Thermotropic Liquid-Crystalline Copoly(ester amide) Containing a Flexible Spacer in the Main Chain

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ABSTRACT: Thermotropic behavior was observed in a number of aromatic copoly(ester amides) containing a flexible spacer based on 4,4'-dicarboxyl-1,10-diphenoxydecane, di-acetylated *p*-aminophenol and di-acetylated hydroquinone with or without di-acetylated aromatic diamine. The copoly(ester amide) was synthesized by melt polycondensation accompanied by the removal of acetic acid. The introduction of up to 50 mol% of *p*-aminophenol units, *i.e.*, 25 mol% of the amide group, gave thermotropic liquid crystalline copoly(ester amide), though the thermotropic behavior disappeared at a greater concentration of *p*-aminophenyl units. A thermotropic copoly(ester amide) was prepared with *p*-phenylenediamine, 4,4'-diaminodiphenylmethane or 4,4'-diamino-3,3'-dimethoxybiphenyl as an amino group-containing monomer when it was used together with *p*-aminophenol as an essential amino-monomer. In the last case, up to 60 mol% of amide groups was allowed to afford thermotropic liquid crystallinity. The polymer structure and thermotropic nature were examined by solid-state and solution ^{13}C NMR spectroscopy, differential scanning calorimetry, polarizing microscopy, and IR spectroscopy.

KEY WORDS Copoly(ester amide) / Melt Polycondensation / Thermotropic Liquid Crystallinity / Amide Group / Solid-State ^{13}C NMR / Solution ^{13}C NMR / Differential Scanning Calorimetry / Mesophase Range / Nematic Threaded-Schlieren Texture / Droplets Texture /

Aromatic polyamides and polyesters have opened a new field of liquid-crystalline polymers with high strength and high modulus.¹⁻³ In general, aromatic polyamides are of lyotropic liquid crystalline, whereas aromatic polyesters are of thermotropic nature. Thermotropic polyamides $\{\text{COC}_6\text{H}_4\text{O}(\text{CH}_2)_{10}\text{OC}_6\text{H}_4\text{CONHC}_6\text{H}_3(\text{X})\text{C}_6\text{H}_3(\text{X})\text{NH}\}$, prepared by polymerization of 4,4'-dichloroformyl-1,10-diphenoxydecane and 3,3'-disubstituted-4,4'-diaminobiphenyl, have been reported.⁴ Strictly speaking, these are poly(ether amides), though di-alkoxy portions in the poly(ether amides) are regarded as spacers to reduce transition temperatures. Synthesis of thermotropic liquid crystalline samples of wholly aromatic copoly(ester amides), in which *p*-aminophenol was used as an amino-containing component

has been reported.^{5,6} In the copoly(ester amide), however, the percentage of amide linkages included in all polymeric linkages was not so high. Recently, the synthesis of aliphatic-aromatic poly(ester amide) with thermotropic liquid crystalline character was reported.⁷

Lenz and coworkers have synthesized various thermotropic polyesters with flexible spacers to lower the melting point.⁸ Recently, we reported that solid-state ^{13}C NMR spectra of thermotropic polyesters with di-alkoxy spacers can provide exact information on their solid structures.⁹

If di-alkoxy spacers are introduced in polymer backbone to lower the melting point and the liquid crystallinity measurement is carried out by use of both conventional polarizing

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microscopy and solid-state ^{13}C NMR spectroscopy, it might be easy to synthesize and characterize thermotropic copoly(ester amide).

In the present work, we synthesized thermotropic copoly(ester amide) containing up to 25 mol% of amide linkages, which are introduced by polycondensing di-acetylated *p*-aminophenol or di-acetylated *p*-aminophenol and di-acetylated *p*-substituted aromatic diamine in combination as amide-forming components, and 1,10-dioxydecamethylene as a flexible spacer.

EXPERIMENTAL

4,4'-Dicarboxy-1,10-diphenoxydecane (1)

1 was obtained by alkaline hydrolysis of 4,4'-dicarbethoxy-1,10-diphenoxydecane (**2**). **2** was prepared according to the Griffin and Havens' method.¹⁰ In a 1 l three-necked flask, *p*-hydroxybenzoic acid ethyl ester (Tokyo Kasei Co.) (33.2 g, 0.20 mol) was dissolved in 25 ml of dimethylformamide (DMF) under nitrogen atmosphere. Anhydrous sodium carbonate (26.5 g, 0.25 mol) and 0.10 mol 1,10-dibromodecane were added to the reaction flask, followed by the addition of 25 ml of DMF. The mixture was heated for 6 h in an oil bath maintained at 140°C and refluxed with continuous stirring. It was allowed to cool to approximately 50°C and then poured into 5 l of cold water. The solution containing the precipitated solid was kept overnight in a refrigerator. The precipitate was washed three times with water, and was filtered. Thereafter, it was recrystallized from 95% ethanol and finally dried under vacuum at 60°C for 48 h. The yield of **2** was 28.5 g (61%). mp 105°C (lit.¹¹ 108.5–110°C). **2** (23.5 g, 0.05 mol) was added to 500 ml of a 10% (w/v) solution of potassium hydroxide in 95% ethanol. The resulting suspension was stirred under reflux for 6 h. It was then diluted with 5 l water and warmed to 60°C, thoroughly dissolving the potassium salt of 4,4'-dicarboxy-1,10-diphenoxydecane. Concentrated hydrochloric acid

was added to the warm solution until it was acidic to pH test paper. After the solution was allowed to cool overnight, the deposit crude **1** was filtered and washed with water. It was purified by recrystallization from a DMF–95% ethanol mixture. Yield, 14.3 g (69%). mp 277°C (lit.¹¹ 273–274°C).

Di-Acetylated *p*-Aminophenol and Aromatic Diamines

Commercial *p*-aminophenol (Tokyo Kasei Co.) mp (155°C) and *p*-phenylenediamine (Tokyo Kasei Co.) (mp 305°C) were used without further purification. 4,4'-Diaminodiphenylmethane (25 g) was acetylated with 50 ml of acetic anhydride and 45 ml of pyridine for 12 h at room temperature. Yield of 4,4'-diacetamidodiphenylmethane was 34.4 g (97%). mp 233°C (lit.¹² 236–237°C). 4,4'-Diamino-3,3'-dimethoxybiphenyl (5 g) was acetylated in the same manner. The yield of 4,4'-diacetamido-3,3'-dimethoxybiphenyl was 4.3 g (64%). mp 242°C (lit.¹³ 242–243°C).

Polymerization

1 (1 or 2 g scale), di-acetylated *p*-aminophenol, di-acetylated hydroquinone, and di-acetylated aromatic diamines were polymerized using 10 mg of $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ as a catalyst in the stream of nitrogen. As an example, the case of 10P20H is described. **1** (2 g, 4.83×10^{-3} mol), di-acetylated *p*-aminophenol (0.186 g, 9.7×10^{-4} mol), di-acetylated hydroquinone (0.750 g, 3.86×10^{-3} mol), and zinc acetate (10 mg) were heated in a glass polymerization tube successively at 100°C for 1 h, at 150°C for 1 h, and at 240°C for 1 h, and then polymerized at 300°C for 5 h under the stream of nitrogen until evolution of acetic acid practically ceased. Thereafter, the polymerization was continued at 300°C for 2 h under vacuum. The lumpy polymer obtained was ground. Yield, 2.0 g (85%).

Measurements

Thermal properties of the polymers were

measured using a Perkin-Elmer DSC-2 calorimeter. The heating and cooling rates were maintained at $20^{\circ}\text{C min}^{-1}$. The peak top was taken as a phase transition temperature. The visual and photographic observations were carried out with a polarizing microscope equipped with a Mettler FP85 hot stage. Solid-state and solution ^{13}C NMR spectra were recorded using a JEOL GX270 spectrometer (6.34 Telsa, 67.8 MHz frequency) with a CP/MAS unit.⁹ In the case of solid-state measurement, contact time was 2 ms and recycle time of pulse was 5 s. A bullet-type Kel-F rotor contained approximately 300 mg of sample. The solution spectrum was taken on a 1% polymer solution in a mixture of

40% 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) and 60% pentafluorophenol (PFP) at 27°C . The absorption of TCE- d_2 was used as an internal standard (74.5 ppm downfield from tetramethylsilane reference).

RESULTS AND DISCUSSION

Preparation of Thermotropic Aromatic Copoly(ester amide) with a Flexible Spacer

A copoly(ester amide) (3) was prepared by the melt polycondensation of 4,4'-dicarboxy-1,10-diphenyldecane, di-acetylated *p*-aminophenol, and di-acetylated hydroquinone according to eq 1. 1,10-Dioxy-decamethylene was used as a flexible spacer group. The results

of polycondensations and thermal measurements are shown in Table I. The yield was 82–89%, a loss is mostly due to loss of the polymer attached to the glass polymerization tube. Reduced viscosities of the polymers were in the range of 0.22–0.31 dl g^{-1} .

A copoly(ester amide) containing 20% *p*-

aminophenol units, 10P20H, exhibited a nematic phase at 232°C (T_m) and became isotropic at 324°C (T_i).

A polyester with a similar structure, 10HQ, showed lower T_m by 7°C and higher T_i by 2°C than respective transition temperatures of the copoly(ester amide). As the *p*-aminophenol

Table I. Thermal properties of thermotropic copoly(ester amide)s (3)^a

Polymer	Molar ratio			T_m	T_i	$T_i - T_m^b$	Yield	η_{red}
	A	B	C	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	%	dl g^{-1}
10HQ	100		100	225	326	101	82	0.59
10P20H	100	20	80	232	324	92	85	0.25
10P30H	100	30	70	234	317	83	86	0.22
10P40H	100	40	60	244	309	65	85	0.22
10P50H	100	50	50	244	290	46	86	0.23
10P60H	100	60	40	—	248	0	89	0.31

^a Measured by DSC.

^b $T_i - T_m$, mesophase temperature range.

unit increased, T_m increased and T_i decreased. However, copoly(ester amide) containing more than 60% of *p*-aminophenol did not exhibited thermotropic liquid crystal behaviors. A poly(ester amide) containing 50 mol% of amide groups, obtained from *p*-aminophenol and methoxy-*p*-phenylenedicarboxylic acid, has afforded anisotropic melt.⁵ In our study, the copoly(ester amide) containing a long di-alkoxy spacer showed thermotropic liquid crystal behavior in the case of low amide group content.

The mesophase temperature range was 92°C for 10P20H, and reduced with increasing amide groups to afford 46°C in a polymer containing 50% of aminophenol unit, 10P50H.

The synthesis of polyamides from *p*-phenylenediamine alone as an amide-forming component did not give thermotropic liquid crystalline polyamides. Thus, *p*-phenylenediamine was used together with *p*-aminophenol.

The results of copolymerizations consisting of four monomers, that is, 4,4'-dicarboxy-1,10-diphenoxydecane, di-acetylated *p*-aminophenol, di-acetylated *p*-phenylenediamine and di-acetylated hydroquinone, are shown in Table II. A copoly(ester amide) 10PHD-1 containing 5 mol% of *p*-aminophenol unit and 5 mol% of *p*-phenylenediamine unit was thermotropic, indicating T_m of 196°C and T_i of 306°C. In this copoly(ester amide) series, both T_m and T_i increas-

ed with amide content, and the mesophase temperature range, T_i-T_m , decreased. Up to 15 mol% of both *p*-aminophenol and *p*-phenylenediamine units, an amide content of up to 22.5 mol% exhibited thermotropic liquid crystalline nature, while beyond this content a copoly(ester amide) 10PHD-4 did not show it.

The reason why the *p*-aminophenol units in these copoly(ester amides) help to form liquid crystalline phase might be due to a decrease in the symmetric nature of the polymer backbone, that is, asymmetry originates from different bonding orders of the aminophenol unit in the polymer backbone, $-NHC_6H_4CO-$ and $-OCC_6H_4NH-$. It is assumed that this disorder might cause a decrease in hydrogen bonds between amide groups. It has been reported that a polyester with an alternating arrangement of mesogenic units did not show a mesophase.¹⁴

When di-acetylated 4,4'-diaminodiphenylmethane, which can not generate a thermotropic liquid crystalline copoly(ester amide) in a case of single use, was used as an amide-forming component together with di-acetylated *p*-aminophenol, a thermotropic copoly(ester amide) was obtained (5). The results of copolymerizations consisting of four monomers are shown in Table III. Although introduction of 15 mol% each of *p*-aminophenol and 4,4'-diaminodiphenylmethane led to thermotropic liquid crystallinity, no meso-

Table II. Thermal properties of thermotropic copoly(ester amide)s (4)^a

Polymer	Molar ratio				T_m	T_i	$T_i-T_m^b$	Yield
	A	B	C	D	°C	°C	°C	%
10PHD-1	100	5	90	5	196	306	110	91
10PHD-2	100	10	80	10	233	308	75	89
10PHD-3	100	15	70	15	260	323	63	92
10PHD-4	100	20	60	20	—	298	0	91

^a Measured by DSC.

^b T_i-T_m , Mesophase temperature range.

Table III. Thermal properties of thermotropic copoly(ester amide)s (5)^a

Polymer	Molar ratio				T_m	T_i	$T_i-T_m^b$	Yield
	A	B	C	D	°C	°C	°C	%
10PHMT-1	100	10	80	10	225	297	72	92
10PHMT-2	100	15	70	15	180	250	70	92
10PHMT-3	100	20	60	20	—	270	0	92

^a Measured by DSC.^b T_i-T_m , Mesophase temperature range.**Table IV.** Thermal properties of thermotropic copoly(ester amide)s (6)^a

Polymer	Molar ratio				T_m	T_i	$T_i-T_m^b$	Yield
	A	B	C	D	°C	°C	°C	%
10PHMD-1	100	10	80	10	215	308	93	92
10PHMT-2	100	15	70	15	203	300	97	92
10PHMT-3	100	20	60	20	193	295	100	92
10PHMT-4	100	25	50	25	170	280	110	95
10PHMT-5	100	30	40	30	160	273	118	95
10PHMT-6	100	35	30	35	155	277	122	98
10PHMT-7	100	40	20	40	145	270	125	94

^a Measured by DSC.^b T_i-T_m , Mesophase temperature range.

phase was observed with 20 mol% each of the two amines.

Diacetylated 4,4'-diamino-3,3'-dimethoxybiphenol and *p*-aminophenol were employed

in equimolar amounts of 10–40 mol% as amide-forming components according to eq 2, giving thermotropic copoly(ester amide) (6) (Table IV). In this case, the maximum

content of the amide groups was 60 mol%. In the case of 10 mol% each of the two components, T_m and T_i were 215°C and 308°C,

respectively. Although both T_m and T_i decreased with an increase in the amide content, lowering in T_m was larger than T_i . Thus, the

mesophase temperature range expanded with amide content. The wide mesophase temperature range might be due to enlarged asymmetry caused by 3,3'-dimethoxy substituents in the 3,3'-disubstituted-4,4'-diaminobiphenyl unit. We assume that rotation around the biphenyl C-C bond changes the geometrical position of the methoxy groups in the rod-like polymer chain, then fixing the following structural units (Figure 1).

Griffin and coworkers reported that a ther-

Figure 1. Probable conformational isomerism for 3,3'-dimethoxy-4,4'-diaminobiphenyl units.

motropic polyamide was prepared by solution polymerization of 4,4'-dichloroformyl-1,10-diphenoxydecane with 4,4'-diamino-3,3'-dimethoxybiphenyl.⁴ The polyamide showed T_m of 256°C and T_i of 276°C, indicating that it has a high T_m and narrow mesophase range 20 degree. It is noteworthy that the copoly(ester amide) obtained in our study show a wide mesophase range.

Solid-State CP/MAS ^{13}C NMR Spectra of Copoly(ester amide)

Solid-state CP/MAS ^{13}C NMR spectrum of the copoly(ester amide) 10P20H was measured with a sideband-free pulse sequence, as shown in Figure 2.

In the solid-state spectrum, alkylene carbons in the di-alkoxy portion appear as sharp peaks at 27–70 ppm, in which C_γ is at 27.7 ppm, and C_β , C_δ , and C_ϵ overlap at 32.5 ppm, and C_α

Figure 2. 67.8 MHz ^{13}C NMR spectra of 10P20H: (A) solution spectrum obtained in TCE-d_2 and PFP; (B) solid-state spectrum which is free of spinning sidebands.

neighboring to an oxygen appears at 68.5 ppm. Aromatic carbons arise at 110–170 ppm. The assignment of individual absorption was carried out by reference to the previous paper⁸ and the substituent effect of the ^{13}C chemical shift.¹⁵

For poly(*p*-phenylene terephthalamide), the nonequivalence of the four ortho carbons in the terephthalic moiety has been reported.¹⁶ In the previous paper,⁹ we observed the nonequivalence of ortho carbons to an alkoxy group in a thermotropic polyester having a hexamethylene spacer in the polymer backbone and concluded that it originated from all-*trans* conformation of the hexamethylene moiety. However, in Figure 2 for 10P20H, the 2 and 2' carbon, *i.e.*, ortho carbons, are not separated, being similar to the absorptions of the heat-treated thermotropic polyester prepared by low temperature solution polymerization and then heated at a high temperature.⁹ Since the poly(ester amide) were obtained by polycondensation at 300°C, it is considered that the polymers have already been subjected to heat-treatment.

Although ester and amide carbon absorptions were separately observed at 168.7 and

171.3 ppm in the solution spectrum, respectively, they overlapped at 170 ppm in the solid-state spectrum. IR spectra of 10P20H and 10P50H clearly indicated the existence of CONH, with the NH and CO absorptions appearing around 3400 cm^{-1} and 1680 cm^{-1} , respectively.

Thermotropic Liquid-Crystal Phase

All these polymers showed typical nematic textures by observation on a hot-stage of a polarizing microscope (Figures 3A–C). A thermotropic polyester obtained with 4,4'-dichloroformyl-1,10-diphenoxydecane and hydroquinone has shown a nematic threaded-Schlieren texture.¹⁷

A copoly(ester amide), 10P20H, which contained 20 mol% of *p*-aminophenol, exhibited a texture similar to a threaded-Schlieren texture (Figure 3A). On the other hand, 10P50H showed a droplet texture when measured in the descending temperature cycle from an isotropic melt (Figure 3B).

It was revealed that copoly(ester amide) containing four components display textures slightly different from the three component copoly(ester amide). A copoly(ester amide),

Figure 3. Photomicrographs of nematic phase from copoly(ester amide), (A) threaded texture of 10P20H, taken at 250°C, (B) droplets texture of 10P50H, taken near T_i , (C) Schlieren texture of 10PHD-2, at 250°C (magnification $\times 150$).

10PHD-2, containing 10 mol% of *p*-phenylenediamine unit showed a typical Schlieren texture having a brightly colored pattern in the limited range of 280–290°C (Figure 3C). Other thermotropic copoly(ester amide) displayed individual nematic textures depending on the composition and measuring temperature.

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