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Synthesis and characterization of a family of wholly aromatic thermotropic liquid crystalline copolyesters

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SUMMARY

A family of melt processable, wholly-aromatic thermotropic liquid crystal copolyesters are prepared, which are characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry and polarized optical microscopy. The copolyesters exhibit broad nematic-mesophase temperature ranges without isotropic transitions and excellent thermal stability. The kinetics of melt polycondensation of the copolyesters is also investigated.

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) offer great potential in the combination of ease of processability and superior mechanical properties. In order to make TLCPs processable, the polymers are usually modified in several ways, such as copolymerization of different mesogenic monomers; incorporation into the main chain of flexible spacers, bulky side groups, kinks or crankshafts (1-3). Based on copolymerization, kinks or crankshafts seem to be effective and feasible, which has been used in several commercialized TLCPs, such as Xydar and Vectra (4-6). One of the excellent kinks is para-substituted bisphenols which when used in a limited amount, can change the molecular packing, reduce the melting point of the polymer and produce mesophase behavior, with most of the mechanical properties retained (7, 8). In this report, a series of fully aromatic TLCPs are synthesized by polycondensing terephthalic acid (TPA), isophthalic acid (IPA) and p-hydroxybenzoic acid (HBA) with one of the following bisphenols: 4,4'-dihydroxydiphenyl (BP), 4,4'-dihydroxydiphenyl methane (BPM), 4,4'-dihydroxydiphenyl propane (BPA) or 4,4'-dihydroxydiphenyl sulfone (SDP). The mole ratio of HBA/bisphenol/TPA/IPA is 60/20/14/6. The corresponding copolyesters are termed as TIHBP, TIHBPM, TIHBPA and TIHSDP, respectively. The basic mesophase and thermal behavior of the copolyesters are surveyed for further processing application.

EXPERIMENTAL

Synthesis of the Copolyesters

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The hydroxy groups of the monomers were acetylated before polymerization and the copolyesters were prepared by melt transesterification. Adding p-acetoxybenzoic acid, acetylbisphenol, TPA, IPA, zinc acetate and antimony trioxide into a 250-mL three neck flask, the mixture was heated and stirred under a dry nitrogen atmosphere by the use of a salt-bath at 200 ^oC to melt the mixture. The melt was heated from 200 ^oC to 330 ^oC over a period of 250 min, and for 30 min at 330 ^oC with the flask being evacuated to 1 torr, and then flushed with dry nitrogen while being allowed to cool to room temperature. The polymer was ground and extracted in a Soxhlet with acetone for 24 h, and then dried in a vacuum oven fro 8 h.

The kinetic measurements were based on monitoring the amount of acetic acid evolved during the reaction. The collecting flasks for acetic acid were removed at scheduled time intervals and the amount of acetic acid was determined by titration with standard sodium hydroxide. The reaction extent (p) was then calculated by the following relationship:

p = (moles of functional group reacted) / (moles of initial functional groups).

Characterization of the Polymers

The copolyesters were analyzed by using an FT-IR20SX infrared spectrophotometer: KBr wafer, number of scanning lines 32, and resolution 4 cm^{-1}.

Thermal analysis data of the copolyesters were obtained by using a Dupont-1090 differential scanning calorimeter at a heating rate of 20 ^oC/min in a nitrogen atmosphere. Both temperature and heat flow scales were calibrated with high purity standards such as benzoic acid or tin. The temperature of endothermal maximum was taken as the melting point T_m of the polymer. Each copolyester was measured twice. First, each sample was heated from room temperature to its degradation point (T_d). Second, the sample was heated to a temperature (10 ^oC) above its melting point and quenched by liquid nitrogen to ambient temperature. The quenched sample was then reheated to T_d. The second run was designed for glass transition (T_g) measurement.

The optical properties of the mesophase were measured by using a Leitz-Wetzlar polarized microscope. The powdered sample was placed between two cover glasses to form a film and then heated under nitrogen on a hot-stage to the melt state. The morphology of the mesophase was surveyed under crossed polarizers and photographed.

RESULTS AND DISCUSSION

Figure 1 and Figure 2 indicate that reaction extent increases with reaction time and finally reaches a limit at a constant temperature. Further increases of temperature decreases the melt viscosity and accelerates the evaporation of by-products or small molecules and thus speeds up the polycondensation. The reaction temperature, however, should never exceed the melt thermodegradation temperature.

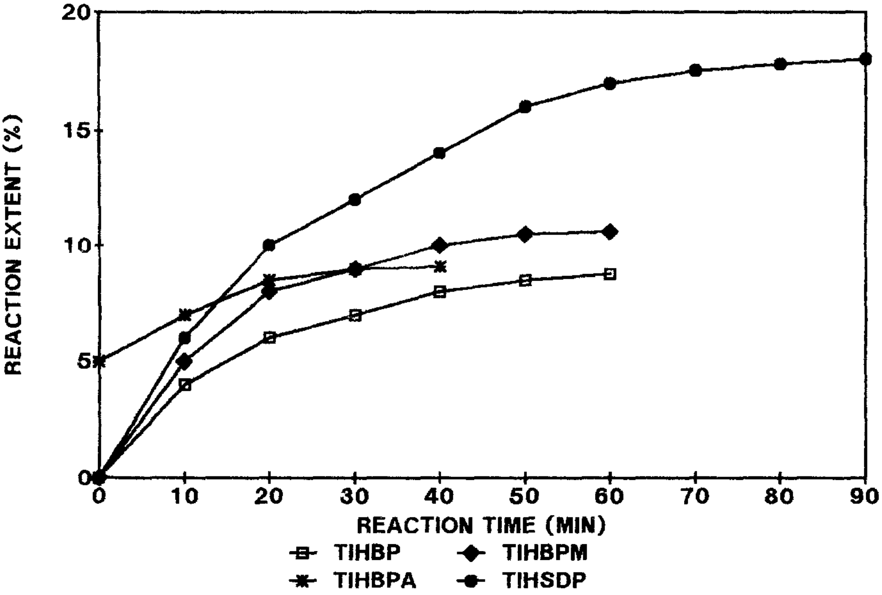


Figure 1. Reaction extent versus reaction time at 200 °C.

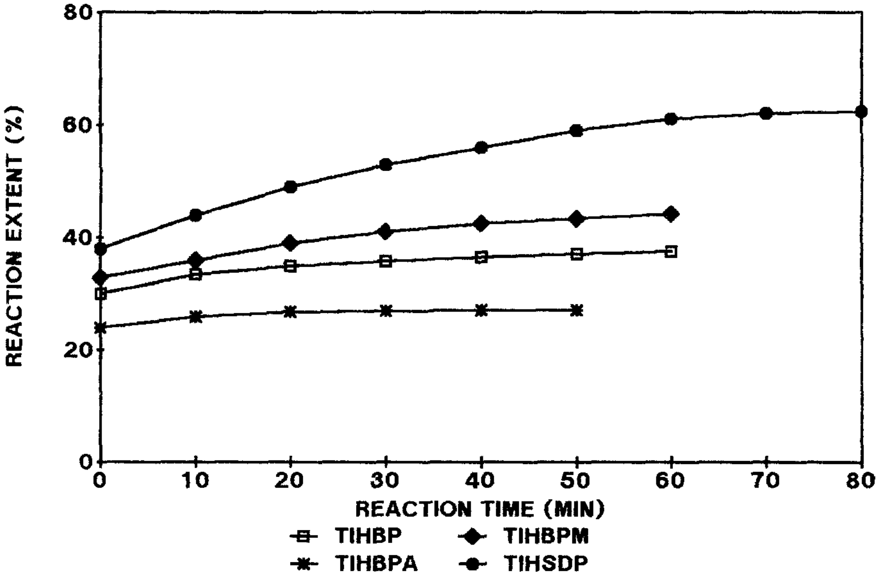


Figure 2. Reaction extent versus reaction time at 235 °C.

The relationship between the reactant concentration X and time t during the early-stage polycondensation is shown in Figure 3. The well-defined linearity between 1/X and t indicates that the reaction rate obeys second-order kinetics as shown in equation (1), where k is the rate constant and C is a constant.

$$-dX/dt = kX^2 + C \qquad (1)$$

The rate constants k are then derived from the slope of the straight lines in Figure 3 and listed in Table 1.

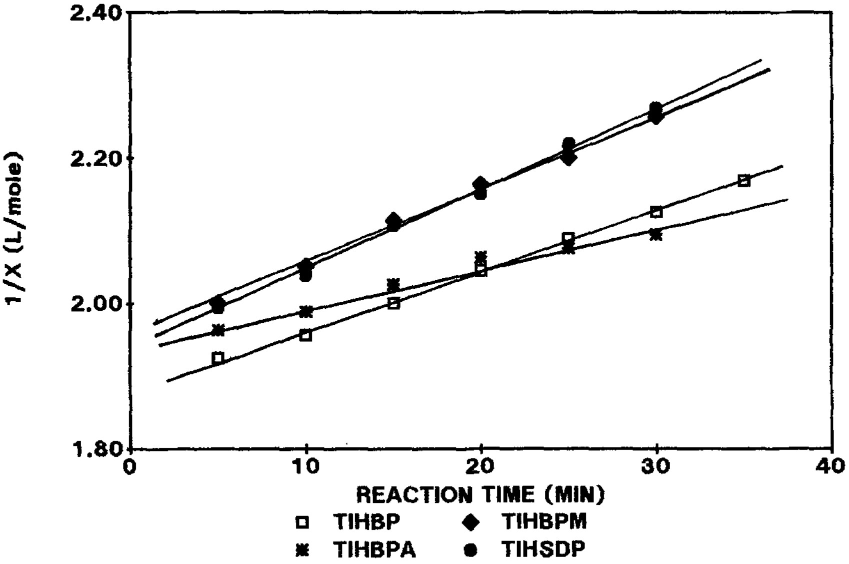


Figure 3. Plots of 1/X versus reaction time at 215 °C.

Table 1. Rate Constants for Melt Polycondensation

Copolyester sample	Rate constant (L $mole^{-1}$ min^{-1})
TIHBP	8.53×10^{-4}
TIHBPM	1.06×10^{-3}
TIHSDP	1.24×10^{-3}
TIHBPA	5.50×10^{-4}

It was found that the rate constants follow this sequence: $k_{TIHSDP} > k_{TIHBPM} > k_{TIHBP} > k_{TIHBPA}$, which is believed to be related to the structure of the functional group between two benzene rings of the bisphenol monomer. The resonance and inductive effects of $-SO_2-$ and $-CH_2-$ render SDP and BPM more reactive than BP. The isopropyl group causes BPA to be the least reactive in the series.

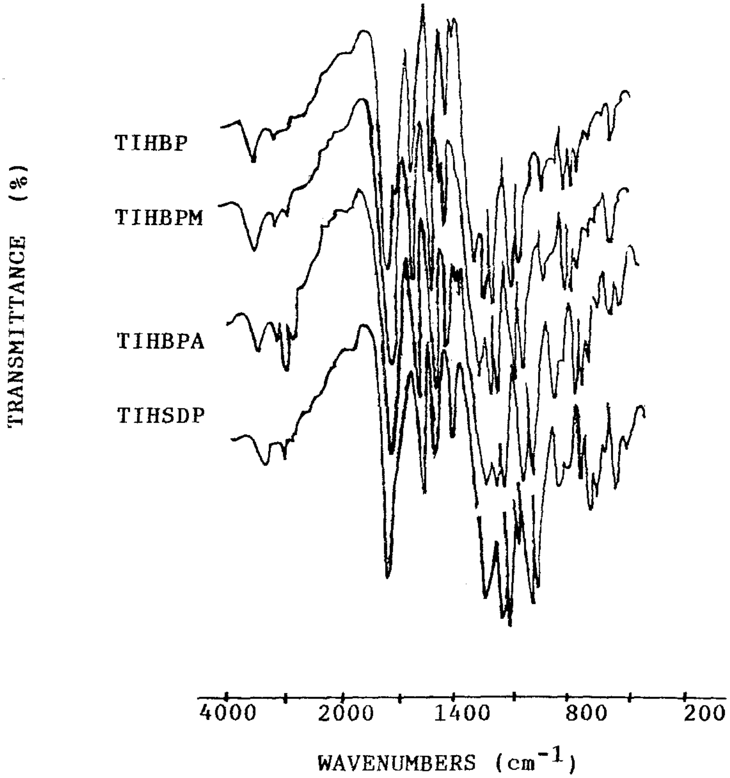
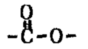
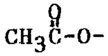


Figure 4. FTIR spectra of the bisphenol family copolyesters.

Figure 4 shows the infrared spectra of the copolyesters. An analysis of the spectra is given in Table 2.

Table 2. Infrared Analysis of the Copolyesters

Absorption peak (cm^{-1})	Vibration type	Indicating
2800-3200	C-H stretching	 *
1600, 1500 and 1410	C=C stretching	
690, 760, 890 and peaks of *	C-H out-of-plane bending	
820 and peaks of *	C-H out-of-plane bending	
1735	C=O stretching	 $-\overset{\overset{O}{\|}}{C}-$
1160, 1200, 1260 and 1735	C-O-C asymmetric stretching	 $-\overset{\overset{O}{\|}}{C}-O-$
1260 and 1735	C-O-C asymmetric stretching	 $CH_3\overset{\overset{O}{\|}}{C}-O-$

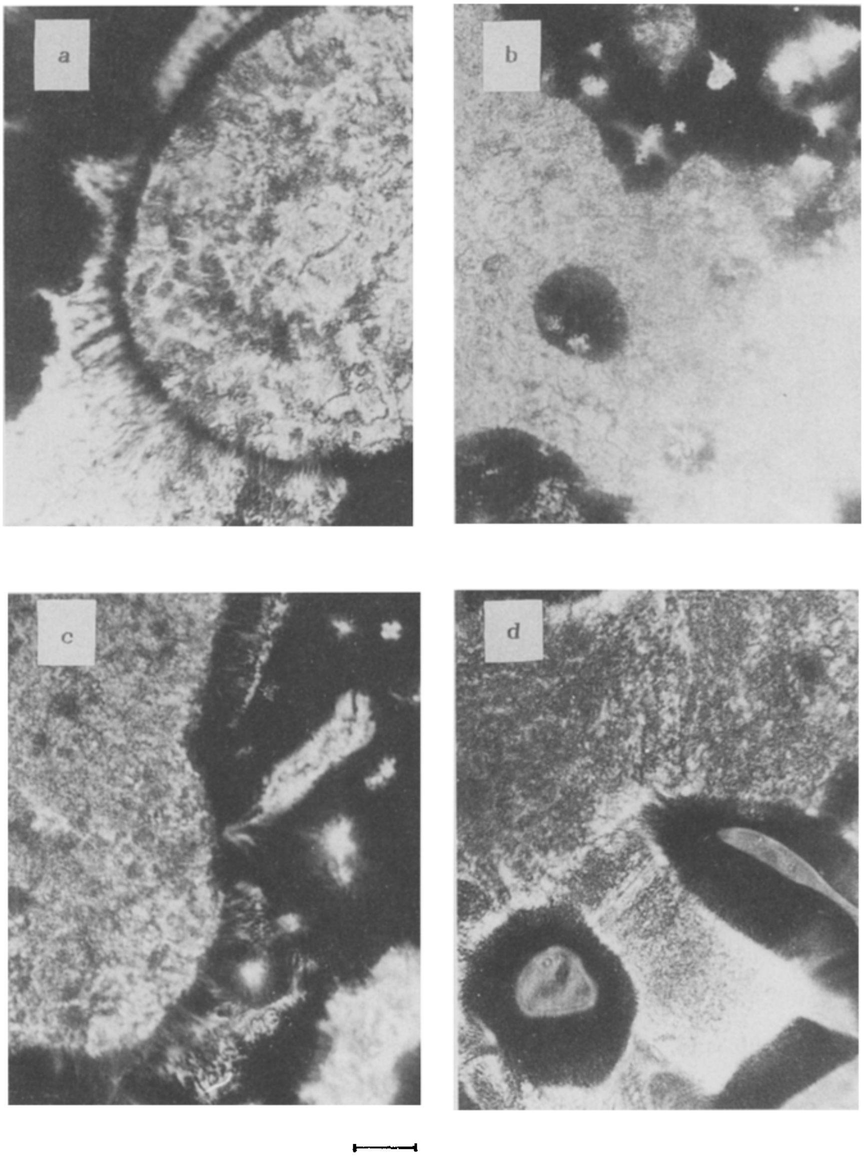


Figure 5. Optical micrographs of the copolyesters under crossed polarizers: (a) TIHBP, (b) TIHBPM, (c) TIHBPA, (d) TIHSDP.

In addition to the analysis above, the absorbance at 1375 cm^{-1} in TIHBP is characteristic of diphenyl while the peaks at 1438 cm^{-1} and 2800 cm^{-1} in TIHBPM are characteristic absorbances of the $-CH_2-$ group. Peaks at 2870-2928 cm^{-1}, 1463 cm^{-1} and the split peak at 1360-1390 cm^{-1} in TIHBPA is due to the isopropyl group, while the strong absorbance at 1108 cm^{-1} in TIHSDP results from the S=O symmetric stretching vibration.

The thermodynamic parameters of the copolyesters, as measured by DSC, are shown in Table 3. The samples melt into nematic mesophases as in Figure 5, at melting temperature T_m. The mesophase behavior decreases with increasing non-linearity of the bisphenol structure, which has been quantitatively studied (9). Each copolyester shows multiple endotherms instead of an isotropic transition by DSC of the degradation (T_d). The multiple peaks are due to a broad distribution of molecular weight. The broad mesophase temperature ranges (>70 ^{o}C) are quite favorable for melt-processing of copolyesters. The small melting enthalpies indicate that it is difficult for the copolyesters to form regular and perfect crystals because of the rigid cores of the mesogenic groups and long chains. There are no very obvious exothermal crystallization transitions due to the low degree of crystallization in the polymers. For each sample, however, the quench effect, as mentioned in the experimental section, causes the T_m to become negligible while T_g becomes stronger due to further increase of amorphous regions. When compared with conventional polymers, the copolyesters show excellent thermal stability as indicated by their T_ds due to the rigid chain structures.

Table 3. Thermodynamical Parameters of the Copolyesters

Copolyester sample	TIHBP	TIHBPM	TIHBPA	TIHSDP
Tm (K)	604.2	559.0	583.2	565.1
ΔHm (J g^{-1})	4.96	4.56	2.08	2.72
ΔS_m (J kg^{-1} K^{-1})	8.21	8.15	3.57	4.81
T_d (K)	675.8	636.1	669.4	639.8
$T_d - T_m$ (K)	71.6	78.6	86.2	74.7
T_g (K)	485.5	368.9	385.5	441.5

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