

The Preparation and Properties of Segmented-Chain Liquid Crystalline Polyesters Based on 4,4'-Dihydroxybiphenyl by Interfacial Polycondensation

Ali Jannesari, Seyed Reza Ghaffarian, Faramarz Afshar Taromi, Naser Mohammadi

Polymer Engineering Department, Amirkabir University of Technology, P.O. Box 15875/4413, Tehran, Iran

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ABSTRACT: Thermotropic homopolyesters were prepared through interfacial polycondensation of 4,4'-dihydroxybiphenyl with sebacoyl chloride. The optimal conditions of the process, in terms of the best yield, were studied through investigating the type of organic phase, amount of phase transfer agent, time and temperature of reaction, and volume ratio of aqueous to organic phase. The structure of the sample that had the best yield ($53.235\% \pm 5\%$) was determined by means of elemental analysis, infrared spectra, and X-ray. The effect of the molar ratio of the monomers on the yield and inherent viscosity was investigated. The inherent viscosity of the samples varied between 0.095 and 0.25 dL/g. The mesophase formed at elevated temperatures was

studied by differential scanning calorimetry, polarized light microscopy, and depolarizing transmittance measurements. Our observations revealed that poly(4, 4'-diphenyl sebacate), in contrast to previous reports that suggest this polymer is smectogenic, could produce nematic phase. It could be concluded that the chemical structure ordering of the poly(4, 4'-diphenyl sebacate) plays a significant role in its liquid crystalline behavior. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1594–1606, 2005

Key words: 4,4'-dihydroxybiphenyl; interfacial polycondensation; polyester; thermotropic liquid crystalline polymer

INTRODUCTION

Liquid crystalline polymers (LCPs) continue to fascinate scientists and technologists alike, with new materials being synthesized at an ever increasing rate, leading to well defined structure-property relationships in these materials. Main-chain LCPs are an important type of LCPs, and have superior anisotropic nature and a combination of desirable properties. These LCPs have high mechanical properties, good heat resistance, extremely low moisture take-up, and superior stability to chemicals.¹

Introduction of flexible segments to separate mesogenic groups placed in the main chain from each other is one of the basic methods that can be used to reduce the transition temperatures of LCPs by disrupting the perfect regularity of simple but intractable *para*-linked aromatic polymers.²

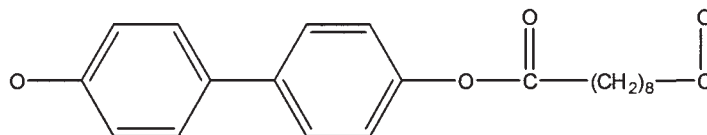
For a very practical reason, virtually all segmented-chain LCPs are polycondensated. Polycondensation is a versatile way to connect two prebuilt molecular sections in alternating sequence just like flexible and rigid segments are. By far the largest numbers of segmented-chain LCPs are polyesters.³ Semiflexible ho-

mopolyesters, having rigid and flexible segments in the repeating unit, are attractive because varying the length of the flexible segment can control the transition temperatures.⁴ One of the most interesting of them is the homologous series of polyesters prepared from 4,4'-dihydroxybiphenyl and aliphatic dibasic acids.^{5–10} The repeating unit of these polyesters can be represented as (Scheme 1).

It was reported that this series exhibits a unique odd-even effect in that the mesophase is nematic for polymers having an odd number of methylene units in the dibasic acid and smectic for the even-membered series.⁶ Since direct polyesterification between diacids and diols at high temperatures do not generate high molecular weight polyesters, the synthesis of these polyesters was mainly carried out by means of melt transesterification of 4,4'-diacetoxybiphenyl and diacids.⁵ One problem in aromatic polyester synthesis from acetates is the color of the final polymer, because it mostly is preferred to be as color-free as possible. One of the major culprits for side reactions is ketene, which can react to introduce possibly colored materials. Ketene has been detected in these polymerizations and is formed by decomposition of the acetate end group.^{11–13} One way to prevent the side reactions is to use mild conditions (e.g., low temperature) for the polyesterification.

It was found out that the highest values of reduced viscosity and the best yield were obtained by use of

Correspondence to: A. Jannesari (alijannesari@yahoo.com).



Scheme 1

interfacial polycondensation.^{14,15} Interfacial polycondensation involves the polymerization of two complementary monomers at the interface of two immiscible phases. The advantage of an interfacial polycondensation is that it provides a simple and quick route to synthesize polymers. Because its reaction energy is low, polymerization can generally be conducted at a low temperature. Only a short polymerization time is needed to synthesize polymers that are thermally unstable.

Basic features of interfacial polycondensation and parameters influencing polymer formation at the interface were first described by Morgan and colleagues.¹⁶ It was established that properties of the polymers synthesized in this way are considerably, and sometimes significantly, influenced by a number of various factors, such as the quality of the reagents, the type of the organic phase, the concentration of the monomers, excess of the hydrochloride acceptor, temperature and time of the reaction, and the contribution of type and quantity of the catalyst.¹⁷⁻²⁰ To the best of our knowledge, other researchers have not reported the conditions of the preparation of (4,4'-dihydroxybiphenyl) alkanedioic acid polyesters through interfacial polycondensation. The purpose of this study is to determine the effects of some material and processing parameters on the conditions of interfacial polycondensation and to define structure and thermal behav-

ior of the segmented liquid crystalline homopolyesters based on a 4,4'-dihydroxybiphenyl rigid segment and a flexible segment arising from aliphatic dibasic acid chlorides (sebacoyl chloride).

EXPERIMENTAL

Materials

4,4'-dihydroxybiphenyl m.p. 275–280°C, as the rigid monomer, was from Merck (Germany) and recrystallized from methanol before use. Sebacoyl chloride m.p. –5 to –3°C, as the flexible monomer, was purchased from Fluka (USA); and benzyl triethyl ammonium chloride m.p. 230–235°C, as the phase transfer agent, and other chemical reagents were purchased from Merck (Germany) and used as received.

Preparation of polymers

4,4'-dihydroxybiphenyl was mixed with the acid absorbent, sodium hydroxide, and the phase transfer agent, benzyl triethylammonium chloride, in the aqueous phase, and the aliphatic dibasic acid chloride was dissolved in the organic phase. The aqueous solution was located in a 250-mL two-necked round bottom flask equipped with a thermometer and a dropping funnel. This set was placed into a water bath

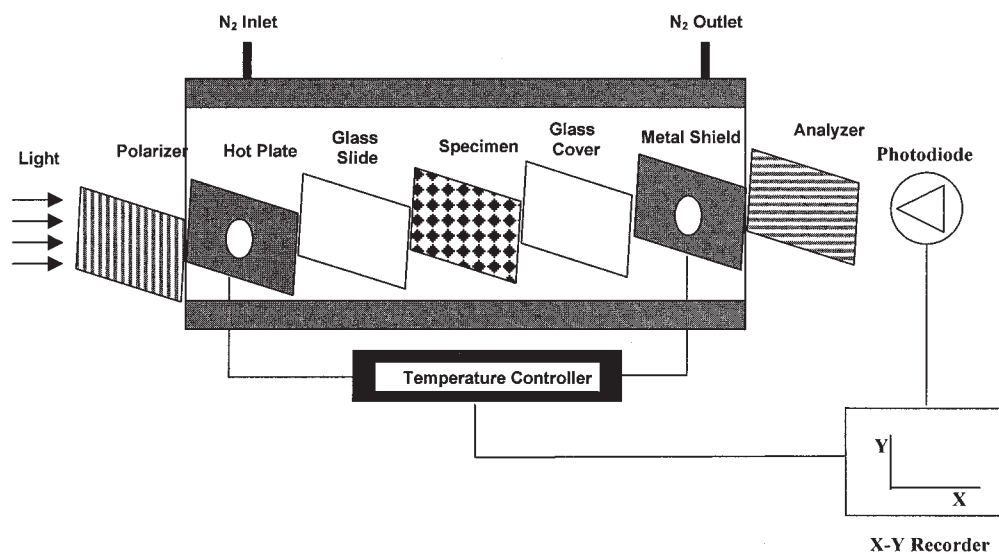


Figure 1 Schematic diagram of experimental apparatus for depolarizing transmittance measurements.

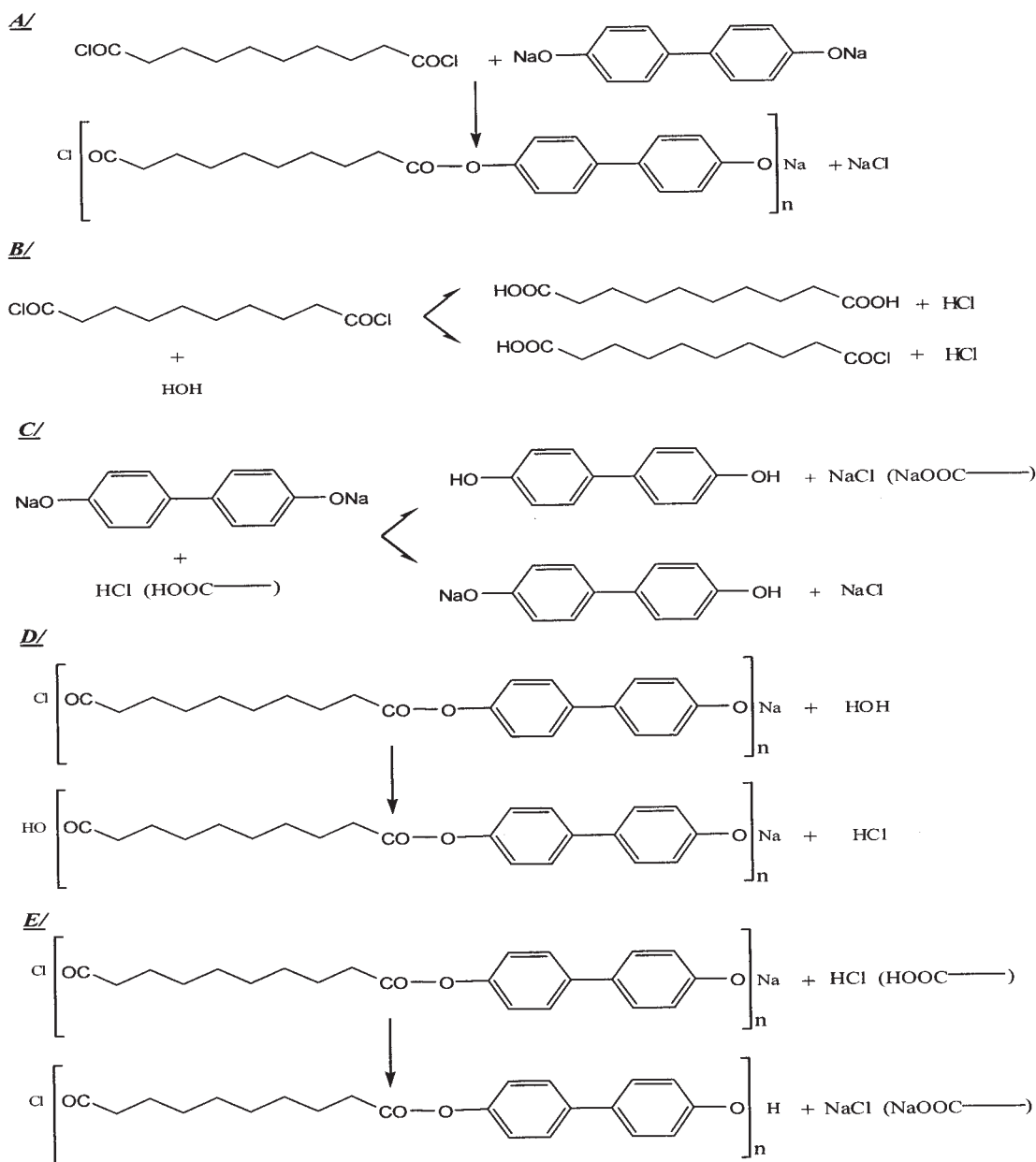
TABLE I
The Effect of Reaction Temperature on the Yield of the Polyester

Yield of reaction (%)	Reaction temperature range (°C)			
	0-4	10-15	20-25	30-35
	9.958 ($\pm 5\%$)	21.749 ($\pm 5\%$)	13.312 ($\pm 5\%$)	9.894 ($\pm 5\%$)

Conditions of the reaction: volume ratio of aqueous to organic phase 0.5 : 1; mole ratio of chloride acid to diol monomer 1.5 : 1; rate of chloride addition 15 min; time of reaction (after completing chloride addition) 30 min; catalyst 5%; organic phase: benzene/hexane (1 : 1).

equipped with a temperature controller. During thorough mixing, the organic solution was added within 15 min at a constant rate. After the addition of the acid

chloride was completed, the stirring was continued for a certain time and then acidified with hydrochloric acid. The isolated polycondensation product was fil-



Scheme 2

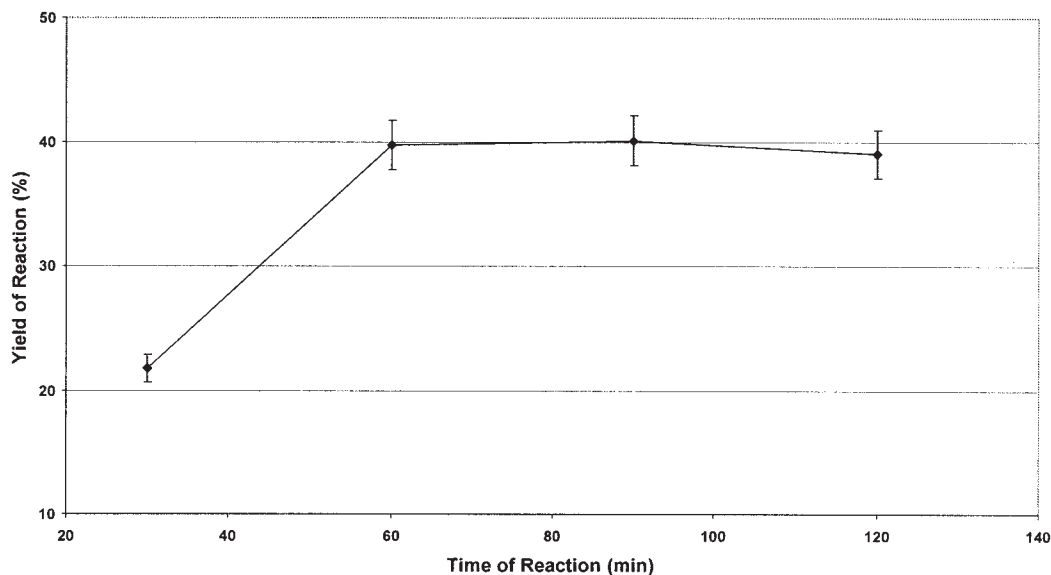


Figure 2 The effect of time of reaction (after completing the chloride addition) on the yield of the polyester. Conditions of the reaction: volume ratio of the aqueous to the organic phase 0.5 : 1; mole ratio of chloride acid to diol monomer 1.5 : 1; rate of chloride addition 15 min; catalyst 5%; temperature of reaction 10–15°C; organic phase: benzene/hexane (1 : 1).

tered and washed with acetone (100mL) and hot water (3 times 100mL) and then with methanol. The polymer was dried to constant weight at 60°C under vacuum conditions (about 48 h).

Characterization

Inherent viscosities of the polyesters were determined at 25°C using 0.5 g/dL solutions in a 60/40 mixture by weight of phenol and tetrachloroethane. Ubbelohde viscometers were used without kinetic energy correction since the solvent flow time exceeded 100s. FTIR spectra were recorded on a Perkin–Elmer system 2000 spectrophotometer. Thermal studies were performed with a DSC (TA Instrument 2010 model) at a scanning rate of 10°C/min. To enhance the thermal contact between the samples and the heat source and omit the thermal history effects, the samples in the form of a powder were first melted to take up the shape of the aluminum sample pan, then cooled at 10°C/min, and after that heated again with a rate of 10°C/min. Optical microscopic studies were performed with a Leica DMR polarizing microscope equipped with a hot stage (Linkam LTS 350). The variations of the depolarizing transmittance of the polyester with temperature were obtained through measurements of the exposure time using a Leica MPS 60 automatic exposure time measuring unit attached to the microscope. The reciprocal of this time was anticipated to be proportional to the intensity of light transmitted through the sample. The transmitted intensity of depolarized light through the polyesters during heating, at a constant rate of 10°C/min and under inert atmosphere, was

measured. The block diagram of the system that was used for this mean is shown in Figure 1. The X-ray diffraction pattern was recorded by a Simens D5000 diffractometer using graphite monochromatized CuK α radiation.

RESULTS AND DISCUSSION

Polyester synthesis

First, we attempted to optimize the conditions of the polymerization through determining the influence of the various parameters on the yield of the reaction. They were type of the organic phase, concentration of the monomers, temperature and time of the reaction, volume ratio of organic to aqueous phase, and quantity of the catalyst. Then, the aim was to study the effect of the proportion of the starting materials on the molecular weight (inherent viscosity) of the products.

TABLE II
The Effect of the Type of the Organic Phase on the Yield of the Polyester

Organic phase	Yield of reaction (%)
Xylene	32.266 ($\pm 5\%$)
Chloroform	28.418 ($\pm 5\%$)
Tetrachloromethane	22.139 ($\pm 5\%$)
Benzene/hexane (1 : 1)	39.728 ($\pm 5\%$)

Conditions of the reaction: volume ratio of aqueous to organic phase 0.5 : 1; mole ratio of chloride acid to diol monomer 1.5 : 1; rate of chloride addition 15 min; time of reaction (after completing chloride addition) 60 min; catalyst 5%; temperature of reaction 10–15°C.

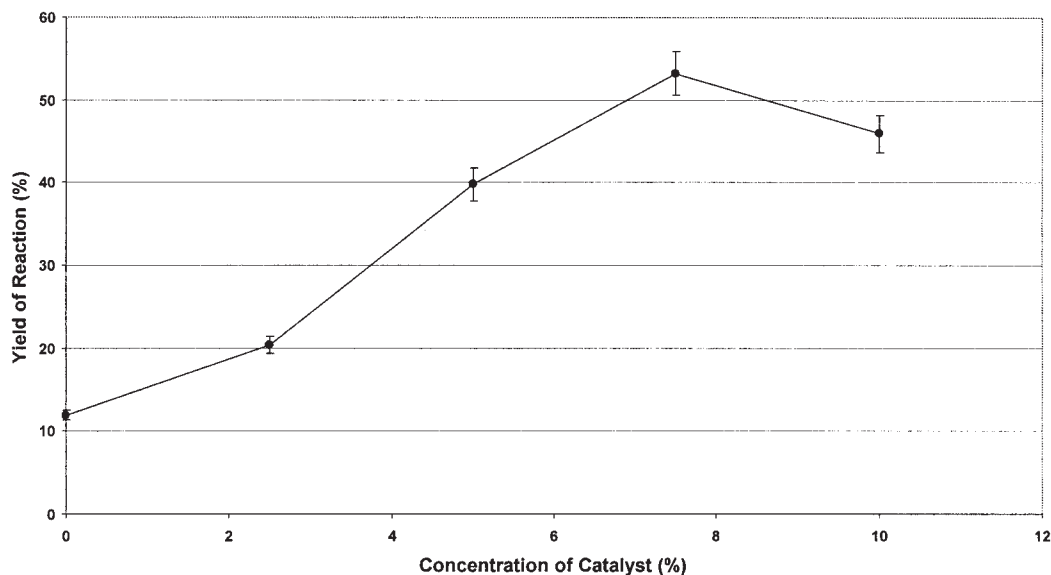


Figure 3 The effect of the concentration of the catalyst (% by weight of the diol monomer) on the yield of the polyester. Conditions of the reaction: volume ratio of the aqueous to the organic phase 0.5 : 1; mole ratio of chloride acid to diol monomer 1.5 : 1; rate of chloride addition 15 min; time of reaction (after completing chloride addition) 60 min; temperature of reaction 10–15°C; organic phase: benzene/hexane (1 : 1).

It must be noted that all reactions were carried out in a nonequivalence condition of proportion of the starting material to obtain low molecular weight polyesters containing reactive end groups (COOH or OH). Finally, the structure and the behavior of the liquid crystalline polyester obtained at the optimal condition, in terms of the reaction yield, were investigated.

At first, with respect to the previous works and the results of our preliminary experiments, the reaction of polymerization was performed in the initial reaction condition, which was set as follows: the rate of the addition of the organic phase about 15 min, the time of the reaction after the addition of the organic phase 60 min, the volume ratio of organic to aqueous phase 2 : 1, the mole ratio of diol to acid chloride monomers was 1 : 1.5, the amount of sodium hydroxide was a small excess (0.3 mol) in comparison with the stoichiometric quantity of the diol monomer, the amount of benzyl triethyl ammonium chloride was 5% by weight of the diol monomer, and a mixture of benzene-hexane (1 : 1) was used as the organic phase.

To investigate the influence of the temperature of the reaction on the yield, the interfacial polycondensation was carried out at temperature ranges of 0–4°C, 10–15°C, 20–25°C, and 30–35°C. The results of these experiments are given in Table I.

It can be seen from these results that the highest yield of the polyester was obtained at the temperature range of 10–15°C. In carrying out polycondensation at the boundary where one of the phases is aqueous, the following types of concurrent reactions are possible (Scheme 2).

The first of these reactions goes in the direction of the result we desire in the synthesis of the polyester. The others, on the contrary, hinder its formation by converting the initial substances or the growing chains into nonreactive materials, that is, causing rupture of the chains. The reduction in the yield of the polyester with a rise of the temperature may be explained by a growth in the role of these reactions. Their rates, no doubt, increase at elevated temperatures. The decrease of the yield of the reactions at a lower temperature range could be attributed to the insufficient energy required to proceed with the reaction.

The temperature of the reaction was then chosen to be 10–15°C, and the time of reaction, after completing the acid chloride addition, was then investigated. As shown in Figure 2, the favorable time of the reaction is about 60 min. It seems that at this time the reaction reaches some kind of steady state condition.

The influence of the kind of organic phase on the yield of the polyester was then examined. The applied organic phase and the obtained results are listed in Table II. It has been shown that the kind of organic phase influences the yield of the polyester. The best yield was obtained with benzene-hexane (1 : 1) as the organic phase. It can be seen that the correct choice of solvent has considerable impact on the yield of the polyesters.

A number of substances have been proposed as catalysts for interfacial polyesterification.²¹ The most common catalyst that is proposed is benzyltriethylammonium chloride (BTEAC), which also was used in this study. Referring to Figure 3, it can be seen that the

TABLE III
The Effect of the Volume Ratio of the Aqueous to the Organic Phase on the Yield of the Polyester

	Volume ratio of aqueous to organic phase		
	0.5 : 1	1 : 1	1.5 : 1
Yield of reaction (%)	53.235 ($\pm 5\%$)	38.545 ($\pm 5\%$)	22.685 ($\pm 5\%$)

Conditions of the reaction; volume ratio of aqueous to organic phase 0.5 : 1; mole ratio of chloride acid to diol monomer 1.5 : 1; rate of chloride addition 15 min; time of reaction (after completing chloride addition) 60 min; catalyst 7.5%; temperature of reaction 10–15°C; organic phase: benzene/hexane (1 : 1).

yields of the polyester improved by increasing the amount of BTEAC as catalyst. The best yield was obtained in 7.5% by weight of the diol monomer. In higher amounts of BTEAC, the yield of the reaction was reduced. It is probably because BTEAC also promotes the diffusion of water molecules and increases the hydrolysis side reaction in the organic phase.

The influence of the volume ratio of the aqueous to the organic phase on the value of yield of the polyester was studied using different quantities of water on the same quantity of organic solvent. The volume ratio of the aqueous to the organic phase was based on the acid chloride concentration in the organic phase of 0.1M/L, and the obtained results are listed in Table III.

The ratio of the starting materials exerts a great influence on the magnitude of the molecular weight and also affects the yield of the polymer. Figures 4 and 5 show how the inherent viscosity and the yield of the

polyesters vary with the ratio of the starting materials. The polyesters are designated, on the basis of the mole ratio of the starting materials, by the letters PB (n : m), where (n : m) is the mole ratio of sebacyl chloride to 4, 4'-dihydroxy biphenyl.

As can be observed, the polyesters obtained with an excess of sebacyl chloride were characterized by higher inherent viscosities than those obtained with an excess of 4, 4'-dihydroxy biphenyl. Korshak and co-workers²² explained these variations by a partial hydrolysis of the sebacyl chloride, which compensates for the presence of an excess of the acid chloride, in fact diminishing this excess.

According to Dae-won Park and colleagues,^{23,24} the mechanism for aqueous/organic two-phase condensation polymerization can be proposed as in Figure 6, where CIR'Cl is the biselectrophilic (sebacyl chloride), HOROH is the bisnucleophilic (4,4'-dihydroxybiphenyl), $^-ORO^-$ is the bisnucleophilic anion, and Q^+ is the phase transfer cation.

In accordance with the above mechanism, the bisnucleophilic anion located in the aqueous phase ion pairs with two phase transfer cations (eq. (2)) and is transferred into the organic phase, where it reacts with the biselectrophilic (eq. (3)). Chung-Yu Wang and co-workers²⁵ illustrated the kinetic mechanism of the interfacial polycondensation of bisphenol A with terephthaloyl/isophthaloyl dichloride following the model shown in Figure 7. They suggested that the reaction of the bisnucleophilic anion with biselectrophilic in the bulk of the organic phase to be the rate-determining step. So it would be expected that the

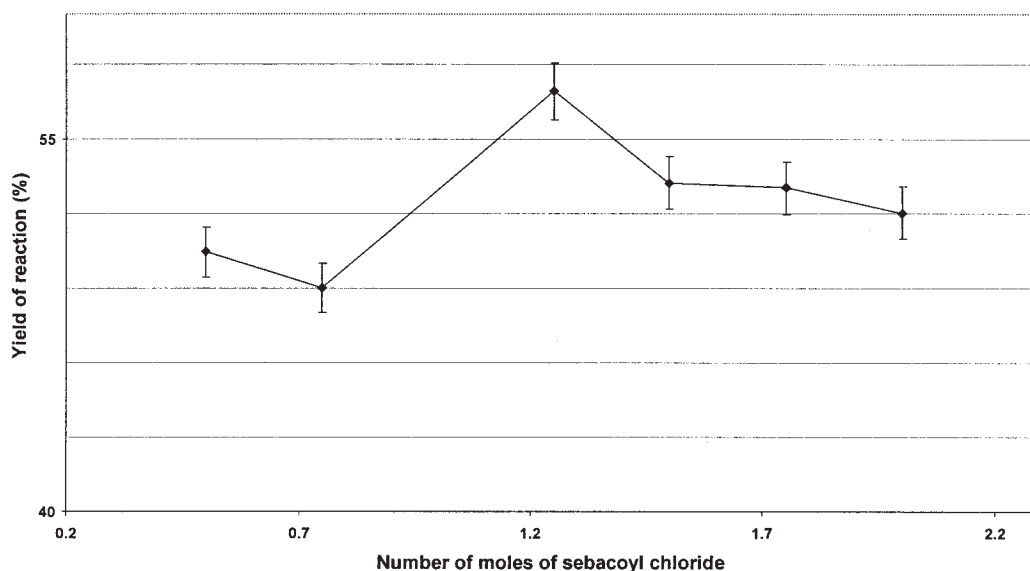


Figure 4 The effect of the mole ratio of chloride acid to the diol monomer (n : 1) (n is the number of moles of sebacyl chloride) on the yield of the polyester. Conditions of the reaction: volume ratio of chloride acid to diol monomer (n : 1); rate of chloride addition 15 min; time of reaction (after completing chloride addition) 60 min; catalyst 7.5%; temperature of reaction 10–15°C; organic phase: benzene/hexane (1 : 1).

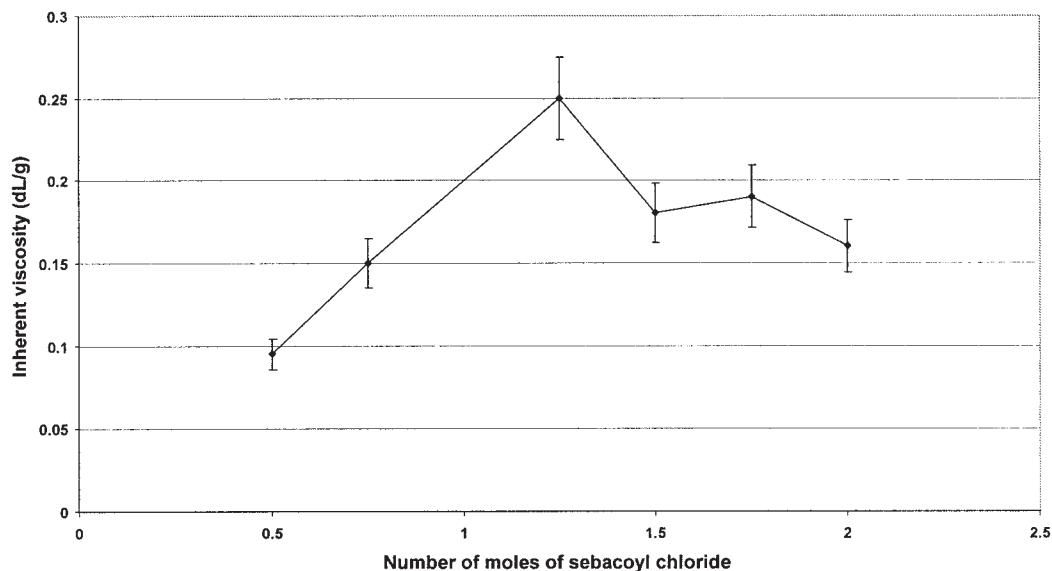


Figure 5 The effect of the mole ratio of chloride acid to the diol monomer ($n : 1$) (n is the number of moles of sebacyl chloride) on the inherent viscosity of the polyester. Conditions of the reaction: volume ratio of the aqueous to the organic phase 0.5 : 1; mole ratio of chloride acid to the diol monomer ($n : 1$); rate of chloride addition 15 min; time of reaction (after completing chloride addition) 60 min; catalyst 7.5%; temperature of reaction 10–15°C; organic phase: benzene/hexane (1 : 1).

yield increases with polarity of the organic phase, because the complex of bisnucleophilic anion and phase transfer cation is difficult to transfer from the aqueous phase to the organic phase, which has low polarity.

Surprisingly, when we used different types of organic phases for polyester synthesis, the yield increased in the order of (benzene/hexane) > xylene > chloroform > dichloromethane, as shown in Table II. This order is in contrast to the solvent polarity. The trend of changes in dielectric constants and solubility of water in these organic solvents is shown in Figure 8.²⁶

As has been illustrated in Figure 8, by increasing the solubility of water in the organic phase, the yield of reaction was lowered. This may be correlated to the competition of two parallel reactions, which can occur simultaneously in the organic phase. These are the reactions of sebacyl chloride with water (hydrolysis side reaction), which is an undesirable reaction and could lead to a decrease in the yield of the polyester, and with biphenolate (polymerization), which is a desirable reaction and increases the yield of the polyester. It seems that by changing the organic phase, the hydrolysis side reaction became a perceptible factor, which could affect the yield in our experiments.

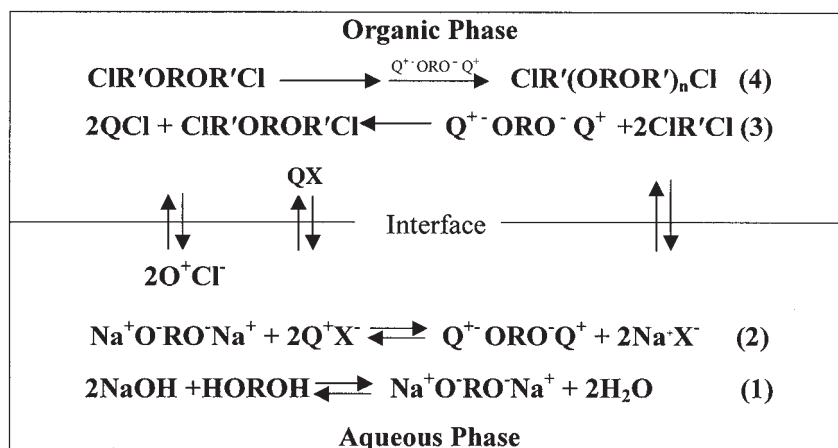


Figure 6 Mechanism of the reaction of polyesterification from sebacyl chloride and 4,4'-dihydroxy biphenyl using phase transfer agent (HOROH = 4,4'-dihydroxy biphenyl, CIR'Cl = sebacyl chloride, QX = quaternary ammonium salt).^{23,24}

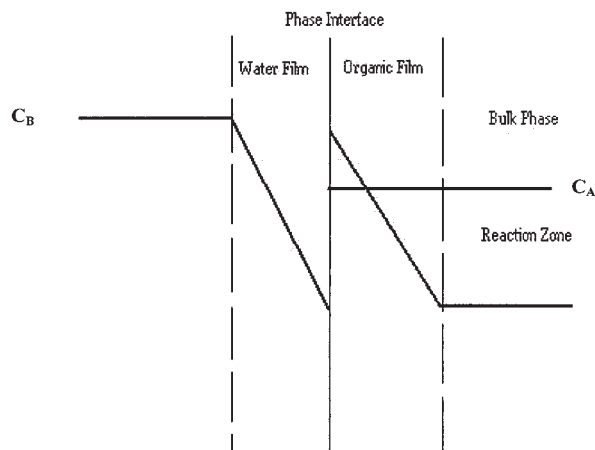


Figure 7 Interface behavior for the stirred interfacial polycondensation, proposed by Wang and coworkers,²⁵ where C_B is the concentration of the coordinated compound of bisphenolate and BTEAC in the aqueous phase and C_A is the average concentration of phthaloyl dichloride in the organic phase.

The effect of the ratio of the starting materials on liquid crystallinity behavior

To determine the influence of the molecular weight (inherent viscosity) of the polyesters on the temperature transitions, the depolarizing transmittance of the samples was performed at a constant heating rate of 10°C/min. Viney²⁷ considered a monodomain sample viewed between crossed polars in monochromatic light. The formula for transmitted intensity was derived as follows:

$$I/I_0 = \text{Sin}^2[2\theta]\text{Sin}^2[(nd/\lambda)(n_2 - n_1)] \quad (5)$$

where I is the depolarized light intensity that is transmitted through the sample and I_0 is the polarized light intensity that is incidental on the sample; the experimental set up was adjusted in a manner that this latter value could be considered constant in our experiments. λ is the wavelength of light, d is the thickness of the specimens, $\Delta n = (n_2 - n_1)$ is the birefringence, and θ is the angle between the vibration direction in the specimen and the vibration direction of transmitted light since the liquid crystalline polyesters that were prepared in this work are not aligned and they are polydomain. Therefore, we considered the intensity of the transmitted depolarized light through the samples as the summation of the depolarized light fluxes that transmitted through each of the domains. This has been shown schematically in Figure 9. So, the above equation can be written as follows:

$$(I/I_0)_{\text{total}} = \sum (I/I_0)_i = \sum \{ \text{sin}^2[2\theta_i] \text{Sin}^2 \times [(nd/\lambda)(n_2 - n_1)_i] \} \quad (6)$$

In this way, $(I/I_0)_{\text{total}}$ could be considered as a criterion for the birefringence and consequently as a measure for the liquid crystallinity of the samples.

Figure 10 shows the depolarizing transmittance plots of the homologous series of PB ($n : m$) samples against temperature. The PB (1.25 : 1) sample demonstrates the higher clearing point, and PB (0.5 : 1) shows clearly the lower clearing point. The isotropization temperatures present a descending trend for the samples, with the number of moles of sebacyl chloride (Fig. 11). It is of interest that the liquid crystalline texture of the PB (0.5 : 1) sample differs significantly from the others. Blumstein and coworkers²⁸ have al-

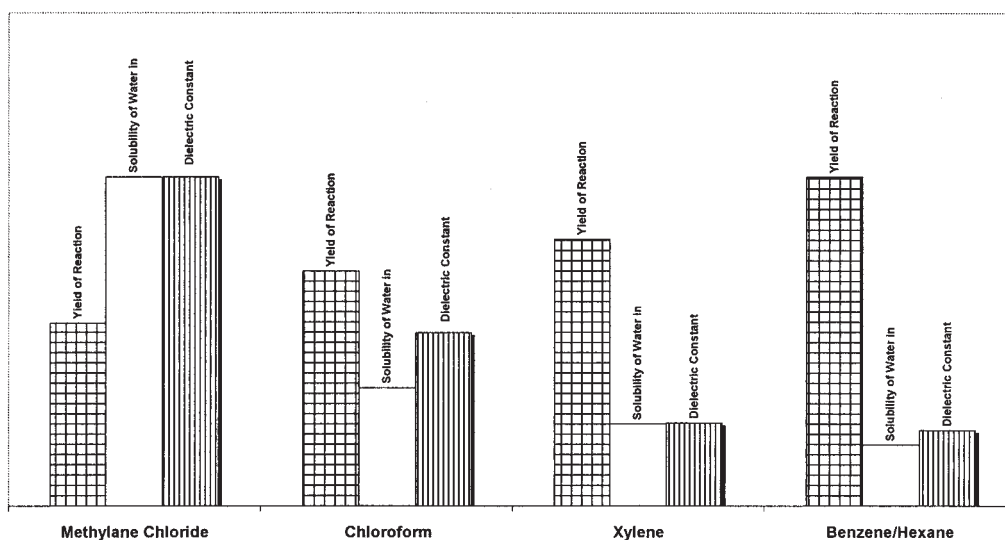


Figure 8 The trend of the obtained yield (crossed bars), the solubility of water (white bars), and the dielectric constant (ribbed bars) for different organic phases, which were used in our experiments.²⁶

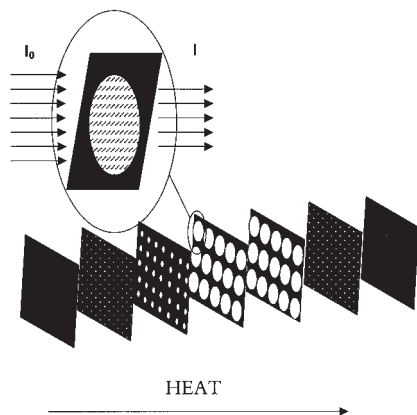


Figure 9 Schematic plan of the emergence of liquid crystalline microdomains in the samples and the depolarized light fluxes that transmitted through each of the domains. I is the depolarized light intensity that is transmitted through the sample, and I_0 is the polarized light intensity that is incidental on the sample.

ready reported that the nature of polymer chain terminations may have an effect on the mesomorphic behavior of segmented liquid crystalline polymers. They found out that a systematic reduction of the isotropization temperature for a group of segmented-chain liquid crystal polymers with a degree of polymerization ranging from ~ 6 to ~ 10 as the ratio between aromatic to aliphatic terminal groups increases at constant average molecular weight. Figure 12 illustrates the polarized photomicrographs of the mesophases of the PB (0.5 : 1) and PB (2 : 1) samples as they appear on cooling from the isotropic phase. Upon cooling of the isotropic melt of PB (0.5 : 1), the nematic

phase begins to separate at the clearing point in the form of typical droplets that, after further cooling, grow and coalesce to form large domains. As can be seen in Figure 12(a), the disclinations in the PB (0.5 : 1) sample produce the characteristic Schlieren with dark brushes that join at certain points. In contrast, the mesophase in the PB (2 : 1) sample appears as elongated particles reminiscent of the batonnets seen in the conventional smectic phase [Fig. 12(b)].

Surprisingly, our observations identify that poly(4, 4'-diphenyl sebacate), contrary to Blumstien and co-workers⁹ and Krigbaum and colleagues⁶ who suggested that this polymer in different molecular weights is always smectogenic, may appear as nematic texture in some cases. In fact, the chemical structure ordering of poly(4, 4'-diphenyl sebacate) plays an important role in its liquid crystalline behavior. On the other hand, this explanation can demonstrate that the observations that were made by Strzelecki and Van Luyen,¹⁰ in some conditions, could not be wrong. These authors reported that poly(4, 4'-diphenyl sebacate) is nematic. The PB (0.5 : 1) sample contains polymer chains that have the mesogenic sequence as terminal groups, while the PB (2 : 1) sample is composed of chains with the flexible spacer as terminal groups. Therefore, it is plausible to expect that the clearing temperature of PB (0.5 : 1) shows a great difference in comparison to the PB (2 : 1) sample. On the other hand, the decrease of the isotropization temperatures of the samples with the number of moles of sebacoyl chloride in excess exhibits that the range of the molecular weight of the homologous series of PB ($n : m$) is below 10,000 units.²⁹

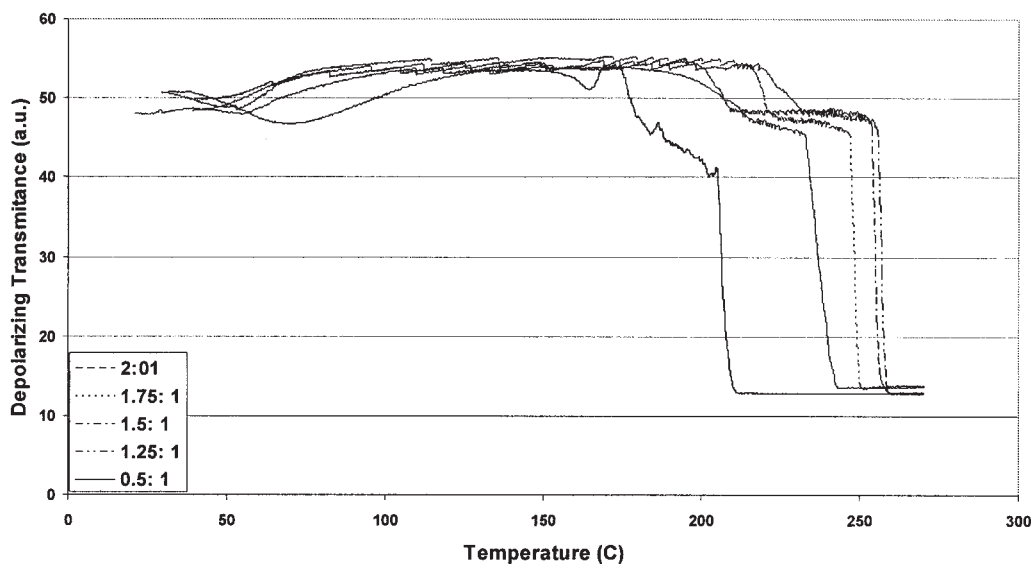


Figure 10 The depolarizing transmittance plots of the homologous series of PB ($n : m$) samples against temperature.

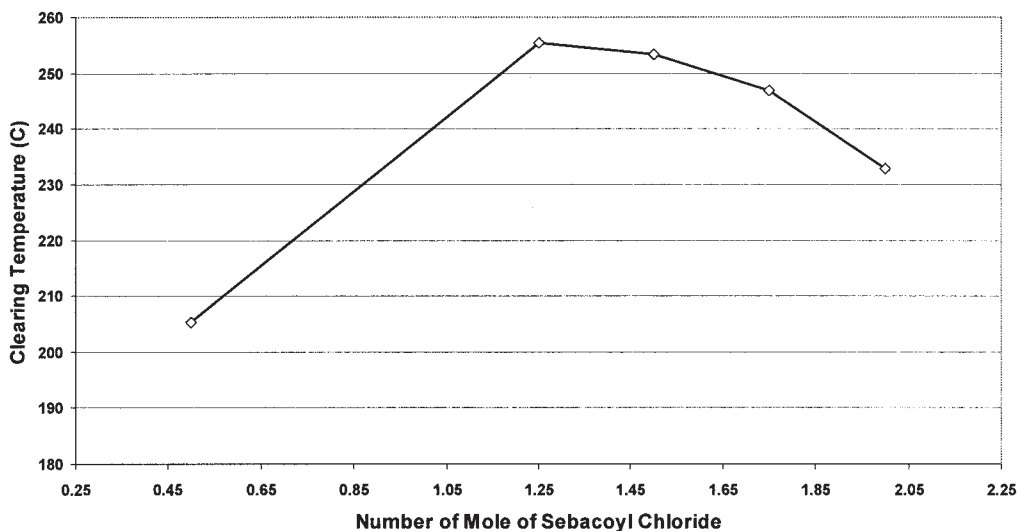
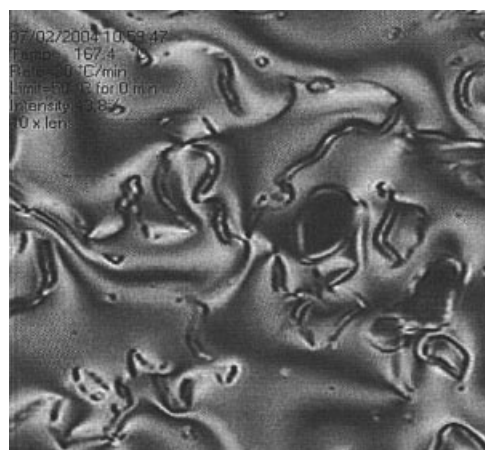


Figure 11 The isotropization temperatures of the homologous series of PB ($n : m$) samples, with different numbers of moles of sebacoyl chloride.

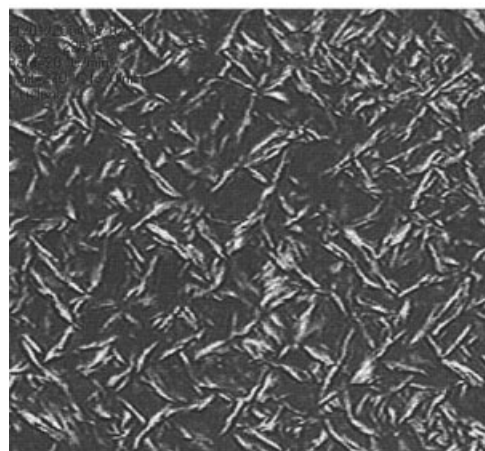
Structural, thermal, and mesomorphic properties

We shall next describe the structural features and the behavior of the liquid crystallinity of the synthesized polyesters. The infrared spectrum of PB (1.5 : 1) is presented in Figure 13. The important feature of the FTIR spectrum of PB (1.5 : 1) is the broad band characteristic of the OH group extending from 3200 cm^{-1} to 3400 cm^{-1} . The absorptions around 3040 , 2926 , and 2851 cm^{-1} are attributed to aromatic CH stretching and asymmetrical and symmetrical CH stretching in CH_2 , respectively. The ester carbonyl band appears at 1754 cm^{-1} in the spectrum of PB (1.5 : 1). On the lower frequency side of the ester carbonyl band, there is an inflection, which can be assigned to the carbonyl group of terminal COOH groups of each polymer chain (1707 cm^{-1}).

The result of elemental analysis of PB (1.5 : 1) is: C (74.67%), H (6.36%), and N (0%). Figure 14 shows the DSC curve and the temperature dependence of the depolarizing transmittance of the PB (1.5 : 1) sample in two forms (pressed powder and melted). A total of four endothermic peaks can be observed at $155\text{--}160$, $180\text{--}185$, $205\text{--}210$, and $230\text{--}260^\circ\text{C}$. The transmittance quickly starts to increase at around the DSC peak temperature of $205\text{--}210^\circ\text{C}$, while above 235°C (in the pressed powder form) it reaches a maximum and then decreases rapidly. In the melted form, the sample at around 232°C transformed to a biphasic state and finally began to show its isotropic state at 252.9°C . In combination with optical microscopic observation, PB (1.5 : 1) melts and transforms from the crystalline to the smectic state, which starts at about 206°C and completed at about 255°C , and then transforms from the smectic to the isotropic state in roughly a sharp manner. As illustrated for PB (1.5 : 1) in Figure 15, the



(A)



(B)

Figure 12 The polarized photomicrographs of mesophases of PB (0.5 : 1) (a) and PB (2 : 1) (b) samples, magnification $100\times$.

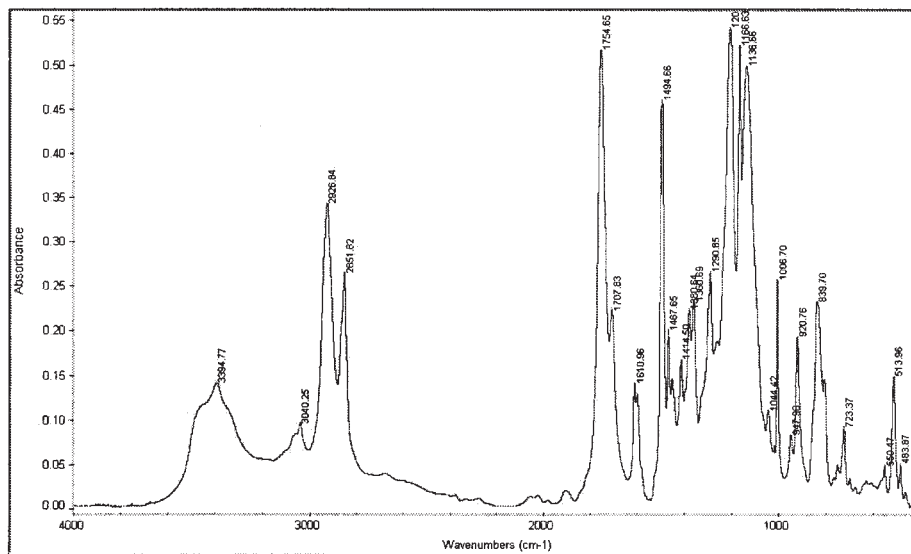


Figure 13 FTIR spectrum of PB (1.5 : 1).

birefringent texture is apparent. Elongated particles, reminiscent of the batonnets seen in conventional smectics, are observed for PB (1.5 : 1).

The observed small changes in the depolarizing transmittance of PB (1.5 : 1) correspond to the peaks on the lower temperature side (155–160 and 180–185°C). These transitions in DSC tracing can be attributed to a partial melting or a phase transition in the solid state.

Referring to Figure 14, the DSC thermogram of PB (1.5 : 1) has a broad endothermic peak around 230–260°C, which is related to the transition from the

anisotropic to the isotropic state. On the other hand, it also has some additional peaks on the lower temperature side. This thermal behavior was already observed by Krigbaum and coworkers.⁶ They suggested that the endothermic peaks of poly (4,4'-biphenyl sebacate) are broad for samples having inherent viscosity less than 0.4 dL/g. PB (1.5 : 1), in our work, in contrast to similar samples with the same inherent viscosity (0.18 dL/g), which were prepared through melt condensation (*trans*-esterification), was synthesized at low temperature (10–15°C); therefore, it has

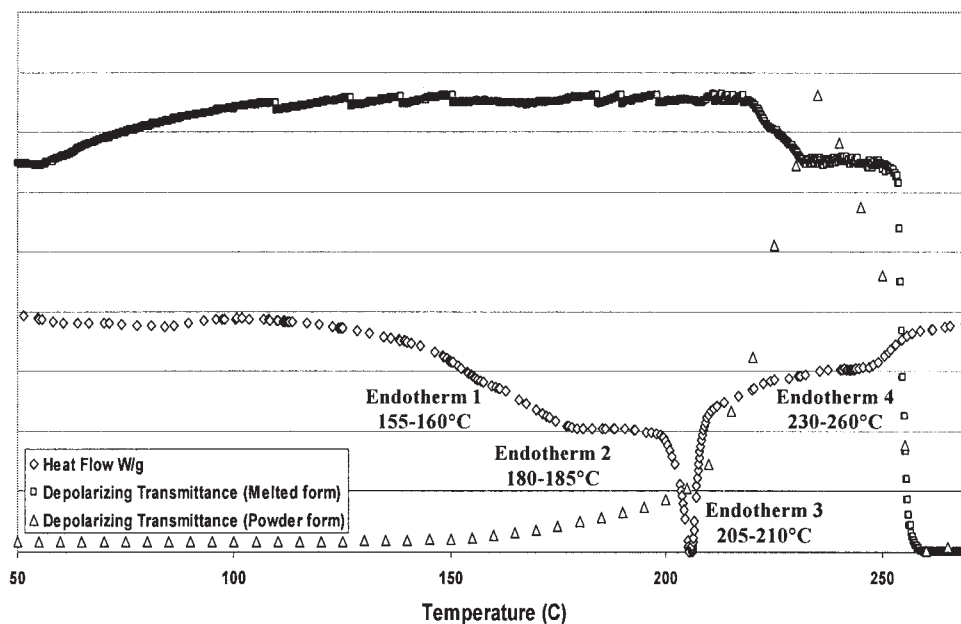


Figure 14 DSC heating curve (\diamond) and depolarizing transmittance (melted form) (\square) and depolarizing transmittance (powder form) (\blacktriangle) of PB (1.5 : 1), heating rate 10°C/min.

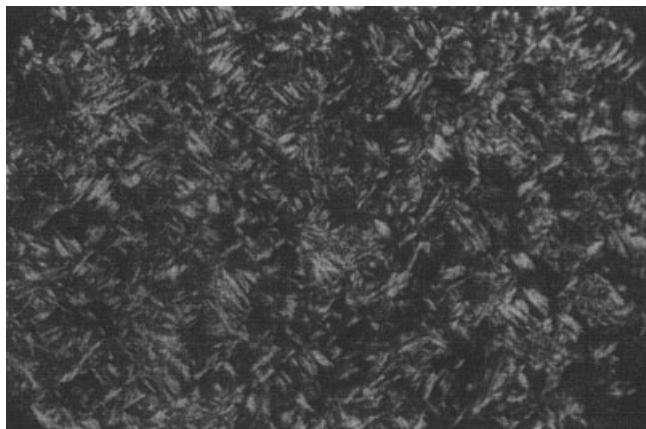


Figure 15 Polarized photomicrograph of PB (1.5 : 1), magnification 100 \times .

experienced a different thermal history than them. To clarify the effect of this difference on the thermal behavior of PB (1.5 : 1), whether it has any effect on their thermal behavior, we have annealed the sample at 270 $^{\circ}$ C (above the isotropization temperature). There were no considerable changes in the DSC tracing of the annealed sample in comparison with the sample without any thermal treatment.

Figure 16 shows a diffractogram obtained by a wide-angle X-ray diffractometer for PB (1.5 : 1), which exhibited sharp diffracted peaks. There are five outer reflections corresponding to Bragg spacing of 4.1136, 4.1592, 4.2720, 4.3105, and 4.3529 \AA .

The sharp reflection peaks are found in the diffraction diagram of PB (1.5 : 1) at room temperature, indicating a high degree of crystallinity. The degree of crystallinity of PB (1.5 : 1) was calculated according to eq. (7) and was found to be 45–55%.

$$D_c = S_c / (S_c + S_a) \quad (7)$$

Here, S_c is the area of the sharp Bragg reflections corresponding to the crystalline part of the polymer, and S_a is the area of the broad amorphous peak.

CONCLUSIONS

The thermotropic segmented-chain liquid crystalline polyester of 4,4'-dihydroxy biphenyl and sebacoyl chloride was prepared by interfacial polycondensation. On the basis of our experimental data, the best yield for polyesters was obtained by using benzene-hexane (1 : 1) as an organic phase, the volume ratio of the aqueous to the organic phase 1 : 2, temperature of the reaction 10–15 $^{\circ}$ C, the catalyst (benzyl triethyl ammonium chloride) amount of 7.5% by weight of 4,4'-dihydroxy biphenyl, and time of the reaction 60 min.

The experimental results of the effect of the mole ratio of acid chloride to the diol monomer on the molecular weight (inherent viscosity) of the polyesters revealed that the samples, which were synthesized with an excess of sebacoyl chloride, were characterized by higher inherent viscosity than those that were obtained with an excess of 4,4'-dihydroxy biphenyl. On the other hand, our observations revealed that poly(4, 4'-diphenyl sebacate), in contrast to previous reports that suggest this polymer is always smectogenic, could emerge nematic in some cases. Indeed, the chemical structure ordering of poly(4, 4'-diphenyl sebacate) plays a significant role in its liquid crystalline behavior.

Differential scanning calorimetry and polarized optical microscopic studies, along with depolarizing transmittance measurements, demonstrated PB (1.5 : 1), with mole ratio of acid chloride to diol monomer 1.5 : 1, to be smectogenic at a temperature range about 205 to 255 $^{\circ}$ C. X-ray diffraction measurements showed that PB (1.5 : 1) has a high degree of crystallinity, of about 45–50%, at room temperature.

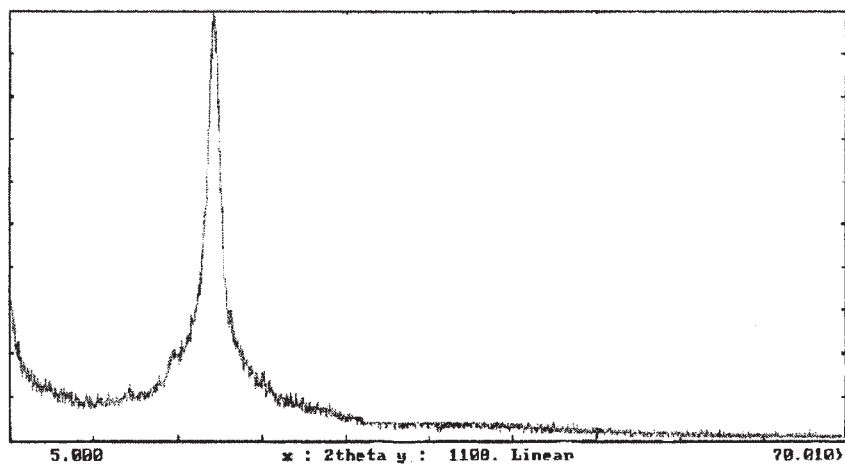


Figure 16 Wide angle X-ray diffractogram of PB (1.5 : 1).

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