

Thermotropic Mesomorphic Polyesters. I. Copolyesters of Terephthalic Acid, Hydroquinone, and Flexible Diols

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Synopsis

A new series of copolyesters has been synthesized by low-temperature solution polycondensation of terephthaloyl dichloride hydroquinone and flexible diols such as 1,2-propane diol, 1,4-butanediol, diethylene glycol, (*cis*) 1,4-cyclohexanediol and (*cis* + *trans*) 1,4-*bis*(hydroxymethyl) cyclohexane. The copolyesters are all insoluble and display thermotropic mesophases at relatively lower transitions than other commercially important systems. The transition temperatures, the crystallinity, and thermal characterization are reported.

INTRODUCTION

Thermotropic liquid crystalline polymers are a relatively new class of high performance materials that have received considerable attention recently.¹⁻¹⁸ Rigid polymers like poly(hydroquinone terephthalate) are nonmesomorphic with decomposition temperature in excess of 500°C and are not melt processable.¹⁹ Major interest of polymer scientists lies in structurally modifying these to generate melt-processable mesophasic polymers.

A variety of approaches have been applied to reduce the crystal perfection and the crystal lattice energy with the specific objective to decrease the melting ranges of these rigid rod polymers and to generate thermotropic mesophasic liquid crystalline polymers. These have included the use of non-rigid groups (flexible spacers) in the main chain to reduce the aspect ratio of mesogen,²⁰ the placement of substituents on the mesogenic group to disrupt regularity of the repeating units,²¹ the use of nonlinear cycloaliphatic comonomers (Kinks)^{22,23} and crankshaft monomers (2,6-disubstituted naphthalene).²⁴ The copolymerization of different mesogens,²⁵ differently substituted mesogens²⁶ and altering the synthetic route are the alternate strategies to decrease the mesogenic transition temperature of thermotropic polymers. Copolymers with random placement of repeat units have lower transition temperatures than ordered copolymers.²⁷

We are interested in the development of commercially viable thermotropic mesophasic polymers with lower mesomorphic transition temperatures than those reported in patent literature. In this communication we report the synthesis of a new series of low melting thermotropic mesophasic copolyesters from terephthaloyl dichloride, and equimolar quantities of hydroquinone and

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flexible diols such as 1,2-propanediol, 1,4-butanediol, diethylene glycol, (*cis*) 1,4-dihydroxycyclohexane and (*cis* + *trans*) 1,4-*bis*(hydroxymethyl) cyclohexane. The transition temperatures, thermal stability in air, and crystallinity data are also reported.

EXPERIMENTAL

Monomer Synthesis and Purification

Terephthaloyl dichloride was synthesized and recrystallized by standard procedure.²⁸ 1,2-Propanediol, diethylene glycol, and 1,4-butanediol were dried over activated 4Å molecular sieves for a few days before use. *Cis* 1,4-dihydroxy cyclohexane was dried in desiccator over potassium hydroxide pellets. Methanol present in 1,4-*bis*(hydroxymethyl) cyclohexane (*cis* + *trans*) was distilled off azeotropically with toluene and dried before use. Dichloroethane (DCE) used as solvent, pyridine used as acid acceptor, and hydroquinone were purified by standard methods.

Polymer Synthesis

The polymers were synthesized by low-temperature solution polycondensation. Terephthaloyl dichloride (10 mmol) was dissolved in 40 mL of dry dichloroethane (DCE) in a stoppered conical flask. Then, 5 mmol of the flexible diol dissolved in DCE/pyridine 1/1 v/v mixed solvent system was added dropwise to the acid chloride solution with stirring, and allowed to react at room temperature (25°C) to form the prepolymer. After 24 h, hydroquinone (5 mmol) dissolved in 20 mL of DCE/pyridine solvent system was added to the reaction mixture and stirred for an additional 24 h at room temperature (25°C) to form the copolyester. The copolyesters precipitated out during the second stage of the polyesterification reaction. The precipitate was poured into fivefold excess of methanol, to quantitatively precipitate the copolyester, filtered, and dried to a constant weight in vacuum oven at 50°C, for 4 h.

Polymer Characterization

The thermogravimetric analysis of the copolyesters (20–25 mg) were evaluated in air with a Netzsch STA-409 thermal analyzer at a heating rate of 10°C/min. The mesomorphic temperature of the copolyesters were observed on a Koffler hot-stage polarizing microscope. The polymer sample was placed between glass slides and heated at a constant rate. The wide-angle X-ray scattering patterns of the copolyesters, in the as-precipitated state, were scanned at a rate of 2000 cps between 2θ range of 5° to 40°. Scans of intensity versus 2θ were obtained. Copolyesters used for the study were in the form of powders.

RESULTS AND DISCUSSIONS

Random copolyesters can be prepared by solution polycondensation by simultaneous and sequential addition. In the present system, terephthaloyl dichloride, hydroquinone, and an additional flexible diol are the reactants.

Hydroquinone and flexible diol could be added simultaneously, or sequentially to the terephthaloyl dichloride solution to form the copolyester. In sequential addition either hydroquinone or the flexible diol could be added first. We observed that simultaneous addition of both diols, as well as initial reaction of the acid chloride with hydroquinone, results in nonmelting polyesters that decomposed at elevated temperature ($> 400^{\circ}\text{C}$). Independently, in separate experiments to prepare homopolyesters of terephthaloyl dichloride with the flexible diols and hydroquinone by low-temperature solution polycondensation, we have determined that hydroquinone is more reactive toward terephthaloyl dichloride than the flexible diol. Also, the homopolyester of the rigid diol with terephthaloyl dichloride precipitated out while those of the flexible diols remained in solution. The polyesterification of terephthaloyl dichloride with hydroquinone was completed in 5 min, while that between terephthaloyl dichloride and flexible diols needed several hours, at room temperature.²⁹ Thus, simultaneous addition of hydroquinone and flexible diol to a solution of terephthaloyl dichloride results in long rigid blocks of the rigid diol and acid, thereby resulting in copolyesters which do not display mesomorphism. Hence, in the synthesis experiments, flexible diols were reacted with terephthaloyl dichloride first to form oligomers with acid chloride end groups interposed by flexible diol moieties. Hydroquinone was then allowed to react with oligomeric diacid chloride to complete the copolyesterification. The copolyesters synthesized would have a predominantly ordered structure of the flexible diol-diacid-rigid diol-diacid, with a partial randomization of the diol distributions along the polymer chain. The molar average of these correspond to that schematically shown in Table I. A number of mixed solvent systems are known that solubilize main chain rigid rod-flexible spacer-type mesophasic thermotropic polyesters.³⁰ Copolyesters synthesized in this study did not dissolve in any of these solvents. Thus, their inherent insolubility has commercial importance, as the polymers are resistant to chemical environments. It is reported that the number-average molecular weights of thermotropic polyesters, prepared by low-temperature solution polyesterifications, are in the range of 4000–12000.³¹ The copolyesters in this study tended to precipitate out during polyesterification. Thus, the polyesters are essentially oligomers⁹ and the molecular weight distribution will be very wide.

Our objective is to develop thermotropic polyesters with low crystal to mesophasic transition temperatures ($< 275^{\circ}\text{C}$) that will be amenable to conventional processing equipment used for other engineering thermoplastics. Thermotropic mesophasic polymers display extensive shear thinning in the mesophasic state resulting in parallel-oriented domains. The materials developed by processing in this state exhibit superior performances over that of the same polymer processed in the isotropic state.¹³ The mesophase to isotropic transition temperatures of thermotropic copolyesters vary linearly with comonomer compositions between the clearing temperatures of the corresponding homopolyesters.³² However, the crystal to mesomorphic transition temperatures deviate from ideality. This transition temperature is the lowest for copolyesters with equimolar compositions (50/50).^{26,32} Generally at this composition, the mesophase formed is stable over a much broader temperature range.²⁶ The minimum observed at this composition is due to the extensive disruption of the crystal lattice. The rigid rod polyester, poly(hydro-

TABLE I
Synthesis and Characterization of Copolyesters

No.	Copolyester code	Polymer structure	Flexible Spacer R	Temperatures (°C)	
				T_m^a	T_d^b
1	PQT ^c			> 400	> 400
2	I	do		276	> 360
3	II	do		250	283
4	III	do		252	325
5	IV	do		284	> 360
6	V	do	 (cis + trans)	245	272

^a Crystal to mesophasic transition temperatures.

^b Temperature at which decomposition starts.

^c PQT = poly(oxy-1,4-phenylene oxy carbonyl-1,4-phenylene carbonyl).

quinone terephthalate), melts with decomposition above 500°C ,¹⁹ without displaying mesomorphism. Modification of this homopolyester by the incorporation of flexible diol results in considerable lowering of its clearing temperature and mesophases are observed, as seen from Table I. The crystal to mesophasic and mesophasic to isotropic transition temperatures are dependent on number-average molecular weight. Above a critical degree of polymerization, the molecular weight dependence levels off.³² Since our copolyesters were all synthesized under identical reaction conditions, with common rigid diol, the molecular weight distribution in all these copolyesters will be similar. The differences in the mesophase transition temperatures observed (Table I) are due to intrinsic thermal characteristics of the polymers and are influenced by nature of the flexible spacers. The crystal-mesomorphic transition temperatures of the copolyesters vary as follows: $\text{IV} > \text{I} > \text{II} \approx \text{III} > \text{V}$. The random copolyesters display mesomorphic phase over a broader temperature

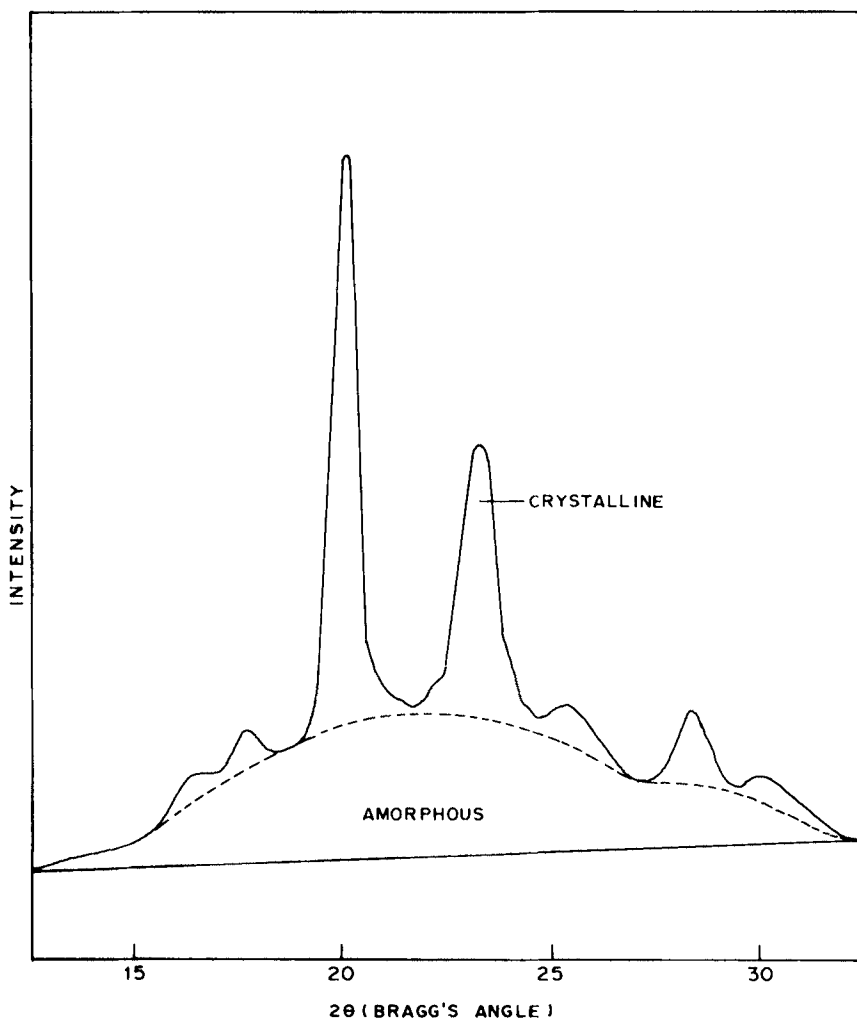
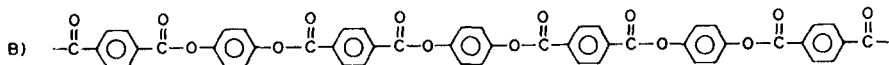
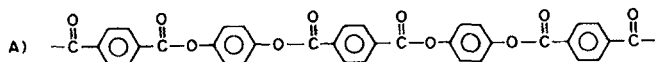


Fig. 1. X-ray diffraction pattern of TA-HQ-BD (50/50) copolyester.

MESOGENS



FLEXIBLE SPACERS

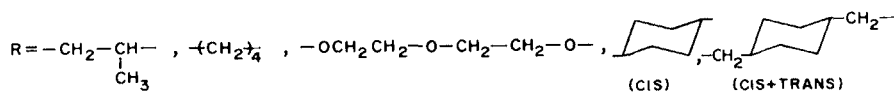
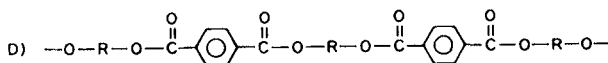
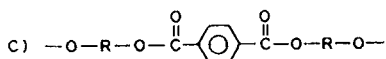


Fig. 2. Mesogens and flexible spacers present in copolyester.

range than that observed for rigid rod-flexible spacer copolyesters of ordered structures.^{26,32} In random copolyesters the mesogenic moiety is not an exact one. In addition to the three-ring systems shown in Figure 1, 5- and 7-ring mesogenic moieties are also present. These larger mesogens presented in Figure 2 will show transitions to mesomorphic state at higher temperatures. These transitions are superimposed on each other resulting in the formation of more stable mesophase. The flexible spacers in random copolyesters do not conform to the aliphatic diol moieties alone. Longer flexible spacers represented in Figure 2 are also probable. These longer spacings induce transition to mesomorphic state at lower temperatures than that observed in commercial system. This enhances the temperature range over which the mesophasic state is stable.

Lenz et al. have reported a number of ordered rigid rod-flexible spacer-type liquid crystalline polyesters with similar mesogenic moieties.²¹ Polycondensation of mesogenic oligomers with similar, but nonmesogenic oligomers have been shown to form liquid crystalline copolyesters with lower phase transition temperatures.²⁶ These are predominantly block copolyesters with a specific mesogenic moiety, unlike the random copolyesters reported in this study. Thus, it is imperative that degree of randomization plays a significant role in determining mesomorphic stability.

In copolyester IV, the ether group of diethylene glycol can take part in hydrogen bonding. This increases crystal lattice energy, thereby shifting its transition to higher temperature. The mesophasic transition temperature of other copolyesters followed the observed trend, copolyester I > II \approx III > V. This is due to increasing dilution of the mesogenic moieties in these copolyesters. Copolyester II and III have similar transition temperatures. Thus, cyclization of aliphatic diols neither decreases the flexible spacer length nor increases the ordered packing. All the copolyesters decomposed before

TABLE II
X-Ray Diffraction Data

Polymer code	Percent crystallinity	<i>d</i> spacings (Å)			
I	51.4	4.51 (s)	3.86 (m)	3.19 (m)	3.00 (m)
II	39.7	4.51 (s)	3.82 (m)	3.17 (m)	2.98 (w)
III	38.9	4.47 (s)	3.84 (m)	3.16 (m)	3.00 (w)
IV	38.7	4.34 (s)	3.80 (m)	3.15 (m)	3.00 (w)
V	30.1	3.78 (w)	3.15 (m)	2.98 (m)	
PQT	53.2				

Abbreviations: s: strong, m: medium, w: weak, PQT: poly(oxy-1,4-phenylene oxy carbonyl-1,4-phenylene carbonyl).

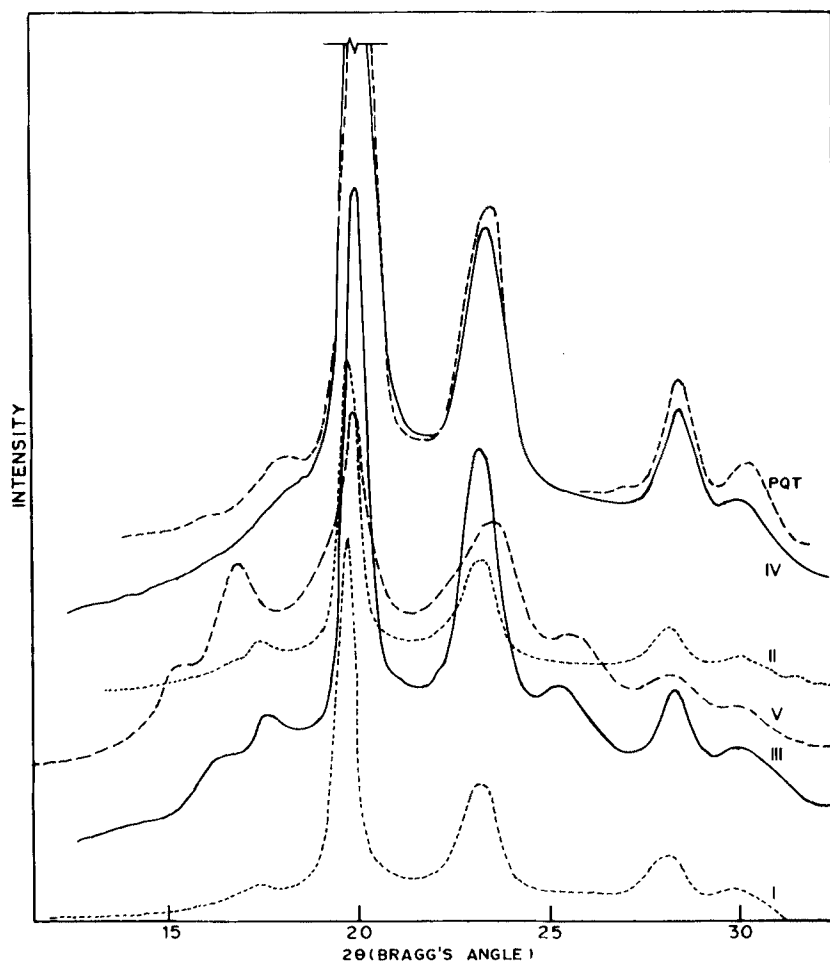


Fig. 3. X-ray diffraction patterns of TA-HQ copolyesters with flexible diols.

isotropization, due to large concentrations of chain ends in these low-molecular weight polyesters.

The copolyesters investigated are all crystalline at room temperature. The degree of crystallinity of the precipitated copolyesters were evaluated at room temperature by taking the ratio of area of crystalline region to the total area³³ as shown in Figure 1. These are presented in Table II (Fig. 3). The ordinate in Figure 3 is an arbitrary scale. To superimpose the scattering pattern observed for the different copolyester in one figure, the respective ordinates have been shifted upward. The percent crystallinity of nonmelting rigid-rod polyester poly(hydroquinone terephthalate), is found to be 53.2 (Table II). To obtain polymers with lower mesophase transition temperatures, the crystal lattice energy and crystallinity need to be reduced. Modification of the rigid-rod polymer by the incorporation of the flexible diols decreased the degree of crystallinity. The crystallinity of the copolyesters follows the trend copolyester I > II \approx III IV > V. The copolyester I has crystallinity similar to the homopolymer PQT (Table II). The methyl group is known to disrupt the chain packing marginally. The Van der Waal radii of methyl group is 2Å and it can be packed between the chains without an appreciable disruption of the

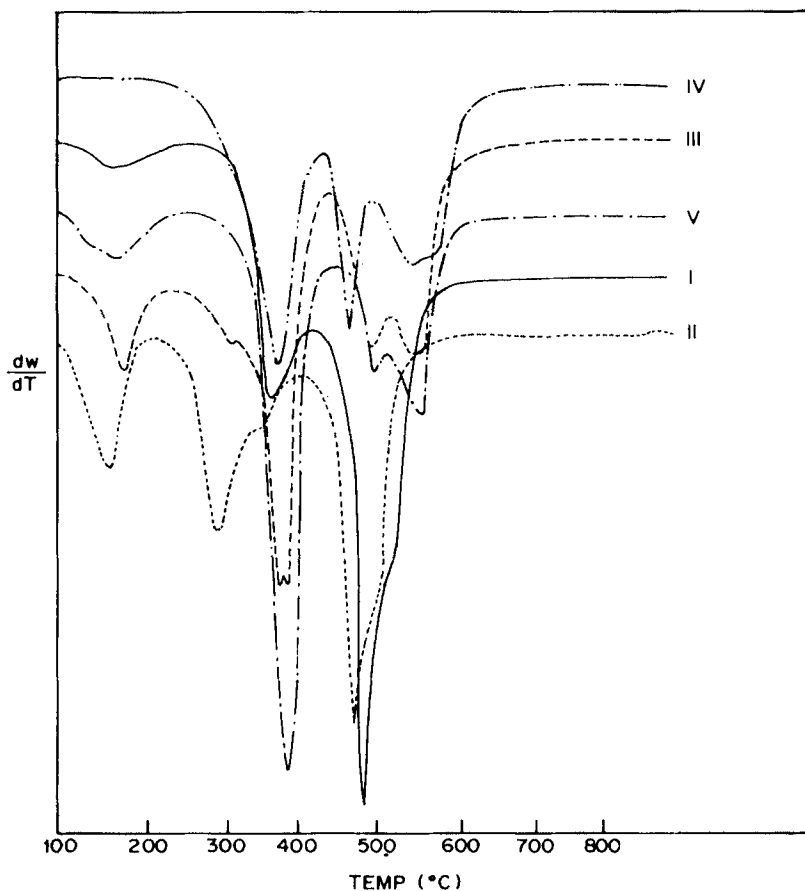


Fig. 4. Differential thermal gravimetric analysis of TA-HQ copolyesters with flexible diols.

TABLE III
Thermal Stability of Copolyesters in Air

Polymer code	Temperature (°C)						600
	300	350	4000	450	500	550	
	Percentage of decomposition						
I	17.2	30.0	34.2	63.5	88.3	90.8	90.8
II	36.5	47.3	47.9	55.8	90.6	90.6	90.6
III	6.0	25.2	51.0	66.1	74.1	95.0	95.0
IV	6.0	25.7	42.8	54.3	66.3	83.1	92.6
V	9.9	20.5	59.3	62.8	75.8	95.0	95.0

crystalline lattice and interchain forces.³⁴ The degree of crystallinity of copolyesters II, III, and IV are lower than that of copolyester I. Of these, copolyester II has *cis* 1,4-disubstituted cyclohexane ring with a restricted rotational freedom, while copolyesters III and IV consist of aliphatic spacers. The linear aliphatic spacers in copolyesters III and IV inherently have a restricted rotational freedom due to the rigid mesogen polyesters. Copolyester V consisting of mixture of *cis* and *trans* isomers of 1,4-*bis*(hydroxymethyl) cyclohexane has the lowest crystallinity. Thus, packing is more extensively disrupted by using mixture of *cis* and *trans* isomers (copolyester V) than by substitution (copolyester I). The *d* spacings and relative intensities observed for these copolyesters are presented in Table II. The effect of annealing on the percent crystallinity of the copolyesters has not been investigated. Further studies with model compounds and homopolyesters are also essential to predict the exact crystal structure.

Thermogravimetric analysis of these polymers were evaluated in air. This determines the maximum use temperature and optimum processing temperatures for these copolyesters. The thermograms are presented in Figure 4. Copolyestification with flexible diols decreases the thermal stability very dramatically. The decomposition profile is complex. It probably involves scission at polymer chain ends. The extent of degradation at different temperatures determined in dynamic mode of 10°C/min are presented in Table III. The contribution of the end groups to the degradation can be decreased by increasing the molecular weight of the copolyesters. The thermal stability of the copolyesters will then be better. Further work is underway to develop high molecular weight copolyesters by acidolysis type transesterification reactions.

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