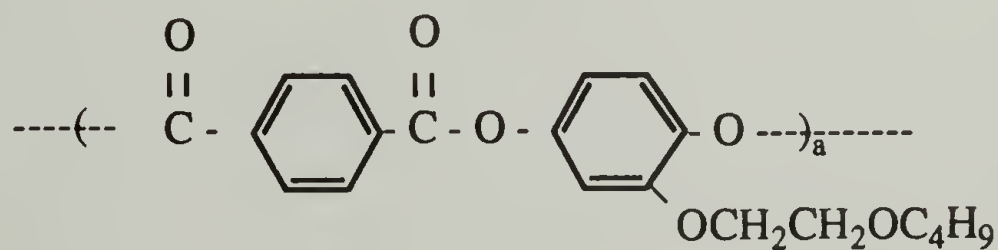


Fig. 2.1: Structure of poly(2-butoxyethoxy-1,4-phenylene terephthalate)

## Experimental

### Materials

All chemicals were obtained from Aldrich Chemical Co. Terephthaloyl chloride was purified by sublimation. The solvent used for polymerization, methylene chloride, was distilled over phosphorus pentoxide. All the other chemicals were used without further purification.

### Monomer synthesis

The monomer synthesis is a 3 - step reaction starting with the commercially available 3, 4 - dihydroxybenzaldehyde.<sup>14</sup> The schematic of the reaction is given in Fig. 2.2. A detailed description of the synthesis is given below.

In the first step, 2 - butoxyethyltosylate was synthesized by slowly adding one mole ( 191.0 g ) of powdered tosyl chloride to an aqueous sodium hydroxide solution ( which was prepared by dissolving 2 moles ( 80.0 g ) of NaOH in 300 mL of water ) containing 1 mole ( 118.2 g ) of 2 - butoxyethanol. Addition was done over a period of 45 minutes and the reaction mixture was vigorously stirred at 20 ° C for 5 h. The product, which was separated from the aqueous layer as an oil, was extracted with 500 mL of methylene chloride. The organic layer was washed successively with 10 % NaOH solution and water, and then dried over anhydrous sodium sulfate overnight. Methylene chloride was evaporated ( on a rotary evaporator ) to yield 2 - butoxyethyltosylate as an oily liquid. Traces of the organic solvent was removed by using a vacuum pump. Yield = 95 %

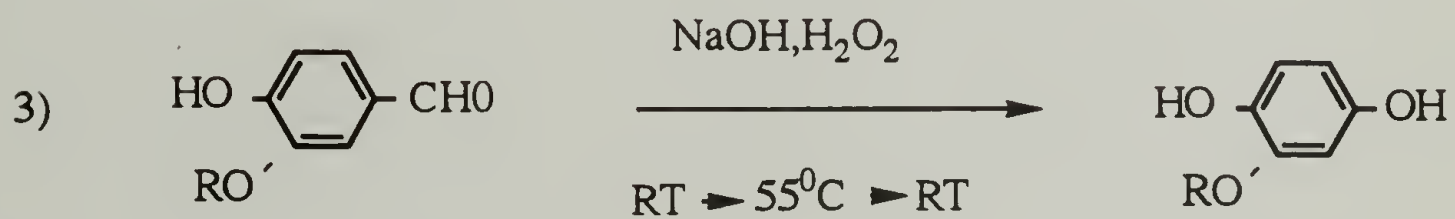
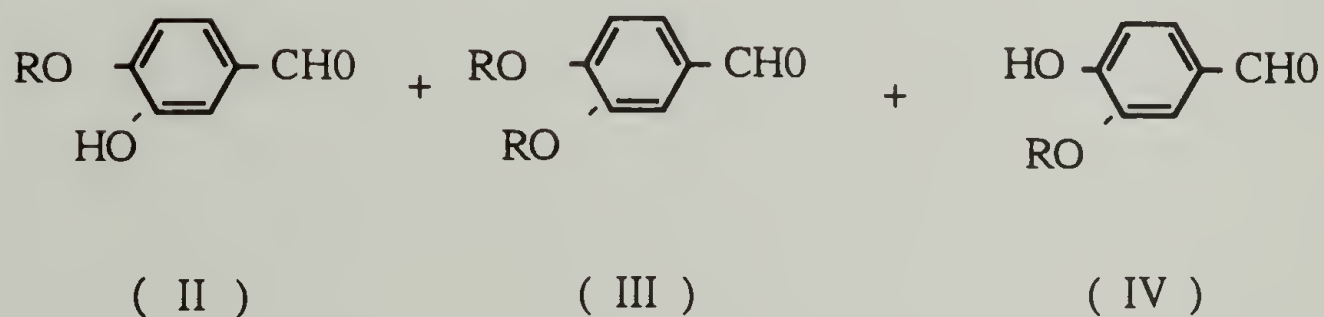
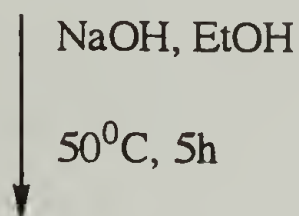
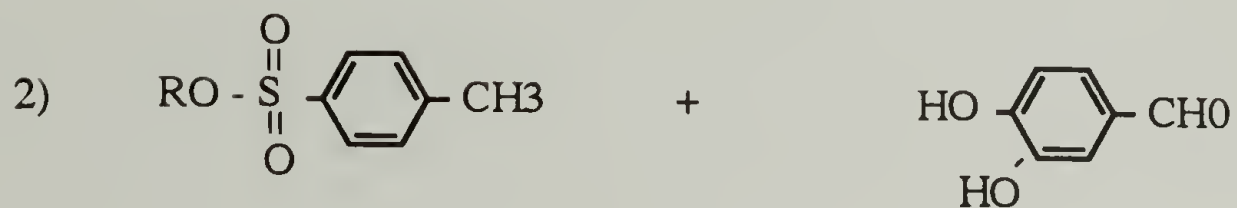
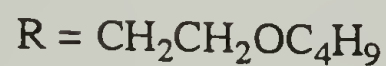
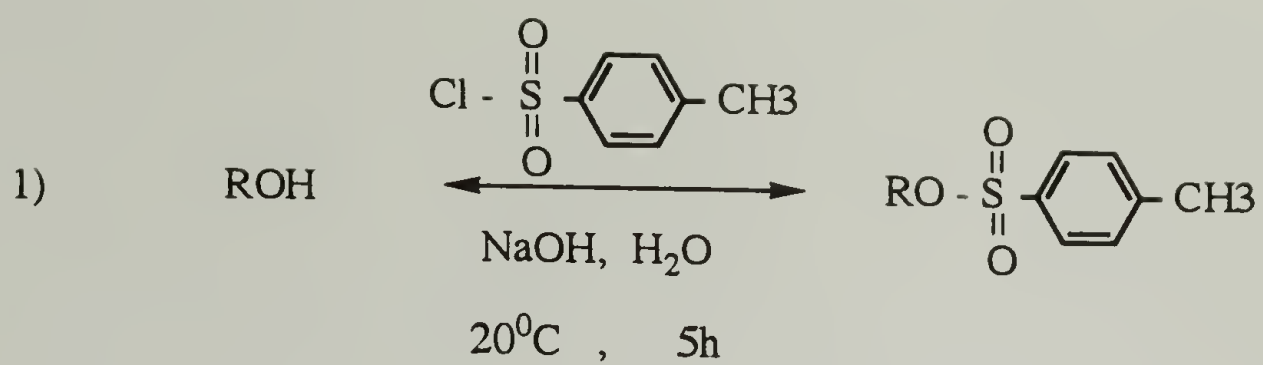


Fig. 2.2 : Synthesis of 2-alkoxyhydroquinone



In the second step, 0.4 mole of 2 - butoxyethyltosylate ( 108.86 g ) and 320 mL of a 10 % aqueous NaOH solution were added to a solution of 0.4 mole ( 55.2 g ) of 3,4 - dihydroxybenzaldehyde in 660 mL of ethanol. The reaction mixture was vigorously stirred for 5 h at 50 °C under an inert atmosphere, after which the solvent was evaporated and the product was dissolved in 200 mL water and extracted with 5 x 150 mL of ether. The ether layer was washed with water and dried over anhydrous sodium sulfate overnight. After evaporating the ether solvent, 3,4 - bis ( 2 - butoxyethoxy ) benzaldehyde was obtained as an orange colored oily liquid. The remaining aqueous solution was acidified with dil. HCl and extracted with 4 x 150 mL of ether. The ether layer was washed successively with 5 % NaHCO<sub>3</sub> ( 3 x 150 mL ), with water ( 3 x 150 mL ) and dried over anhydrous sodium sulfate. The ether was then distilled off, and an oily product was obtained which is a mixture of compounds ( II, III, IV ) as shown in Fig. 2.2. This oil was dissolved in chloroform and Skelly - F solvent was added to it until the solution became cloudy. Upon standing overnight in the refrigerator, crystals of unreacted 3,4 - dihydroxybenzaldehyde formed and were filtered out. The solution was kept in the refrigerator for more than a week to ensure the complete removal of the starting compound. The solvent was then evaporated from the solution, and the resultant oil was used without further purification in the next step. Yield = 38 %.

In the third step, 20.86 g of the crude product from the second step was dissolved in NaOH solution ( 6.6 g / 235 mL ) under an argon atmosphere in a Nalgene flask. A 30 % H<sub>2</sub>O<sub>2</sub> solution ( 10 mL ) was injected into the flask quickly. The solution temperature increased to 55 °C, after which it was allowed to reach room temperature, then kept there for 2 h. The deep brown alkaline solution was acidified with dilute HCl and extracted with 4 x 150 mL ether. The ether was washed successively with 4 x 150 mL of saturated sodium metabisulfite solution and

3 x 150 mL of distilled water. The ether solution was dried over anhydrous sodium sulfate overnight. the product was pre - purified by short column chromatography using silica gel ( 100 mesh ). After evaporation of the ether solvent, a yellowish orange oil was obtained. Skelly - F was added to the orange residue to crystallize the compound and kept in the refrigerator overnight. Depending on the purity, the compound would take from 5 minutes to 1 week to crystallize. Yield ( 58 % ). Purification was done by recrystallization from a mixture of chloroform / Skelly F ( 5 : 2 ). The melting point of the monomer was 86 ° C.

Elemental Analysis :      Observed - C ( 63.99 % ) H ( 8.08 % )  
   Expected - C ( 63.70 % ) H ( 7.96 % )

### Polymer synthesis

Solution polymerization was done using methylene chloride as the solvent. To a 500 mL 3 - neck flask, were added 0.03943 mole ( 8.897 g ) of 2 - butoxyethoxy hydroquinone and 0.08 mole ( 11 mL ) of triethylamine as the acid - acceptor. Then 200 mL of methylene chloride was cannulated into the flask followed by vigorous agitation to form a solution. Thereafter a solution of 0.0394 mole ( 8 g ) of terephthaloyl chloride in 200 mL methylene chloride was added slowly to the reaction mixture, and the contents of the flask were stirred for 24 h with a magnetic stirrer at room temperature, and then refluxed for 24 h. At the conclusion of the refluxing period, the mixture was cooled to room temperature and was added to a 3 - fold excess methanol. The polymer was filtered from the solution to obtain 13.5 g of product. The polymer product was dried and then extracted with acetone / methanol in a Soxhlet extractor to obtain a more pure polymer at a yield of 89 % ( 12.5 g ). The viscosity of the polymer solution in p - chlorophenol at 50 ° C was 0.4 dL / g.

## Characterization methods

Viscometry was done to get a relative idea of the molecular weight of the polymer. The GPC analysis could not be done because of the insolubility of the polymer in common organic solvents. The polymer was dissolved in p - chlorophenol at high temperatures and the inherent viscosity measured at 50 °C for a polymer concentration of 0.5 g / dL using a Cannon - Ubbelohde viscometer. The phase transition temperatures were measured on a differential scanning calorimeter ( Perkin - Elmer II ), under a nitrogen flow with a heating and cooling rate of 20 °C / min. The temperature axis of the DSC thermogram was calibrated prior to use with reference standards of high purity indium. The peak maxima were chosen as the phase transition temperatures. A second heating cycle after slow cooling as well as a cooling cycle for a sample heated up to 300 °C were recorded. For the study of the mesophases formed by the polyester, polymicrographs were taken with a 35mm camera mounted on a Carl - Zeiss polarizing light microscope equipped with a hot stage ( Mettler FP - model ). The polymer sample, placed between 2 microscope cover glasses, was heated well above its melting transition on a hot plate melting point apparatus and rapidly quenched. The mesophase behavior was then observed as a function of temperature on the hot stage.

## Results and Discussion

### Molecular weight / IV

In general, wholly aromatic polyester have limited solubilities in most solvents because of the rigid - rod structures of these polymers. Highly polar solvents like trifluoromethanesulfonic acid, p - chlorophenol or pentafluorophenol have to be used to solubilize them for inherent viscosity ( IV ) measurements. Standard curves for the correlation of the inherent viscosity and molecular weight have been obtained for a rigid - rod polymer, poly ( phenyl - 1,4 - phenyleneterephthalate )<sup>22</sup> where the



absolute molecular weights were determined by low angle LASER light scattering. This technique could be applied to our system provided a suitable solvent and apparatus is available. The inherent viscosity measured for PBEHT in p - chlorophenol at 50<sup>0</sup> C gave a value of 0.4 dL / g. Calculations were done using the equation,  $\eta_{inh} = \ln \eta_r / C$

where  $\eta_r$  = relative viscosity =  $t / t_0$

$t$  = time taken by solution

$t_0$  = time taken by the solvent

### Thermal analysis

Thermogravimetric analysis done under conditions of nitrogen and air showed that the polymer was very stable up to 350<sup>0</sup> C.

The DSC thermograms of main - chain LCPs are usually complicated. The samples show a glass transition ( positive  $\Delta C_p$  ), melting ( endotherm ) and mesophase - mesophase or mesophase - isotropic liquid transitions ( endotherms ). On cooling, the mesophase - isotropic & mesophase - mesophase transitions are completely reversible, but a marked super - cooling is generally observed for the crystal - mesophase and crystal - crystal transitions.<sup>23-25</sup> It is also observed that the lowest temperature mesophase can be frozen in the glassy state. The DSC thermograms of PBEHT are shown in Fig. 2.3 and Fig. 2.4 for the second heating cycle and the subsequent cooling cycle respectively. The analysis showed that the polymer softened over a broad range of 190 - 228<sup>0</sup> C. This temperature should also correspond to crystal - nematic transition, ultimately melting around

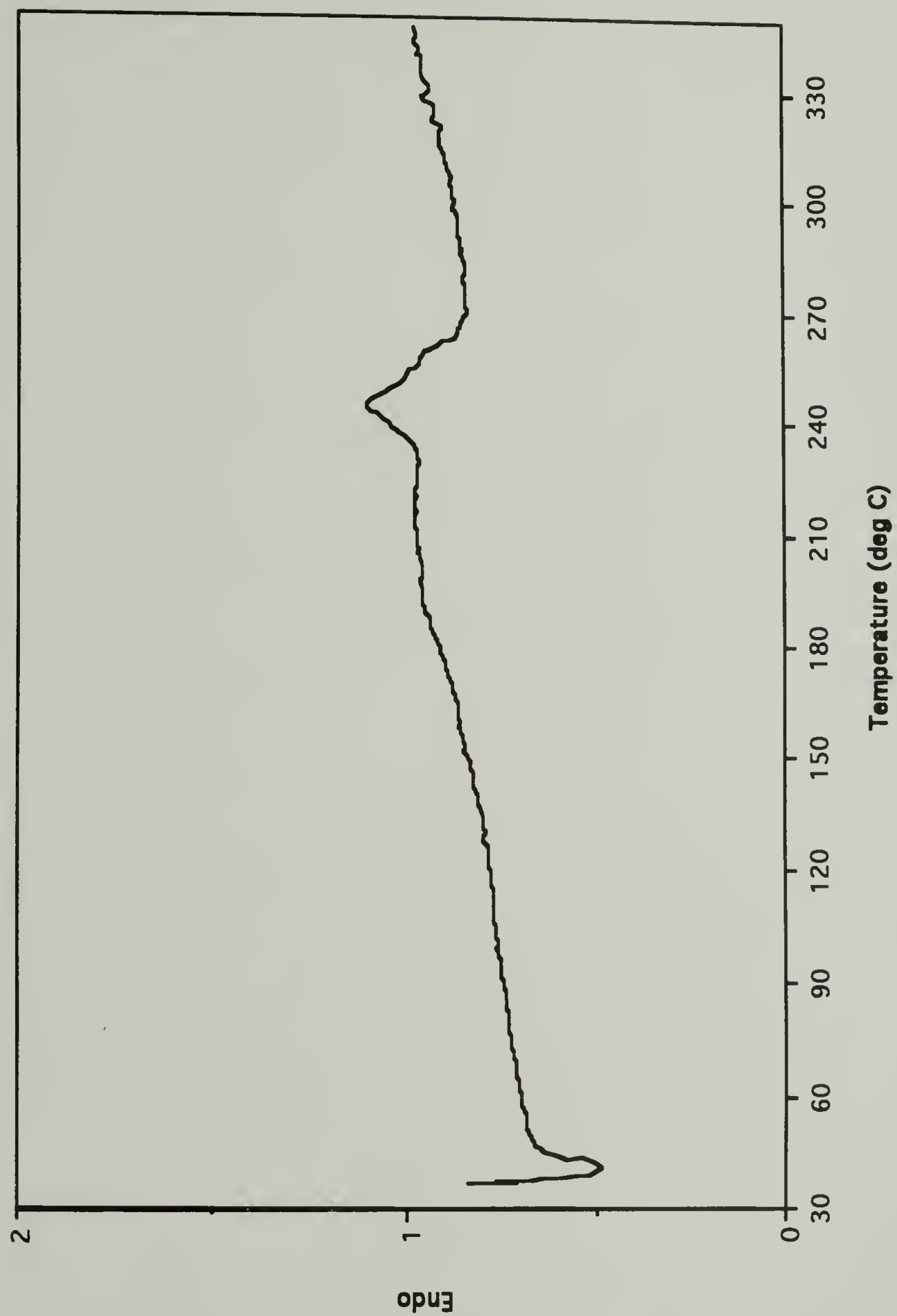


Fig 2.3 : DSC trace of PBEHT recorded on the second heating at a rate of 20 deg C/min.

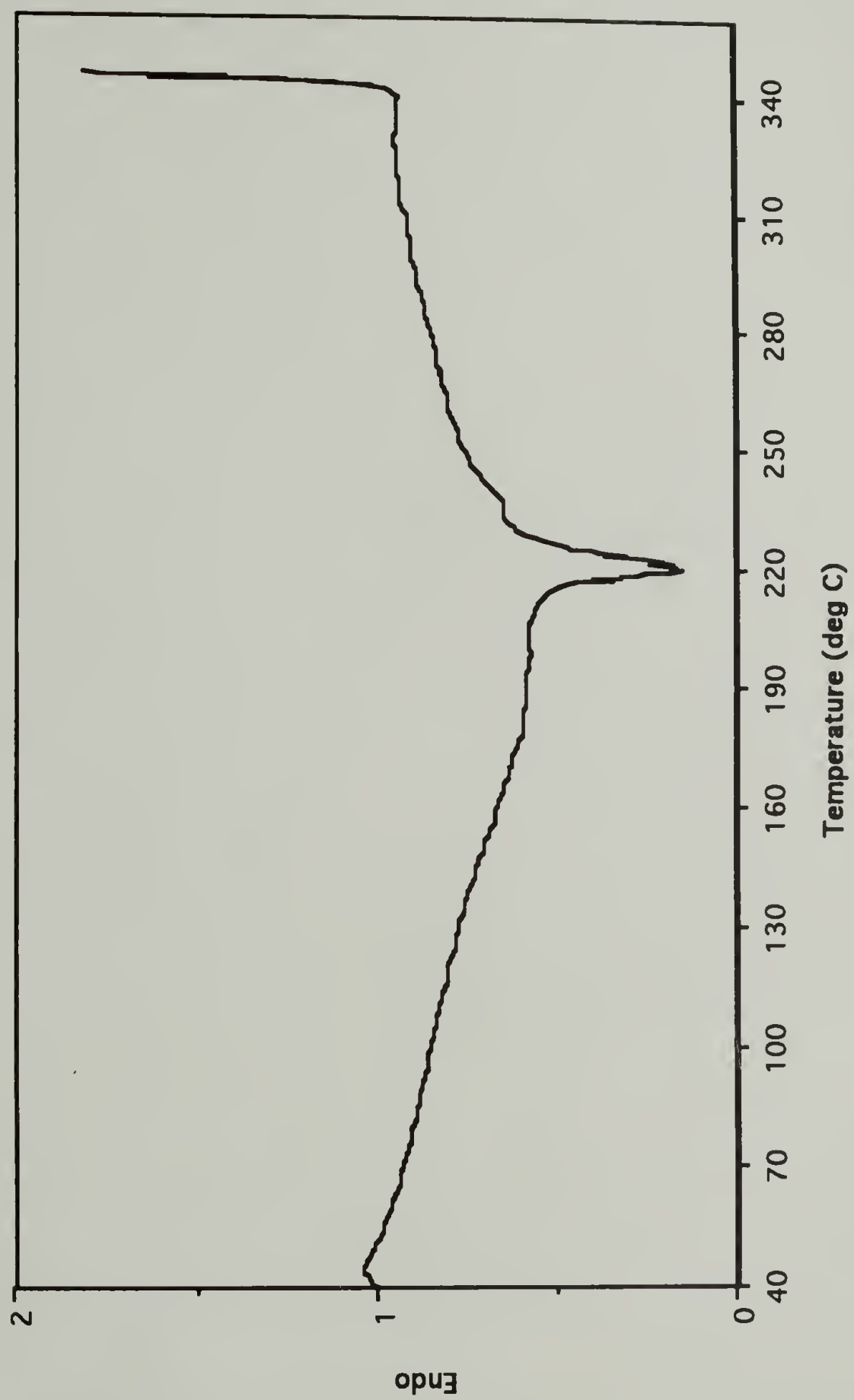


Fig. 2.4: DSC trace of PBEHT recorded on the second cooling at a rate of 20 deg C/min.

240 °C. A fairly well - defined endotherm corresponding to a nematic - nematic transition was seen around 245 °C and this assignment has been confirmed by optical microscopy. The cooling cycle showed an exotherm peaking around 220 °C, which probably corresponds to a mesophase - crystal transition as indicated by the massive super - cooling. The transition temperatures were fairly reproducible in subsequent heating and cooling cycles.

### Optical Polarizing Microscopy

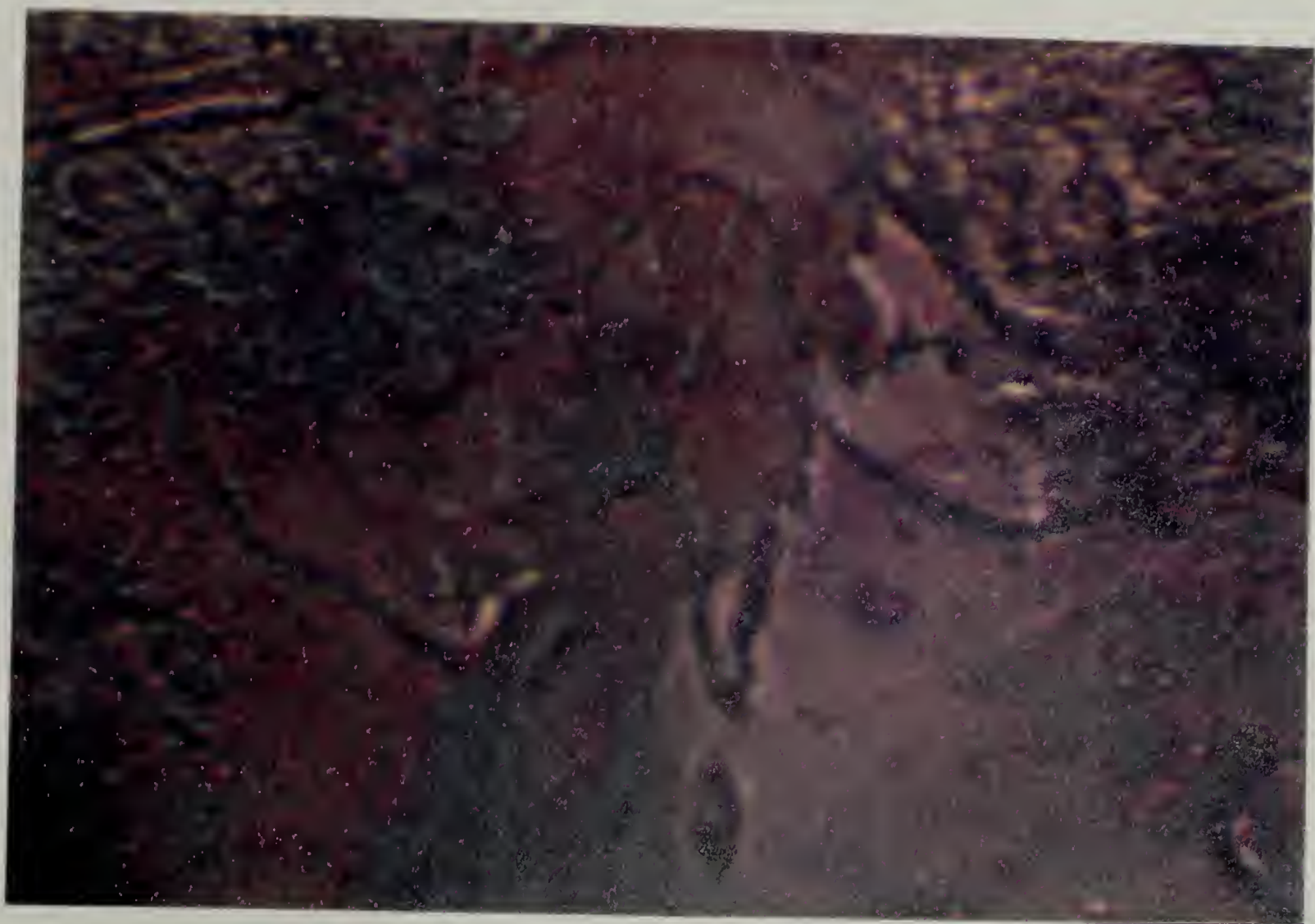
The appearance of a particular texture of the melt is usually a function of the structure ( order ) of the mesophase, and it is often possible to directly identify the type of mesophase present by this method. The various optical features which are characteristic of each mesophase structure can be obtained from consulting books with photographic illustrations which have been published on this subject.<sup>26</sup>

The optical micrographs of the polyester, PBEHT, at various temperatures are given in the following pages ( Fig. 2.5 - 2.6 ). A threaded texture indicative of a nematic phase was observed at room temperature. There is a massive organization of the liquid crystalline state as the temperature is raised. When the temperature increases, the number of threads diminished and simultaneously, the threads became loose and shrunk in length. Formation of closed loops followed by their disappearance to give a homogenous color pattern was observed around 245 °C, which is the temperature corresponding to the second endotherm in the DSC. An intense movement within the melt and scintillation effects due to a directly observable brownian motion is a characteristic of nematic mesophase and observed in the sample up to 320 °C. The sample was not heated above that temperature as degradation may set in and hence the isotropization temperature could not be determined.



**Fig. 2.5: Optical micrographs of PBEHT ( Mag. = 400 X )**

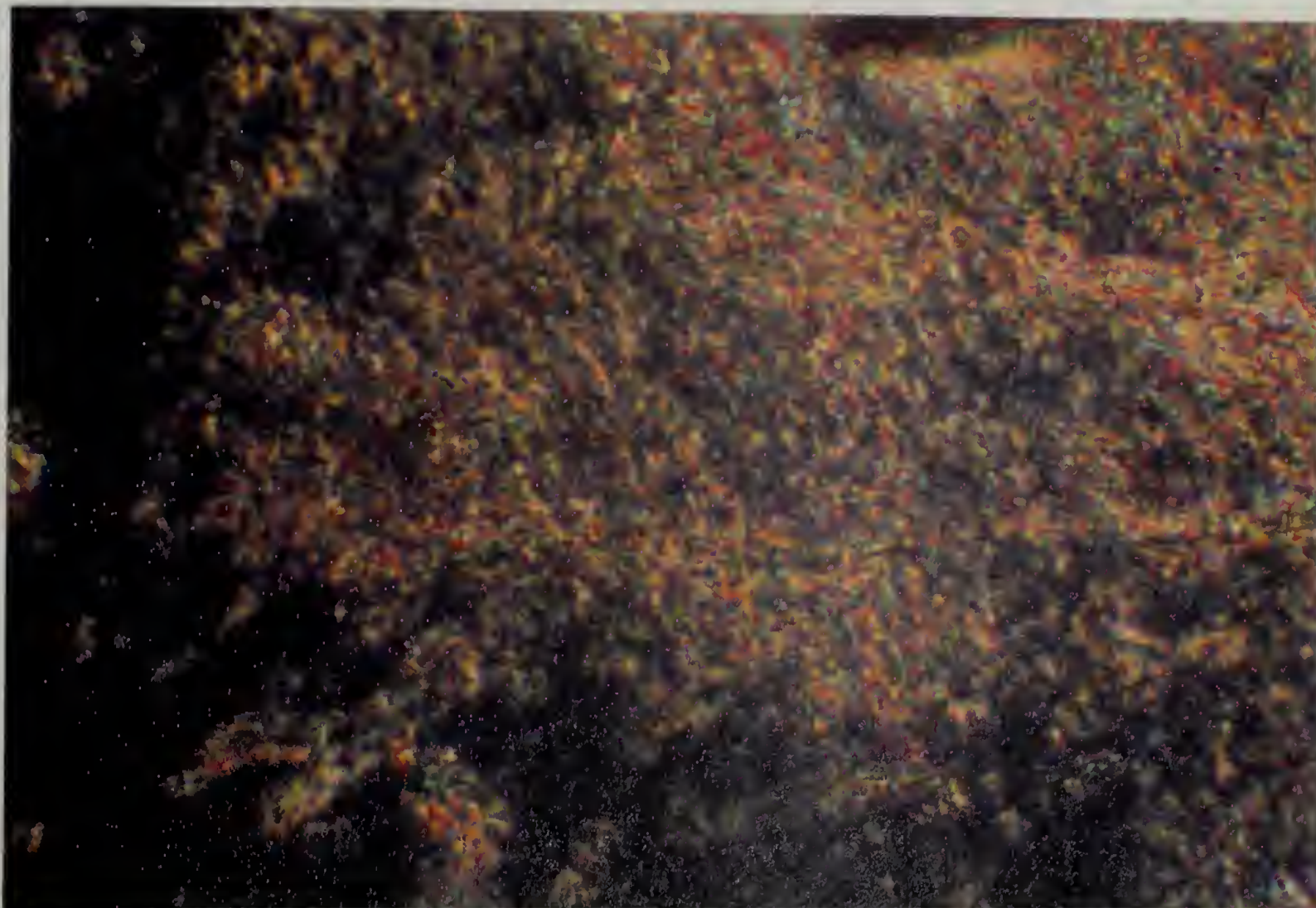
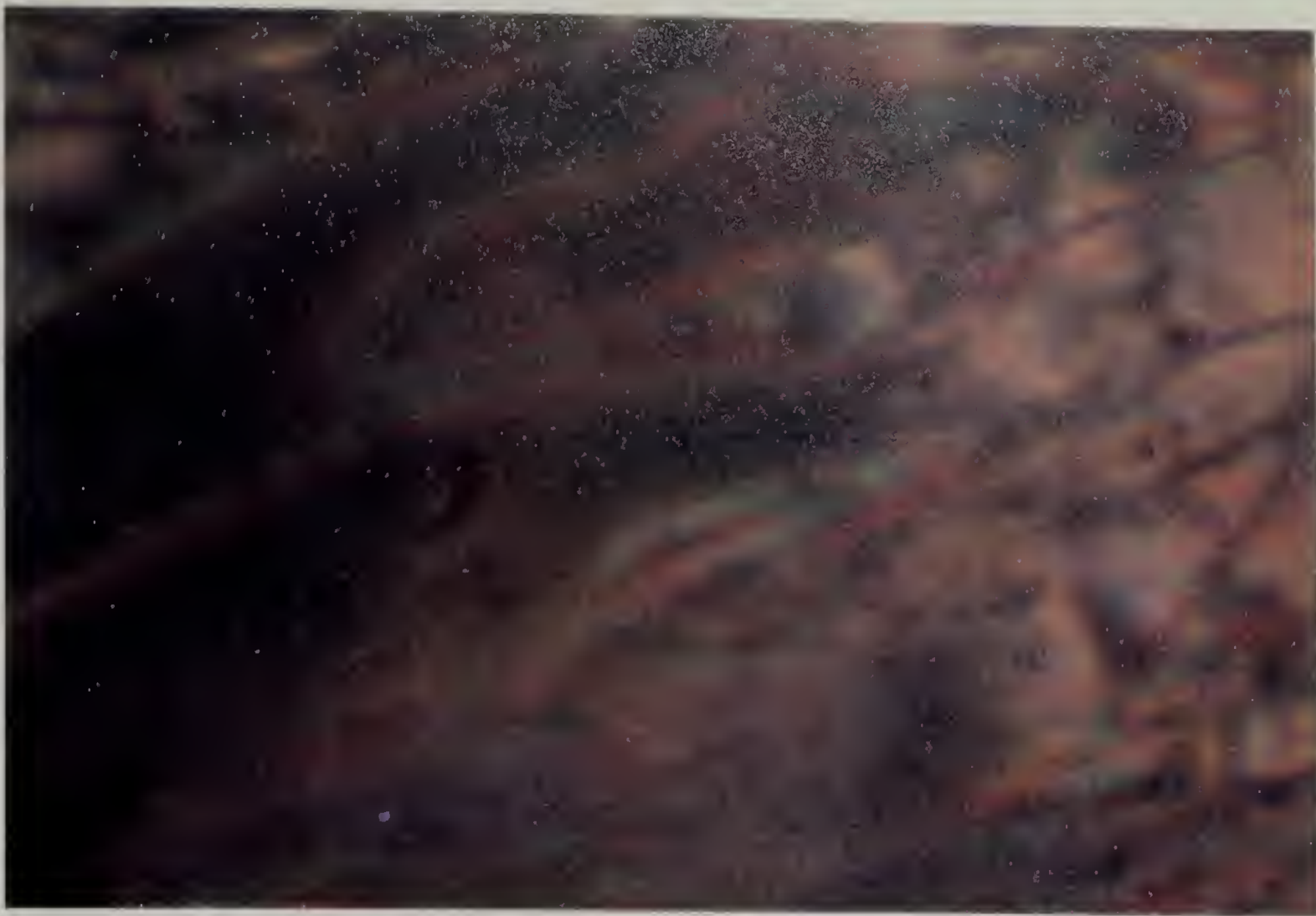
- a ) Observed mesophase of the polymer quenched to room temperature from the nematic mesophase**
- b ) Observed mesophase of the polymer heated up to 245 ° C at a rate of 10 ° C / min.**



**Fig. 2.6: Optical micrographs of PBEHT ( Mag. = 400 X )**

- a ) Observed mesophase of the sample heated upto 300  
° C at a rate of 10 ° C / min**
- b ) Observed mesophase of the polymer at 220 ° C  
cooled down from 320 ° C at a rate of 10 ° C / min**







A homeotropic texture caused by a spontaneous orientation of the sample was also observed at high temperatures. This texture occurs when the long axes of the mesogenic groups are at right angles to the glass surfaces. In the homeotropic regions, the field of view remains uniformly dark as the slide or stage is rotated. However, if the cover - glass is touched, the original dark field of view brightens instantly.

### Rheological studies of the blends

#### Introduction

Melt blending studies of PBEHT with PET were done by Dr. Farris's group in UMass. A summary of the mechanical properties of fibers of a 20 % blend of the sample is given in Table. 2.5 :

Table. 2.5 : Mechanical properties of PET & PBEHT blend fiber

	Modulus (GPa)	Stress (MPa)	Strain ( $\Delta L / L$ )	Shrinkage ( % )
20% PBEHT / PET (DR=8.0)	13.4	600	20.5	9.0
PET (DR=8.0)	19.3	1110	7.1	15.0

As it is seen from the table, PBEHT was not very good as a reinforcing agent but the thermal shrinkage of the blend was much smaller compared to pure PET. It was observed that it was much easier to fiber spin the blends which points out to

the viability of using the LCP in a much smaller amount as a processing - aid for PET. It was necessary to quantify these observations by doing some rheological measurements, both in the dynamic and steady mode.

In order to characterize polymeric fluids, it is customary to use simple, well - defined flows. The two main flows are simple shear and simple elongational. In shear flow, material planes move relative to each other without being stretched, whereas in extensional flows the material elements are stretched. When these flows are carried out in a manner in which the rheological properties no longer change with time, the flows are termed steady simple shear flow or simple elongational flow. Typically, simple shear flow is generated in cone and plate, plate - plate or couette devices.<sup>27-29</sup> Simple extensional flow is generated by devices in which a cylindrically shaped specimen is deformed in such a manner that the length increases exponentially with time.

Besides the experiments which are carried out under steady state conditions, there are also a number of transient flow experiments which are used to characterize complex fluids.

*Steady shear flow*: Three material functions can be defined for this kind of flow (viz.) Primary normal stress differential coefficient ( $\Psi_1$ ), secondary normal stress coefficient ( $\Psi_2$ ) and shear stress ( $\sigma$ ) which are all related to viscosity ( $\eta$ ) and shear rate ( $\Gamma$ ). For LCPs, the steady shear viscosity was found to have a power law dependence on shear rate for more than two decades.<sup>30</sup> The viscosity of blends or pure PET as a function of temperature will give a trend which more closely resembles the conditions in the capillary extruder used for fiber spinning of small quantities of samples.

*Dynamic oscillatory flow*: Small strain dynamic shear flow is the most common flow used to analyze rheological properties of macromolecular fluids. Measurements are usually carried out at strain levels where the stresses are directly proportional to strain. In this experiment, the loss modulus ( $G''$ ) and storage modulus ( $G'$ ) are measured as a function of angular frequency ( $\omega$ ).  $G'$  represents the amount of energy stored per cycle of deformation and  $G''$ , the energy loss / cycle. One can also define a complex viscosity ( $\eta^* = \eta'' - i\eta'$ ), where  $\eta'$  and  $\eta''$  can be obtained from  $G'$  and  $G''$ .<sup>31</sup>

### Experimental

*Sample preparation*: The PET and LCP components of the blends were tumble mixed for 24 h at room temperature and then compression molded into a disc at 280 °C for 30 s. The disc was then ground and sifted. After redrying the blends, the dynamic oscillatory and steady shear data were obtained on a Rheometrics Dynamics Spectrometer RDS - 7700. Cooling experiments on all blends were conducted in the dynamic oscillatory mode and step shear mode at a frequency of 10 rad /sec and a gap of 1mm in a parallel plate arrangement with a plate radius of 12.5mm. Parallel plate geometry with the same dimensions were used for steady (step) shear measurements too.

### Results and Discussion

*Dynamic mode*: In Fig. 2.7, is shown the complex viscosity as a function of temperature (cooling curves) of the blends and a reference PET. Such experiments give an idea about the degree of supercooling of a material (i.e.) the difference between DSC determined melting point and the temperature at which the material actually begins to solidify (indicated by the sharp rise in viscosity) upon cooling from a temperature above its melting point. The larger this degree of supercooling,



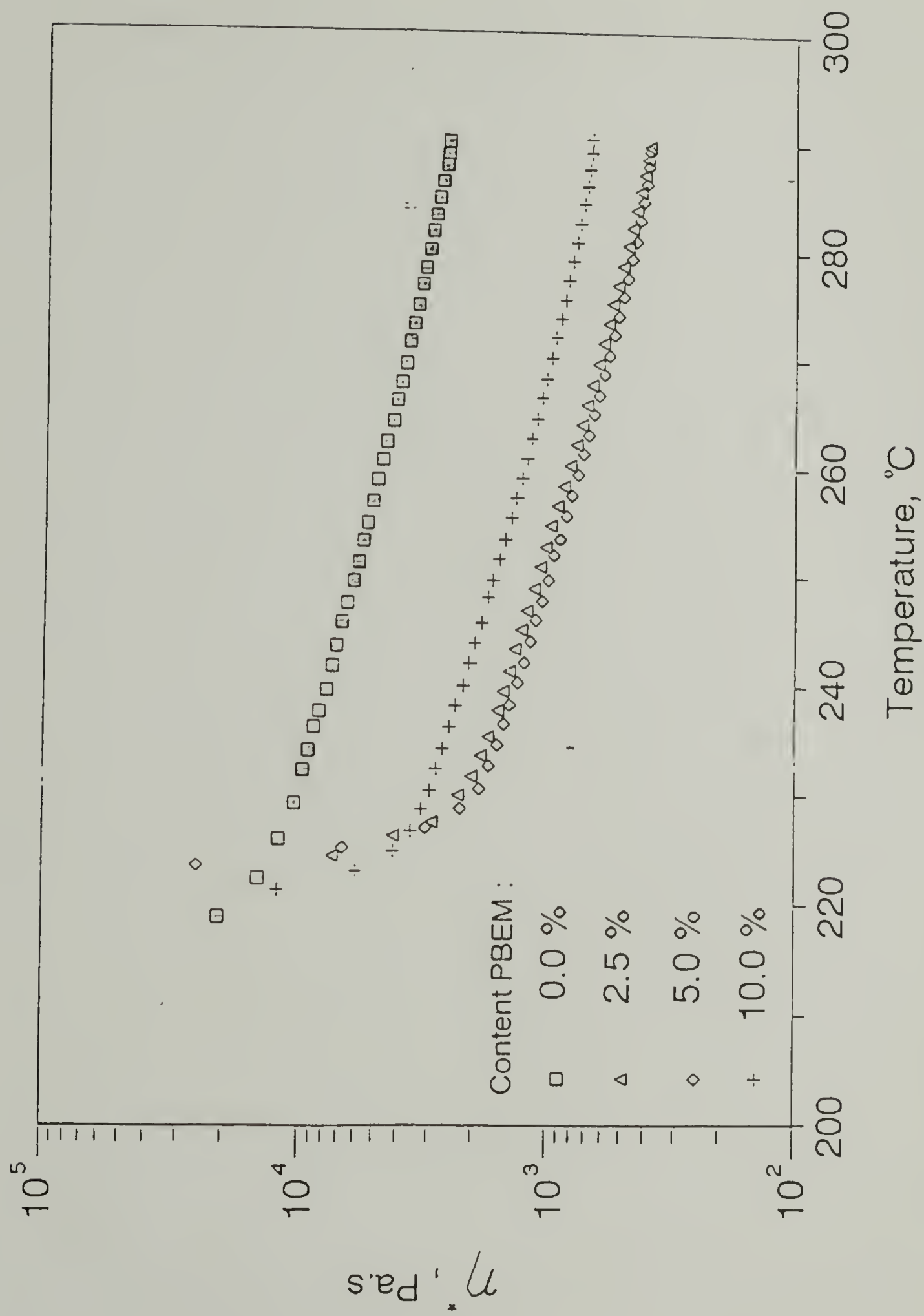


Fig. 2.7 : Viscosity measured in the dynamic mode Vs Temperature for the PBEHT blends with PET

the greater is the window for processing. Also blending of LCP with PET results in a lower viscosity ( about a decade ) than that of the flexible coil polymer itself. The 10 % blend is slightly more viscous than the 2.5 and 5 % blends in the processing range. We do not have an explanation for this peculiar behavior.

*Steady mode* : Step shear tests on the blends also indicate a similar trend as shown in Fig. 2.8. The viscosities used in the plot are the averages of the values obtained for different shear rates at every temperature. All the blends show almost identical viscosity values and about a decade lower than that of PET at temperatures greater than 220 °C. The difference is highest at 270 °C which implies that the blends can be processed easily at a much lower temperature than that for the pure PET. Thus the LCP could be comfortably used as a processing - aid at concentrations as small as 2.5 %.

### Conclusions

A 3 - step monomer synthesis, optimized for earlier systems was employed to prepare a new monomer, 2 - butoxyethoxy hydroquinone. Solution polymerization of the monomer with terephthaloyl chloride in methylene chloride lead to the formation of a thermotropic LC polyester, with an inherent viscosity of 0.4 dL / g. The polymer was stable up to 350 °C and melted around 240 °C. It exhibited a nematic texture under crossed polars and there was a distinct LC - LC transition at 245 °C shown by DSC and confirmed by optical microscopy. Thus the transition temperatures were conveniently in the processing temperature range of PET.

Melt blending studies showed no significant mechanical reinforcement of PET by the LCP, but there was a reduction in thermal shrinkage for the blends as

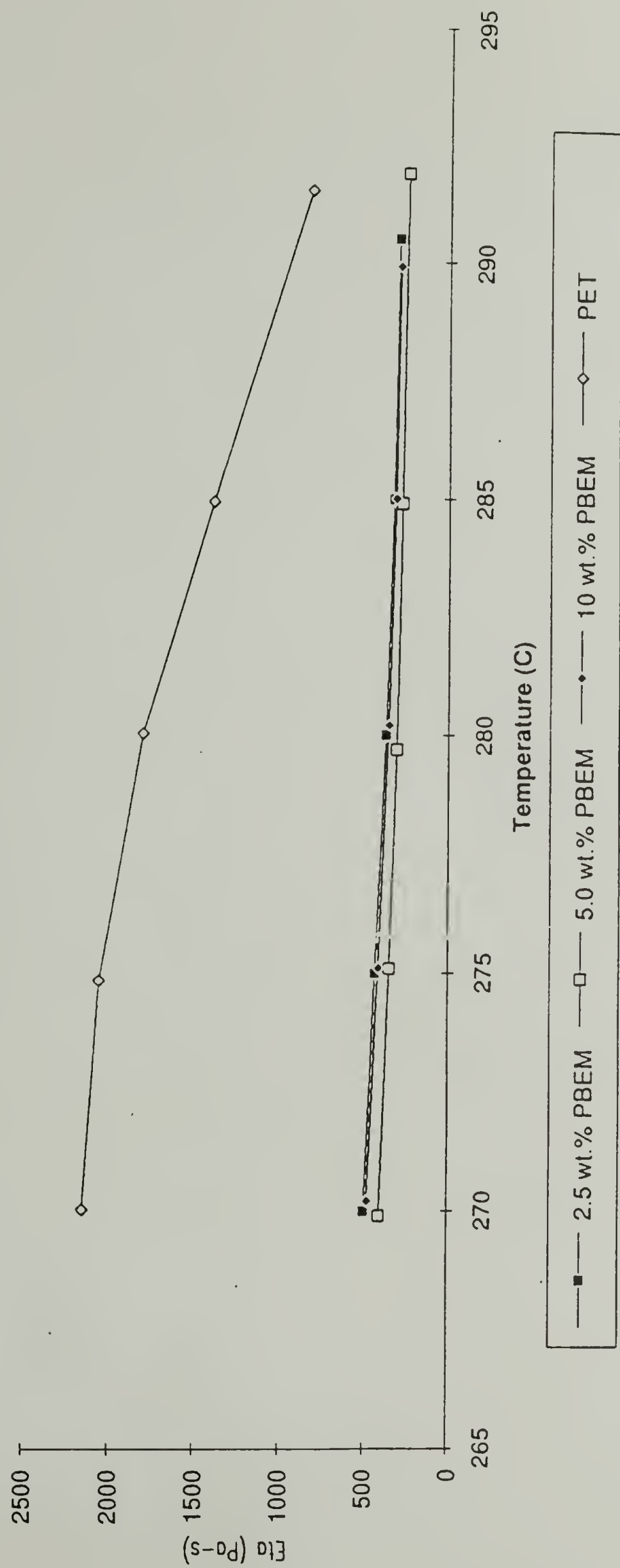


Fig. 2.8 : Steady shear viscosity Vs Temperature for the PBEHT blends with PET



compared to PET. Also a decrease in melt viscosity of the blends was observed which facilitated processing. Quantification of this observation was done by rheological measurements. As expected, a quantitative decrease in the viscosity of the PBEHT blends was observed as compared to PET, even for a concentration as low as 2.5 %. This would make the polymer interesting as a processing - aid too.

#### Future work

The preparation of the oxyethylene substituted hydroquinones as described in Fig. 2.2 is highly cumbersome 3 - step process. The total synthesis time is about 2 weeks and the yields are poor as one gets a mixture of products which have to be tediously separated. It would be interesting to try some alternative routes for the synthesis of these monomers. Preliminary work was done in the project of optimizing monomer synthesis, but could not be completed due to lack of time!

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## CHAPTER 3

### SYNTHESIS AND CHARACTERIZATION OF PEHT SYSTEMS - HOMOPOLYMER AND COPOLYMERS

#### Introduction

An introduction to thermotropic liquid crystalline main - chain polyesters containing asymmetrically substituted hydroquinone is already given in Chapter II. The primary purpose of the introduction of the pendants is to lower the transition temperatures of the aromatic polyesters with rigid back - bones, which in turn would facilitate their processing. Another approach that has been followed to achieve the same purpose has involved the synthesis of LC copolyesters containing non - mesogenic units.<sup>1</sup> Lenz and co - workers investigated the effect of adding a non - mesogenic unit into a linear mesogenic polymer and found that LC properties are retained up to 80 % of the non - mesogenic units. In another study from the same lab, copolyesters with mesogenic ( chlorohydroquinone ) and non - mesogenic ( bisphenol ) units were made and it was observed that the anisotropy in the copolymers varied greatly with composition.<sup>2</sup> Polymers with high percentage of mesogenic units formed a nematic mesophase, and as the percentage of mesogenic units was decreased, a biphasic mesophase was observed. Other investigators have studied the synthesis and characterization of random copolyesters ( Fig. 3.1 ).<sup>3-9</sup>



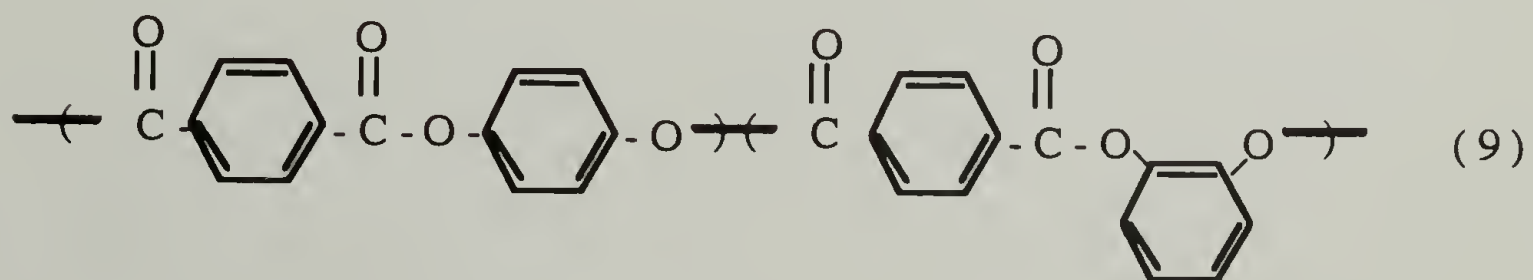
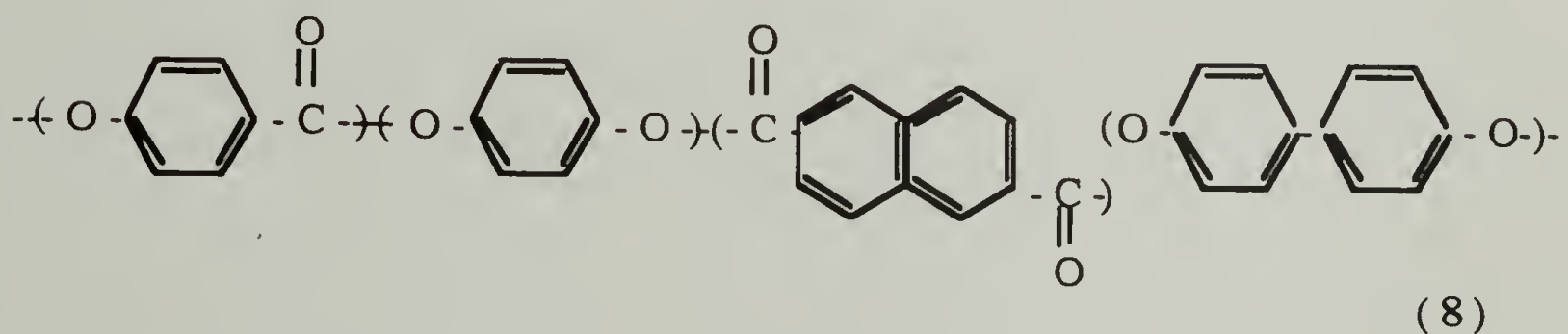
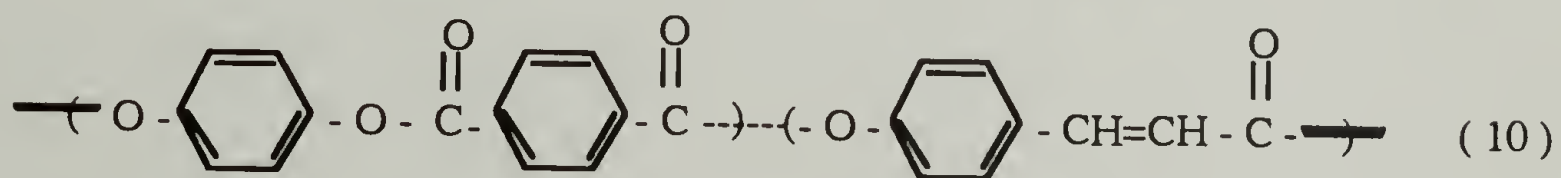
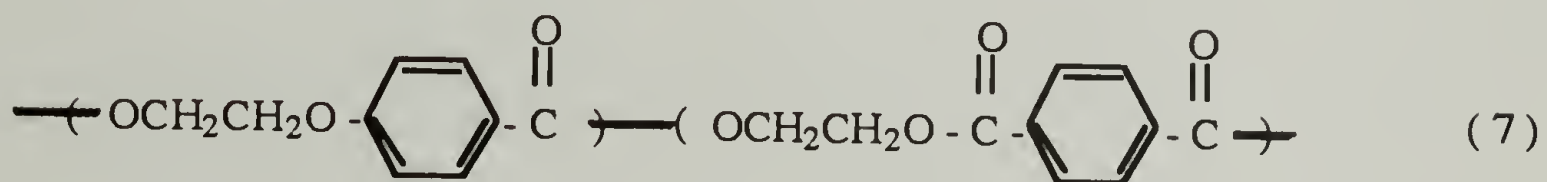
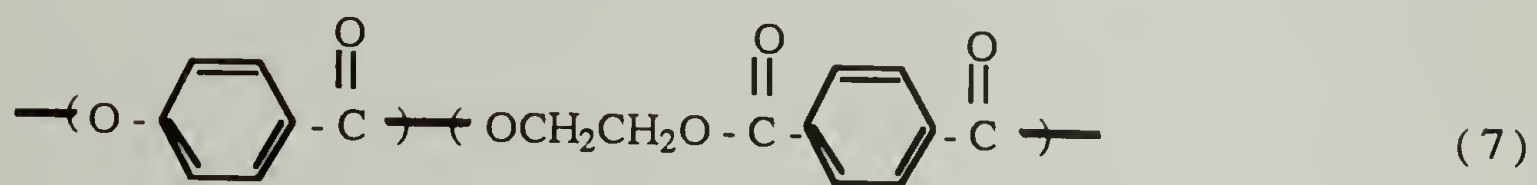
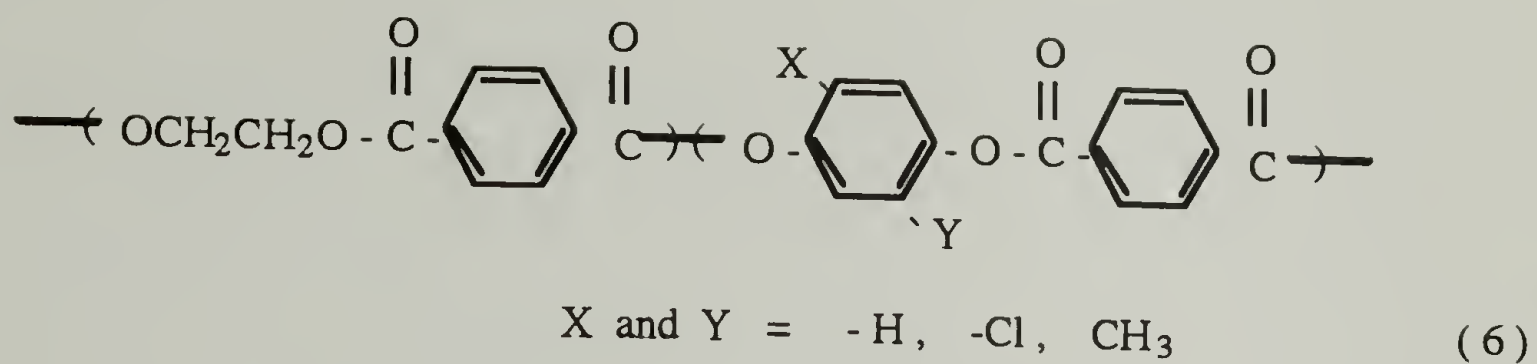


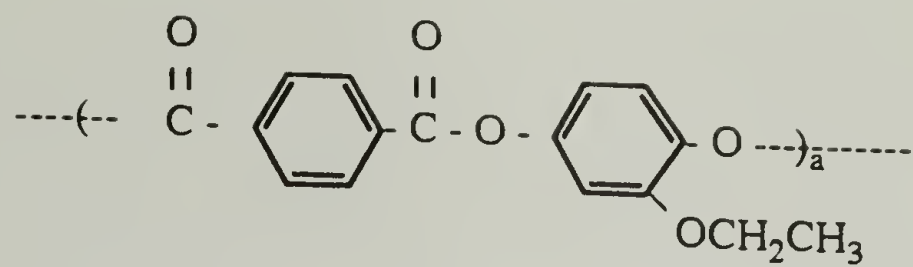
Fig. 3.1 : LC polyesters containing non-mesogenic units

For the 'Molecular Composites Project' sponsored by AKZO, new polymers had to be synthesized which could be used as components in molecular composites with flexible coil PET as the matrix. One approach was the synthesis of polymers with functionalities exhibiting specific interactions with the matrix as described in chapter II. Compatibilization could be further enhanced by the introduction of PET / PBT segments in the LC copolyester due to the interaction of the isotropic segments in the melt state.

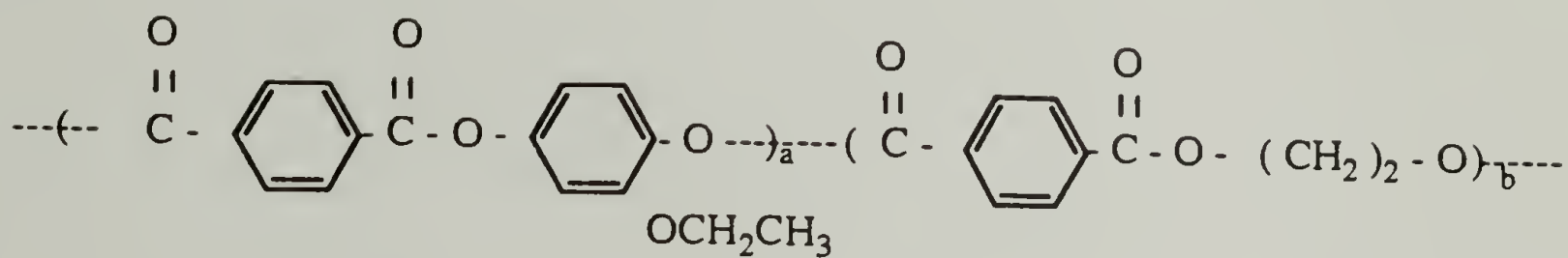
Of the various oxyethylene groups available for substitution on the hydroquinone, the monoethoxy functionality would be the most convenient as regards monomer synthesis. The problem of tedious monomer synthesis can be circumvented by opting for this system which involves a much simpler 1 - step reaction starting with the commercially available 3 - ethoxy - 4 - hydroxy benzaldehyde.<sup>10</sup> The homopolymer and a series of random copolyesters of the ethoxy hydroquinone with ethylene glycol and terephthaloyl chloride were synthesized and characterized by A. Tendolkar from our lab.<sup>11</sup> The results of the studies are summarized in Table. 3.1.

It was thought that the block copolymers containing ethoxyhydroquinone moieties should show further enhanced compatibility with PET and properties could also be tailored by adjusting the block sizes. Hence research work was focused on the synthesis of the monomer and optimization of the copolymerization conditions.

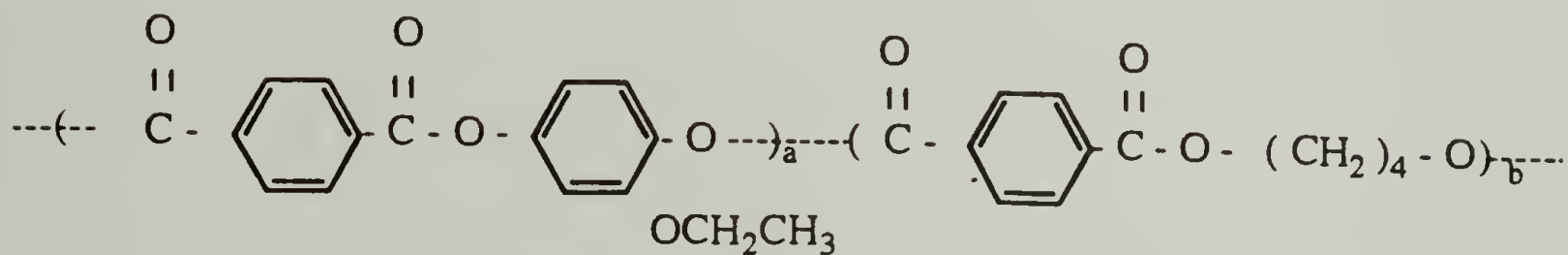
The objective of this chapter is to describe the synthesis and characterization of homopolymer and copolyesters based on ethoxyhydroquinone, ethylene glycol / butanediol and terephthaloyl chloride moieties ( Fig. 3.2 ). Optimization of conditions to get high molecular weight PET copolyesters is described here.



( PEHT )



P(EHT) / (ET)



P(EHT) / (BT)

Fig. 3.2 : Structures of PEHT and P EHT/(ET/BT) copolyesters

Table. 3.1 : Properties of random copolyesters containing PEHT & PET

Polymer composition (PEHT : PET)	$\eta$ inherent (dL/g)	$T_m$ ( $^{\circ}$ C )	$T_{lc-lc}^{**}$ ( $^{\circ}$ C )	Texture
100 : 0	0.70	200	267	Nematic
80 : 20	0.63	205	262	Nematic
60 : 40	0.60	206	267	Nematic
40 : 60	0.52	205	275	Biphasic
20 : 80	0.45	230	-	Biphasic
0 : 100	0.37	256	-	Crystalline

\*\* - Transition from a dense threaded nematic to a birefringent, schlieren texture

The thermal and morphological characterization of the copolyesters by DSC and cross polarized optical microscopy is also discussed here. The compositional and sequence distribution analysis of the random and block copolyesters using  $^1\text{H}$  NMR is described in detail. WAXD work done to assign some DSC peaks in the blocky copolymers is also described here.

### Experimental

#### Materials

All of the chemicals except bis ( hydroxyethyl ) terephthalate [ BHET ] were purchased from Aldrich chemical Company. BHET was obtained from Poly Sciences and recrystallized from acetone. Terephthaloyl chloride was purified by sublimation. The solvents used for polymerization, methylene chloride [ MC ], tetrachloroethane



[ TCE ] and 1 - chloronaphthalene [ 1 - CN ] were distilled over phosphorus pentoxide, potassium carbonate and calcium hydride respectively, the latter under reduced pressure. Triethyl amine and pyridine were also distilled over calcium hydride before use.

### Monomer Synthesis

The synthesis of monoethoxyhydroquinone is a 1 - step reaction starting with the commercially available 3 - ethoxy - 4 - hydroxybenzaldehyde.<sup>12</sup> The schematic of the reaction is given in Fig. 3.3. A detailed description of the synthesis is given below :

In a Nalgene flask, 40 g ( 0.241 mol ) was dissolved in sodium hydroxide solution ( 19.3 g / 689 mL ) [ 0.482 moles ] under an Ar atmosphere. A 30 % hydrogen peroxide solution [ 29.5 mL = 0.289 moles ] was injected into the flask quickly. The solution temperature increased to 60<sup>0</sup> C, after which it was allowed to reach room temperature, then kept there for 2 h. The deep brown alkaline solution was acidified with dil. HCl and extracted with 4 x 150 mL of ether. The ether was washed successively with 4 x 150 mL of saturated sodium metabisulfite solution and 3 x 150 mL water. The ether solution was dried over anhydrous sodium sulfate overnight. After evaporation of the ether solvent, 200 mL chloroform was added to crystallize the compound immediately. After filtering off the monomer, the filtrate was kept in the refrigerator to ensure complete crystallization of the compound. If the monomer is dark, color can be removed by using animal charcoal. Pure white product was obtained by a sublimation process at 120<sup>0</sup> C under vacuum.

Yield = 70 %. The melting point of the monomer was 110<sup>0</sup> C.

Elemental Analysis: Expected - C ( 62.33 % ) H ( 6.49 % )

Observed - C ( 62.32 % ) H ( 6.46 % )

$^1\text{H}$  NMR (  $\text{CH}_3\text{COOD}$ , ppm ) : 1.3 ( t, 3H ), 3.95 ( q, 2H ), 6.2 ( d, 1H ),  
6.4 ( s, 1H ), 6.58 ( d, 1H ), 8.1 ( s, 1H ), 8.76 ( s, 1H ).

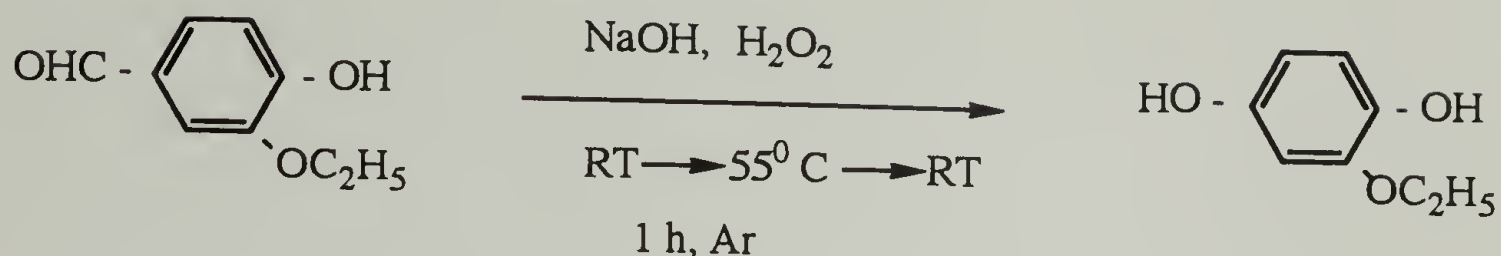


Fig. 3.3 : Synthesis of 2-ethoxyhydroquinone

The synthesis of bis ( hydroxybutyl ) terephthalate [ BHBT ] was more cumbersome and the procedure described by Hasslin et al was followed.<sup>13</sup>

In a 1 liter, three - neck round bottomed flask fitted with condenser / reflux column, pressure equalizing addition funnel, inert gas inlet and mechanical stirrer, was added 100g ( 1.11 mol ) of 1,4 - butanediol, 35 mL ( 0.43 mol ) of pyridine, and 200 mL tetrahydrofuran [ THF ]. The solution was purged with purified argon for 15 minutes. Subsequently 60 g ( 0.3 mol ) of terephthaloyl chloride in 100 mL of THF was added dropwise over a 30 minute period into a vigorously stirred reaction pot.

The cloudy yellow solution was brought to reflux for 1 h at which time the solution cleared. The yellow solution was then distilled by rotovap at 40 °C until half the original volume of THF remained. The remaining solution was poured over 1 liter of ice water. The solid precipitate was then filtered off and dissolved in 300 mL of absolute ethanol. This solution was heated to reflux and hot filtered. The solution was cooled to 15 °C for 5 h. The resulting precipitate was the crude product of the 2.5 mer. The filtrate was further cooled to 0 °C for 12 h, filtered

and was then poured over ice water. The resulting precipitate was filtered, dried and recrystallized twice with ethyl acetate.

Yield = 35 %. The melting point of the product was 72 ° C.

$^1\text{H}$  NMR (  $\text{CDCl}_3$ , ppm ) : 1.6 - 1.9 ( m, 8H ), 3.71 ( t, 4H ),  
4.36 ( t, 4H ), 8.07 ( s, 4H )

The purity of the product was confirmed by HPLC.

### Polymer synthesis

#### *Homopolymer synthesis<sup>14</sup>*

Solution polymerization was done using methylene chloride as the solvent. To a 500 mL 3 - neck flask, were added 0.039 mole ( 8.897 g ) of 2 - ethoxy hydroquinone and 0.078 mole ( 10.8 mL ) of triethylamine as the acid - acceptor. Then 100 mL of methylene chloride was added into the flask with vigorous agitation to form a solution. Thereafter a solution of 0.039 mole ( 7.92 g ) of terephthaloyl chloride in 100 mL methylene chloride was added slowly to the reaction mixture, and the contents of the flask were stirred for 24 h with a magnetic stirrer at room temperature, and then refluxed for 24 h. The polymer started precipitating after 30 minutes of stirring. At the conclusion of the refluxing period, the mixture was cooled to room temperature and was added to 1000 mL methanol. The polymer was filtered from the solution to obtain 10.1 g ( 80 % yield ) of product. The polymer product was dried and then extracted with acetone in a Soxhlet extractor to obtain a more pure polymer. The inherent viscosity of the polymer solution in p-chloro phenol at 50 ° C was 0.42 dL / g at a polymer concentration of 0.5 g / dL.

#### *Random copolymer synthesis<sup>11</sup>*

This procedure illustrates the preparation of random copolymers with a ratio of 60 : 40 of ethoxyhydroquinone : ethylene glycol .



To a 1 - liter flask were added 6 g ( 0.039 mol ) of an ethoxyhydroquinone, 1.6014 g ( 0.026 mol ) of ethylene glycol, and 18 mL ( 0.0649 mol ) of triethylamine as an acid - acceptor. Then 300 mL of methylene chloride was added to the flask and the reactants were stirred vigorously with a magnetic stirrer until dissolution occurred. Then 13.18 g ( 0.0649 mol ) of terephthaloyl chloride dissolved in 200 mL methylene chloride was added slowly to the reaction mixture, and the contents of the flask were stirred for 24 h at room temperature, and then refluxed for 24 h. The solution became turbid after about 30 minutes. The reaction was terminated by adding the cooled reaction mixture to 1500 mL of methanol, and the polymer was filtered from the solution to obtain 16 g of crude polymer ( 93.2 % ). The polymer was dried and then extracted in a Soxhlet extractor using methanol to obtain a more pure polymer at a yield of 87.4 %. The inherent viscosity measured in a mixture of p - chlorophenol / TCE ( 60 / 40 v / v ) at 26.1 ° C was 1.1 dL / g.

$^1\text{H}$  NMR (  $\text{CH}_3\text{COOD}$ , ppm ) : 1.47 ( t, 3H ), 4.29 ( q, 2H ), 4.98 ( s, 4H ),  
7.18 ( m, 2H ), 7.6 ( s, 1H ), 8.28 - 8.58 ( m, 8H )

The 70 : 30 random copolymer was also synthesized in an identical manner.

### *Block copolymer synthesis*

A one - reactor reaction procedure was adopted for making the block copolymers as illustrated in Fig.3.4.

This procedure illustrates the low temperature preparation of the block copolymer with a ratio of 50 : 50 of ethoxyhydroquinone : ethylene glycol and a block size ratio of 6 : 6. To a 500 mL three - necked flask were added 6.0 g ( 0.0236 mol ) of BHET, 25 mL pyridine and 200 mL tetrachloroethane. The flask was fitted with a condenser, an argon inlet and outlet and a teflon stirrer. After dissolving the BHET in TCE & pyridine, 6.394 g ( 0.0314 mol ) of terephthaloyl



chloride dissolved in 200 mL of tetrachloroethane was cannulated into the flask. The temperature was increased to  $90^{\circ}\text{C}$  and maintained at that temperature for 3 h. At the end of that period, the solution was slightly turbid and at this stage, 7.992 g (0.0393 mol) of terephthaloyl chloride was added to the vessel under a positive flow of Argon. After 10 minutes, 7.279 g (0.0472 mol) of ethoxyhydroquinone was added to the reaction mixture and enough solvent was added to keep the reactants in solution. At this point, the solution becomes cloudy due to the evolution of HCl. The temperature was increased to  $100^{\circ}\text{C}$  and the polymerization was carried out for 20 h to give a pale yellow, slightly cloudy solution. the reaction was terminated by cooling the reaction mixture to room temperature and pouring it into 1500 mL of methanol. The mixture was then filtered to obtain 27.5 g of polymer. The crude polymer was extracted in a Soxhlet extractor using methanol / acetone (50 : 50) for about a day and after drying in a vacuum oven at  $90^{\circ}\text{C}$  for about 3 days, about 86 % of pure polymer was obtained. The inherent viscosity was 0.3 dL / g measured in 4 - chlorophenol at  $50^{\circ}\text{C}$  at a concentration of 0.5 g / dL.

$^1\text{H}$  NMR (  $\text{CH}_3\text{COOD}$ , ppm ) : 1.3 ( m, 3H ), 4.11 ( m, 2H ), 4.81 ( s, 4H )  
7.007 (m, 2H ), 7.28 ( m, 1H ), 8.12 - 8.42 ( m, 8H )

The following illustrates the high temperature preparation for the block copolymer with a ratio of 50 : 50 of ethoxyhydroquinone : butanediol and a block size ratio of 6 : 6. A 500 mL three - neck flask was fitted with a water condenser, an argon inlet and outlet, a dropping funnel and provided with a teflon stirrer. The flask was heated and completely flushed with argon to remove any moisture and 6 g (0.0194 mol) of BHBT and 100 mL of 1 - chloronaphthalene [ 1 - CN ] was charged into it. A solution of 5.239 g (0.0259 mol) terephthaloyl chloride in

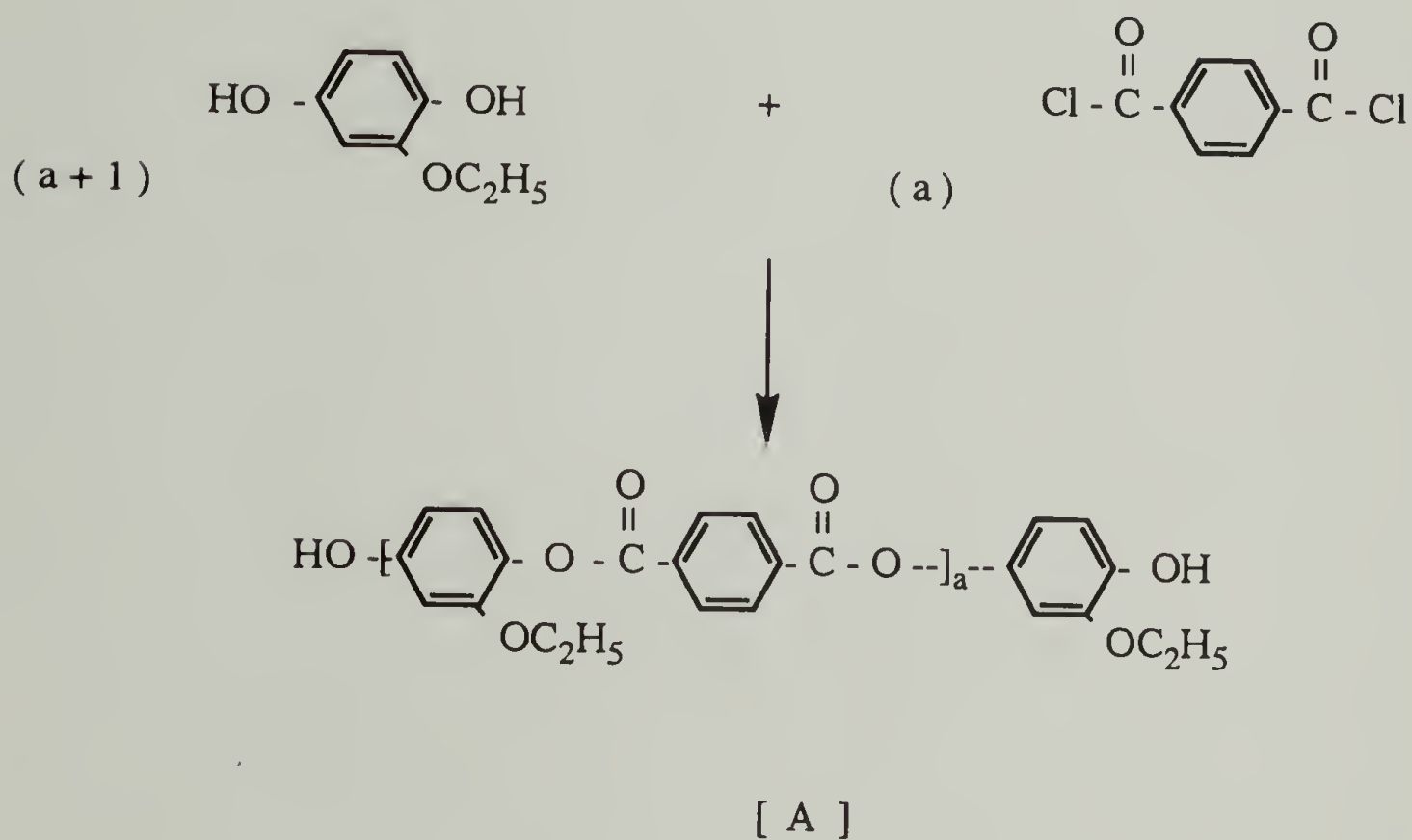
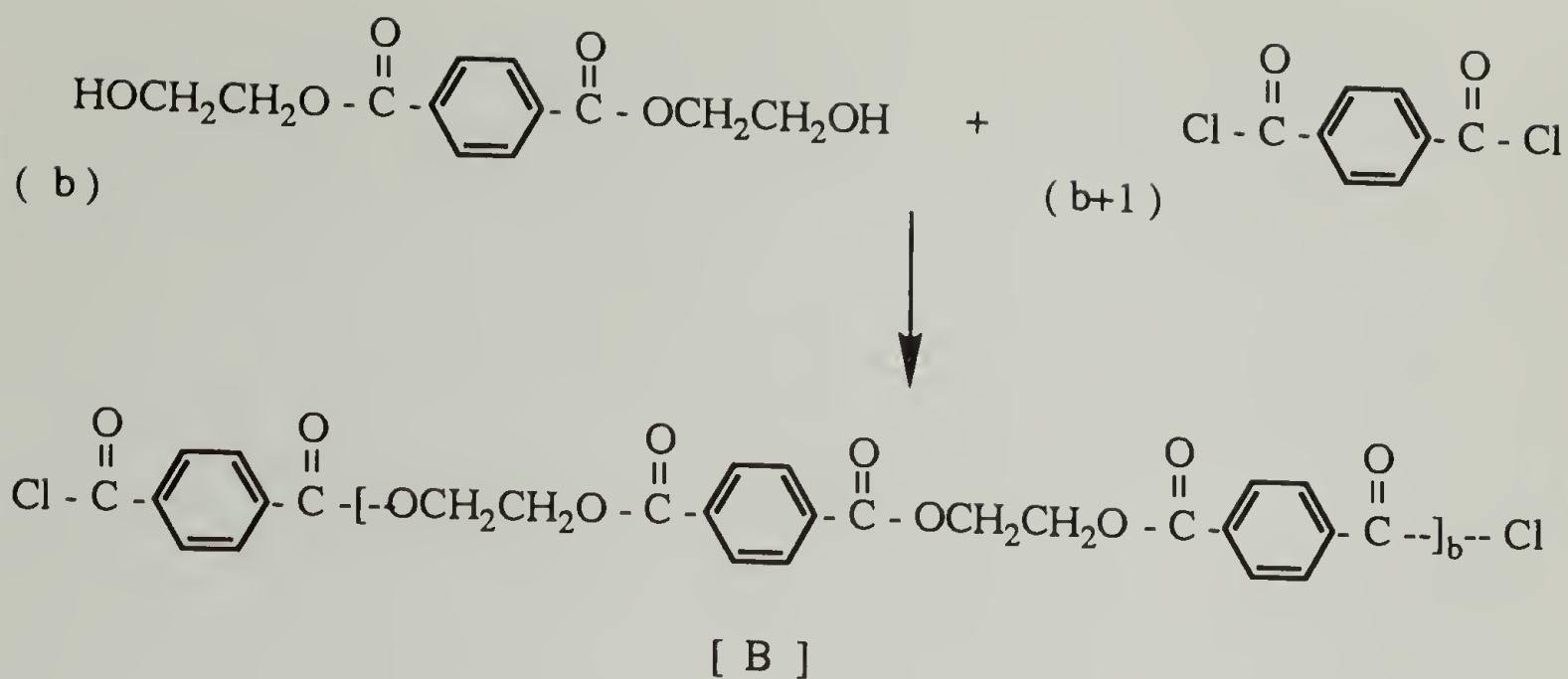


Fig. 3.4 : Synthesis of block PEHT/(ET/BT) copolyesters

200 mL 1 - CN was placed in the dropping funnel and added dropwise to the reaction mixture at 100 °C. At the end of 5 h, 6.549 g ( 0.0323 mol ) of terephthaloyl chloride was added to the flask followed by the addition of 5.638 g ( 0.0388 mol ) of ethoxyhydroquinone after 10 minutes. The temperature of the reaction mixture was increased to 190 °C and the polymerization was maintained for 42 h. At the end of the period, a gel - like material was formed which was dissolved in excess 1 - CN and the hot reaction mixture poured into 1500 mL methanol to yield white, fibrous polymer particles. After filtering the polymer, it was washed by stirring in hot, boiling methanol for 3 - 4 h and then dried in a vacuum oven for 3 - 4 days at 90 °C. About 17 g of the pure polymer was obtained. The inherent viscosity was 1.1 dL / g in a 60 : 40 ( v / v ) mixture of p - chlorophenol / tetrachloroethane at 26.5 °C at a concentration of 0.1 g / dL.

<sup>1</sup>H NMR ( CH<sub>3</sub>COOD, ppm ) : 1.29 ( m, 3H ), 2.04 ( M, 3H ), 4.11 ( m, 2H ), 4.52 ( s, 4H ), 6.99 (m, 2H ), 7.27 ( m, 1H ), 8.11 - 8.40 ( m, 8H )

#### Optimization of block copolymerization conditions

Different batches of the PET block copolymers were synthesized varying a number of reaction conditions like the solvent, acid - acceptor, temperature of the reaction and reaction time corresponding to Stage - II as well as the ratio of the block sizes. Some modifications of the process described in the earlier section were also tried out such as a two - pot reaction procedure with the two stages of the reactions done separately and then mixed. Also a reverse one - pot reaction was attempted wherein the ethoxyhydroquinone was reacted in Stage - I followed by the addition of BHET. The reaction conditions used for the representative batches of polymerization are summarized in Table. 3.2. Essentially, there are 4 types of block copolymers differing in composition as listed in the table.

Table. 3.2 : Reaction conditions for the synthesis of PEHT/ET copolyesters with varying block size ratios

Block size ratio PEHT : PET	Solvent	Acid -acceptor	Time ( Stage II )	Temperature ( Stage II )
3 : 6	TCE	Pyridine	19 h	100
5 : 6	TCE	Pyridine	19 h	100
6 : 6	TCE	Pyridine	20 h	100
6 : 6	1 - CN	--	37 h	200
6 : 4	1 - CN	--	29 h	185

Solid phase polymerization to enhance the molecular weight of the PET block copolymers was also tried.<sup>15</sup> To achieve this, one of the copolymer samples was ground to a fine powder and subjected to heat treatment at 150 - 185 °C for two days. As expected, a 50 % increase in inherent viscosity of the sample was measured but the sample color changed from white to orange. This technique could be further optimized for enhancing the molecular weight of the PET block copolymers.

Also a number of experiments were performed to study the effect of reaction conditions on the molecular weight of the 60 / 40 PEHT / PET random copolymer. The experimental conditions are summarized in Table. 3.3.



Table. 3.3 : Reaction conditions for the synthesis of a series of 60/40 P EHT/ET random copolyesters

Reaction solvent	Acid - acceptor	Reaction temperature ( <sup>0</sup> C)
MC	Triethyl amine	45
TCE	Pyridine	100
TCE	Pyridine	45
TCE	Triethyl amine	50
1 - CN	Triethyl amine	50
1 - CN	-	200

A few batches of the PEHT / PBT copolymers were also synthesized and the reaction conditions are summarized in Table. 3.4. Based on the properties of the PET block copolymers, only the 6 : 6 PBT block copolymer was synthesized, but in two different solvents.

Table. 3.4 : Reaction conditions for the synthesis of P EHT/BT block copolyesters

Block size ratio PEHT : PBT	Solvent	Acid acceptor	Time ( Stage II )	Temp ( <sup>0</sup> C ) ( Stage II )
6 : 6	TCE	Pyridine	20 h	100
6 : 6	1 - CN	--	42 h	190

#### Characterization methods

Viscometry was done to get a relative idea of the molecular weight of the polymer. The GPC analysis could not be done because of the insolubility of the

polymer in common organic solvents. The polymer was dissolved in a mixture of p - chlorophenol / TCE ( 60 / 40 v / v ) and the inherent viscosity measured at 26.1° C for a polymer concentration of 0.5 g / dL using a Cannon - Ubbelohde viscometer.

Thermogravimetric analysis was done using a DuPont TA instrument under air as well as nitrogen. The phase transition temperatures were measured on a differential scanning calorimeter ( Perkin - Elmer IV, Perkin - Elmer VII and DuPont 2000 ), under a nitrogen flow with a heating and cooling rate of 20 ° C / min. The temperature axis of the DSC thermogram was calibrated prior to use with reference standards of high purity indium. The peak maxima were chosen as the phase transition temperatures.

WAXD studies were undertaken to assign the endotherms observed in the DSC spectra of blocky copolymers. For WAXD studies, a Statton II camera and a point collimated Ni filtered Cu K $\alpha$  radiation was used. As the measurements have to be done at temperatures as high as 280 ° C, the powder samples had to be filled in the X - ray capillaries under inert conditions and sealed using super glue in the glove bag. The capillaries were further sealed using an oxygen flame and the height of the tube adjusted according to the requirements of the heater. An exposure time of 10 - 12 h was needed to get sharp, clear X - ray photographs.

For the study of the mesophases formed by the polyester, polymicrographs were taken with a 35mm camera mounted on a Carl - Zeiss polarizing light microscope equipped with a hot stage ( Mettler FP - model). The polymer sample, placed between 2 microscope cover glasses, was heated well above its melting transition on a hot plate melting point apparatus and rapidly quenched. The

mesophase behavior was then observed as a function of temperature on the hot stage.

Extensive  $^1\text{H}$  NMR analysis was done to get the composition and sequence distribution in the various copolymers synthesized. This was mainly done to get an idea of the degree of randomness in these copolyesters. A Bruker model attached to a IBM - 200 was used to collect the spectra and do quantitative integration of the peaks for calculation of the composition and sequence distribution values.  $^{13}\text{C}$  NMR analysis was also done for representative polymers where the peaks were assigned correctly, but quantitative work was not possible using the resolution available. A Varian XL - 300 operating at 300 MHz in deuterated solvents was used for this purpose.

For the PBT copolymer exhibiting a high viscosity value, a torsion rectangular test using a frequency rate of 10 rad / sec, a strain of 0.2 and a heating rate of  $1^\circ\text{C} / \text{min}$  was performed in a RDS - 7700 to get the glass transition temperature of the LCP. The sample film about 1.62 mm thick with an area of  $10.1 \times 6.2 \text{ mm}^2$ , was prepared by compression molding.

Also a transmitted light intensity ( TLI ) measurement was done to confirm the phase transitions in some of the copolyesters. For example, at the melting point a sudden decrease in the intensity of the transmitted light through the sample is expected. A thin film of the sample made between two cover - glasses at high temperature was used for measurement. The experimental setup for TLI measurement is displayed in Fig. 3.5.

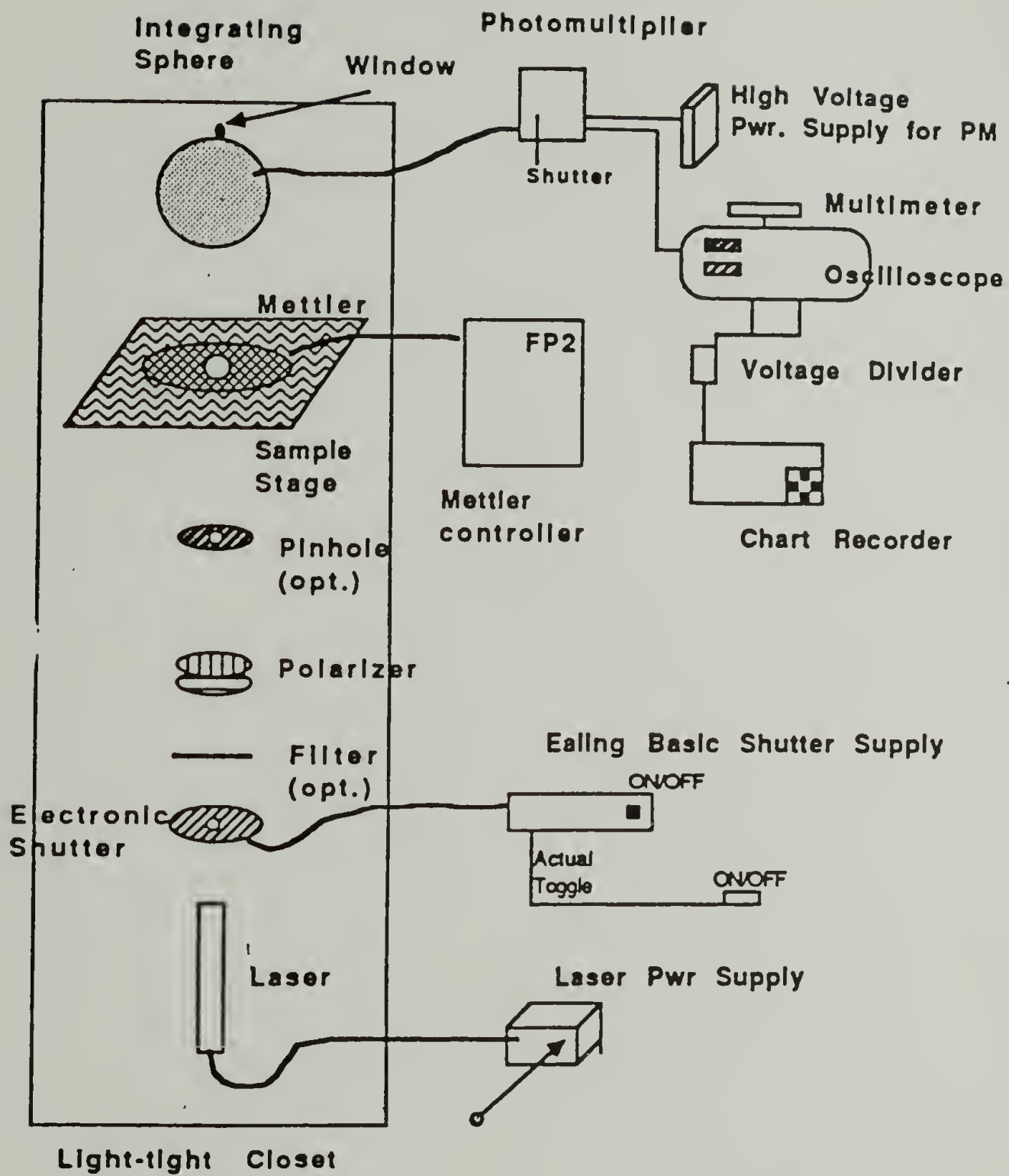


Fig. 3.5 : Experimental set - up for TLI measurements



## Results and Discussion

### Homopolymer

The rigid rod polymer was found to be soluble only in strongly polar solvents like trifluoroacetic acid and p - chlorophenol. The inherent viscosity measurement in p - chlorophenol at a concentration of 0.5 g / dL gave a value of 0.4 dL / g. The calculations are described in Chapter 2.

The DSC analysis showed the presence of two endotherms in the heating cycle as shown in Fig.3.6. The first peak at 257 °C was assigned to the melting of the polyester or a crystal - nematic transition and the second at 270 °C, a transition from one LC phase to another. The latter assignment was corroborated by optical microscopy evidence. The cooling cycle showed an exotherm around 223 °C, which probably corresponds to the mesophase - crystal transition as indicated by the massive super - cooling.

Stir - opalescence was clearly visible in the melting point apparatus. The optical micrographs at various temperatures are given in the following pages, Fig.3.7 and Fig. 3.8. A dense threaded texture indicative of a nematic phase was observed at room temperature. On heating, the texture changed to a highly colored schlieren pattern around 270 °C. The sample remained birefringent up to 320 °C and probably isotropization sets in around the degradation temperature of 350 °C.

### PET block copolymers

The thermal and optical properties along with the viscosity values for the representative PET copolymers are summarized in Table 3.5. The DSC thermograms of the 6 : 6 PEHT : PET block copolymer synthesized in tetrachloroethane at 100 °C

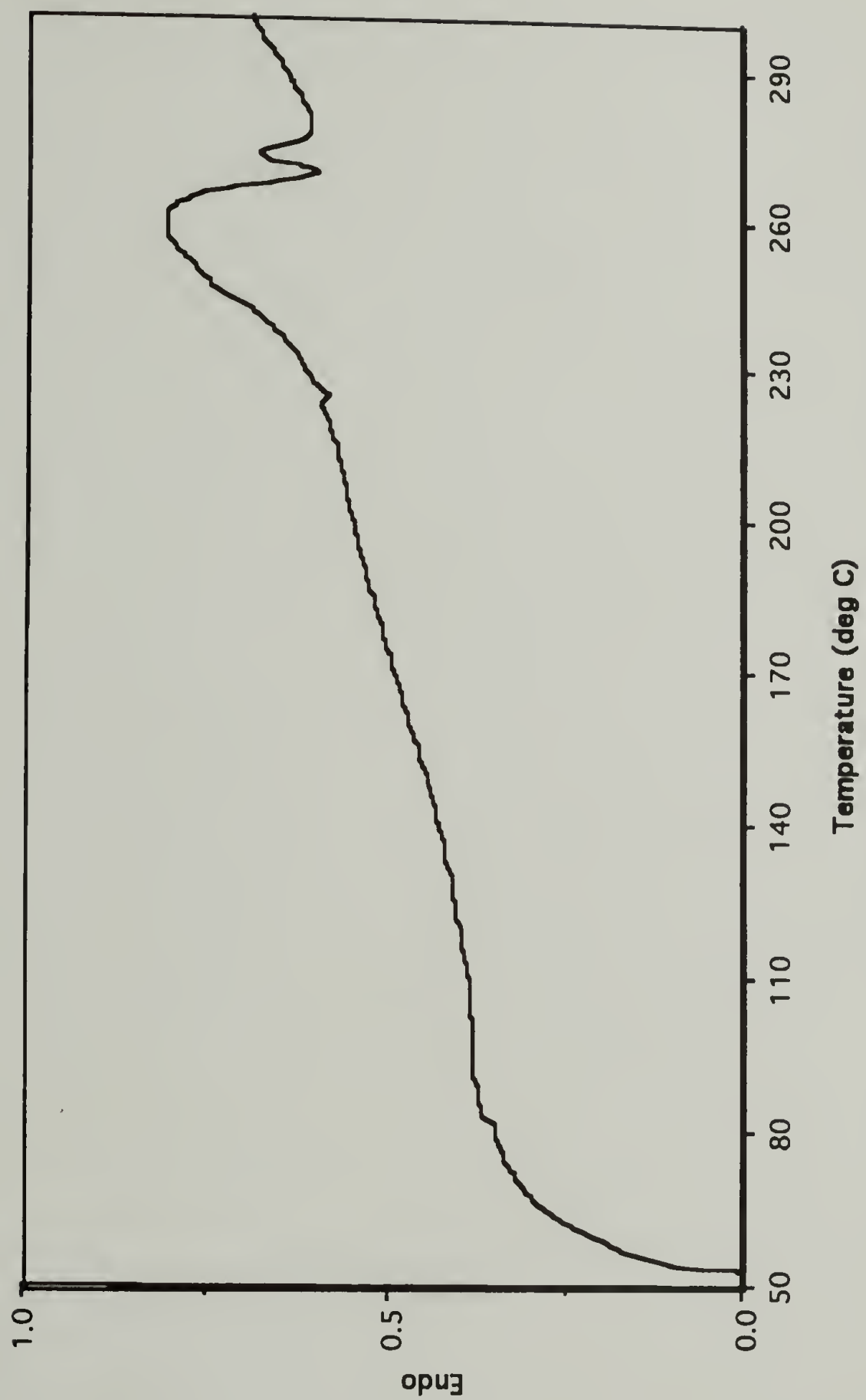


Fig. 3.6: DSC trace of PEHT recorded on the second heating at a rate of 20 deg C/min.

Fig. 3.7: Optical micrographs of PEHT ( Mag. = 400 X )

- a ) Observed mesophase of the polymer quenched to room temperature from the nematic mesophase
- b ) Observed mesophase of the polymer heated up to  $270^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$ .



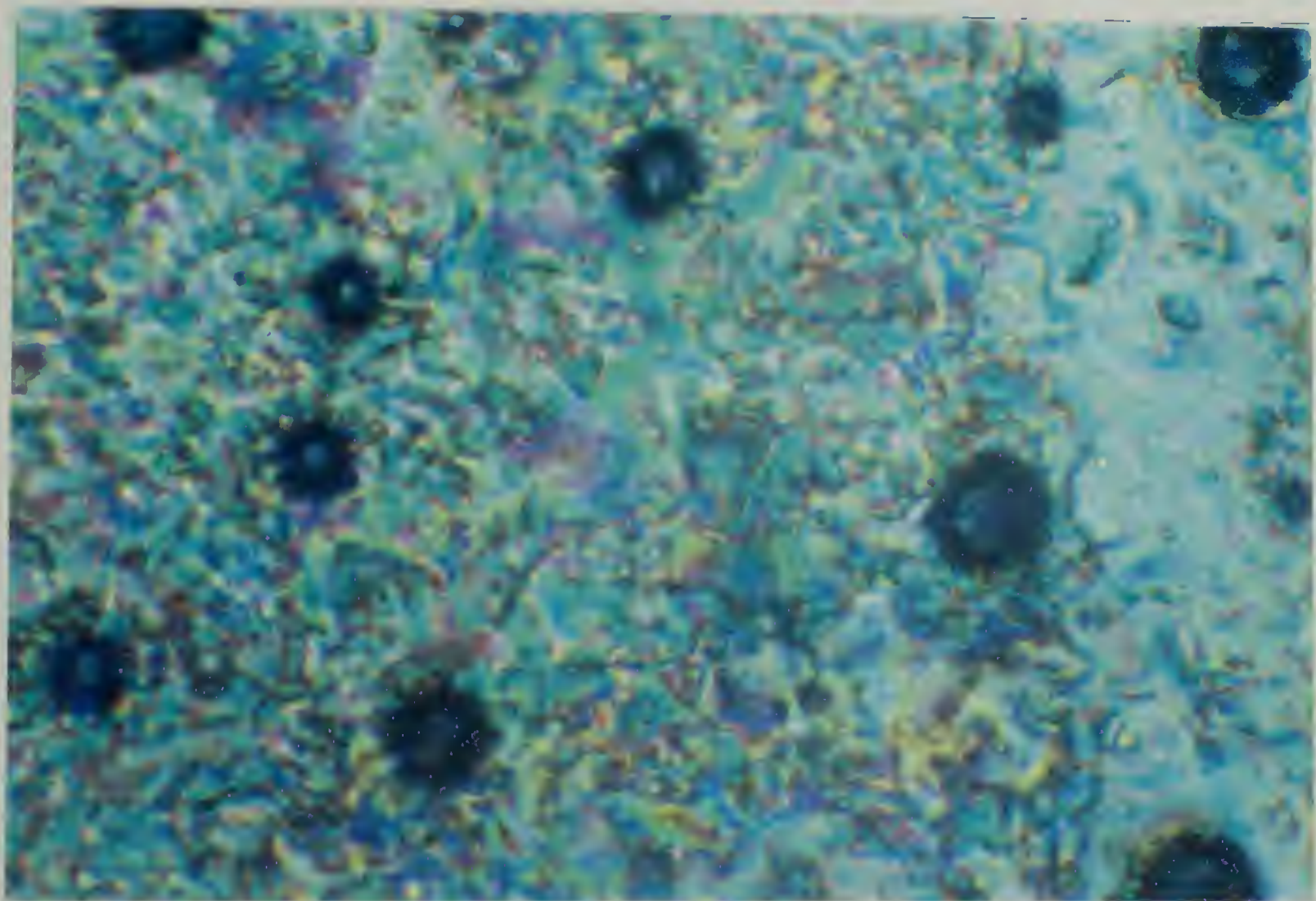
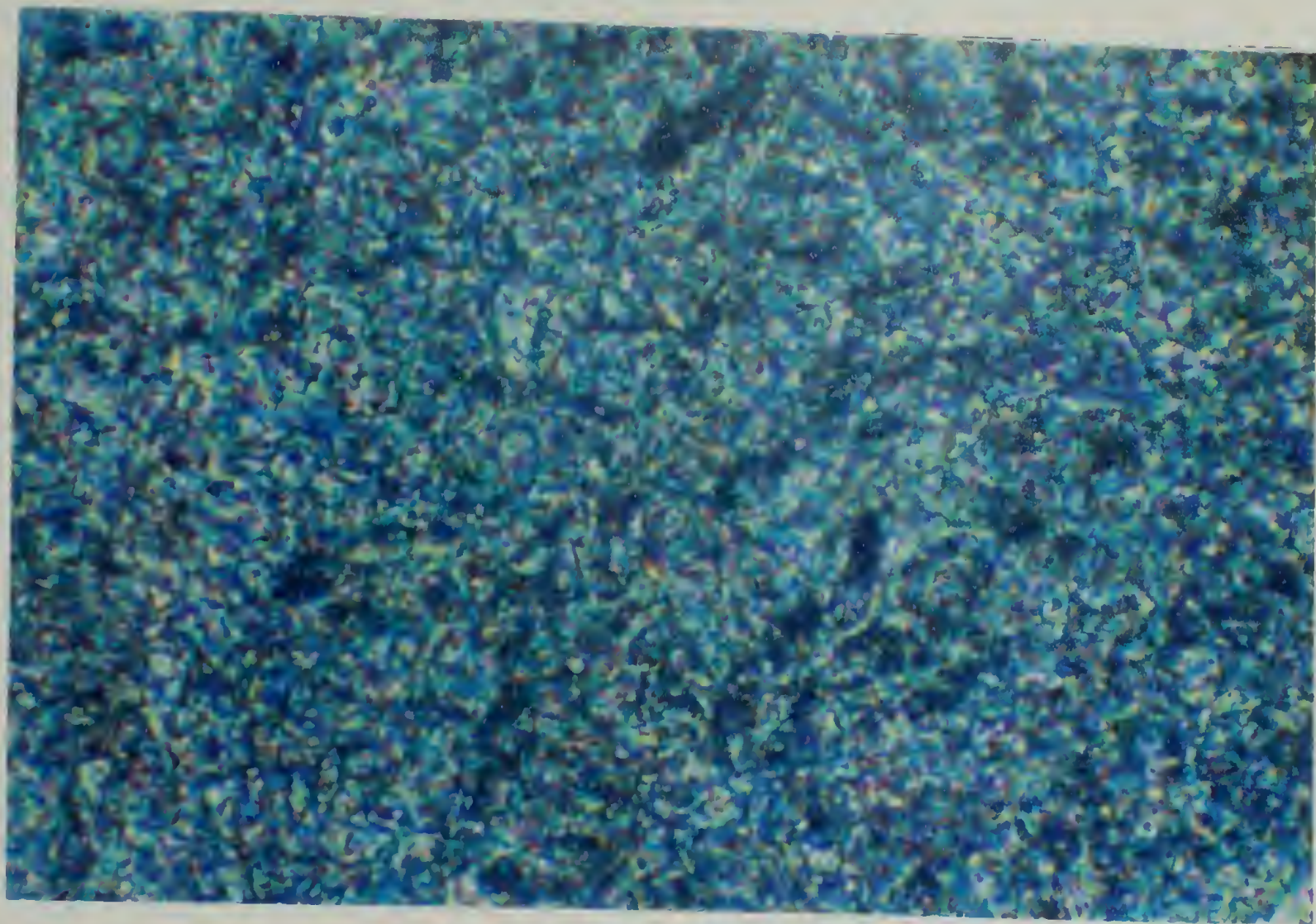
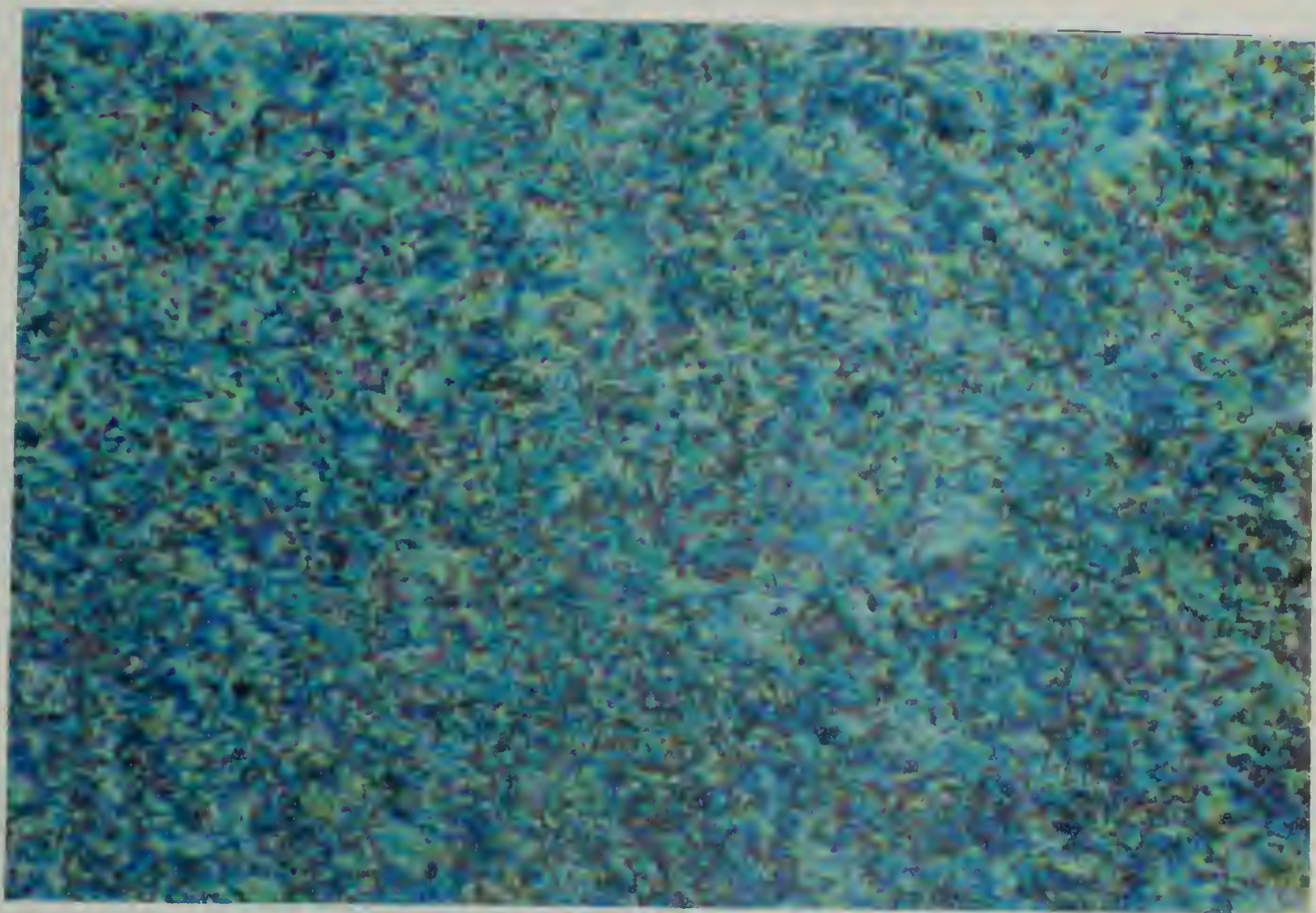
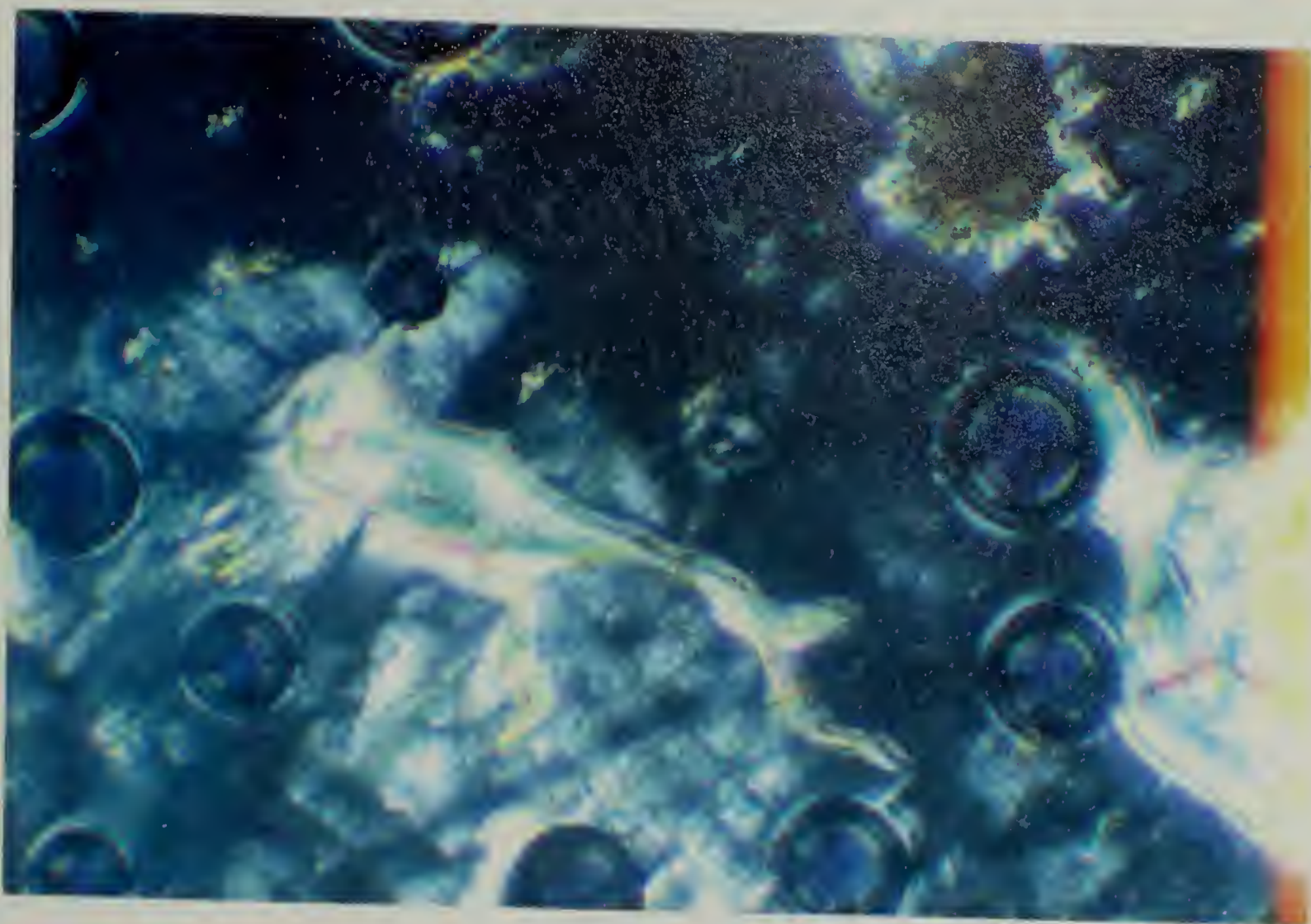




Fig. 3.8: Optical micrographs of PEHT ( Mag. = 400 X )

- a ) Observed mesophase of the sample heated up to  
300 ° C at a rate of 10 ° C / min
- b ) Observed mesophase of the polymer cooled to room  
temperature from 320 ° C at a rate of 10 ° C / min





( P50 ) as well as the optical micrographs corresponding to the sample are given in Fig. 3.9 - 3.12.

The inherent viscosities were measured in a mixture of p - chlorophenol / TCE ( 60 / 40 v / v ) at a concentration of 0.5 g / dL. It was observed that high viscosities could not be obtained for the block copolyesters by varying any of the conditions. High temperature polymerization in 1 - Chloronaphthalene also yielded a poor molecular weight which leads one to suspect a side - reaction at temperatures around 200 °C. To verify whether degradation of the polymer at high temperatures was due to the reaction of ethylene glycol end - groups, the argon outlet was connected to a trap containing 2,4 - dinitrophenyl hydrazine reagent. It was expected that if acetaldehyde was the side - product, an orange precipitate corresponding to the 2,4 - dinitrophenyl hydrazone should be formed in the trap. As the precipitate was not formed, it was concluded that this was not the side - reaction occurring. An alternative reaction that could be taking place leading to a disruption in the stoichiometry would be the formation of cyclic oligomers of PET at high temperatures and higher dilution conditions. It has been shown that formation of rings as opposed to linear chains is thermodynamically favored at high temperatures.<sup>16-19</sup> It has also been shown that the cyclic trimer is present in the highest concentration in PET.<sup>20-22</sup>

The DSC thermogram of the 6 : 6 block copolymer shows 3 distinct endotherms, the assignment of which would be fully confirmed only by high temperature X - ray studies. It can be postulated that the lower endotherm at 223 °C, observed in the second heating cycle of the copolymer, probably corresponds to the melting point of PET segments while the higher temperature endotherms correspond to the mesogenic segment. By comparison with the

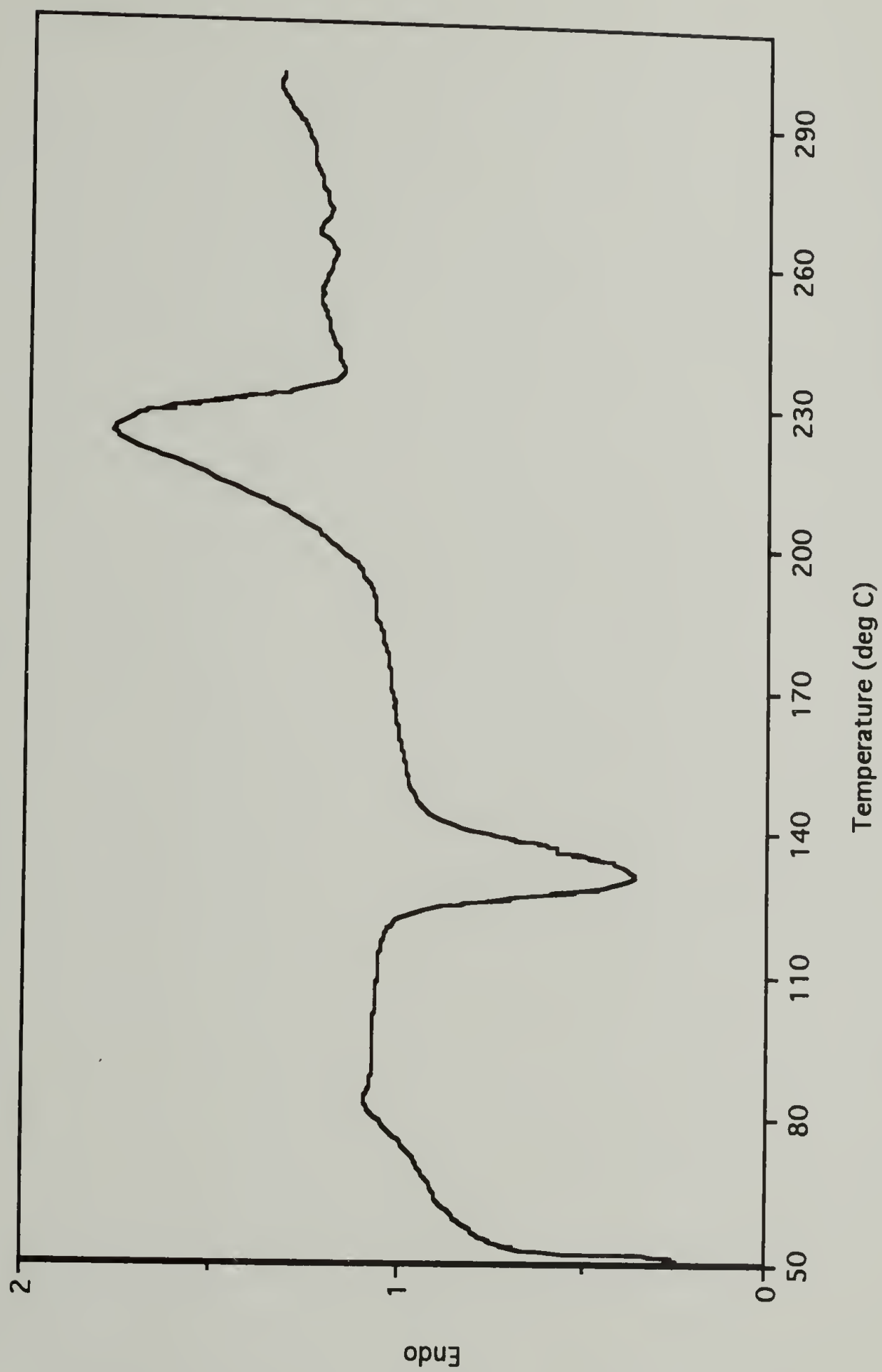


Fig. 3.9: DSC trace of P EHT/ET copolyester, P50, with a block size ratio of 6:6, for the second heating at a rate of 20 deg C/min.



Fig. 3.10: Optical micrographs of P EHT/ET copolyester  
with a block size ratio of 3 : 6 (Mag. = 400 X)

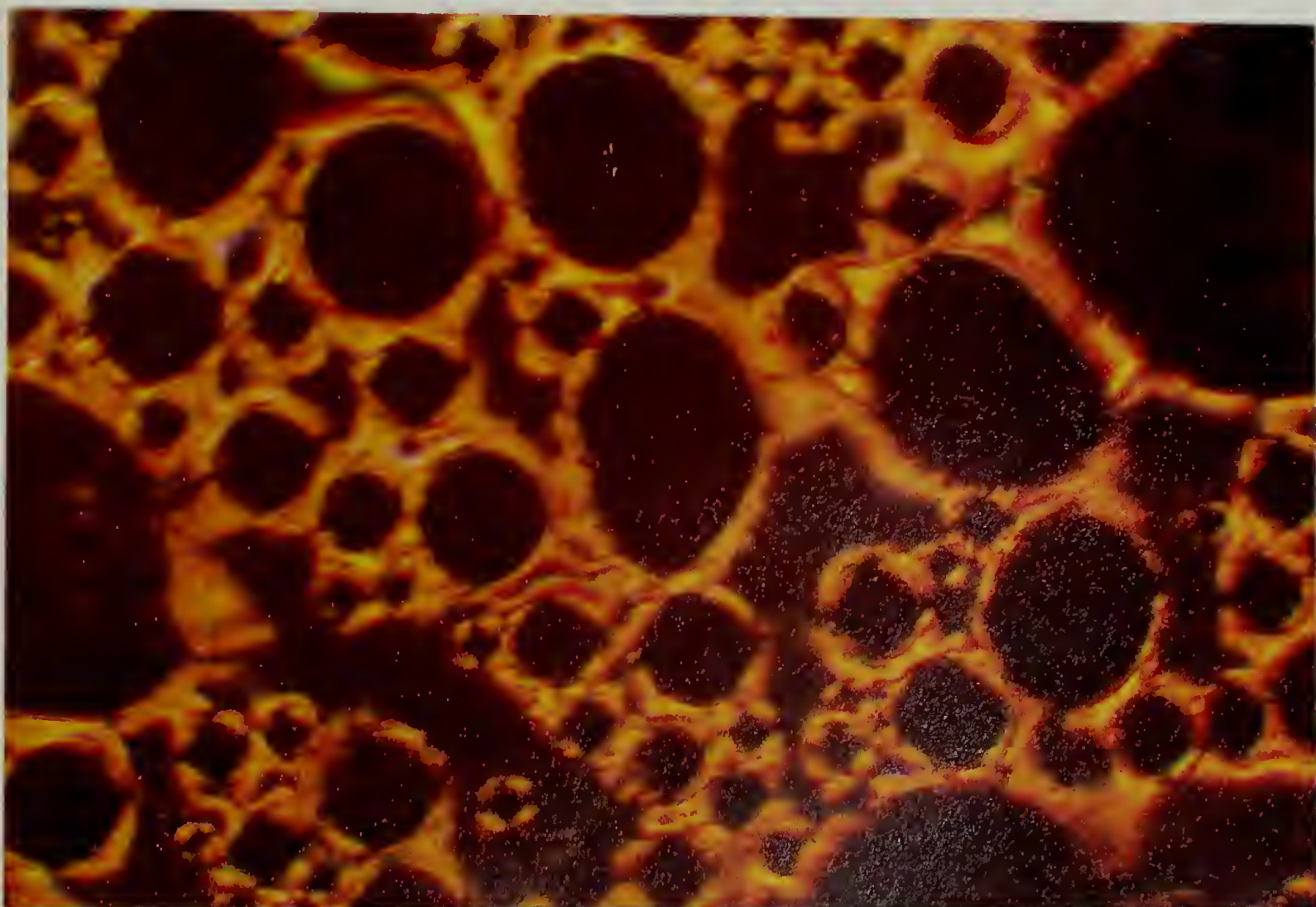
- a ) Observed mesophase of the polymer quenched to room temperature from the nematic mesophase
- b ) Observed mesophase of the polymer heated up to  $246^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$ .



Fig. 3.11: Optical micrographs of P EHT/ET copolyester, P50, with a block size ratio of 6 : 6 ( Mag. = 400 X )

- a ) Observed mesophase of the polymer quenched to room temperature from the nematic mesophase
- b ) Observed mesophase of the polymer heated up to  $271^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$ .





**Fig. 3.12: Optical micrographs of P EHT/ET copolyester, P50,  
with a block size ratio of 6 : 6 ( Mag. = 400 X )**

- a ) Observed mesophase at room temperature for a sample  
heated upto  $320^{\circ}\text{C}$ , cooled down at a rate of  $10^{\circ}\text{C} /$   
min and annealed at  $200^{\circ}\text{C}$  for 1 h**
- b ) Observed mesophase for sample ( a ) reheated upto  $240^{\circ}$   
 $\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$**



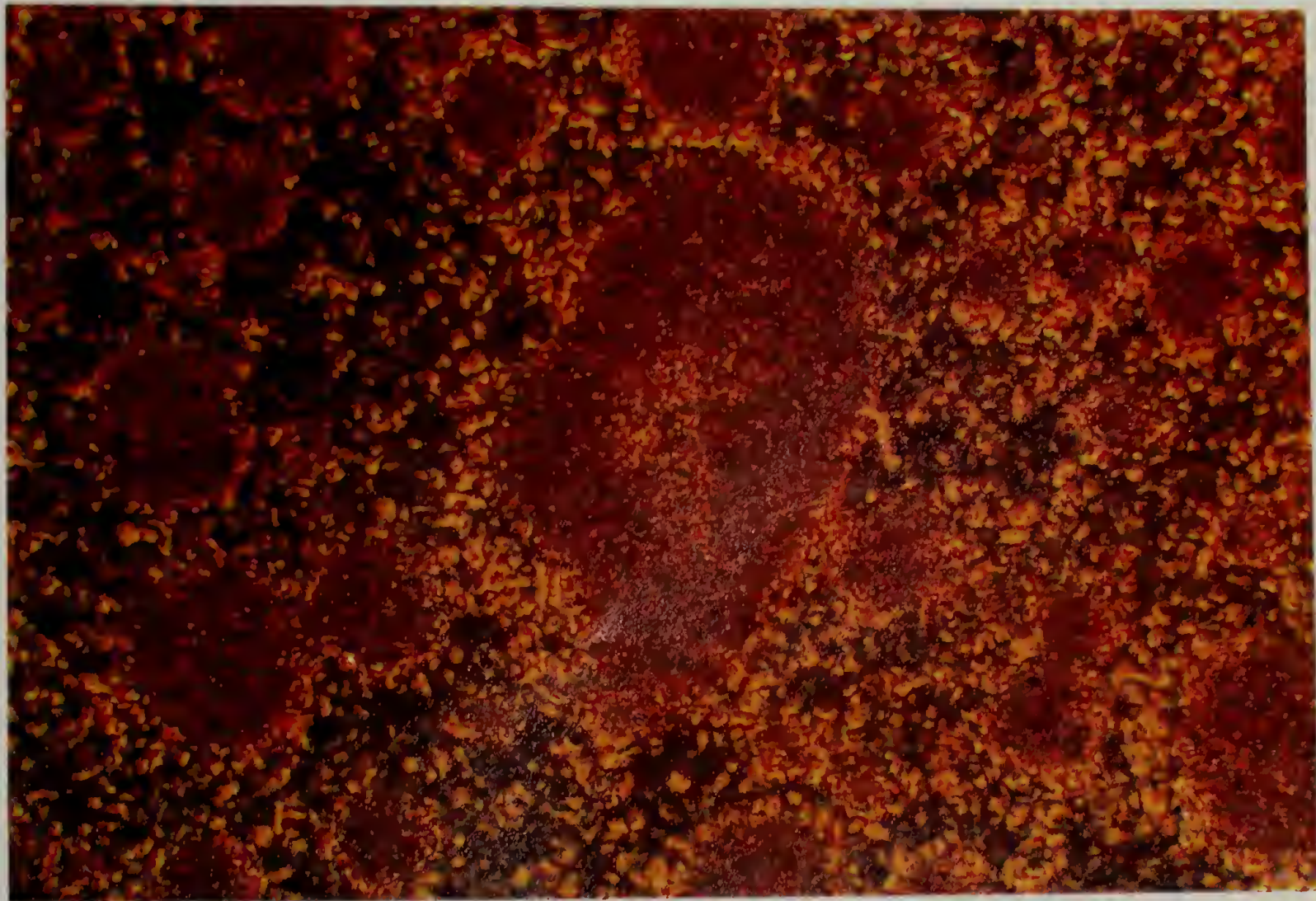
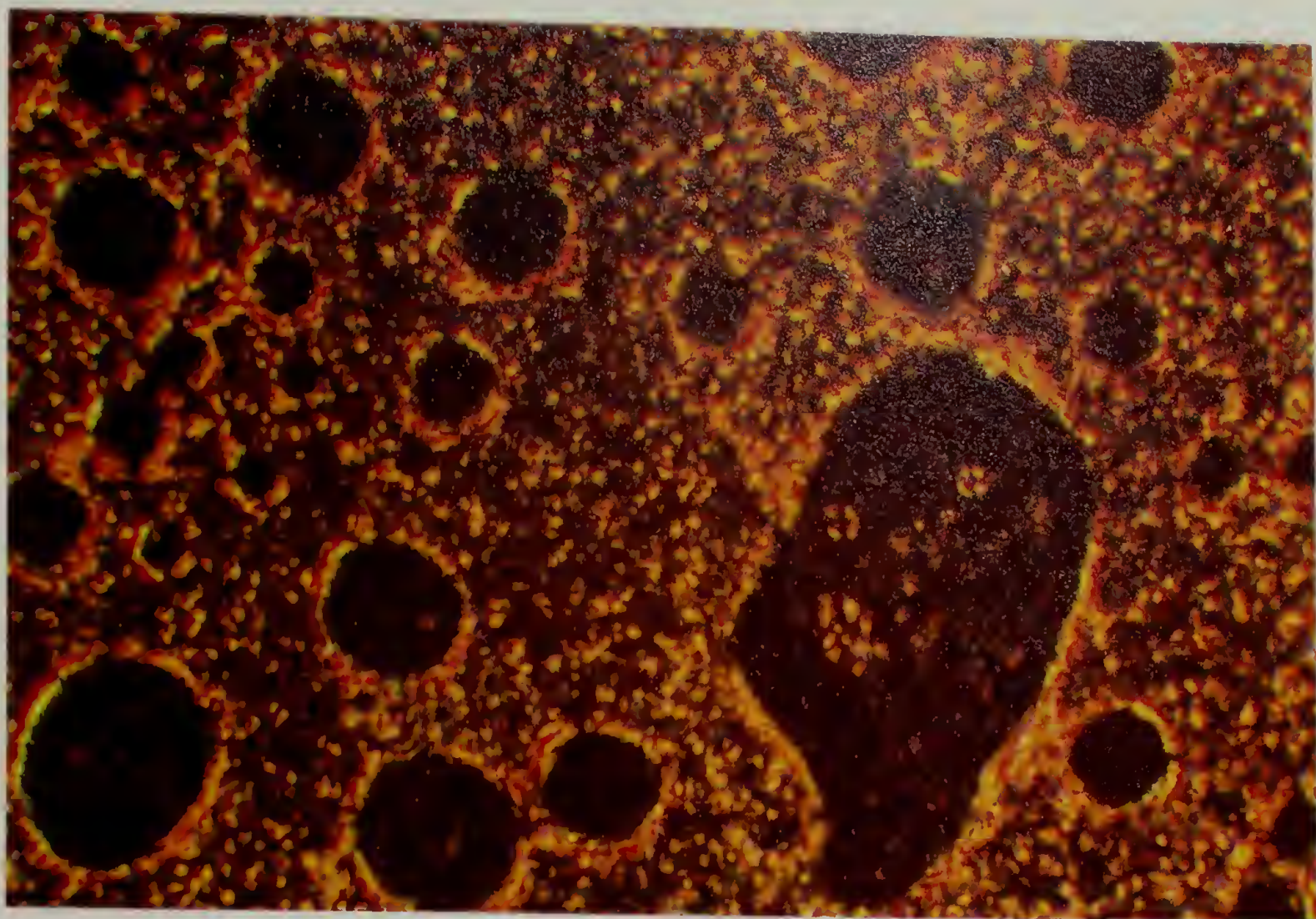




Table. 3.5 : Summary of properties of PEHT/ET block copolyesters

PEHT : PET	Inherent vis. dL / g	Texture	T <sub>peak</sub> ° C	T <sub>g</sub> ° C
3 : 6	0.6	Spherulitic	241	77
5 : 6	0.1	Nematic (When quenched )	223	75
6 : 6	0.3	Biphasic ( At high temps)	223 254 266	80 ( for quenched samples )
6 : 4	0.45	Nematic	215 225	
PEHT	0.4	Nematic	257 267	

thermogram of the homopolymer, the peak at 245<sup>0</sup> C may correspond to the crystal - nematic transition of the PEHT segments and the peak at 266<sup>0</sup> C to the transition from one liquid crystalline phase to another. The peak values are reproducible in subsequent heating cycles. The cooling shows a single exotherm at 211<sup>0</sup> C, which may correspond to the crystallization of the PET segments. When the sample is heated up to 320<sup>0</sup> C and quenched using liquid nitrogen, a glass transition is observed around 80<sup>0</sup> C and a cold crystallization around 136<sup>0</sup> C, which is much lower than the value of 149<sup>0</sup> C obtained for pure PET. Probably, the mesogenic segments act as a nucleus for the PET segments to crystallize on. Annealing at

temperatures just above the different endotherms did not provide any extra information.

The optical micrographs of the PET copolymers were quite interesting too. As the ratio of the PEHT : PET block sizes were varied from 3 : 6 to 6 : 6 to 6 : 4, an interesting change from spherulitic to biphasic to totally nematic pattern was observed at high temperatures under crossed polars.

Elaborating on the optical microscopy results for the PEHT / PET block copolymer with a block size ratio of 6 : 6 ( P50 ), it is obvious from Fig. 3.11 that at temperatures higher than 230 °C, there is the presence of distinct liquid crystalline and isotropic phases. The birefringence in the melt remained up to 320 °C and there is a distinct transition to a highly colored Schlieren texture around 270 °C in the LC domains. On cooling down slowly, PET crystal growth was observed within the isotropic phase as in Fig. 3.12. The size of the crystals depended on the rate of cooling, annealing conditions etc. These crystals melted around 230 °C, when heated again and this corresponds to the first melting endotherm in the DSC thermogram. From the above results, one could conclude that the 6 : 6 block copolymer showed typical characteristics of a " dual chemidomain " system both in the solid and the liquid crystal state.<sup>23-24</sup> The phase separated domains of different compositions may be due to the distinct blockiness of the system and this hypothesis has been confirmed by detailed <sup>1</sup>H NMR analysis described in a later section. The isotropic domains may be composed of PET rich isotropic melt as well as the fraction of low molecular weight PEHT segments that have isotropized.

### PET random copolymers

The thermal and optical properties of the 60 PEHT / 40 PET ( RP60 ) and 70 PEHT / 30 PET ( RP70 ) copolyesters are summarized in Table. 3.6. The DSC thermograms and the optical micrographs corresponding to RP60 are given in Fig. 3.13 - 3.15.

Table. 3.6 : Summary of properties of P EHT/ET random copolyesters

	Inherent viscosity dL / g	Stoichiomet ric composition PEHT : PET	NMR composition PEHT : PET	Randomnes number	DSC ° C	Optical microscopy
RP60	1.1	60 : 40	57 : 43	0.31	235 266 288	nematic
RP70	0.8	70 : 30	77 : 23	0.38	236 261 289	nematic

The inherent viscosities of the random copolymers synthesized in methylene chloride was measured to be as high as 1.1 to 1.3 dL / g in a mixture of p - chlorophenol / tetrachloroethane ( 60 / 40 v / v ) at 26.1 ° C. This high inherent viscosity value was especially interesting in light of the observations made with the block copolymers. So a series of experiments were done to evaluate the effect of reaction conditions on molecular weight of the copolymer and this is listed in Table. 3.7. Some of the immediate conclusions that we could draw from the table is that triethyl amine is more effective than pyridine, probably due to its higher basicity and that low molecular weight polyesters are obtained at higher temperatures due to the reasons given in the earlier section.



**Fig. 3.13 : DSC traces of P EHT/ET copolyester, RP60, in the ratio 60/40**

- a) First heating at a rate of  $20^{\circ}\text{C} / \text{min}$
- b) First cooling at a rate of  $20^{\circ}\text{C} / \text{min}$
- c) Second heating at a rate of  $20^{\circ}\text{C} / \text{min}$
- d) Third heating of a sample, quenched from  $320^{\circ}\text{C}$ , at a rate of  
 $20^{\circ}\text{C} / \text{min}$

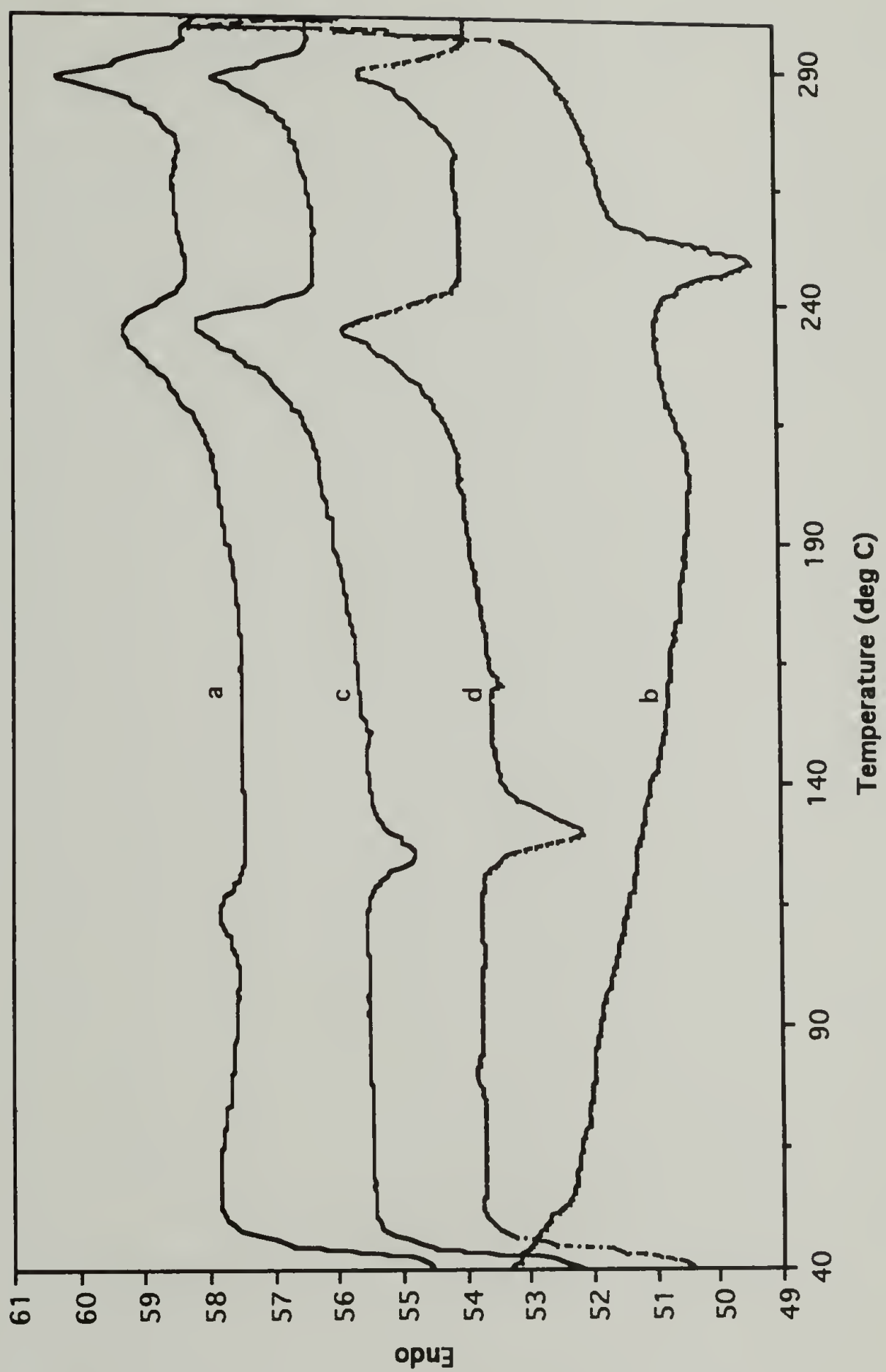


Fig. 3.14: Optical micrographs of P EHT/ET copolyester in the ratio 60/40 ( Mag. = 400 X )

- a ) Observed mesophase of the polymer quenched to room temperature from the nematic mesophase
- b ) Observed mesophase of the polymer heated up to  $271^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$ .







**Fig. 3.15: Optical micrographs of P EHT/ET copolyester in the ratio 60/40 ( Mag. = 400 X )**

- a ) Observed mesophase at room temperature for a sample heated upto  $320^{\circ}\text{C}$ , cooled down at a rate of  $10^{\circ}\text{C} / \text{min}$  and annealed at  $200^{\circ}\text{C}$  for 1 h**
- b ) Observed mesophase for sample ( a ) reheated upto  $240^{\circ}\text{C}$  at a rate of  $10^{\circ}\text{C} / \text{min}$**

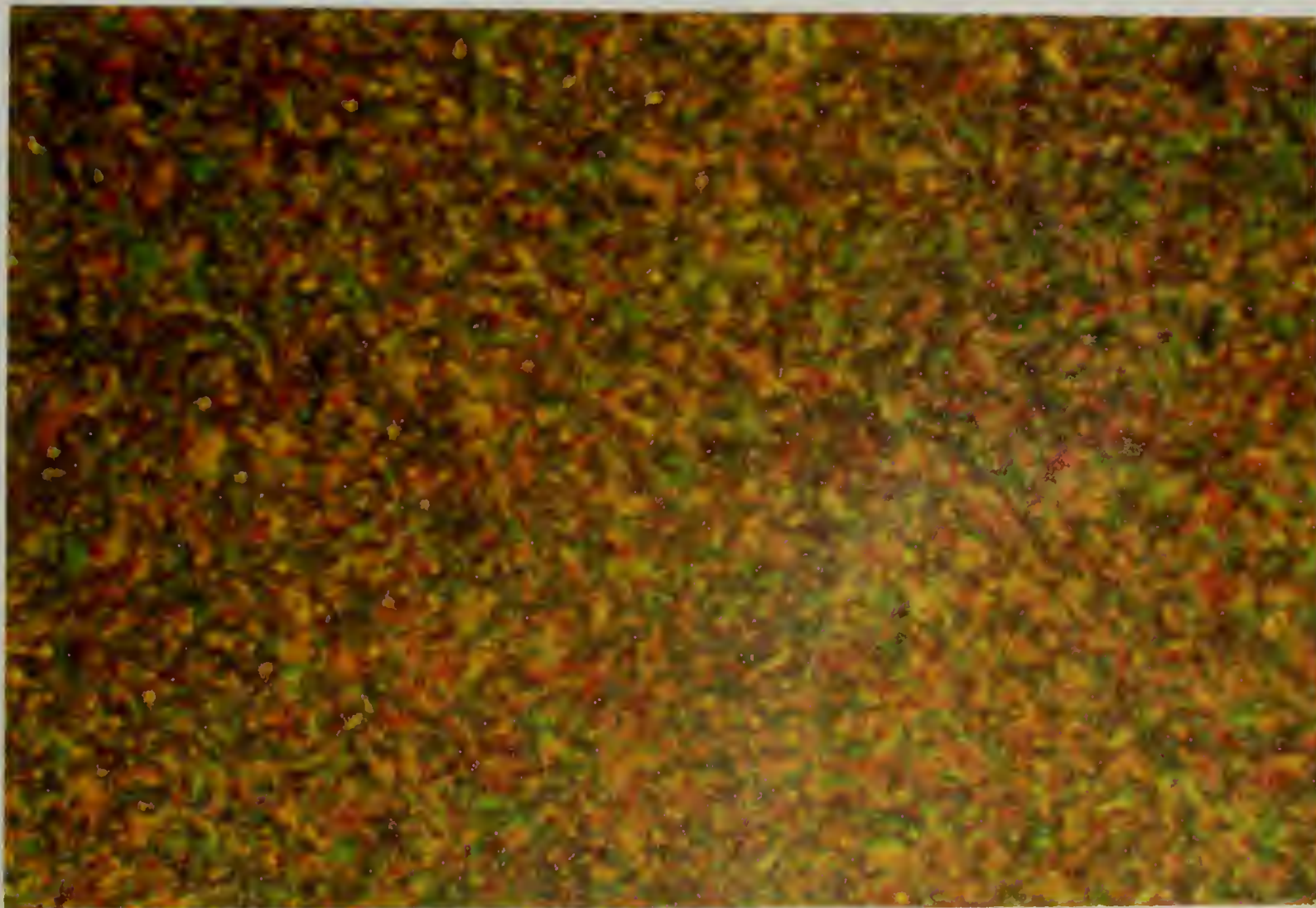




Table. 3.7 : Effect of reaction conditions on molecular weight of random  
60/40 PEHT/ET copolyesters

Reaction solvent	Acid -acceptor	Reaction temperature ( $^{\circ}$ C)	Inherent viscosity (dL / g )
MC	Triethyl amine	45	1.1
TCE	Pyridine	100	0.37
TCE	Pyridine	45	0.24
TCE	Triethyl amine	50	0.6
1 - CN	Triethyl amine	50	0.64
1 - CN	-	200	0.2

Thermogravimetric studies showed that the polymers were stable up to 350  $^{\circ}$ C. The DSC thermograms are very similar to the PET block copolymers and the peaks can be assigned in a similar manner. The cooling cycle shows two distinct exotherms though. The sharp exotherm at 250  $^{\circ}$ C probably corresponds to the nematic - crystalline transition of the PEHT segments and the broader exotherm at around 210  $^{\circ}$ C to the crystallization of the PET segments.

The optical micrographs of the random copolyesters did not show the biphasic texture at high temperatures and resembled the liquid crystalline homopolymer, PEHT. A dense threaded nematic texture was obtained at room temperature which changed to highly colored Schlieren texture around 290  $^{\circ}$ C.

### PBT block copolymers

The thermal and optical properties of the two samples of PBT copolymers synthesized are listed in Table. 3.8. The DSC thermograms and optical micrographs of the PEHT / PBT copolymer with a block size ratio of 6 : 6 and synthesized in 1 - CN, PCBT, are given in Fig. 3.16 & Fig. 3.17.

Table. 3.8 : Summary of properties of PEHT/BT block copolyesters

PEHT : PBT	Inherent viscosity dL / g	Texture	T <sub>peak</sub> ° C
6 : 6 ( TCE )	0.28	Biphasic ( At high temperatures	139 198
6 : 6 ( 1 - CN )	1.1	Nematic ( up to 330 ° C )	202

The inherent viscosity of the 6 : 6 PBT block copolymer synthesized in TCE was 0.28 dL / g as measured in p - chlorophenol at 50 ° C. On the other hand, the high temperature polymerization in 1 - CN yielded a copolymer of inherent viscosity of 1.1 dL / g as measured in p - chlorophenol / TCE ( 60 / 40 v / v ) at 26.5 ° C. The concentration of the latter solution was 0.1 g / dL.

The DSC thermogram showed a broad endotherm around 205 ° C for the high molecular weight PCBT, which probably corresponds to the melting point of the PBT segments. Because of the high viscosity, even in the melting point apparatus,

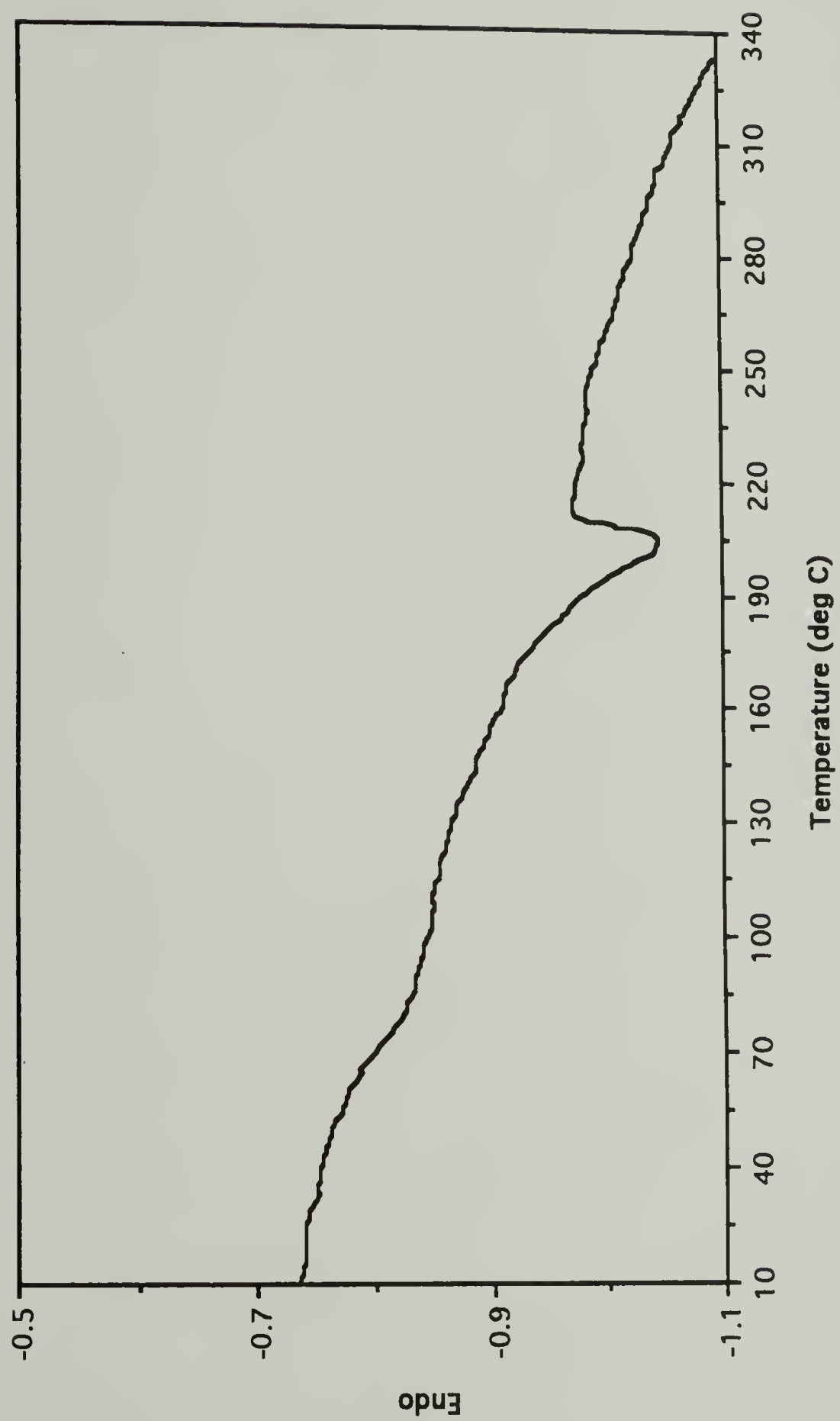
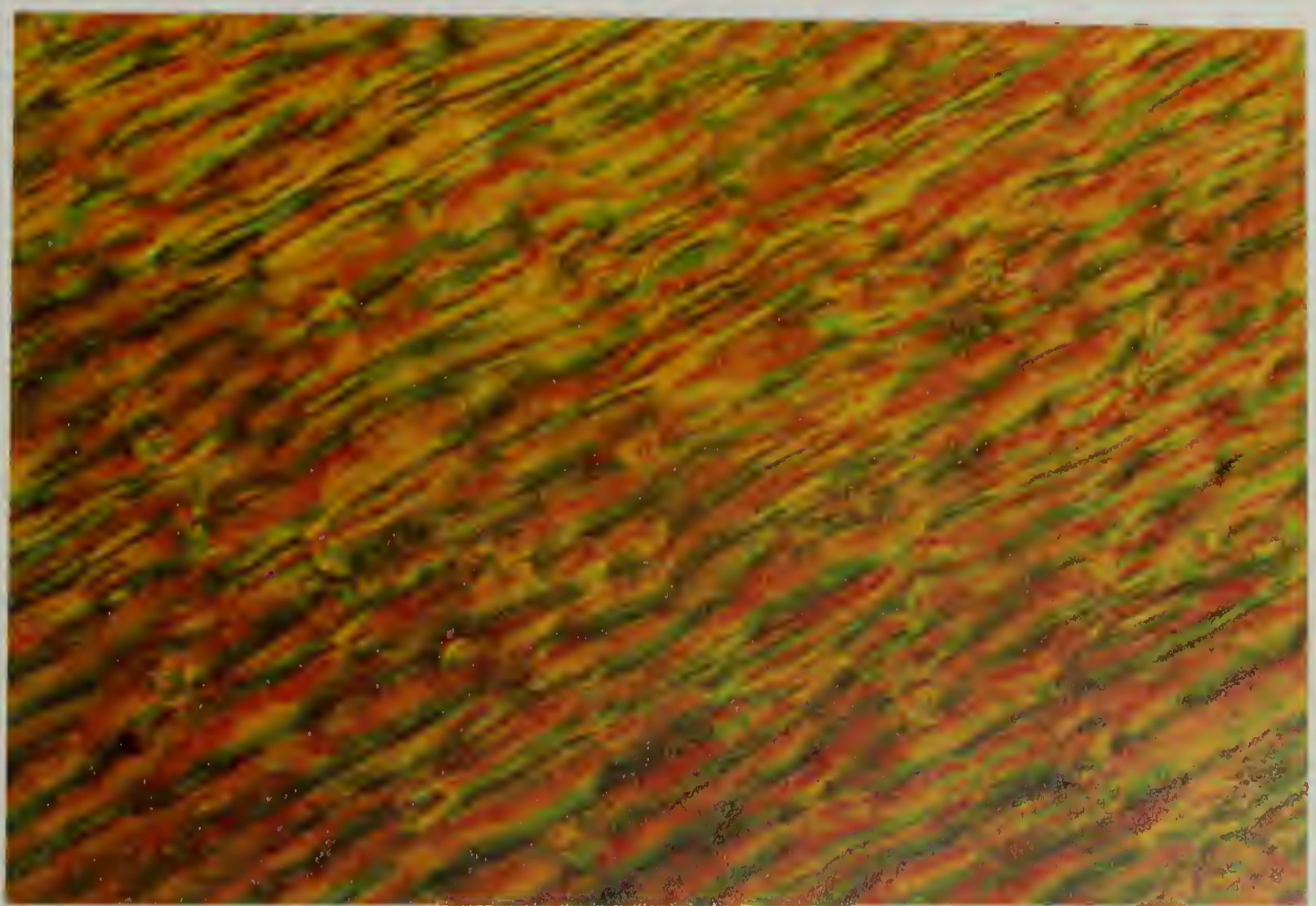


Fig. 3.16: DSC trace of P EHT/BT copolyester, PCBT, with a block ratio of 6:6, for the first heating at a rate of 20 deg C/min.



Fig. 3.17: Optical micrographs of P EHT/BT copolyester  
with a block size ratio of 6 : 6, [ PCBT ]  
( Mag. = 400 X )

- a ) Observed mesophase of polymer heated up to  
180 ° C for a solution cast sample film
- b ) Observed mesophase of the polymer heated up to  
320 ° C at a rate of 10 ° C/min





the polymer softened around  $160^{\circ}\text{C}$ , but did not flow until  $350^{\circ}\text{C}$ . Stir opalescence was observed over a wide region too. As the polymer did not flow, a thin film could not be obtained by melting. Hence the copolymer was dissolved in 1,1,1,3,3,3 - hexafluoroisopropanol and a thin film was obtained by solution casting in teflon molds. The film was transparent and isotropic under cross - polars at room temperature. On heating, crystallization set in around  $160^{\circ}\text{C}$  and at  $180^{\circ}\text{C}$ , a dense threaded nematic texture was observed. The pattern remained the same up to  $340^{\circ}\text{C}$ . The film showed good toughness and mechanical integrity. The polymer with a lower inherent viscosity had properties very similar to the PET copolymer.

In the torsion rectangular test, the plot of the storage and loss moduli as a function of temperature gave a value for the glass transition temperature as illustrated in Fig. 3.18. It was around  $82^{\circ}\text{C}$  for the high molecular weight PCBT. This was around the same temperature obtained for glass transition by DSC measurements, Fig. 3.16.

### $^1\text{H}$ NMR Analysis

The structural regularity in the alternation of units for copolymers has a decisive influence on the physical and mechanical properties of the materials. High resolution NMR spectroscopy has been successfully used for the analysis of the structure of products of copolycondensation.<sup>25-32</sup> Formulae were derived for use with NMR spectra for calculating the degree of randomness, average lengths of comonomer blocks in products of copolycondensation, and the structure of some copolyesters was analyzed on a quantitative basis in the cited papers.



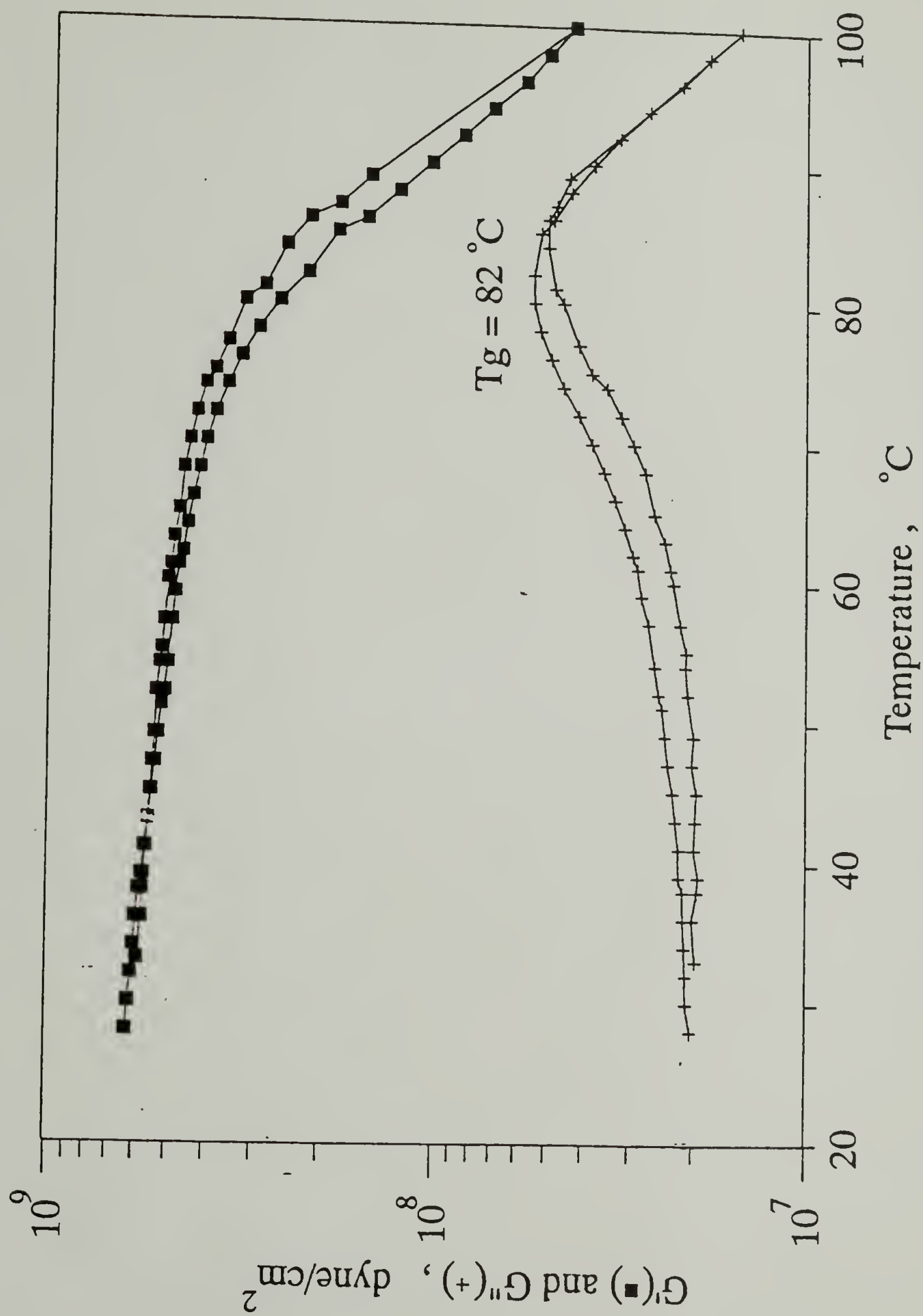


Fig. 3.18 : Dynamic moduli Vs Temperature for a P EHT/BT copolyester with a block size ratio of 6 : 6, PCBT, in a torsion rectangular test

The type of analysis used in our study can be explained in detail by taking a representative polymer, PCBT, which is the P EHT/BT copolyester with a block size ratio of 6:6. The NMR spectra corresponding to this polymer are represented in Fig. 3.19 and Fig. 3.20. The different peaks in Fig. 3.19 were assigned by the comparison of the spectrum with that of the homopolymers. The composition of the copolyester could be found from the integrated intensities of A, B, C & D peaks in Fig. 3.19. From the figure, one can say that A and B correspond to a total of 5 hydrogen atoms and C & D to a total of 8 hydrogen atoms. If the mole fractions of PEHT and PBT segments correspond to  $x$  and  $1 - x$  respectively, it follows that

$$5x / 8(1 - x) = A + B / C + D = Q$$

$$x = 8Q / 5 + 8Q$$

$$\% \text{ PEHT} = P_{\text{EHT}} = 100 x$$

$$\% \text{ PBT} = P_{\text{BT}} = 100 (1 - x)$$

Fig. 3.20 represents the expanded region corresponding to the protons of the terephthalate moiety attached to both butane diol and ethoxy hydroquinone. We can distinguish peaks corresponding to three kinds of terephthalate protons ( - T - ), a singlet for the unit attached to ethoxy hydroquinone on both sides, E - T - E, another for the unit attached to butane diol on either side, B - T - B, and the quartet in the middle corresponding to the asymmetric sequence, E - T - B. The proton signals appear at 8.42, 8.12 and 8.17 - 8.38 respectively. From these three kinds of signals, one can determine the degree of randomness and the average sequence lengths of the two segments in the copolyesters by applying the following analysis :

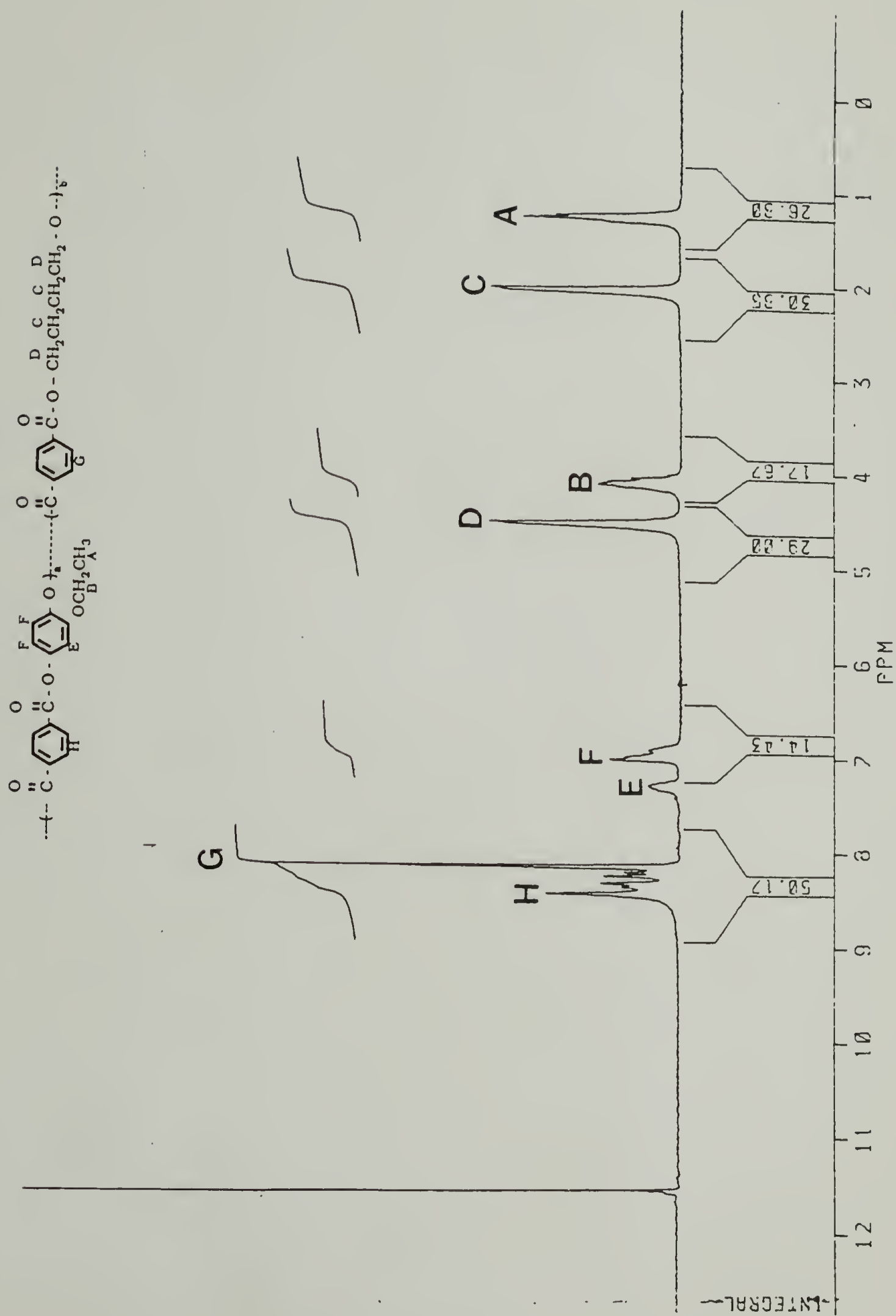


Fig. 3.19 :  $^1\text{H}$  NMR spectra of a P EHT/BT copolyester with a block size ratio of 6:6, PCBT



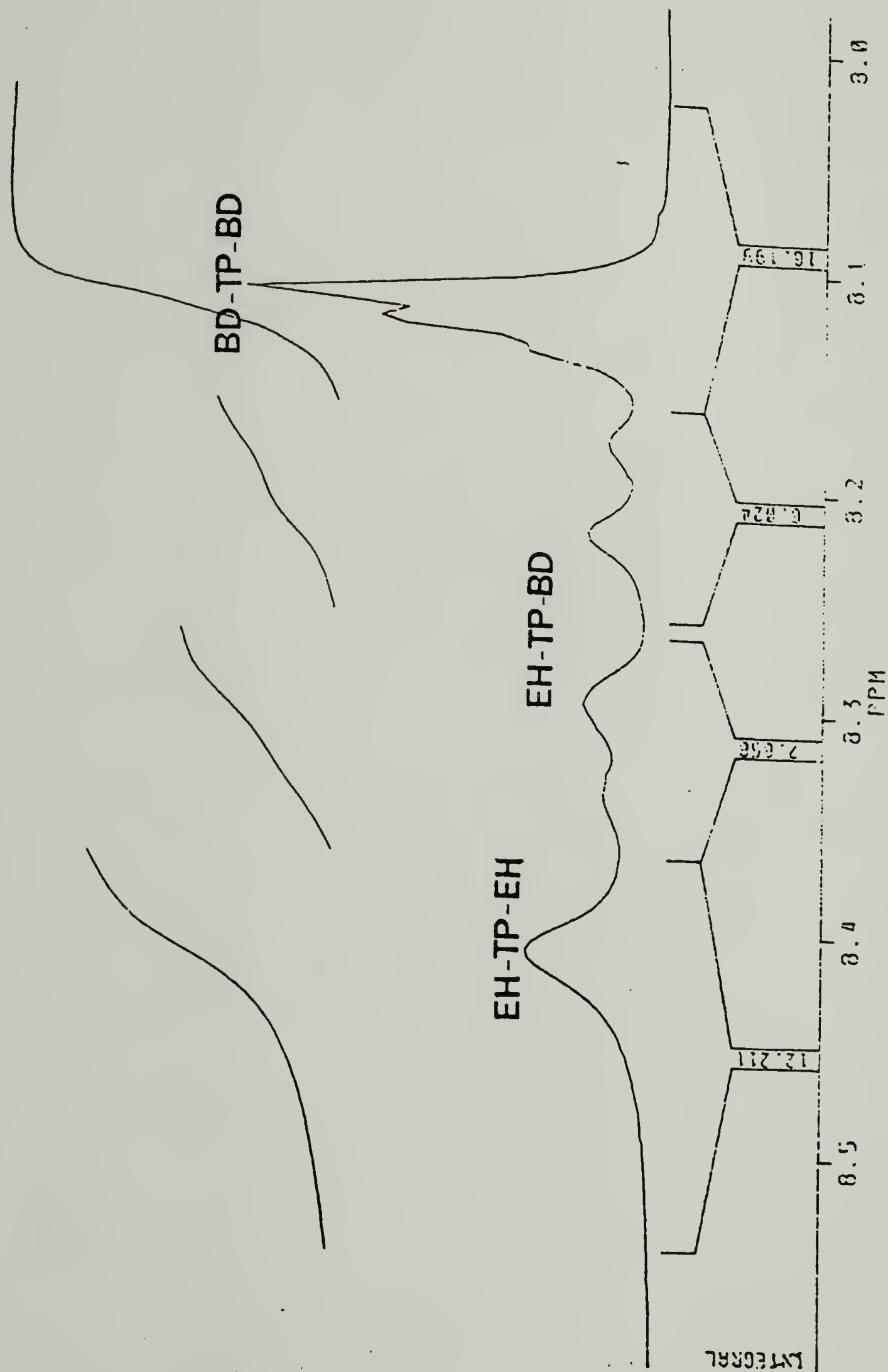


Fig. 3.20 : Expanded  $^1\text{H}$  NMR spectra of a P EHT/BT copolyester, PCBT, for sequence distribution analysis

If one could inspect the units along the PEHT - PBT copolymer chain from one end to the other, the probability of finding a EHT unit next to a BT unit would be

$$P_{EHB} = P_{ETB} / 2 P_{EHT}$$

where  $P_{ETB}$  = Proportion of the integrated intensity of E - T - B to the total intensity of terephthalate units.

$P_{EHT}$  = Molar fraction of ethoxyhydroquinone units.

Similarly a BT unit exists next to a EHT unit with a probability of

$$P_{BEH} = P_{ETB} / 2 P_{BT}$$

where  $P_{BT}$  = Molar fraction of butanediol units

The degree of randomness is defined by

$$\begin{aligned} B &= P_{EHB} + P_{BEH} = P_{ETB} / 2 P_{EHT} P_{BT} \\ &= 0 \text{ [ Pure block copolymer ]} \\ &= 1 \text{ [ Totally random copolymer ]} \\ &= 2 \text{ [ Alternating copolymer ]} \end{aligned}$$

The number average sequence length of a EHT unit [  $L_{nEHT}$  ] and a BT unit [  $L_{nBT}$  ] are given by

$$L_{nEHT} = 2 P_{EHT} / P_{ETB}$$

$$L_{nBT} = 2 P_{BT} / P_{ETB}$$

The NMR analysis of some of the representative copolymers are listed in Table. 3.9. Among the block copolymers synthesized by the 2 - stage process, the PET & PBT copolymers synthesized in tetrachloroethane are found to be blocky as per NMR analysis while a randomization is spotted in the high temperature polymerization products. As per the block copolymerization scheme, the hydroquinone monomers first react with the terephthaloyl chloride to give the rigid-rod oligomers which then react with the PET / PBT oligomers formed in stage I, to

Table. 3.9 :  $^1\text{H}$  NMR analysis of representative PEHT copolyesters

POLYMER	Mol % PEHT Theoretical	Mole % PEHT Found by d NMR	Randomness #	Ln BD / EG	Ln MEH
P50 - TCE 6 PET : 6 PEHT	50	53.5	0.04	11	13
PCBT -TCE 6 PBT : 6 PEHT	50	48	0.3	5	6
PCBT - 1CN 6 PBT : 6 PEHT	50	49.3	0.65	3	3
RP60 - MC 40 PET : 60 PEHT	60	57	0.3	5	7
RP70 - MC 30 PET : 70 PEHT	70	77	0.38	3	11

give the block copolyesters. When the copolymerization is done in tetrachloroethane at  $100^\circ\text{C}$ , the PET oligomers formed in the first stage precipitate from solution leaving the hydroquinone and terephthaloyl chloride monomers to react to give the other oligomer and there is block copolymer formation as expected. On the other hand, when 1-chloronaphthalene is the solvent and the temperature of the second stage is raised to  $200^\circ\text{C}$ , the PET/PBT oligomers remain in solution and compete with the hydroquinone monomer for terephthaloyl chloride to give a random copolyester. As for the blockiness seen in the copolyesters synthesized by heating all the reactants together in one-pot, it may be due to the differences in the reactivities of the ethylene glycol and hydroquinone monomers towards the terephthaloyl chloride and the preferential formation of a certain oligomer which precipitates from solution at the low polymerization temperatures. The various



degrees of randomness observed in a series of 60 : 40 random PET copolyesters synthesized under different reaction conditions are listed in Table. 3.10.

Table. 3.10 :  $^1\text{H}$  NMR analysis of random 60PEHT/40PET copolyesters synthesized under different reaction conditions

Reaction solvent	Acid -acceptor	Reaction temperature ( $^{\circ}\text{C}$ )	Randomness number
MC	Triethyl amine	45	0.3
TCE	Pyridine	100	0.98
TCE	Pyridine	45	0.94
TCE	Triethyl amine	50	1.0
1 - CN	Triethyl amine	50	0.72
1 - CN	-	200	1.0

It can be seen that a random copolymer is obtained in all solvents other than methylene chloride, even at low temperatures. Maybe there is no preferential formation of any one of the oligomers for blockiness to occur in all these cases.

### $^{13}\text{C}$ NMR Analysis

$^{13}\text{C}$  NMR spectra of the homopolymer, PEHT, block copolymer containing PEHT & PET segments, P50, and a copolyester of PEHT with PBT, PCBT, are represented from Fig. 3.21 to Fig. 3.23. The peaks in the spectrum corresponding to the homopolymer, PEHT, were assigned by comparison with theoretical values. Those of the copolymers could be easily assigned by comparison with the spectra of the homopolymers. Quantitative sequence distribution analysis could not be done using this technique as the resolution was quite poor and one could not distinguish

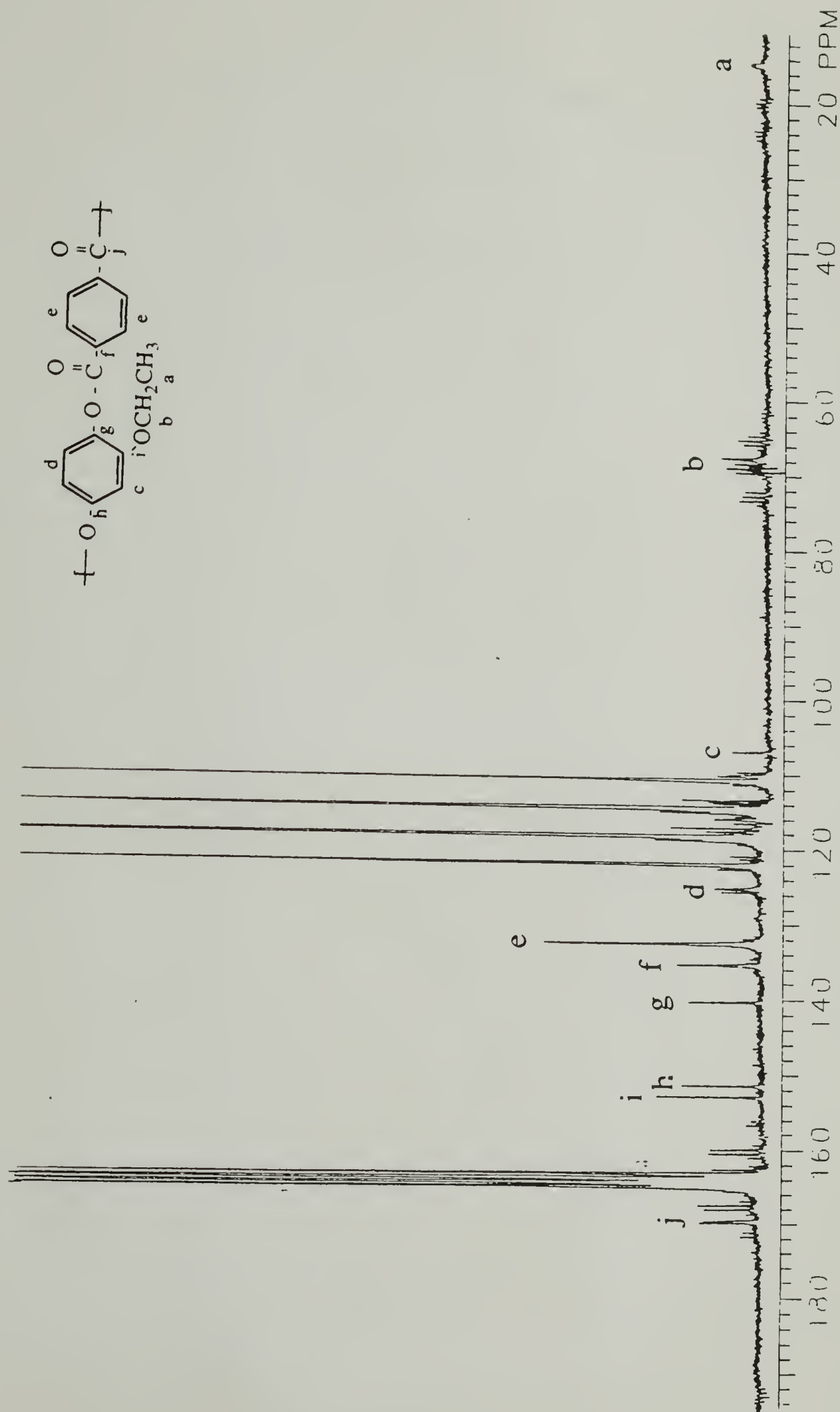


Fig. 3.21 :  $^{13}\text{C}$  NMR spectra of PEHT

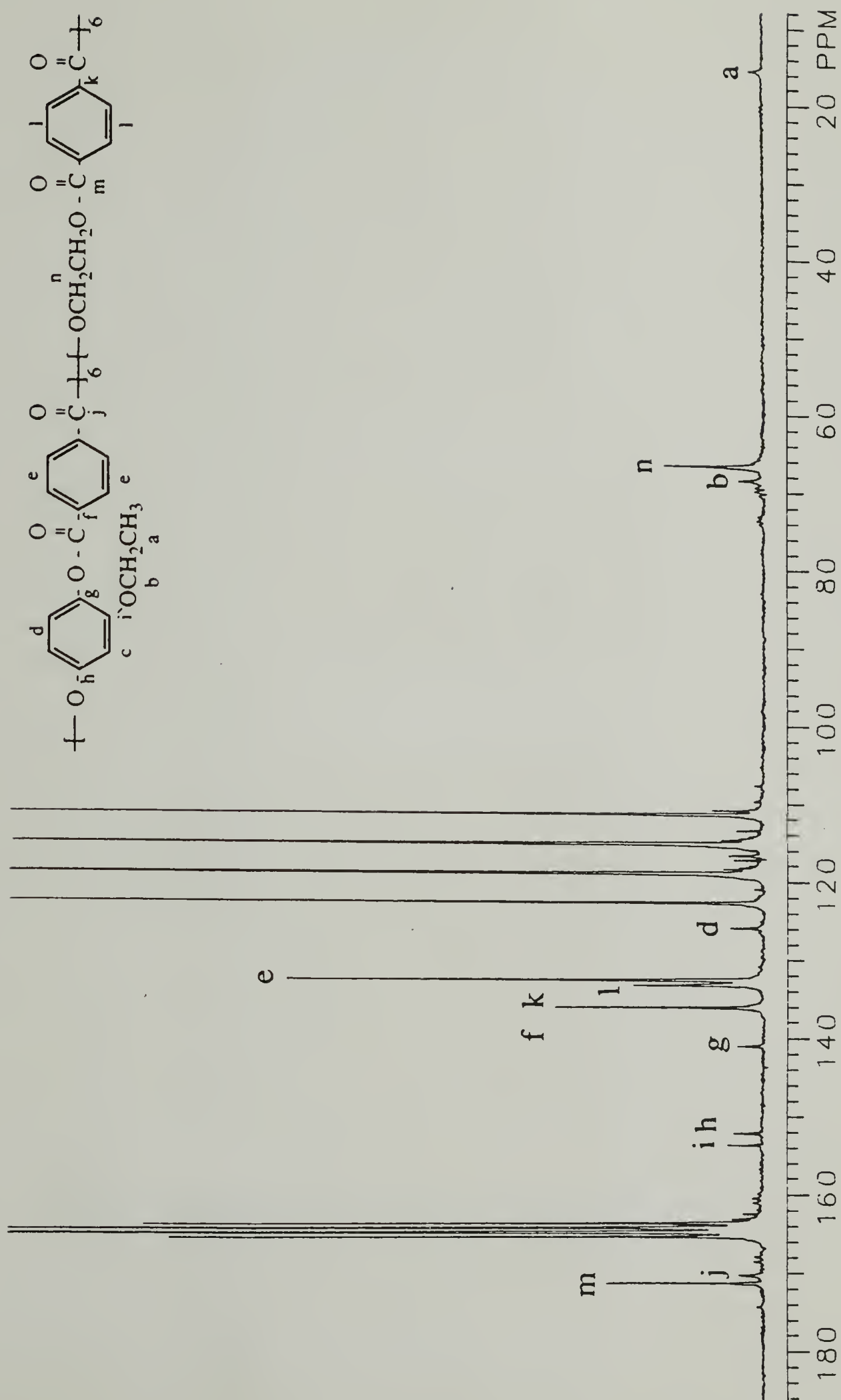


Fig. 3.22 :  $^{13}\text{C}$  NMR spectra of P EHT/ET copolyester, P50, with a block size ratio of 6 : 6



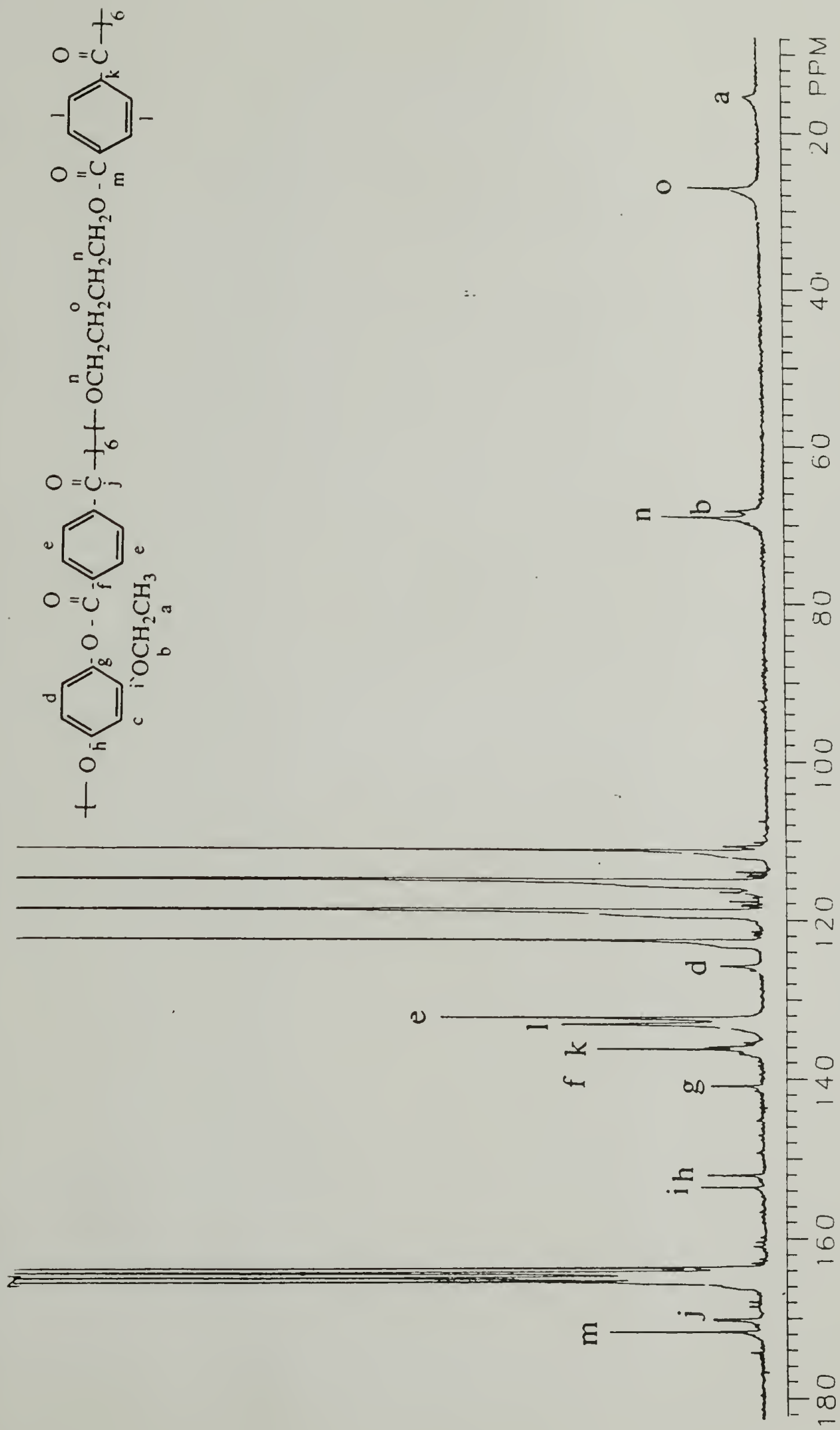


Fig. 3.23 :  $^{13}\text{C}$  NMR spectra of P EHT/BT copolyester, PCBT, with a block size ratio of 6 : 6

the peaks corresponding to symmetric and asymmetric sequences to apply the analysis described in the earlier section.

### Wide angle X-ray diffraction

WAXD is a powerful technique for the characterization of liquid crystalline polymers in general. Valuable information regarding the molecular orientation, type of packing of the mesogens and the order present in the mesophase can be obtained from this technique.<sup>33-35</sup> Qualitative identification of the mesophase in the LCPs can be done through the observation of WAXD patterns of the powdered sample of the polymer. Typically, the diffraction pattern of a powder sample can be divided into the inner rings at small diffraction angles and outer rings at large angles. The inner ring is related to the length of the molecule and indicative of longer layer spacings of the mesogens while the outer ring can be ascribed to the interaction of neighboring parallel molecules. The appearance of either a sharp ring or a broad halo at large angles furnishes a qualitative identification of the mesophase present. A nematic phase gives a diffuse outer halo because of the lack of translational order of the mesogens. The outer diffuse ring typically corresponds to an average intermolecular spacing of 4 - 6 Å<sup>0</sup> in nematic LCPs.<sup>9,36-40</sup> The inner ring may be diffuse too if there is no order in the direction of the long molecular axis of the mesogens.

In our case, WAXD work was attempted mainly to confirm the assignments of the different endotherms in the DSC thermograms of the blocky copolyesters and also to get an idea about the LC - LC transition observed in the homopolymer. For this study, a hot-stage was required to maintain the temperature of the sample at the desired high values when acquiring the X-ray pattern. Our work was very much limited by the non-availability of hot-stages operating beyond 250 °C! But

the comparison of the room temperature powder patterns of the homopolymers and the random copolyester proved to be quite interesting too.

Representative WAXD patterns of the homopolymers, PET & PEHT, and the random & blocky (60 : 40) PET copolyesters are given from Fig. 3.24 to Fig.3.26. Also Table. 3.11 gives the diffraction spacings,  $d$ , calculated for the different polymers. The  $d$  spacings for the rings corresponding to PET were calculated using the Bragg's equation ( viz. )  $\sin \Theta = \lambda / 2 d$  where

$\lambda$  = Wavelength of the X - ray source =  $1.541 \text{ \AA}$  (  $\text{CuK}\alpha$  radiation )

$$\Theta = [ \tan^{-1} r / D ] / 2$$

$D$  = Distance of the film from the camera

$r$  = Radius of the ring whose diffraction spacing is being calculated

The distance of film from the camera,  $D$ , was calculated from the X - ray photograph of a standard calcium carbonate sample. The  $d$  spacings for the nematic rings were calculated using the DeVries modification ( viz. )  $\sin \Theta = 1.229 \lambda / 2 d$ .

The copolyesters showed the characteristic rings corresponding to both the segments, PEHT & PET at room temperature. The X - ray patterns corresponding to the random and blocky copolyesters having the same composition, were quite similar. The random copolymer which had the lowest viscosity and melted around  $240^{\circ} \text{C}$ , was annealed at  $250^{\circ} \text{C}$  for 12 h in the hot stage within the WAXD apparatus. The X - ray pattern corresponding to the heated specimen resembled that of the homopolymer, PEHT, with the rings corresponding to PET missing. Similar studies could not be done with the other polyesters as they were characterized by higher transition temperatures and the hot - stage temperature could not be increased beyond  $250^{\circ} \text{C}$ !



**Fig 3.24 : WAXD patterns for a) PET and b) PEHT**



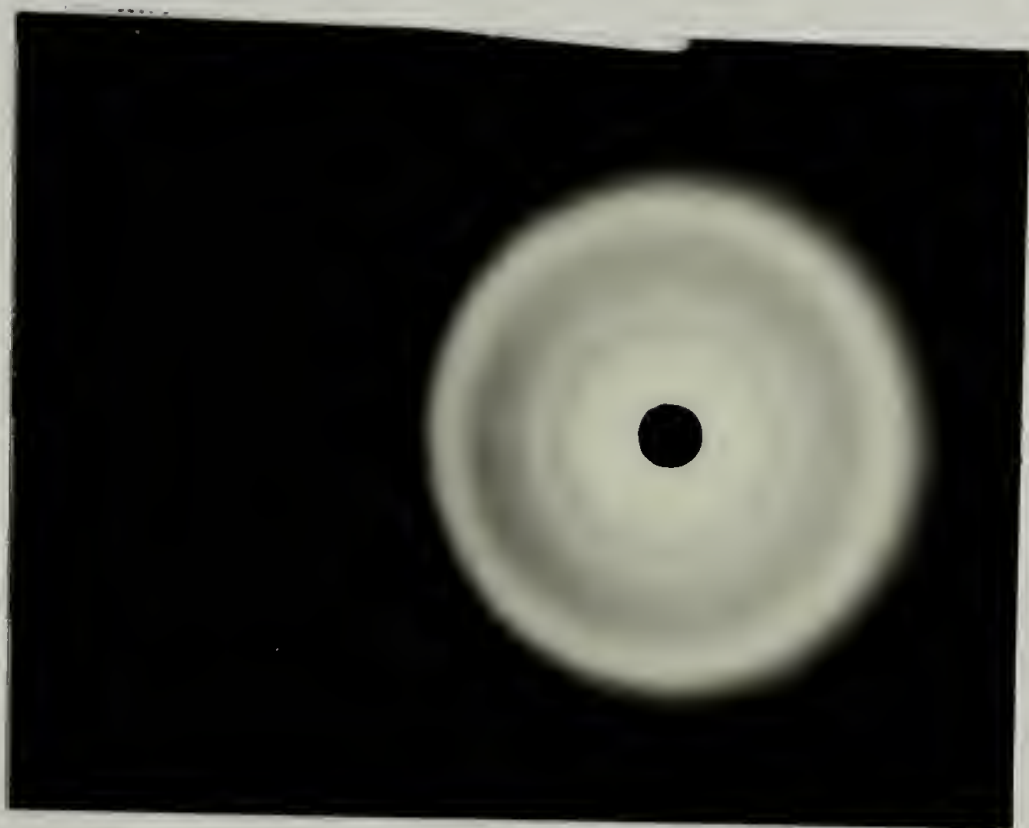
**Fig 3.25 : WAXD patterns for**

**a) Random P EHT/ET at R.T.**

**b) Random P EHT/ET at 245 °C**

,





**Fig. 3.26 : WAXD pattern of blocky P EHT/ET**

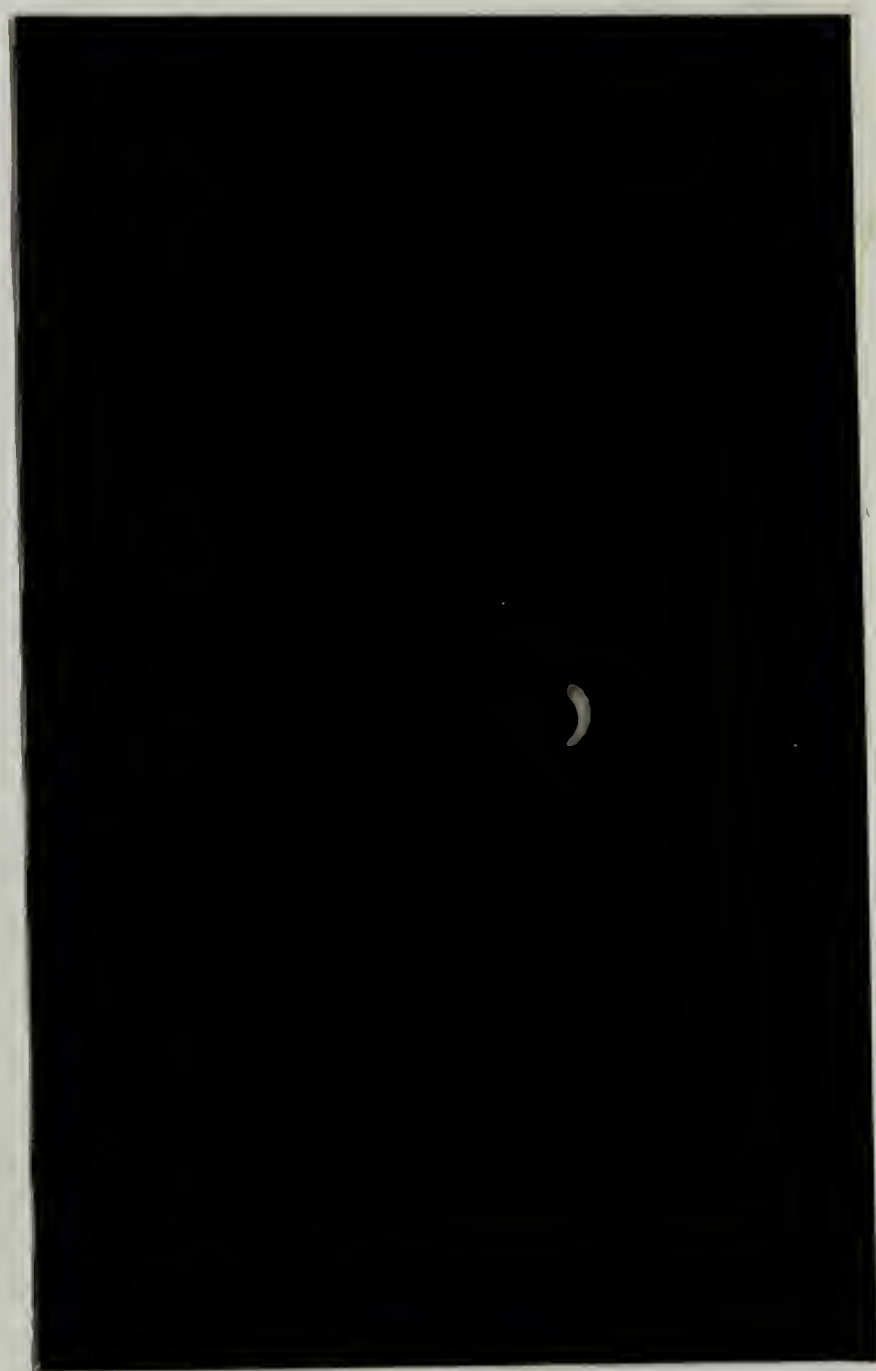




Table. 3.11 : X-ray diffraction spacings calculated for representative polyesters

PE HT r (mm) d (Å <sup>0</sup> )	PE T r (mm) d (Å <sup>0</sup> )	Random r (mm) d (Å <sup>0</sup> )	PEHT/ET r (mm) d (Å <sup>0</sup> )	Blocky r (mm) d (Å <sup>0</sup> )
10.5 (sharp)	-	10.5 (sharp)	7.41	11.5 (sharp)
11.5 (sharp)	-	11.5 (sharp)	6.8	
12.5 diffused	-	13 diffused	6.03	12.5 diffused
-	14.5 (sharp)	14.8 (sharp)	5.36	
-	15.5 (sharp)	16 (sharp)	4.97	
19.0 diffused	20 diffused	19 diffused	5.21	21.5 diffused
-	24 (sharp)	24 (sharp)	3.45	26.5 sharp

### Transmitted light intensity measurements (TLI)

This is a sensitive method for the determination of phase transition temperatures, especially in polymers with very low crystallinity where the DSC measurements fail to show any significant peaks. The principle behind this technique is the measurement of the intensity of transmitted light through the sample as a function of temperature at a constant heating or cooling rate. The TLI measurement scans for three polymers - PET, PEHT & a block copolyester of PEHT / ET with a size ratio of 6 : 6, P50, are displayed from Fig. 3.27 to Fig. 3.29. All the figures represented correspond to the first heating scan of samples previously quenched from 320<sup>0</sup> C in a melting point apparatus.

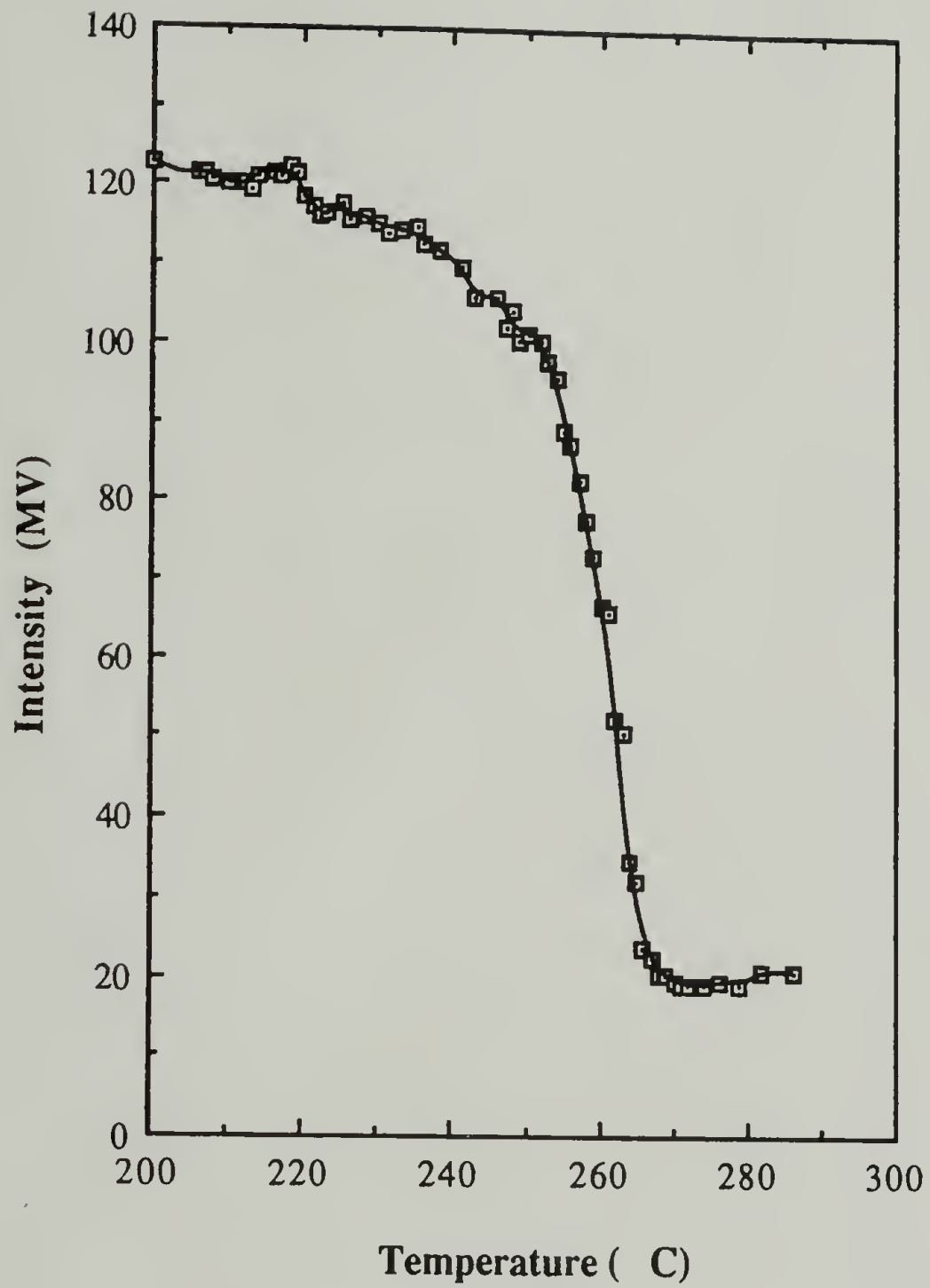


Fig. 3.27 : Transmitted light intensity plots for PET

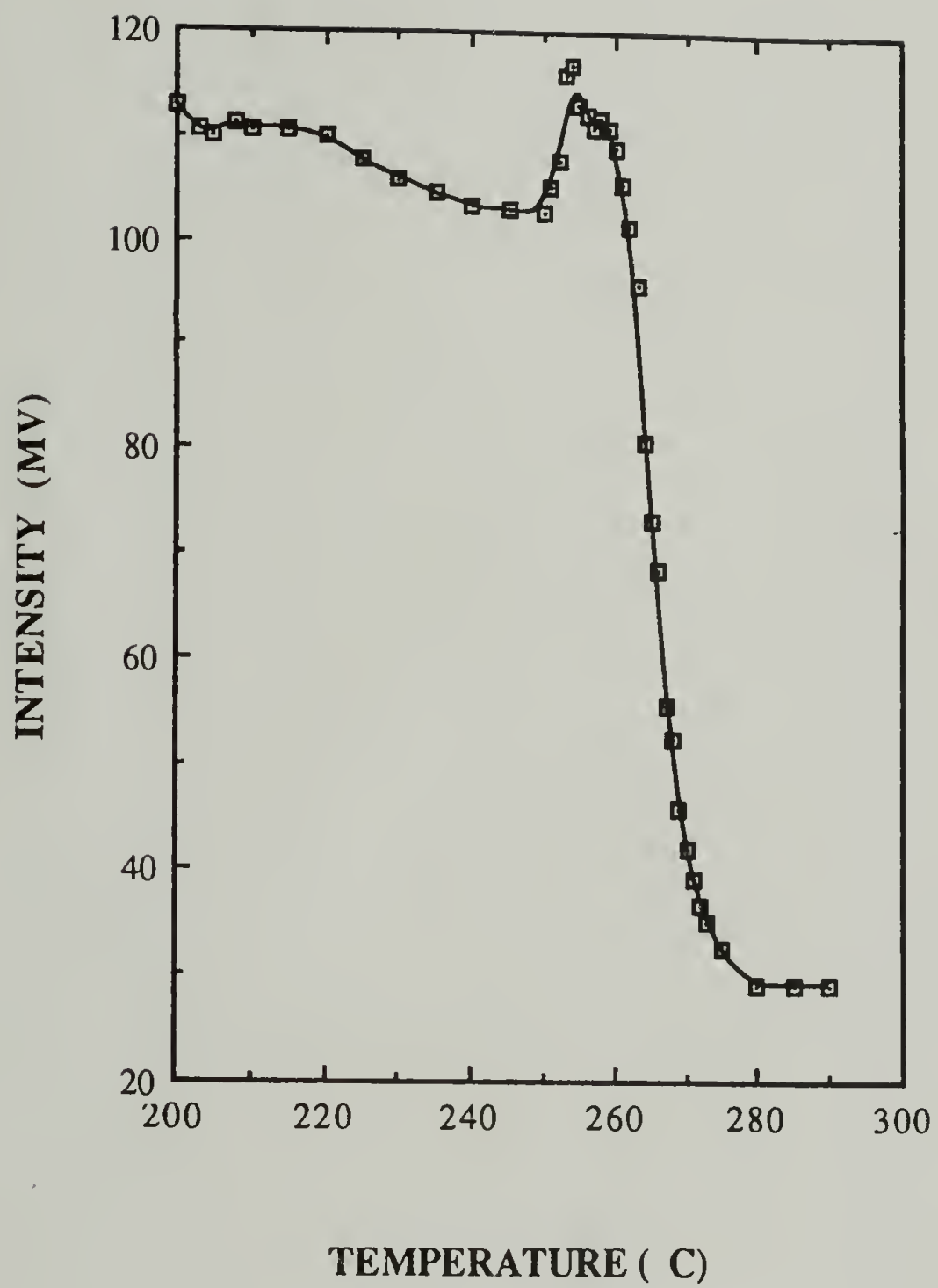


Fig. 3.28 : Transmitted light intensity plots for PEHT



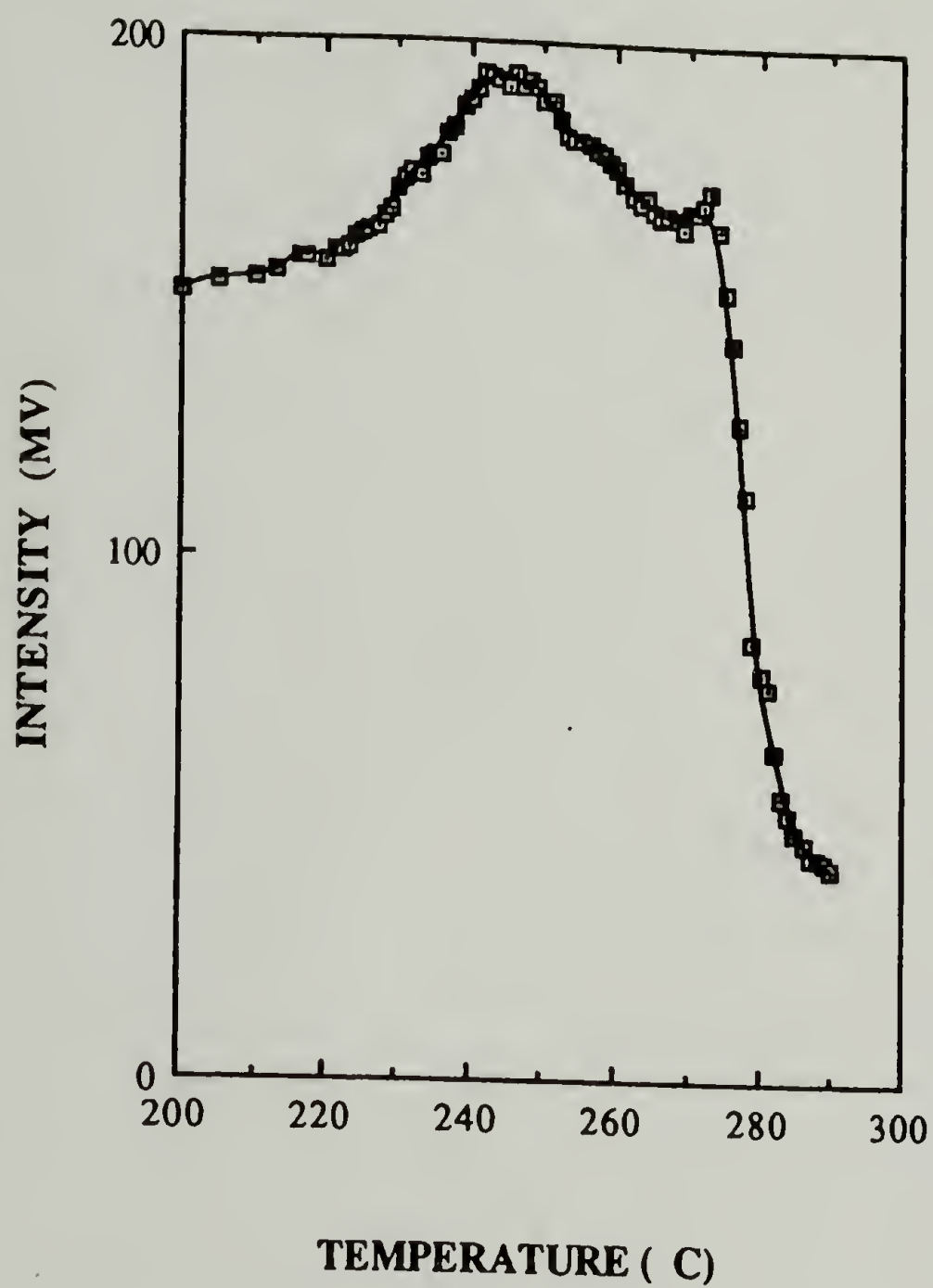


Fig 3.29 : Transmitted light intensity plots for a P EHT/ET copolyester, P50, with a block size ratio of 6 :6

For the PET sample, the intensity of transmitted light decreased at temperatures corresponding to the melting point because of annealing effects. In the case of the homopolymer, PEHT, the intensity of transmitted light increased at temperatures approaching the solid - mesophase and LC - LC transitions. This is consistent with our observations of a polymer flow and a texture change from dense - threaded to a highly colored schlieren pattern at the LC - LC transition, under crossed polars. For the block copolymer, a melting point around 240<sup>0</sup> C and a LC - LC transition at 270<sup>0</sup> C can be confirmed by this sensitive method.

### Summary of properties

A summary of all the important properties of the representative polymers containing the PEHT segment are listed in Table. 3.12.

Table. 3.12 : Summary of properties of representative PEHT copolyesters

Polymer	Solvent	Inherent vis (dL/g)	Randomne ss #-NMR	Tg ( <sup>0</sup> C)	Tpeak ( <sup>0</sup> C)	Texture
PEHT	MC	0.4	-	-	257 270	Nematic
Random 60 PEHT : 40 PET	MC	1.1	0.3	77	235 267 288	Nematic
Block 6 PEHT : 6 PET	TCE	0.3	0.04	80	223 264 276	Biphasic at high temp.
Block 6 PEHT : 6 PBT	TCE	0.28	0.3	-	139 198	Biphasic at high temp.
Block 6 PEHT : 6 PBT	1 -CN	1.1	0.65	-	202	Nematic

### Solution blending studies

Preliminary studies, mostly thermal characterization, on the blends of the P EHT / ET copolymer with a block size ratio of 6 : 6, P50, yielded some interesting results. Blends of various compositions ( 5 %, 10 %, 20 % & 50 % ) of P50 with PET were prepared by co - dissolving the two components in trifluoroacetic acid and reprecipitating in excess methanol. The samples were vacuum dried for 2 - 3 days at 90 ° C. The thermal properties of PET and the blends are listed in Table. 3.13.

Table. 3.13 : Thermal properties of blends of P50 with PET

Blend composition ( % P50 )	T <sub>g</sub> (° C)	T <sub>c</sub> (° C)	T <sub>m</sub> (° C)	D H <sub>m</sub> (cal / g)	T <sub>c</sub> * (° C)
5	81.6	181.4	250.2	3.73	127
10	84.7	171.6	244.5	6.25	120
20	87.8	162.6	234.8	6.46	127
50	87.8	153.4	232.3	4.74	129
PET	84	167	249.9	8.17	142

The most striking trend observed in the table is the decreasing melting point of the blends with increasing P50 content which indicates some compatibility of the two components. Also there is a depression in cold crystallization temperatures for the blends as compared to pure PET. The rigid segments in the block copolymer probably act as hetero - nuclei for the PET to crystallize.



The thermal characterization of 20 % blends of the various representative polymers with high molecular weight AKZO PET was also done. The results of the DSC studies are listed in Table. 3.14.

Table. 3.14 : Thermal properties of 20% blends of representative LCPs with PET

Blend	T <sub>m</sub> (° C)	Δ H <sub>m</sub> (cal / g)	T <sub>C</sub> (° C)	Δ H <sub>C</sub> (cal / g)	T <sub>c</sub> * (° C)
PET (AKZO)	270	7.2	192	- 8.1	148
PEHT + PET	252	5.6	182	-4.21	134
P50 + PET	265	4.8	195	-4.1	122
PCBT + PET	251 270	2.6	183	- 2.54	122

Once again, a single melting endotherm at lower temperature and lower cold crystallization values compared to pure PET is observed for all the blends.

### Conclusions

The PEHT systems were chosen for study because of the convenience of the synthesis of the starting monomer, 2 - ethoxy hydroquinone. Solution copolymerization with PET / PBT components resulted in some very interesting thermotropic copolyesters with transitions in the processing temperature range of

commercial PET. High molecular weight PBT copolymers were obtained by conducting polymerizations at high temperatures (  $200^{\circ}\text{C}$  ) using 1 - chloronaphthalene as the solvent and these polymers yielded thin films of good strength and mechanical integrity. On the other hand, the highest molecular weights for the PET copolymers were obtained by polymerizing at  $50^{\circ}\text{C}$  in methylene chloride using triethyl amine as the acid - acceptor. The extent of randomness in the copolyesters were quantitatively determined by proton NMR analysis. It was observed that totally random copolymers were obtained by high temperature polymerization and blocky copolymers were obtained for the low temperature reactions. Interesting optical micrographs and characteristic DSC thermograms were obtained for the block copolymer systems.

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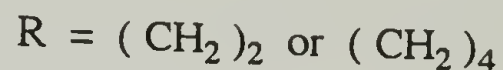
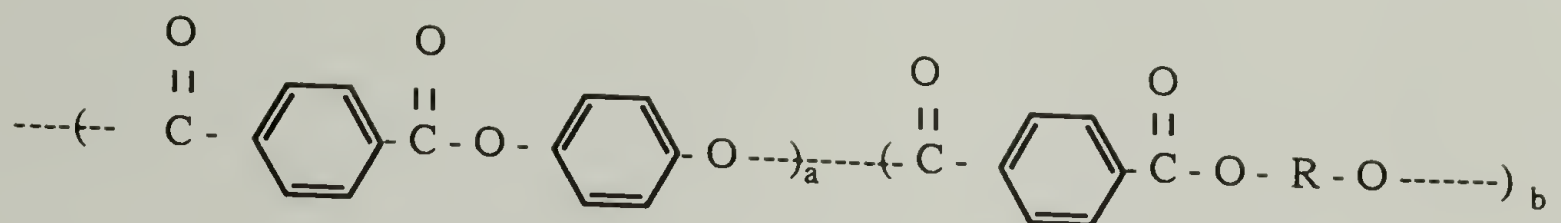
## CHAPTER 4

### SYNTHESIS AND CHARACTERIZATION OF PH ET / BT COPOLYMERS

#### Introduction

The parent, unsubstituted polymer of the two thermotropic polyesters described in the earlier chapters would be poly ( p - phenyleneterephthalate ), which has a melting temperature above  $600^{\circ}\text{C}$ . Even the lower molecular weight polyester has a glass transition around  $267^{\circ}\text{C}$  and a melting point of  $467^{\circ}\text{C}$ , which are too high for proper characterization of the mesophase.<sup>1</sup> One approach to lower these transition temperatures has involved the use of asymmetrically substituted hydroquinones as in the case of the systems described in Chapter II and Chapter III. Another easier approach would be to copolymerize the unsubstituted hydroquinone with the terephthaloyl chloride and flexible units like ethylene glycol / butanediol. Involved monomer synthesis of substituted hydroquinones can be avoided following this route! The presence of the PET / PBT segments would assist in at least partial compatibilization of the liquid crystalline polyester with the isotropic polymer matrix either in the melt or in the solid state.

The objective of this chapter is to describe the synthesis and characterization of block and random copolyesters of the unsubstituted hydroquinone, ethylene glycol / butanediol and terephthaloyl chloride moieties ( Fig. 4.1 ). The thermal and morphological characterization of the copolyesters by differential scanning calorimetry and optical microscopy is also discussed here.



P(HT / ET) or P(HT / BT)

Fig 4.1 : Structure of P HT/(ET/BT) copolyesters

### Experimental

#### Materials

All the chemicals except bis ( hydroxyethyl terephthalate ) [ BHET ] were purchased from Aldrich chemical Company. BHET was obtained from PolySciences and recrystallized from acetone. Terephthaloyl chloride was purified by sublimation. Hydroquinone was purified by recrystallization from acetone. The solvents used for polymerization, methylene chloride [ MC ], tetrachloroethane [ TCE ] and 1 - chloronaphthalene [ 1 - CN ] were distilled over phosphorus pentoxide, potassium carbonate and calcium hydride respectively and the latter under reduced pressure. Pyridine was also distilled over calcium hydride before use.

#### Monomer synthesis

The synthesis of bis (hydroxybutyl terephthalate) [ BHBT ] was done in the exact manner described in Chapter III. This monomer was utilized in the PBT block copolymer synthesis in different solvents.



## Polymer synthesis

### *Random copolymer synthesis*

Only one batch of the random copolymer was synthesized for it to serve as a reference material for comparison with the random PET copolymers containing the substituted hydroquinones. The following procedure illustrates the preparation of a random copolyester with equal amounts of unsubstituted hydroquinone and ethylene glycol.

To a 500 mL flask fitted with an argon inlet and an outlet and a dropping funnel, were added 1 g ( 0.009091 mol ) of an ethoxyhydroquinone, 0.5636 g ( 0.009091 mol ) of ethylene glycol, and 5 mL ( 0.03636 mol ) of triethylamine as an acid - acceptor. Then 100 mL of methylene chloride was added to the flask and the reactants were stirred vigorously with a magnetic stirrer until dissolution occurred. Then 3.691 g ( 0.01818 mol ) of terephthaloyl chloride dissolved in 100 mL methylene chloride was added slowly to the reaction mixture, and the contents of the flask were stirred for 24 h at room temperature, and then was refluxed for 24 h. The polymer started precipitating almost immediately after the completion of addition of terephthaloyl chloride. The reaction was terminated by adding the reaction mixture to 1000 mL of methanol, and the pure white polymer was filtered from the solution. The polymer was dried and then extracted in a Soxhlet extractor using acetone to obtain a more pure polymer.

### *Block copolymer synthesis*

A one -reactor reaction procedure was adopted for making the block copolymers as illustrated in Fig. 4.2. The following procedure illustrates the general preparation of the block copolymers with a block size ratio of 6 : 6 of hydroquinone to ethylene glycol. The PBT copolymers were also synthesized in a similar manner.

To a 100 mL three-necked flask were added 1.0 g (0.003937 mol) of BHET and 25 mL pyridine [ in the case of low temperature polymerization ]. The flask was fitted with a condenser, an argon inlet and outlet and a teflon stirrer. After dissolving the BHET in 100 mL of tetrachloroethane and pyridine or 100 mL of 1-chloronaphthalene, 1.0656 g (0.005249 mol) of terephthaloyl chloride dissolved in 100 mL of TCE / 1-CN was added slowly to the reaction mixture. The temperature was increased to 90 °C and maintained at that temperature for 3 h. When 1-CN is the solvent, a constant flow of argon was used to remove the hydrogen chloride formed. At the end of that period, the solution was slightly turbid and at this stage, 1.332 g (0.006562 mol) of terephthaloyl chloride was added to the vessel under a positive flow of Argon. After 10 minutes, 0.8661 g (0.007874 mol) of hydroquinone was added to the reaction mixture and enough solvent was added to keep the reactants in solution. The temperature was maintained at 100 °C when TCE was the solvent but raised to 190 °C when polymerization was done in 1-CN and reacted for 20 h. At the end of the period, the turbid solution was poured into 1000 mL methanol to yield pure white polymer. In both the cases, the polymer had precipitated quite early in the reaction period. The crude polymer was extracted in a Soxhlet extractor using acetone for about a day and dried in a vacuum oven at 90 °C for about 3 days.

A number of batches of the polymerization were done varying the block size ratio, solvent and corresponding polymerization temperatures. The polymerization conditions and properties of the various hydroquinone polymers are listed in Table. 4.1.

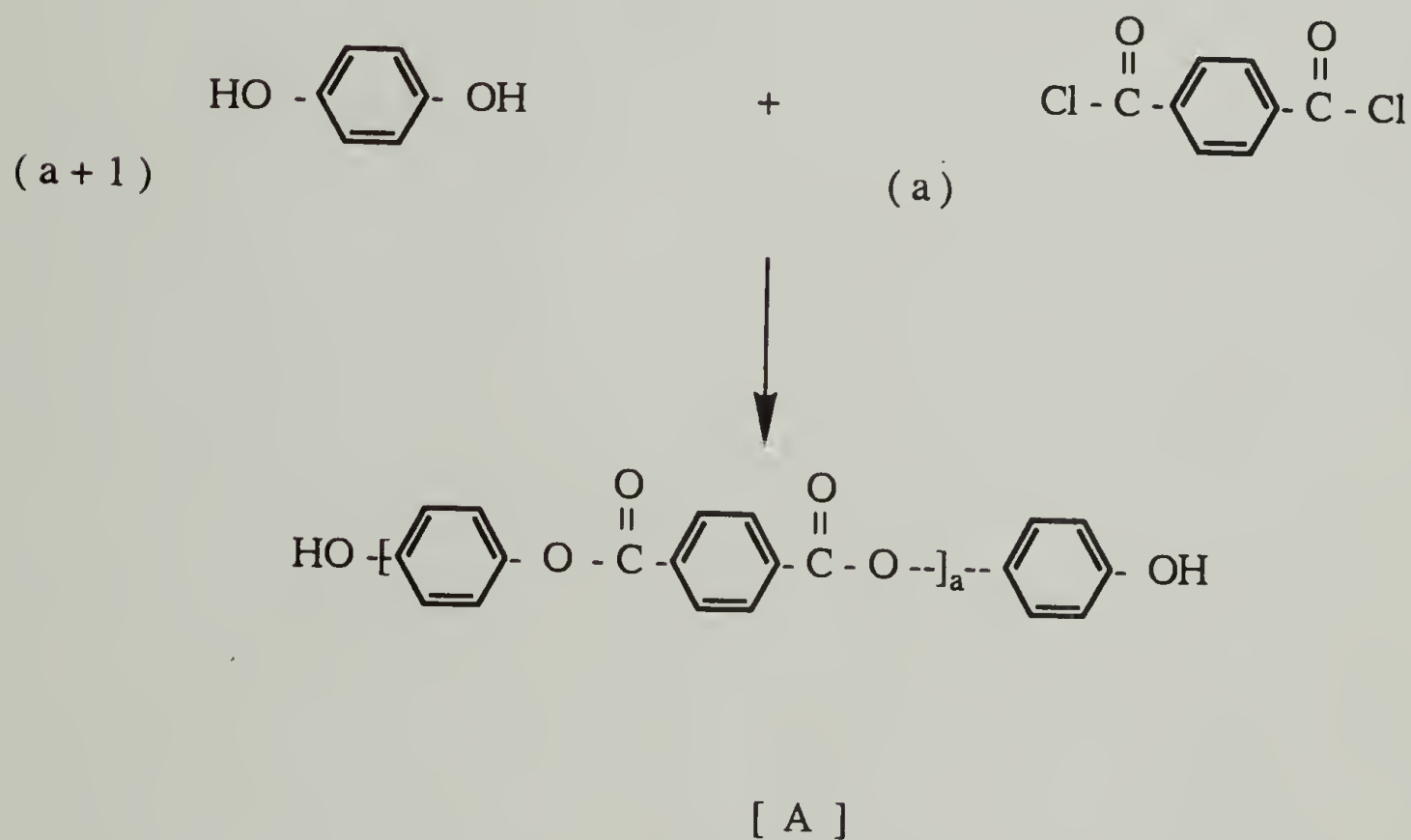
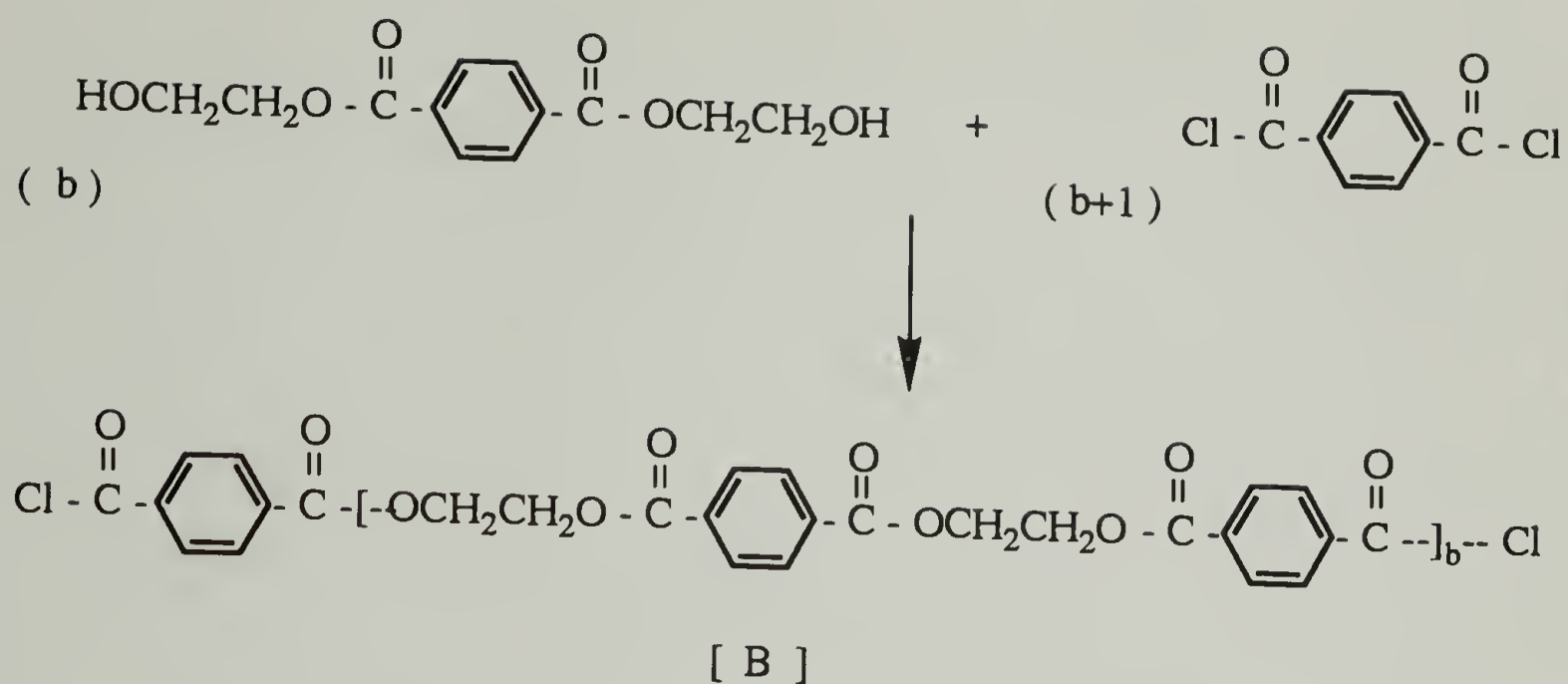


Fig. 4.2 : Synthesis of PHT/(ET/BT) block copolyesters



### Characterization methods

Viscometry could not be done as the polymers were insoluble in even strongly polar solvents like p - chlorophenol, tetrachloroethane and m - cresol. As they were not soluble in d - trifluoroacetic acid too, the NMR analysis could not be done to get the composition and sequence distribution in the copolyesters. The phase transition temperatures were measured on a differential scanning calorimeter ( Perkin - Elmer VII ) under a nitrogen atmosphere with a heating / cooling rate of  $20^{\circ}\text{C} / \text{min}$ . The temperature axis of the instrument was calibrated prior to use with reference standards of high purity indium. For the study of mesophases formed by the copolyesters, polymicrographs were taken with a 35 mm camera mounted on a Carl - Zeiss polarizing microscope equipped with a hot stage ( Mettler - FP 2 model ). The mesophase behavior was observed as a function of temperature on the hot stage.

### Results and Discussion

The thermal and optical properties of the various hydroquinone polymers are listed in Table. 4.1

#### Thermal studies

The DSC thermograms of some representative copolyesters are given in Fig. 4.3 & Fig 4.4. Four different kinds of PET copolymers were thermally characterized. The 50 : 50 random copolyester polymerized in methylene chloride showed 2 distinct endotherms in the first heating cycle corresponding to the melting transitions of the flexible and rod - like segments. When the copolymer sample was cooled down from  $350^{\circ}\text{C}$ , a broad exotherm between  $150 - 200^{\circ}\text{C}$ , corresponding to the crystallization of PET moieties was observed. On heating the sample again, a

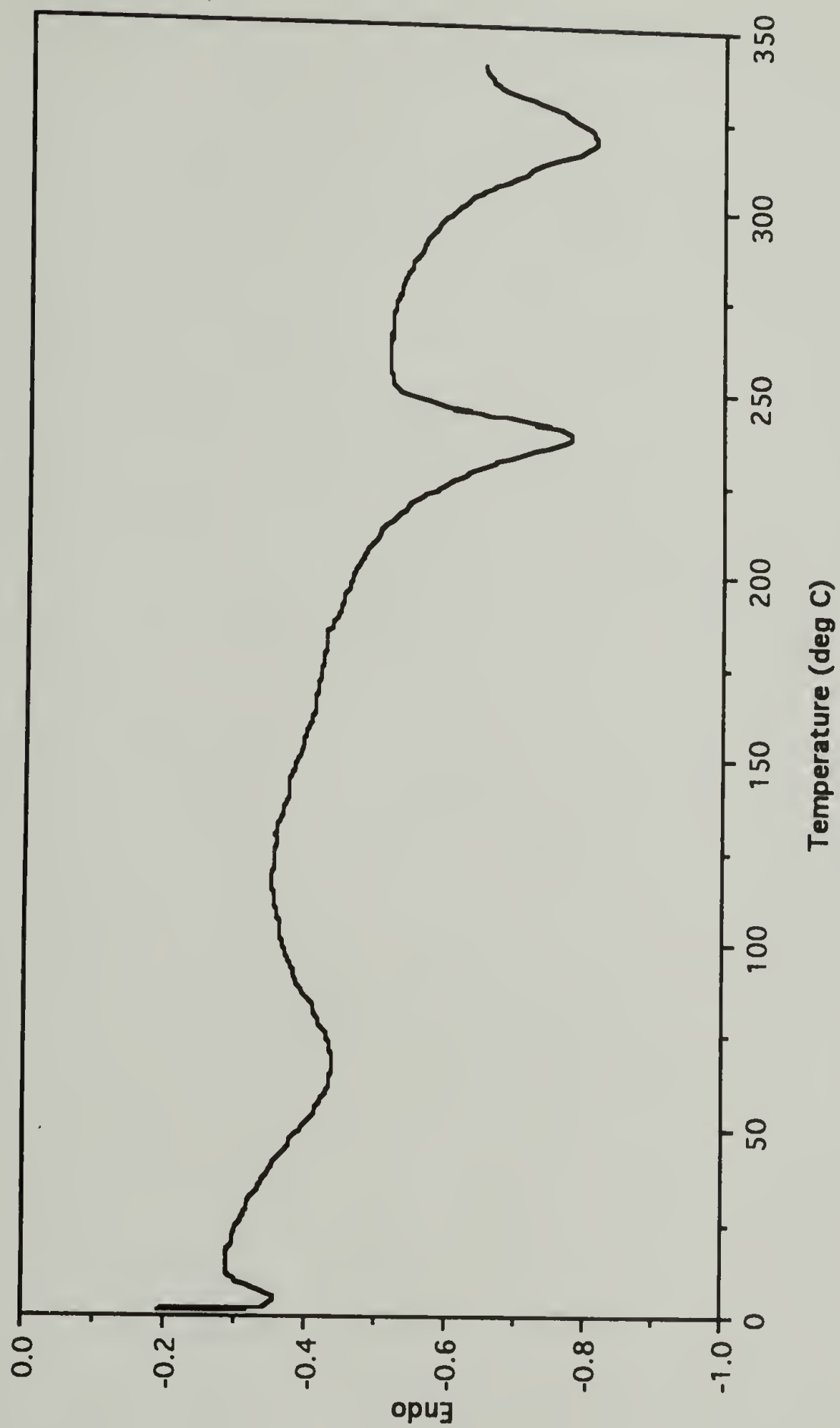


Fig. 4.3: DSC trace of P HT/ET copolyester, PHET-TCE, with a block size ratio of 6:6 recorded on the first heating at a rate of 20 deg C/min.

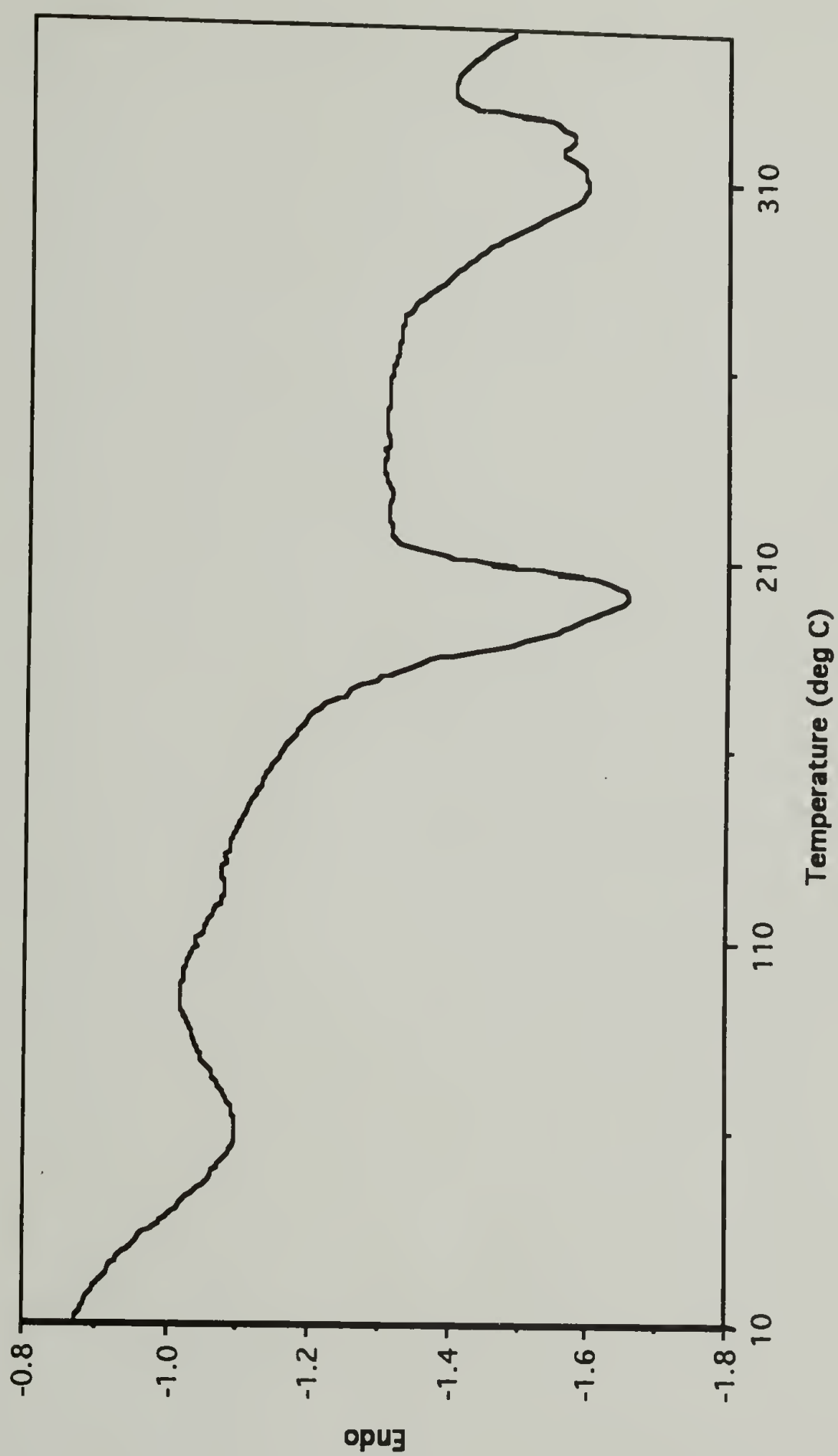


Fig. 4.4: DSC trace of P HT/BT copolyester, PHBT-TCE, with a block size ratio of 6:6 recorded on the first heating at a rate of 20 deg C/min.



Table. 4.1 : Properties of P HT / (ET/BT) copolyesters

Polymer	Reaction solvent	HT / (ET/BT) ratio	Thermal		Transitions,	Texture
1 heating						
2 heating						
<u>Random</u>						
P(HT/ET)	MC	50 : 50	224.2	325.4	233.7	Nematic
<u>Block</u>						
P(HT/ET)	1 CN	3 : 6	205.5	259.2	249.8	Nematic
P(HT/ET)	TCE	6 : 6	237.7	323.2	233.3	Nematic
P(HT/ET)	1 -CN	6 : 6	257.1	331.1	236.2	Nematic
P(HT/BT)	1 -CN	3 : 6	208.2	-	192.3	Nematic
P(HT/BT)	TCE	6 : 6	203.9	312.3	192.3	Biphasic at 300 ° C
P(HT/BT)	1 CN	6 : 6	229.5	325.3	-	

single endotherm was obtained which may be due to the randomization of the polymer at temperatures around 350 °C. The presence of two distinct peaks in the first place may indicate the presence of quite a bit of blockiness in the random copolyester.

The 6 : 6 block copolymers synthesized in both TCE and 1 - CN showed similar behavior, though the transitions were at slightly different temperatures. The copolyester synthesized at high temperatures in 1 - CN exhibited transition temperatures at least 10 - 20 °C higher which may be due to the higher molecular weight of the same. When the block size of the rigid rod was reduced, the peak

corresponding to the melting of the rigid segments also dropped down by 50 °C or so.

Similarly, the PBT copolymers also showed two peaks in the first heating cycle, the first corresponding to the melting of PBT segments around 205 °C and the peak at 315 °C to the melting of the rigid blocks. Similar, but higher transition temperatures were obtained for the copolymer synthesized in 1-chloronaphthalene.

#### Optical polarizing microscopy

All the copolyesters showed stir - opalescence after melting indicating the onset of liquid crystallinity. Optical micrographs corresponding to representative copolyesters are given in Figs. 4.5 - 4.6.

##### 1. PHE3 [ 3 PHT : 6 PET ]

A dense threaded nematic texture is obtained at room temperature for the quench cooled sample. The polymer started flowing only around 347 °C and there was no isotropization up to that temperature.

##### 2. PHET - 1CN [ 6 PHT : 6PET ]

It was difficult to obtain a thin film because of the high viscosity. Nematic texture observed up to 350 °C.

##### 3. PHET - TCE [ 6 PHT : 6 PET ]

A nematic pattern was obtained at all temperatures.

##### 4. RPHET [ Random 50 PHT : 50 PET ]

A nematic texture seen at all temperatures.

**Fig. 4.5: Optical micrographs of P HT/ET copolyester,  
PHET-TCE, with a block size ratio of 6 : 6  
( Mag. = 400 X )**

- a ) Observed mesophase of the polymer quenched to  
room temperature from the nematic mesophase**
- b ) Observed mesophase of the polymer heated up to  
280 ° C at a rate of 10 ° C / min.**



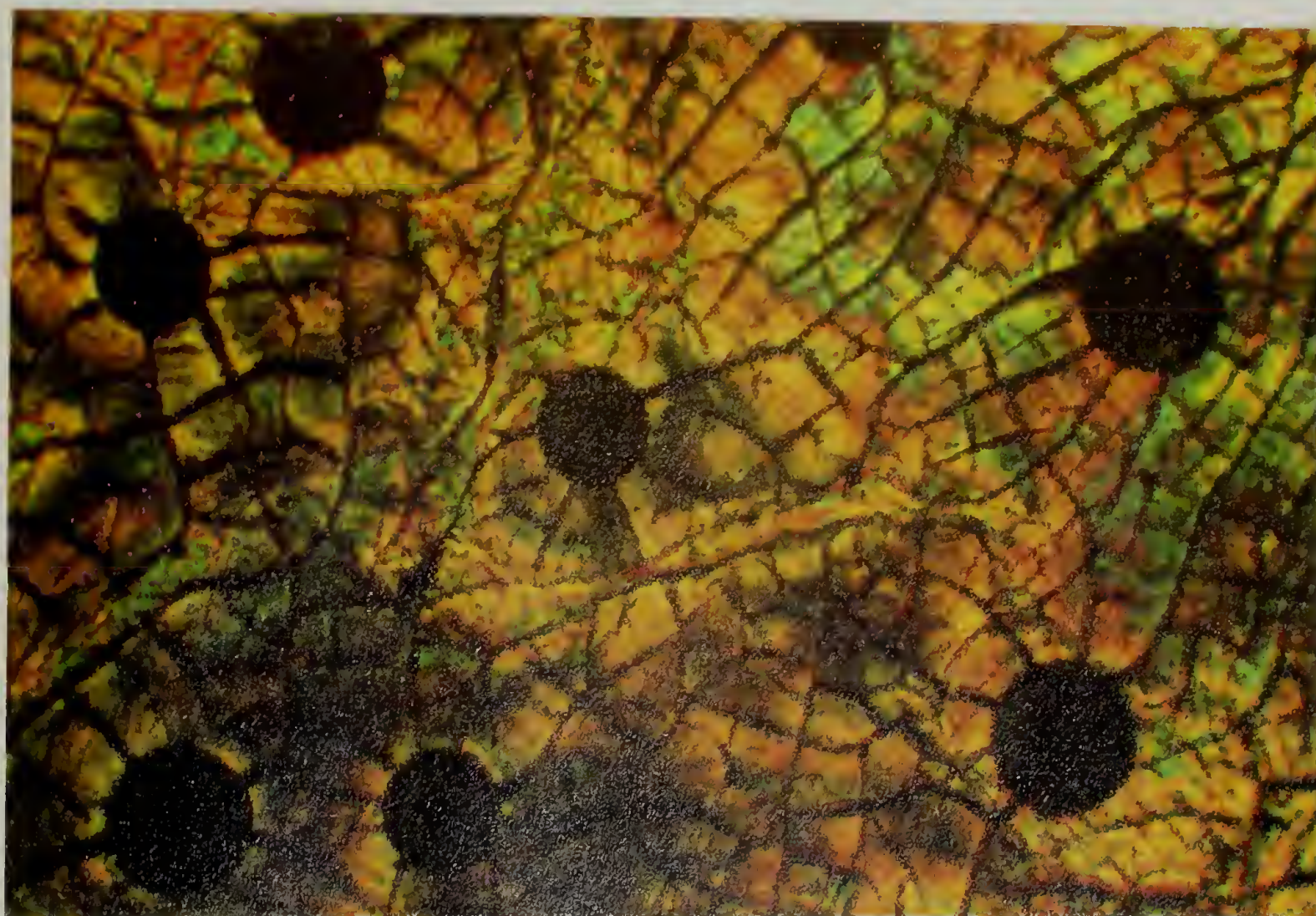
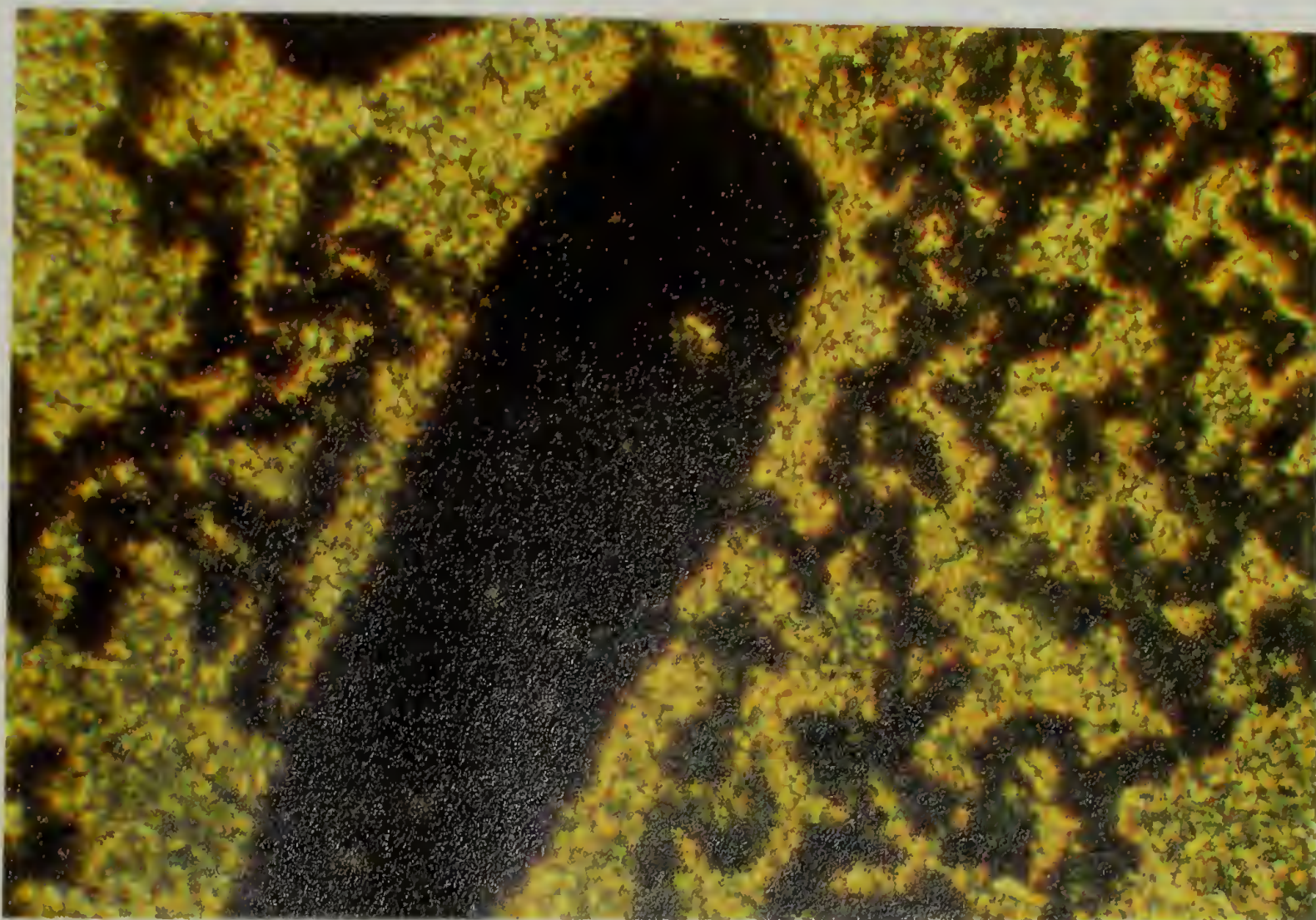
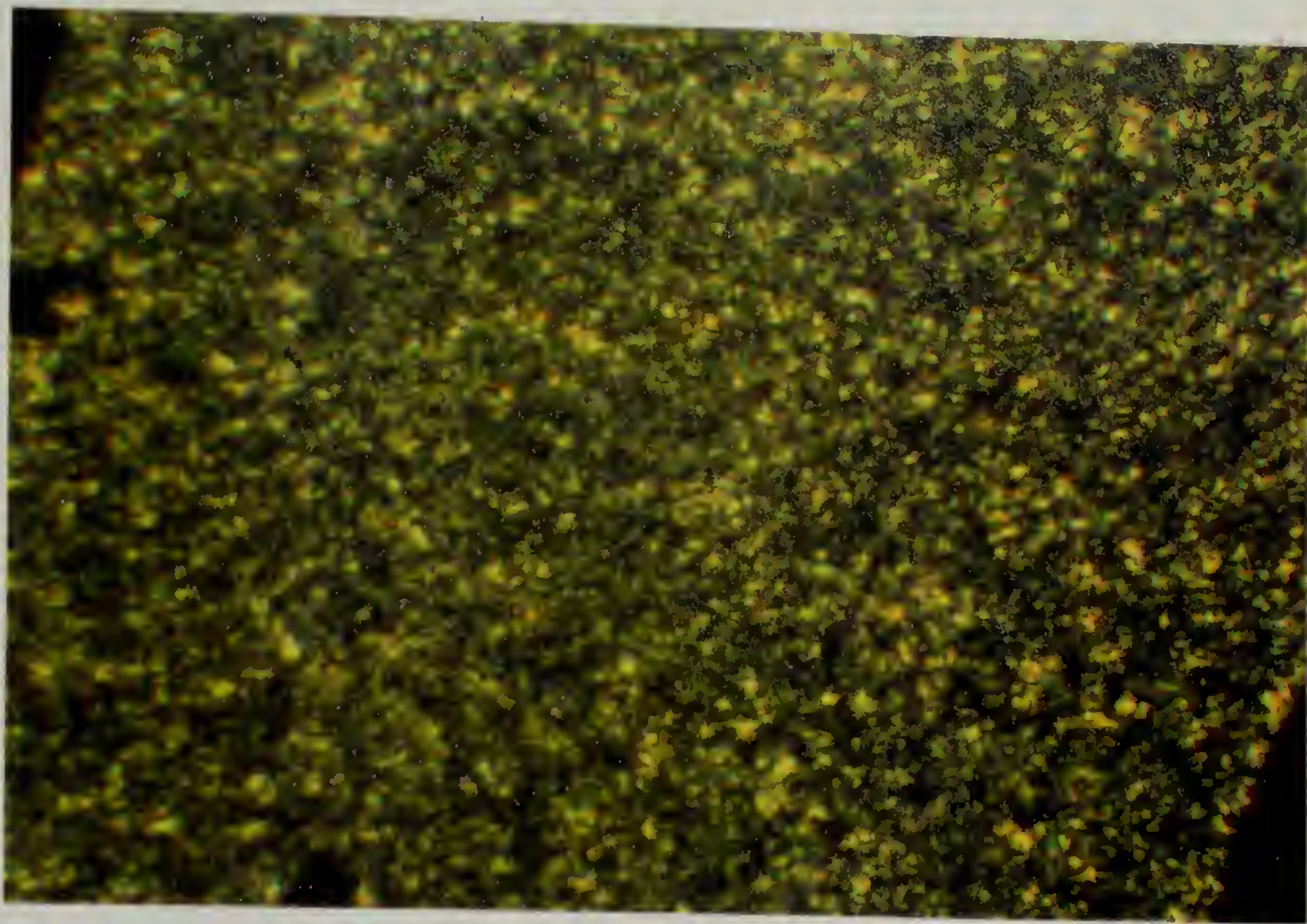




Fig. 4.6: Optical micrographs of P HT/BT copolyester,  
PHBT-TCE with a block size ratio of 6 : 6  
( Mag. = 400 X )

- a ) Observed mesophase of the polymer quenched to  
room temperature from the nematic mesophase
- b ) Observed mesophase of the polymer heated up to  
280 °C at a rate of 10 °C / min.







5. PHB3 [ 3 PHT : 6 PBT ]

It was difficult to obtain a thin film and hazy pattern was obtained at room temperature. The pattern became clearer around 225 °C due to increased flow of polymer sample to give a thinner film.

6. PHBT - TCE [ 6 PHT : 6 PBT ]

A biphasic texture was observed around 275 - 300 °C. Recrystallization within the isotropic matrix was also seen.

7. PHBT - 1CN [ 6 PHT : 6PBT ]

Dense threaded nematic pattern was obtained at room temperature. Isotropization did not set in even around 350 °C.

All the polymers showed unusual spots or black threads during cooling from 350 °C.

### Conclusions

Solution copolymerization with PET / PBT components resulted in the synthesis of thermotropic copolyesters possessing high viscosity and poor solubility characteristics. Only thermal and optical characterization was possible. Thermal studies showed the presence of 2 distinct endotherms for the copolymers in the first heating cycle. The synthesis and study of this set of copolyesters has helped to affirm the utility of pendant groupings on the hydroquinone in bringing down the transition temperatures as well as the solubility of the rigid - rods.

It would be interesting to find better solvents for the copolyesters so that more detailed NMR analysis can be done. Also synthesis of the oligomers may



reduce transition temperatures to the processing range of PET and their utility as a compatibilizing agent evaluated.

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## CHAPTER 5

### CONCLUSIONS AND SUGGESTED FUTURE WORK

#### Conclusions

The main objective of the work was to design and synthesize thermotropic liquid crystalline polyesters which could be blended with flexible coil polymers like PET for the mechanical reinforcement of the latter. The prospectus of this dissertation was to synthesize oxyethylene substituted hydroquinones and their corresponding homopolymer / copolymers containing PET / PBT segments and subsequently characterize the polymer properties. It was thought that the presence of flexible, pendant groups would bring down the transition temperatures of the liquid crystalline polyesters to the processing temperature range of the commercial polymer. It has been demonstrated in literature that incorporation of sites for specific molecular interactions into immiscible polymer systems is a successful route for enhanced compatibilization via a favorable decrease in the enthalpy of mixing. Thus an electrostatic / dipolar interaction between the ether groups of the pendant and the carbonyl groups of the matrix polymer should result in a molecular level mixing of the two components in the blend. The formation of a "molecular composite" or an "in-situ" composite could enhance both mechanical and rheological properties of PET. Also the block and random copolyesters containing the mesogenic moiety as well as the flexible PET / PBT segments could show enhanced compatibility with the coil polymer by the interaction of the isotropic segments in the melt.

The initial investigation [ Chapter 2 ] discussed the preparation and characterization of the 2-butoxyethoxy hydroquinone monomer and the



corresponding homopolymer with terephthaloyl chloride. The objective was to obtain a thermotropic liquid crystalline polyester with transitions in the processing temperature range of PET. This goal was found to be achieved by thermal and optical characterization of the polymer using differential scanning calorimetry and optical microscopy respectively. On blending with PET, no significant reinforcement of the tensile properties of PET was observed, but there was a significant reduction in the melt viscosity of the blends in the processing temperature range even when the LCP was present in very small amounts. This opens up the possibility of using the system as a processing - aid for PET as well as many other commercial polymers.

The next investigation [ Chapter 3 ] evaluated the thermotropic liquid crystalline polymer systems based on ethoxyhydroquinone monomer. The homopolymer, PEHT, with terephthaloyl chloride exhibited liquid crystalline transitions in the processing temperature range of PET. Optimization of synthesis conditions for making the random and block copolyesters of PEHT with PET / PBT components resulted in some very interesting TLCPs. DSC thermograms of the blocky copolyesters showed three distinct endotherms in the heating cycle, the assignment of which was corroborated by optical microscopy and WAXD analysis. In the case of the block copolyesters, as the ratio of the flexible to the rigid block sizes were varied from 6 : 3, to 6 : 6 to 4 : 6, a transition from spherulitic to biphasic to totally nematic texture was observed at high temperatures. High molecular weight PBT copolymers were obtained by conducting polymerizations at high temperatures (  $200^{\circ}\text{C}$  ) in 1 - chloronaphthalene as the solvent. These copolyesters yielded thin films of good strength and mechanical integrity. On the other hand, the highest viscosities were obtained for the PET copolyesters synthesized in methylene chloride at  $50^{\circ}\text{C}$  using triethyl amine as the acid - acceptor.

Proton NMR analysis could be very effectively used to study the degree of randomness in these copolymers and also the sequence distribution in terms of average sequence lengths. Many interesting experiments were done to study the effect of polymerization conditions on the molecular weight and randomness number of the copolyesters and to provide a rationale for the various trends observed. Mostly random copolyesters were obtained at high temperatures even when the polymerization was done according to a two - stage reaction procedure while a large amount of blockiness was observed in the copolyesters synthesized by heating all the reactants together at low temperatures. The melt - blending and mechanical property studies of the blends of these TLCPs shows the random copolyesters to be effective reinforcing agents. The utility of these polyesters in the improvement of the flow properties of their blends is also being evaluated.

In the final investigation, the random and block copolyesters containing the unsubstituted hydroquinone in the rigid segment were synthesized and characterized. All the copolyesters synthesized were found to be highly insoluble in many of the known organic solvents and hence the viscosity measurements and NMR analysis could not be done. Thermal studies showed the presence of two distinct endotherms corresponding to the melting point of both the segments. All the copolyesters were also nematic and remained birefringent to 350 °C.

In this investigation of thermotropic LCPs for molecular composite formation, many systems have been successfully developed for the mechanical reinforcement and improved flow properties of the PET blends. But the lack of a proper rationale for some of the trends observed both on the synthesis and characterization ends warrants further studies which also encompasses the confirmation of specific interactions between the components in the blends by spectroscopy.

### Suggested future work

This dissertation was set-up to design and synthesize thermotropic LCPs, mostly systems containing the oxyethylene substituted hydroquinones for use in "molecular composite" fabrication with PET. Some of the systems have found to improve the mechanical and flow properties of the matrix polymer which justifies further research in this area. Suggested future work on this project is highlighted in the following outline.

The 2-butoxyethoxyhydroquinone homopolymer is found to be very interesting with respect to improvement of flow properties of PET and probably other commercial polymers too. Hence there is potential use for the polyester as a processing-aid in industry. But the current synthesis of the monomer is found to be highly cumbersome and a low yielding reaction making the monomer potentially very expensive. So it should be worth-while to investigate alternative synthesis routes for these kind of monomers. Two of the proposed routes are described in Fig. 5.1 and Fig. 5.2. Both the routes would lead to slightly different monomers as the pendants would be attached to the hydroquinone through a -C linkage, rather than -O.

Novel substitutions on the hydroquinone to yield thermotropic LCPs with lower transition temperatures, say 150 - 200 °C could be synthesized for blending with amorphous polymers like polycarbonate and the blends studied for flow improvement and mechanical reinforcement. Grafting low molecular weight PET oligomers on to hydroquinone and subsequent polymerization may result in a product which is highly compatible with PET. It would also be interesting to evaluate the mechanical properties of the melt spun neat LCP fibers. Fiber spinning



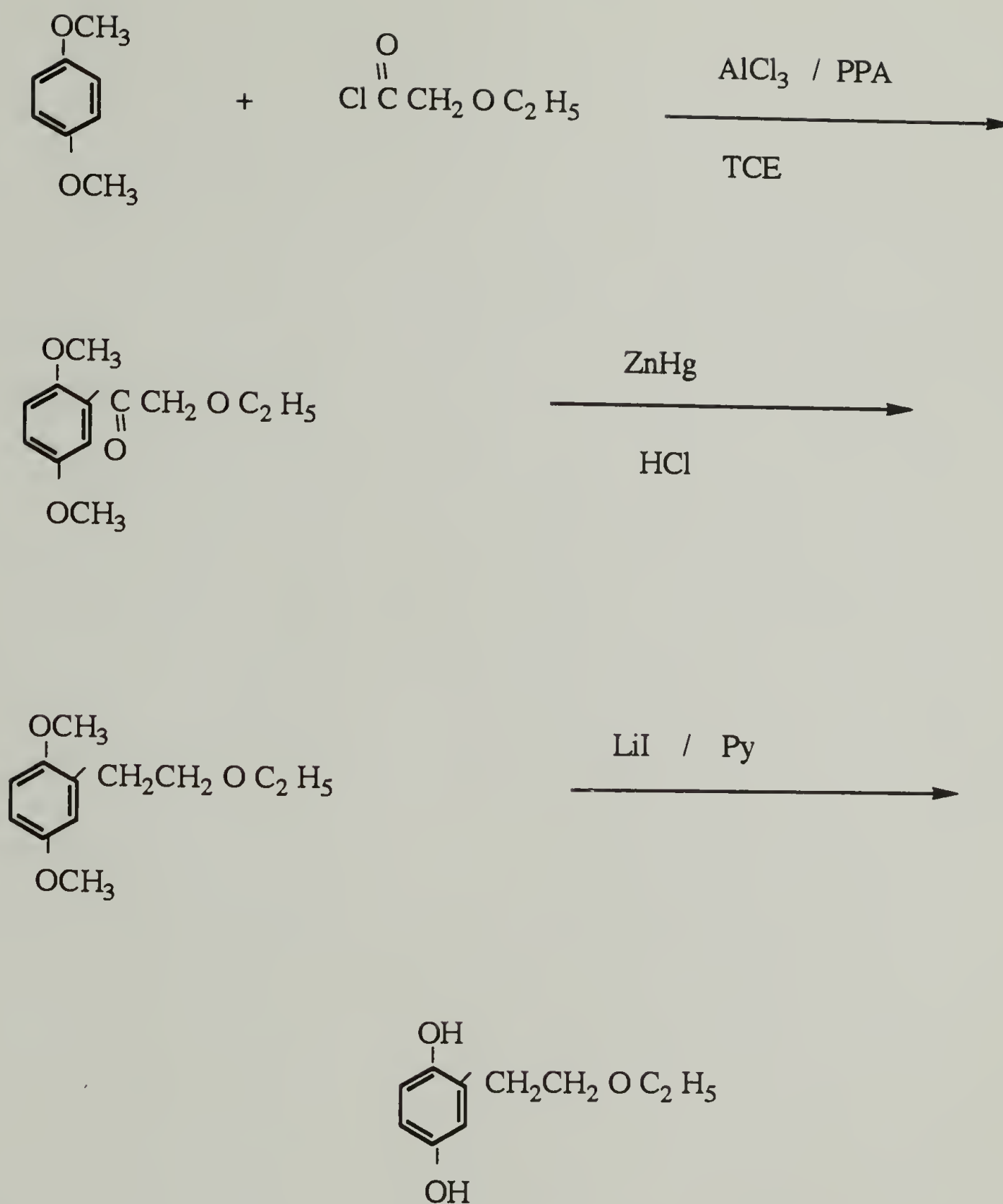


Fig. 5.1 : Alternative route for the synthesis of 2 - alkoxy hydroquinone

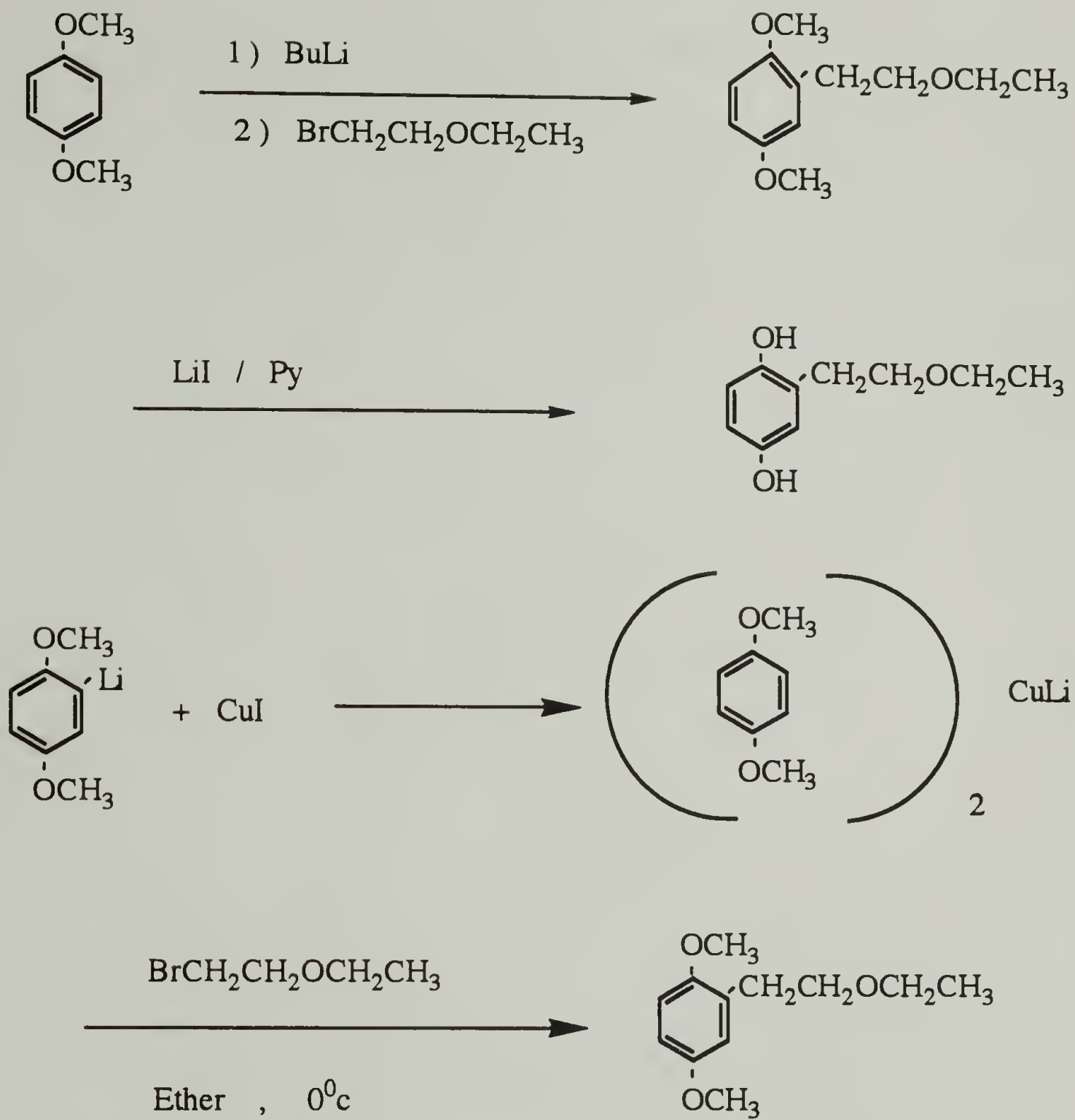


Fig. 5.2 : Alternative route for the synthesis of 2 - alkoxy hydroquinone

of the higher molecular weight LC polyesters like PCBT & RP60 should be feasible and one could compare the properties of these novel LCPs with that of the material which is already available in market.

As we have observed in Chapter IV, the copolymers containing unsubstituted hydroquinones in the rigid segments have high insolubility as well as high transition temperatures. It would be interesting to synthesize a ter polymer containing the unsubstituted hydroquinone, ethoxyhydroquinone and PET / PBT segments. The cost of this system would be much lower than the systems already investigated and would be interesting from an economic point of view if the desired properties are achieved. Also triad systems containing the ethoxyhydroquinone could be an interesting variation of the theme.

The route taken to achieve the goal of forming a true " molecular composite " is based on the assumption that specific interactions are present between the two components of the blends investigated. This has never been proved experimentally and hence it would be interesting to confirm these interactions spectroscopically. Raman spectroscopy could be a powerful tool for picking up the weak electrostatic interactions between the ether group of the pendant and the carbonyl functionality of the matrix polyester.



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