

Thermotropic Liquid Crystalline Copolyesters. I. Synthesis and Thermal Characterization of the Copolyesters of Terephthaloyl Chloride, Hydroquinone, and 1,4-Butane Diol

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SYNOPSIS

A new series of random thermotropic liquid crystalline polyesters (LCPs) was synthesized from terephthaloyl chloride, hydroquinone, and 1,4-butane diol. The copolyester composition was varied by changing the relative mole ratio of hydroquinone and 1,4-butane diol in the feed. All the copolyesters displayed thermotropic liquid crystallinity at relatively low temperatures. Liquid crystalline behavior of the copolyesters has been characterized by polarizing light microscopy and by differential scanning calorimetry (DSC). The effect of copolyester composition on the temperature and thermodynamic parameters related to liquid crystalline transition is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Thermotropic liquid crystalline or mesomorphic copolyesters are now commercially established as high-performance engineering polymers.¹⁻⁵ The driving force for the development of such thermotropic copolyester systems⁶⁻⁸ was (i) the clean, safe, and easy processability via conventional molding techniques and (ii) the outstanding balance of mechanical and thermal properties of the finished products.

A majority of the commercially important or academically interesting thermotropic copolyesters are random, wholly or partially aromatic polymers with *p*-oxybenzoate residues in the main chain. Xydar from Amoco and Vectra of Hoechst-Celanese are wholly aromatic, whereas X7G of Tennessee Eastman is partially aromatic. In the former category, introduction of an unsymmetrical aromatic comonomer brings down the mesomorphic transition temperature to within the normal operating range of a conventional molding equipment. Partially aromatic or semiflexible liquid crystalline polyesters

(LCPs) owe their origin to the patented research in laboratories of DuPont and Tennessee Eastman as early as 1972.⁹ The basis of this work was the rigid rod-flexible spacer concept. These systems have the virtue of lower transition temperatures that can be manipulated by the nature and mole fraction of flexible spacers. The particular choice of *p*-hydroxybenzoic acid as one rigid monomer in commercial thermotropic polyesters has been due to its ready availability and relatively low cost. The use of this monomer in academic research has been due primarily to its ability to generate a given kind of mesogen in the repeat unit of main-chain thermotropic LCPs.

Our aim here has been to develop a novel, new series of random, semiflexible thermotropic copolyesters that are devoid of *p*-oxybenzoate sequences and to study their mesomorphic properties.

This paper deals with the synthesis and thermal characterization of a copolyester system based on terephthaloyl chloride (TPC), hydroquinone (HQ), and 1,4-butane diol (BD). Five different mole ratios of HQ (the rigid diol) to BD (the flexible diol) were employed to generate five different copolyester structures. The mole ratios of HQ to BD in the feed of diols were 0.75 : 0.25, 0.67 : 0.33, 0.50 : 0.50, 0.33 : 0.67, and 0.25 : 0.75.

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EXPERIMENTAL

Materials

Pyridine (Py) and 1,2-dichloroethane (DCE) (both from S. D. Fine-Chem., India) were distilled with the careful exclusion of moisture and stored over activated 4 Å molecular sieves. Pyridine was used as the HCl acceptor, and DCE, as the solvent in the solution polycondensation.

Terephthaloyl chloride (TPC) was synthesized by appropriately modifying an established standard procedure.¹⁰ A 1M stock solution of pure TPC was prepared in DCE for use.

Hydroquinone and 1,4-butane diol (both from Fluka AG, Switzerland) were used after extensive drying. A 1M solution of each diol was prepared in a mixed solvent system containing 16 : 9 (v/v) pyridine and DCE just before synthesis for immediate use.

Copolymer Synthesis

All glassware used in the synthesis work was flame-dried. Copolyesters were synthesized via a room temperature solution polycondensation route in which aliphatic and aromatic diols were added sequentially. A typical polycondensation reaction is described below.

TPC stock solution (60 mL; 0.06 mol) was taken in an Erlenmeyer flask. BD stock solution (V mL; Y mol) was added dropwise to it. The flask was stoppered airtight and left aside for 24 h at room temperature (25°C). A prepolymer with acid chloride end groups was thus prepared. It was reacted *in situ* in the next stage with HQ stock solution [(60- V) mL, (0.06- Y) mol] for another 24 h to form a random copolyester.

The values of V and Y are shown in Table I. The value of Y was varied such that the BD/HQ mole ratios in the feed of diols were 0.25/0.75, 0.33/0.67, 0.50/0.50, 0.67/0.33, and 0.75/0.25. The corresponding copolyesters were designated as HB II, III, IV, V, and VI.

At the end of the second stage, the copolyesters were found to separate out partially from the reaction medium. The reaction products were poured into a fivefold excess of methanol to precipitate out the polymers completely. The copolyesters thus obtained were then freed from traces of pyridine and unreacted monomers, if any, by repeated washing with a 5 wt % aqueous solution of sodium bicarbonate followed by distilled water. The copolyesters were dried in a vacuum oven at 50°C for 2 days. The two-

Table I Stoichiometric Details: Synthesis of HB Copolyesters

Copolyester	Weight in g of			
	HQ	BD	Y	V
HB II	1.6512	4.0560	0.045	45.0
HB III	2.2020	3.6048	0.040	40.0
HB IV	3.3036	2.7036	0.030	30.0
HB V	4.4040	1.8024	0.020	20.0
HB VI	4.9548	1.3524	0.015	15.0

Y = moles of 1,4-butane diol (BD). V = mL of 1M solution of BD. 60 V = mL of 1M solution of hydroquinone (HQ) added.

stage reaction scheme adopted here is outlined in Figure 1.

Thermal Characterization

The copolyesters were examined under a polarizing microscope equipped with a Koffler hot stage. A small amount of an HB copolyester was mounted between a glass slide and a cover slip and heated on the Koffler stage at a constant rate. The mesomorphic transition temperature (T_m) was noted. It is the temperature at which both the fluidity and birefringence (optical texture) began to manifest under a cross-polarized light. The disappearance of birefringence (termed isotropization) was not observable for any of the copolyesters within 325°C (upper working limit of the hot stage).

DSC scans were obtained with a Mettler DSC-30 apparatus interfaced with a thermal analysis data station. A sample size of 5–10 mg was used. The samples were sealed hermetically in standard aluminum pans of comparable mass to the pan used for the reference. All runs were performed at a heating rate of 10 K/min in a dry nitrogen atmosphere. Pure indium was used to calibrate the enthalpy scale, and a standard alloy of In—Pb—Zn, the temperature scale of the DSC. Peak values of the endotherms were determined. Heats and entropies of the melting transitions were estimated on the basis of molar mass of repeat unit (mru). The molar masses of the average repeat units of HB copolyesters II, III, IV, V, and VI are calculated to be 235.2, 233.6, 230.2, 226.8, and 225.2 g/mol, respectively.

RESULTS AND DISCUSSION

Synthesis of Copolyesters

The room-temperature solution polycondensation between TPC and HQ produces a mesogenic inter-

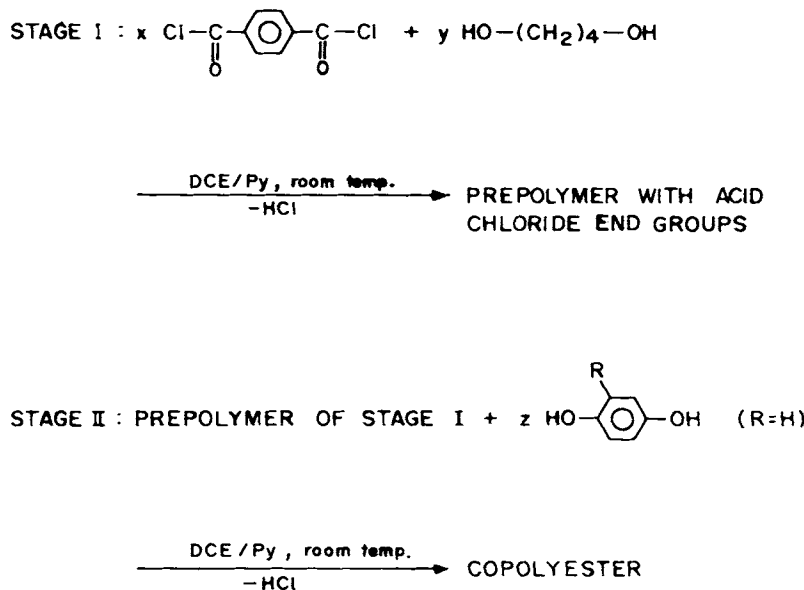


Figure 1 Two-stage copolyester synthesis scheme.

mediate with acid chloride end groups. This intermediate on subsequent *in situ* reaction with BD yielded copolyesters that decomposed at elevated temperatures without melting.¹¹ Another solution polycondensation strategy of simultaneously adding the two diols to TPC resulted in similar nonmelting copolyesters. Larger blocks of TPC and HQ were formed owing to greater reactivity of HQ toward the acid chloride.¹² The polycondensation between TPC and HQ generates a polyester with the liquid crystalline transition temperature above the decomposition temperature. The polymer is insoluble and infusible and decomposes above 600°C.¹³ Copolyesters displaying thermotropicity at lower temperatures were obtained only when a reactive intermediate (prepolymer) was generated from the acid chloride and the aliphatic diol prior to its reaction with HQ *in situ*. The globally averaged structures for the repeat units of these copolyesters are shown in Figure 2. The semiflexible liquid crystalline copolyesters synthesized by us do not conform to the well-defined rigid rod-flexible spacer-type liquid crystalline polymers reported by other research groups.¹⁴⁻¹⁷ The reasons are the following: (i) The directional order of —COO— group positioning is random along the chain of any copolyester. (ii) In a given copolyester composition, there is wide distribution of rigid rod lengths, with a mean around the structure as shown in Figure 2.

Going by the reaction scheme adopted by us, one would expect the synthesized copolyesters to possess predominantly a structure similar to the structures

depicted in Figure 2. Below 50 mol % of the flexible diol in the feed, the prepolymer mix would tend to contain unreacted TPC in higher fractions. When HQ is added to this homogeneous prepolymer mix, one cannot rule out the growth of HQ-TPC-HQ coupled species into a rigid-rodlike polymer, apart from the designed semiflexible polymer species. It is difficult to estimate on a theoretical basis the probability of such growth in this complicated reaction system. Judging from the polarizing microscopic observations, we can say that the probability was extremely small. The presence of nonmelting species (rigid-rodlike polymer from HQ-TPC-HQ) would appear as crystalline specks floating in a birefringent fluid. Such specks were virtually absent for copolyesters II and III, wherein the probability of formation of such rigid-rodlike polyesters does exist. There is, however, very little doubt that the mesogen and the flexible spacer are randomly arranged along the chain.

All the copolyesters were found insoluble in common organic solvents, limiting the study of their solution properties and molecular weight estimations, etc.

Polarizing Microscopy

The transition temperatures, T_m , of the copolyesters are presented in Table II. There is an increase in T_m with increasing HQ content. The isotropization temperature in each case was over 325°C (the upper working limit of the hot stage). The temperature

AVERAGED STRUCTURE	HQ	BD	TA	HB COPOLYESTER DESIGNATION
	0.75	0.25	1.00	II
	0.67	0.33	1.00	III
	0.50	0.50	1.00	IV
	0.33	0.67	1.00	V
	0.25	0.75	1.00	VI

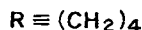


Figure 2 Statistically averaged structures of the HB copolyester.

range, ΔT , over which the mesophases are stable, was then quite broad. Also, the liquid crystallinity was observed even at a level of the flexible spacer as high as 37.5 mol % (corresponding to 75 mol % in the feed of diols), which is usually not possible with a normal rigid rod-flexible spacer-type polymer. Regular textures due to a specific mesophase type are observable in a thermotropic liquid crystalline polymer upon cooling the isotropic melt in a controlled manner, holding the melt isothermally at specific temperatures in the liquid crystalline state for sufficiently long times and then observing it under cross-polarized light. In the present study, such

observations could not be made owing to decomposition accompanying isotropization. However, the specimens were found to be extremely free flowing in the liquid crystalline state. This fluidity would normally arise from a nematic state.

DSC Analysis

Typical DSC traces for HB copolyesters II, III, IV, V, and VI in the first heating cycle are shown in Figure 3. The DSC traces in the first heating cycle were taken for comparison here because the polymers, being the products of a low-temperature solution polycondensation, are expected to possess similar thermomechanical histories during the synthesis stage. Table II lists transition temperatures and thermodynamic data for these copolyesters, as determined from the DSC melt endotherms. We have assumed the transitions to be near equilibrium.

In the DSC thermograms of HB copolyesters II and III, multiple endotherms are observed. This complex thermal behavior has been reported for other thermotropic LCPs with mesogenic units connected by flexible spacers in the main chain.¹⁸ The factors responsible are crystal-crystal transitions, succession of various polymorphic crystal meltings, or reorganizations of preformed imperfect crystals.¹⁸ The very first small endothermic peak (between 142

Table II Transition Temperatures and Thermodynamic Data for HB Copolyesters^a

Copolyester	T_m^b	T_m^c	ΔH_m^d	ΔS_m
HB II	302.8	310.0	6.60	11.46
HB III	284.8	294.0	1.68	3.02
HB IV	202.7	185.0	3.30	6.92
HB V	208.6	179.0	10.52	21.80
HB VI	208.6	174.0	12.46	25.80

^a T values in °C. ΔH_m and ΔS_m values are in KJ/mru and $J/(\text{mru}) \times (\text{K})$, respectively.

^b Peak value of crystal-to-mesophase transition.

^c T values in °C as determined by polarizing microscope.

^d Sum total of ΔH values in crystal-mesophase transition.

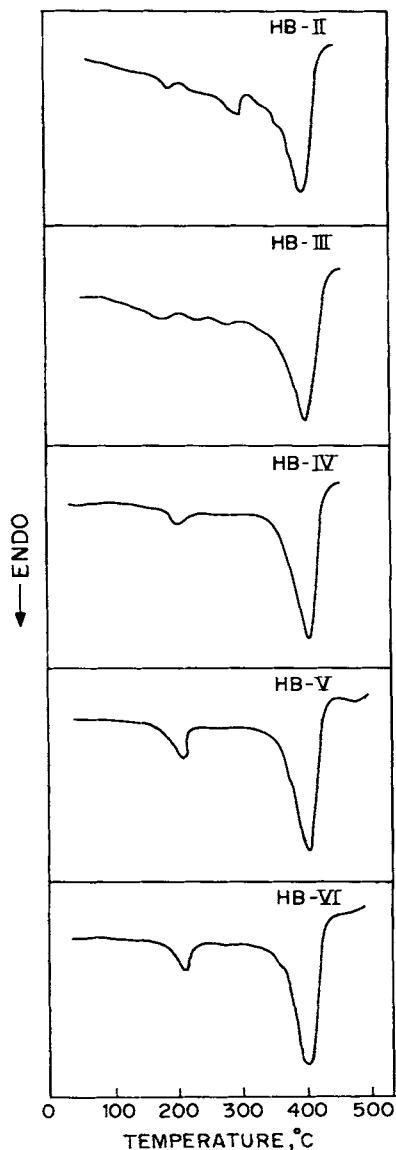


Figure 3 Typical DSC thermograms of HB copolyesters for the first heating cycle.

and 166°C) in the DSC heating curves of these copolyesters is due to the formation of new crystal modifications. No mesomorphic textures were noticeable in this temperature range. Instead, the solid particles glowed. The multiplicity in the melting endotherm was not present in the other three copolyesters where the greater amount of flexible spacers have simplified the crystallite structure.

The peak temperature value of the liquid crystalline endotherm is lowest for copolyester IV, where rigid and flexible diols are equimolar. The occurrence of such a melting-point minimum or an eutectic for the melting transition has earlier been observed in other liquid crystalline polymer systems.^{15,19} The

chains of a semiflexible LCP composition with an equimolar or near equimolar proportion of flexible and corresponding rigid monomers are structurally most random and disordered. Their packing in the solid state therefore becomes least efficient. The LCP system showing an eutectic for the melting transition does not favor cocrystallization of mesogenic units and flexible spacers into a lattice owing to greater differences in their types.²⁰ In the present system, these differences between mesogenic units and flexible spacers have arisen in respect of not only types but lengths also, by varying the composition of the two diols in the feed (Fig. 2). The liquid crystalline endotherms for copolyesters V and VI have the same peak temperature value. This is because the mean mesogenic length responsible for the transition is almost the same in the two cases.

The isotropization in all the cases may have superimposed with the polymer degradation. In fact, the last large peak in all the DSC heating traces can arise out of such superimposition.

The transition enthalpy and entropy of the copolyesters were found to display eutectic behavior, however, with the minima at HB copolyester III. The energy of interaction between polymer chains in the crystalline phase is reflected in the transition enthalpy, ΔH_m . With a higher amount of BD (> 50 mol %) in the diol feed, the spacer segment comprises more and more of butylene terephthalate moieties. This leads to higher chain extension and packing of the spacer part. The much higher ΔH_m for copolyesters V and VI can be attributed to such spacer extension and packing. In the present copolyester system, not only did the relative length of rigid and flexible segments vary but also the type of flexible spacer, upon simply altering the relative mole ratio of the two diols. All these factors have given rise to an interesting set of thermal properties for these *p*-oxybenzoate-free copolyesters.

It is therefore expected, from the thermal characteristics, that copolyester IV would be economical and easier to process from the liquid crystalline melt. This copolyester is endowed with the lowest T_m (202.7°C), a lower ΔH_m (3.30 KJ/mru), and a wider mesophase stability (at least 100°C) before isotropization and decomposition.

CONCLUSION

A series of five random aliphatic-aromatic copolyesters were synthesized by a sequential addition polycondensation methodology. The copolyesters displayed thermotropic character over a wide temper-

ature range and decomposed prior to isotropization. The system differs from conventional rigid rod-flexible spacer-type copolyesters in that the flexible spacer component consisted of crystalline aliphatic-aromatic ester (butylene terephthalate) moieties. The thermotropic character is retained even at a very high dilution of the mesogen, which is not observable in ordered copolyester systems.

REFERENCES

1. A. Blumstein, Ed., *Polymeric Liquid Crystals*, Plenum Press, New York, 1985.
2. L. L. Chapoy, Ed., *Recent Advances in Liquid Crystalline Polymers*, Elsevier, London, 1985.
3. G. W. Calundann, in *High Performance Polymers: Their Origin and Development*, R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier, London, 1986, p. 235.
4. T.-S. Chung, *Polym. Eng. Sci.*, **26**, 901 (1986).
5. S. I. Stupp, *Chem. Eng. Prog.*, **Dec.**, 17 (1987).
6. G. W. Calundann, in *Proceedings of the Robert A. Welch Conferences on Chemical Research XXVI, Synthetic Polymers*, 1982.
7. M. G. Dobb and J. E. McIntyre, *Adv. Polym. Sci.*, **60/61**, 61 (1984).
8. S. L. Kwolek, P. W. Morgan, J. R. Schaeffgen, and L. W. Gulrich, *Macromolecules*, **10**, 1390 (1977).
9. J. L. White, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **41**, 3 (1985).
10. W. R. Sorenson and T. W. Campbell, *Preparative Methods in Polymer Chemistry*, 2nd ed., Interscience, New York, 1968, p. 95.
11. C. Aguilera and I. Luderwald, *Makromol. Chem.*, **179**, 2817 (1978).
12. R. S. Ghadage, PhD Thesis, Department of Chemistry, University of Poona, India, 1989, p. 91.
13. S. G. Cottis, J. Economy, and L. C. Wohrer, Ger. Pat. 2,248,127 (1973); 2,507,066 (1976).
14. C. K. Ober, J.-I. Jin, and R. W. Lenz, *Makromol. Chem. Rapid Commun.*, **4**, 49 (1983).
15. A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough, and R. B. Blumstein, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 877 (1982).
16. W. R. Krigbaum, J. Watanabe, and T. Ishikawa, *Macromolecules*, **16**, 1271 (1983).
17. A. Roviello and A. Sirigu, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 455 (1975).
18. C. K. Ober, J.-I. Jin, and R. W. Lenz, *Adv. Polym. Sci.*, **59**, 1003 (1984).
19. Q. F. Zhou, J.-I. Jin, and R. W. Lenz, *Can. J. Chem.*, **63**, 181 (1985).
20. C. K. Ober and T. L. Bluhm, in *Current Topics in Polymer Science*, R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Eds., Hansser, New York, 1987, Vol. I, p. 249.

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