

Liquid Crystalline Aromatic Polyesters Containing *para*-Linked Dimethylbiphenylene Moieties

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SYNOPSIS

A series of liquid crystalline aromatic polyesters containing 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid and 3,4'-dimethyl-biphenyl-4,3'-dicarboxylic acid was prepared by a melt polycondensation procedure and characterized by elemental analysis, DSC and TMA measurements, and optical polarizing microscopy. An optimal composition of the copolymer having a melting temperature around 300°C is proposed and the rheological behavior is discussed. Most of the mechanical properties of this copolymer were found to be close to those of Vectra A950® used as a reference sample. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The wholly aromatic polyesters are of particular commercial interest due to their potential application as high-performance engineering plastics.¹⁻⁴ The homopolyesters poly(*p*-hydroxybenzoate) [poly(PHBA)], poly(*p*-phenylene terephthalate) [poly(HQu-TPA)], and poly(*p*-phenylene naphthalene-2,6-dicarboxylate) have been known to have a liquid crystalline phase. However, these cannot be processed in the molten state, because they have extremely high melting temperatures.⁵ A number of strategies have been employed to reduce the melting temperature of liquid crystalline polyesters for them to be melt-processed.⁶ The copolymerization of different monomers is known to be one of the most effective techniques for lowering the melting range of wholly aromatic copolyesters: The copolymers consisting of terephthalic acid (TPA), hydroquinone (HQu), and *p*-hydroxybenzoic acid (PHBA) were prepared, but the melting temperature proved to be too high for melt processing. However, incorporation of 4,4'-biphenol gave the desired results.⁷ Krigbaum et al. investigated the effect of substituents on the transition temperatures of poly(HQu-TPA).⁸ Several types of wholly aromatic thermotropic polyesters have been reported.⁹⁻¹⁹ Incorporation of 2,2'-

disubstituted biphenylenes in *para*-linked polyesters does not disturb the rodlike structure of the polymer backbone, but the interchain interactions are weakened because of the noncoplanar conformation of the phenyl rings.²⁰⁻²³ Accordingly, the mechanical strength of the molded resins are lowered due to a reduced crystallinity.

In this contribution, we report on a new type of wholly aromatic, *para*-linked polyesters containing 3,3'-dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA) and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA), which can be melt processed at moderate temperatures.

EXPERIMENTAL

Materials

P-DMBA and Q-DMBA were prepared according to published procedures.²⁴ Other chemicals were commercially available. Hydroquinone was treated with acetic anhydride under reflux to give hydroquinone diacetate.

Polycondensations

In a typical experiment (no. 9 in Table I), P-DMBA 5.406 g (20 mM), Q-DMBA 4.325 g (16 mM), TPA 3.987 g (24 mM), hydroquinone diacetate 11.881 g (61.2 mM), and 4-acetoxybenzoic acid 7.206 g (40

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Table I Characterization of Copolymers of a P-DMBA/Q-DMBA/TPA/HQu/PHBA Series

No.	P	Q (mol%)	TPA	PHBA	Yield (%)	η_{inh}^a (dL/g)	T_m^b (°C)	T_{aniso}^c (°C)	T_d^d (°C)	TMA ^e (°C)	Elemental Analysis ^f	
											C	H
1	15		15	70	94	1.80	338	330	460	360	72.21 (72.02)	3.97 (3.76)
2	15	15		70	98	1.71	241	232	444	273	74.10 (73.71)	4.30 (4.09)
3	10	10	20	60	95	0.98	g	297	454	303	72.11 (72.46)	3.98 (3.84)
4	15	15	20	50	95	1.54	g	286	452	290	73.33 (73.29)	4.14 (4.01)
5	30		20	50	87	1.55	297	296	477	326	72.58 (73.29)	4.11 (4.01)
6	30		30	40	95	2.02	302	295	470	308	73.33 (73.11)	4.22 (3.97)
7	15	15	30	40	94	1.36	g	316	438	310	72.64 (73.11)	3.98 (3.97)
8	10	8	42	40	98	1.43	g	350	450	372	71.72 (71.98)	3.77 (3.75)
9	20	16	24	40	95	1.96	275	294	450	282	73.34 (73.63)	4.07 (4.07)
10	20	20	40	20	94	1.09	g	298	432	340	73.19 (73.60)	4.08 (4.06)

A molar quantity of HQu is practically equal to the sum of P-DMBA, Q-DMBA, and TPA.

^a Inherent viscosity in pentafluorophenol of 0.2 g/dL, at 60°C.

^b Melting temperature from DSC measurements at a heating rate of 20°C/min.

^c Anisotropic melting temperature from optical polarizing microscope.

^d Decomposition temperature from TGA measurements at a heating rate of 20°C/min.

^e Penetrating temperature from TMA measurements at a heating rate of 10°C/min.

^f The calculated value is indicated in parentheses.

^g Not clearly defined.

mM) were placed in a 100 mL sus316-reaction vessel equipped with a stirrer, a Claisen head, and a nitrogen inlet tube. The vessel was immersed into a metal (Sn) bath held at 240°C, and within 2 h, the temperature was gradually increased to 300°C while removing acetic acid with a slow stream of nitrogen. The reaction temperature was then maintained at 300°C in a vacuum (0.1 Torr) for 1 h. After cooling, the product was crushed out: yield 21.7 g (94%). A 1 L sus316-reaction apparatus was used in the production of the test sample for injection molding.

Measurements

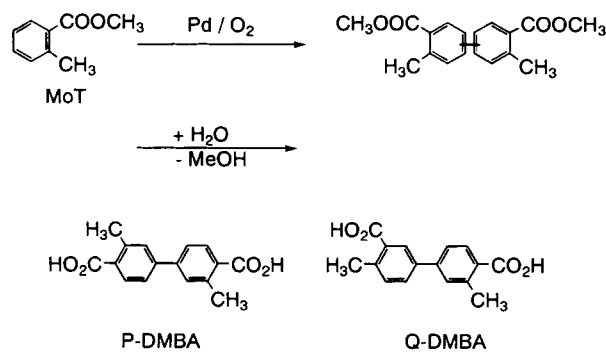
The films used for thermal measurements were pressed at a temperature 20°C above the melting temperature. The differential scanning calorimetry (DSC) measurements were conducted on a Seiko-Denshi DS2000 instrument in aluminum pans at a heating rate of 20°C/min under nitrogen. The glass transition temperature could not be reliably taken from the DSC chart of the polymers. The melting temperatures (T_m) were determined from the endothermic peak in the second heating run of the DSC curves. However, DSC measurements were usually less well defined, showing broad and small melting endotherms. The thermomechanical analysis (TMA) in the penetration mode demonstrated the more obvious thermal information of polymers having too ambiguous T_m 's. TMA measurements were performed on a DuPont 943 TMA instrument

at a heating rate of 20°C/min under nitrogen. The thermogravimetric (TGA) measurements were conducted at a heating rate of 10°C/min under nitrogen. The liquid crystalline textures of the polymers were observed under an optical polarizing microscope equipped with crossed polarizers and a hot stage (Linkam TH600RMS). The viscosities were measured with a Cannon Fenske viscosimeter in pentafluorophenol solution (0.2 g/dL, 60°C). Rheological measurements were performed on a Rheometrics RDS-2 mechanical spectrometer in the cone and plate geometry using 25 mm plates (cone angle 0.1 rad) at 1.0 Hz ($\omega = 6.28$ rad/s). Dynamic data were recorded at a step of 5°C over a range of strain amplitudes of 5–100%. The test pieces for mechanical measurements were injection-molded using a FUNAC 30A machine working at 300°C and the mechanical data were obtained following the ASTM D638 (tensile strength), ASTM D790 (flexural strength), and ASTM D256 (notched Izod strength).

RESULTS AND DISCUSSION

Polymer Synthesis

3,3'-Dimethylbiphenyl-4,4'-dicarboxylic acid (P-DMBA), and 3,4'-dimethylbiphenyl-4,3'-dicarboxylic acid (Q-DMBA) were prepared from an oxidative coupling of methyl *o*-toluate using a Pd catalyst. Dimethyl esters were hydrolyzed to the corresponding



Scheme 1 Synthesis of dimethylbiphenyldicarboxylic acids.

dicarboxylic acids (Scheme 1) as already described.²⁴ A series of aromatic copolyesters (Table I) was prepared by a melt-polycondensation procedure (Scheme 2).

Thermal Properties of Polymers

All the polymers prepared exhibited shear opalescence under microscopic observation with crossed polarizers. The anisotropic melting temperatures (T_{aniso}) of polymers are summarized in Table I. The thermal decomposition temperatures (T_d) were determined by TGA under nitrogen and the results are summarized in Table I. The T_d 's were invariably found in the range 430–480°C, indicating good thermal stabilities at elevated temperatures. Typical TGAs of polymer 9 in nitrogen and in air showed only a little difference in Figure 1 in that a T_d in air (445°C) is slightly lower than in nitrogen (450°C). Although the reaction conditions were not optimized, the molecular weights of the polymers prepared, as indicated by the inherent viscosities, were high enough to be melt-pressed into thin tough films.

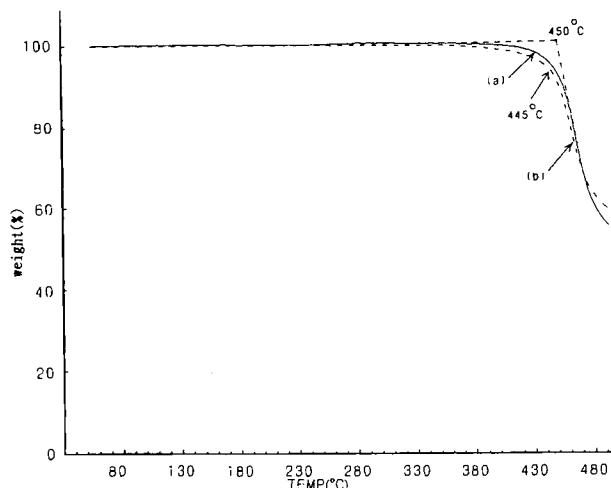
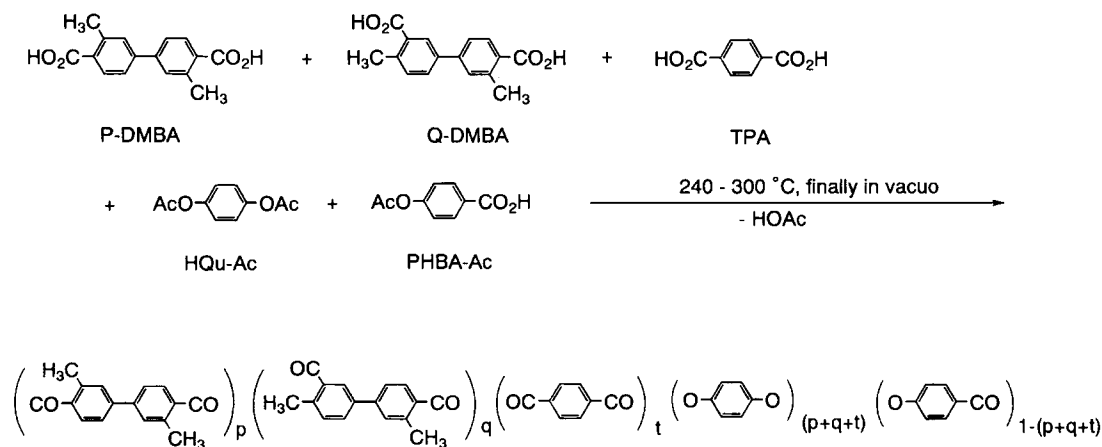


Figure 1 Thermogravimetric analysis of polymer 9 (a) in nitrogen and (b) in air.

Introduction of a P-DMBA/HQu component into poly(PHBA) affords a remarkable reduction of the T_m 's of copolymers, and a minimum melting temperature (200°C) was observed around a 50 : 50 molar ratio of P-DMBA/PHBA in the P-DMBA/HQu/PHBA system (Fig. 2). P-DMBA appears to play a decisive role in lowering the T_m 's of copolymers, whereas a minimum value of about 520°C was reported for the TPA/HQu/PHBA system.⁷ Poly(phenyl-1,4-phenylene biphenyl-4,4'-dicarboxylate) had been earlier prepared and its T_m (393°C) and T_{aniso} (425°C) were reported.²⁵ For comparison, we synthesized the corresponding P-DMBA containing polymer, poly(phenyl-1,4-phenylene 3,3'-dimethylbiphenyl-4,4'-dicarboxylate), which shows a T_m at 240°C and a T_{aniso} at 242°C. Undoubtedly, the T_m of poly(*p*-phenylene biphenyl-4,4'-dicarboxylate) must be much higher than 400°C. This result re-



Scheme 2 Preparation of copolyesters by a melt-polycondensation procedure.

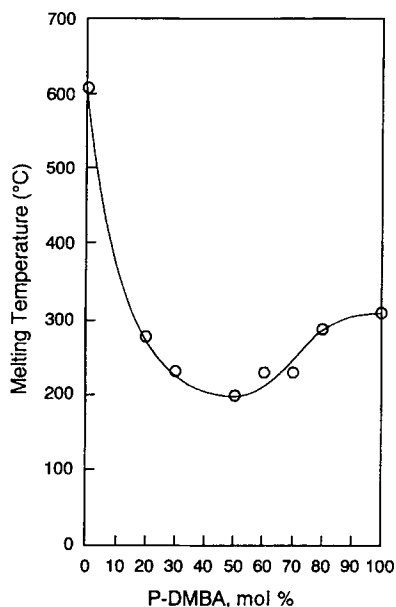


Figure 2 Melting temperature of P-DMBA-PHBA-HQu copolyesters: P-DMBA (mol %) = {P-DMBA/(P-DMBA + PHBA)} × 100; HQu = P-DMBA + PHBA.

vealed that an introduction of methyl groups into the biphenyl moiety remarkably depresses the melting temperatures. At the same time, processability of the copolymer is favorably affected. A number of copolymers containing P-DMBA and Q-DMBA were prepared in a range of comonomer compositions varying from 70 to 20 mol % of the PHBA. Comparing nos. 4 vs. 5 and nos. 6 vs. 7 reveals that P-DMBA and Q-DMBA have almost the same effect on the T_m 's of the copolymers. In the aimed preparations of polymers with a T_m around 300°C for practical use, the preferable composition was attained using a molar ratio of 20/16/24/60/40 = P-DMBA/Q-DMBA/TPA/HQu/PHBA (polymer 9).

Thermal Behavior and Rheology

In the DSC curve of polymer 9, a broad endothermic peak was located at 275°C and an anisotropic melting temperature (T_{aniso}) was observed at 294°C under the optical polarizing microscope. The dynamic storage modulus (G') and the loss modulus (G'') as a function of temperature at $\omega = 6.28$ rad/s are shown in Figure 3. A remarkable drop of the moduli G' and G'' is observed as the temperature is increased from 250 to 300°C. The curve of G' crosses that of G'' at 275°C, which coincides with the melting temperature (DSC). A similar behavior of the moduli was described in the formation of liquid crystalline phases.²⁶

The real part (η') of the complex viscosity calculated by G''/ω has a minimum value of 600 poise at 370°C. Around 370°C, the isotropic phase appears and G'' increases, indicating that the anisotropic phase disappears and the isotropic one becomes predominant. The isotropic phase is attained at 430°C, above which point G'' decreases again. A similar temperature dependence of complex viscosities has been described.²⁷ This behavior corresponds with the DSC and the observation under the optical polarizing microscope.

Mechanical Properties

Mechanical data for polymer 9 are given in Table II. As a reference sample, Vectra A950® (Ref. 28) (copolymer of PHBA and 6-hydroxy-2-naphthoic acid), a commercially available polyester, was subjected to the same test. Of six characteristic values, only the Izod strength of polymer 9 is significantly lower than that of Vectra A950. Both the flexural and tensile strengths of this polymer are reasonably close to those of Vectra A950, but the moduli of polymer 9 are higher. These, however, critically depend on the injection-molding conditions which must be checked in detail. This increase in moduli is likely to be caused by an enhanced linearity of the polymer structure.

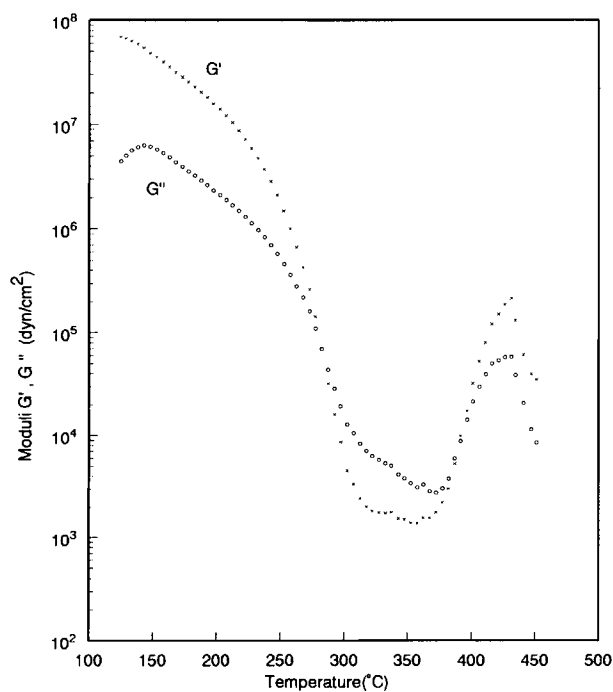


Figure 3 Temperature dependence of moduli G' and G'' for polymer 9.

Table II Mechanical Properties of Polymer 9 and Vectra A950

	Polymer 9	Vectra A950
Tensile strength (kgf/cm ²)	2360	2440
Tensile modulus (kgf/cm ²)	65,700	52,700
Elongation at break (%)	5	8
Flexural strength ^a (kgf/cm ²)	1830	1450
Flexural modulus (kgf/cm ²)	108,200	79,100
Notched Izod (kgf cm/cm)	20	69

^a 3.2 mm thickness.

CONCLUSION

Some practically useful candidates of new wholly aromatic polyesters are proposed. Although some of polymers prepared showed a rather broad melting behavior, a good thermal processability was attained. A preferable composition of a copolymer having a melting temperature around 300°C was elucidated to arise from a molar ratio of 20/16/24/60/40 = P-DMBA/Q-DMBA/TPA/HQu/PHBA (polymer 9). The rheological behavior of this polymer appears suitable for applications and most of important mechanical properties are close to those of a reference sample (Vectra A950).

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