

Lytropic liquid crystalline phase of polyesteramides with different ratio of amide to ester groups in a main chain

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Summary

Various lyotropic liquid crystalline polyesteramides were prepared from 1,3-bis(4-aminobenzoyloxy)benzene, p-phenylene diamine, and terephthalic acid by changing the ratio of amide to ester groups and were observed by using a cross polarized light microscope. The range of liquid crystalline phase becomes wider with increasing the portion of amide groups in a main chain because the chain rigidity becomes higher and the polymer-solvent interaction stronger. In the case of polyesteramides with flexible spacers, the polymer with one p-phenylene group between two ester groups does not form an anisotropic phase but the polymer with the same group between amide groups shows an anisotropy.

Introduction

The anisotropic behavior has been well proved by a lot of literature on lyotropic and thermotropic liquid crystalline(LC) polymers. LC polymers have stimulated the research on theory and application because they form easily a highly oriented state and thus give good mechanical properties. Therefore, there are many reports about the mesomorphicity of rigid and semirigid polymers ; aromatic polyamides(1,2), cellulose derivatives(3,4), and poly(N-alkyl isocyanate)(5,6) are lyotropic but aromatic polyesters(7–10) and polyesteramides(11–14) are thermotropic LC polymers. The thermotropic LC polymers with flexible spacers have been widely studied in order to lower the melting temperature without adversely affecting the range of a mesophase stability.

However, there are several reports on the effects of rigid segments and flexible spacers or non-expanding groups in lyotropic LC polymers(1,2,15). Specially, because of a chain rigidity and extension the aromatic polyester known as a thermotropic LC polymer shows a liquid crystalline phase in solvent(16), and a thermotropic polyurethane has been reported to show a lyotropic liquid crystalline phase(17). Preston and Hofferbert reported that the ether linkage introduced a "kink" into the chain in a solution system(18). Aharoni reported that the aromatic diether was a non-rigid segment(1). In the case of polyesteramide which has amide and ester groups in a main chain, Gopal and Srinivasan studied the solubility of the aromatic polyesteramides(19) and Aharoni reported that the aromatic polyesteramide showed a lyotropic liquid crystalline phase(20).

In this study, three kinds of copolyesteramide are prepared by solution polycondensation and are observed by using a cross polarized light microscope to investigate the liquid crystalline phase of a polyesteramide with different ratio of amide to ester groups in a main chain.

Experiment

(a) Materials

1,4-bis(4-aminobenzoyloxy)benzene(ABHQ-NH₂) was obtained by a catalytic hydrogenation of 1,4-bis(4-nitrobenzoyloxy)benzene (ABHQ-NO₂) in the presence of Raney nickel. ABHQ-NO₂ was prepared from p-nitrobenzoyl

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chloride(Aldrich) and hydroquinone(Aldrich) by a Schotton– Baumann type reaction in the cold mixture of tetrachloroethane and pyridine. After filtration, ABHQ–NO₂ was washed with ethanol and dried in vacuum oven for one day. Then, ABHQ–NO₂ was dissolved in N,N–dimethyl acetamide(DMAc) in the temperature range from 80 to 105 °C and reduced to the ABHQ–NH₂ in the autoclave under the high pressure of hydrogen. 1,6–bis–(4–aminobenzoyloxy) hexane(ABH–NH₂) was prepared in the same manner. Solvents used for the synthesis were reagent grade and were stored over 4A molecular sieves. A concentrated sulfuric acid(Merck, 96%)was used with oleum (65% SO₃ + 35% H₂SO₄, Merck) to make 100% sulfuric acid for the preparation of polymer solution.

(b) Polymerization

HQ polymers were polymerized with the different proportion of ABHQ–NH₂, p–phenylene diamine, and terephthalic acid(or terephthalic dichloride) as shown in Table 1. P6 polymer was prepared from ABHQ–NH₂ and suberic acid, and M6 polymer from ABH–NH₂ and terephthalic acid.

Polymers were prepared by the procedure of Yamazaki and Higashi(21–23) in the solution of N–methyl–2–pyrrolidone(NMP) and pyridine with cosalts, and the reactivity between diamines of ABHQ–NH₂ and p–phenylene diamine in the preparation of HQ polymers was confirmed by the Schotton–Baumann type reaction using the solution of DMAc with 5% LiCl and pyridine.

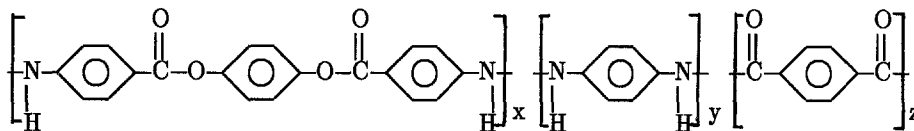
(c) Measurements

The structure of monomers was confirmed by ¹H–NMR spectrum(FT–80A NMR) and Infrared Spectrum (FTIR) in the 4000–400 cm⁻¹ range and the thermal properties of the polymers were measured by using a Perkin–Elmer DSC–2 and DuPont 2000 calorimeter.

The inherent viscosities were measured by using Cannon–Ubbelohde viscometer at 30°C for the polymers in DMAc with 5 wt/vol% dry LiCl. Other solutions were prepared from 100% sulfuric acid under the nitrogen atmosphere for the observation of an anisotropy. The solutions were slightly heated in order to certify the complete dissolution of the polymer and then maintained in the chamber of a constant temperature.

The photographic observations were carried out by using a cross polarized light microscope(Carl Zeiss Laborrux 12 Pols) with heating stage and an automatic camera.

Table 1. Structures and Inherent Viscosities of HQ Polymers.



Polymer code	molar ratio			I.V.
	x	y	z	
HQ1	1		1	0.35
HQ2	0.5	0.5	1	0.32
HQ3	0.33	0.67	1	0.38
HQ5	0.2	0.8	1	0.40
HQ10	0.1	0.9	1	0.33

* by the procedure of Yamazaki and Higashi

Table 2. Structures and Inherent viscosities of P6 and M6 Polymer.

Polymer Code	Structure	I. V.
P6		0.33
M6		0.32

Results and Discussion

The inherent viscosities and structures of polymers are summarized in Tables 1 and 2. All polyesteramide solutions are degraded faster than poly(*p*-phenylene terephthalamide) (PPTA, Kevlar by DuPont, I.V. = 5.1 dl/g) solution because of ester groups in sulfuric acid(16). In addition, when the polymer solutions are heated, the polymers are often degraded because the ester groups take part in hydrolytic and exchange reactions due to sulfuric acid. Therefore, the optical anisotropy of polymer solutions was observed as soon as possible before the degradation of polymer.

Figure 1 (a) shows the photograph of PPTA solution in 100% sulfuric acid by using a cross polarized light microscope(24). This polymer is wholly aromatic ring structures with all-*para*-orientation and a hydrogen bonding from $-\text{CO}-$ and $-\text{NH}-$ (25). Figure 1 (b) shows the photograph of HQ10 polymer solution. In these figures, the texture of HQ10 polymer solution is the typical nematic LC phase like that of PPTA solution(26). The texture of liquid crystalline phase of PPTA solution is clearer than that of HQ10 polymer solution. Probably this seems that in solvent system, PPTA is more rigid than HQ10 polymer with ester linkages.

Figure 2 shows the phase diagram of HQ10 polymer solution. HQ10 polymer shows a liquid crystalline phase in the concentration range from 21 to 27wt% at 20°C. The critical concentration at which a polymer begins to show an anisotropy is about 18wt% at 20°C and 30wt% solution shows the mixture of a liquid crystal and solid. The critical concentration is higher than that of PPTA solution because of a low molecular weight and a poor chain rigidity. As the temperature increases, the anisotropic state is gradually changed into an isotropic phase. The temperature range of anisotropic phase becomes wider with the polymer concentration. That is, 27 wt% polymer solution shows a lyotropic liquid crystalline phase in the temperature range from 20°C to 60°C. As compared with the PPTA solution, this solution shows a narrower temperature range.

Figure 3 (a) shows the photograph of 25 wt% HQ5 polymer solution. The solution shows the anisotropic phase in the concentration range 23–27 wt% at 20°C. The biphasic state of this solution at 20°C is at 21 wt%. In Figure 3, liquid crystalline phase in solution appears at higher concentration with increasing ester group portion in a main chain. Although the ester-(*p*-phenylene)-ester linkage is a rigid segment, it seems that the lyotropic liquid crystallinity of polyesteramide appears at lower concentration with increasing the number of amide groups in a main chain because a mesophase is formed due to not only the chain rigidity but also the hydrogen bondings between amide groups and solvents.

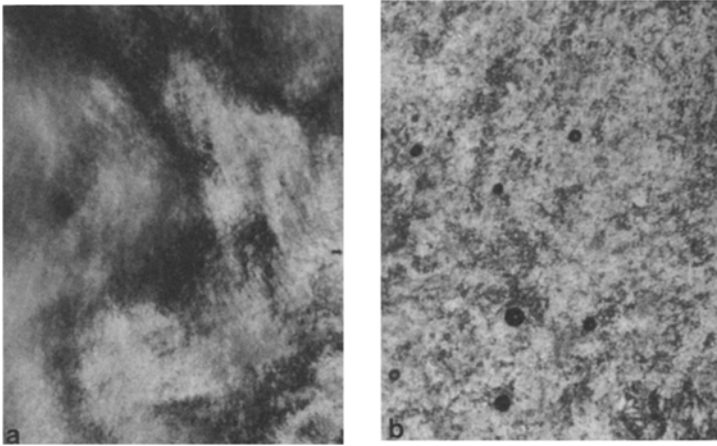


Figure 1. Photographs of Liquid Crystalline Polymer Solution in 100% Sulfuric Acid by using a Cross Polarized Light Microscope.
 (a) 10% PPTA Solution (132X, at 50°C)
 (b) 25% HQ10 Polymer Solution(132X, at 20°C)

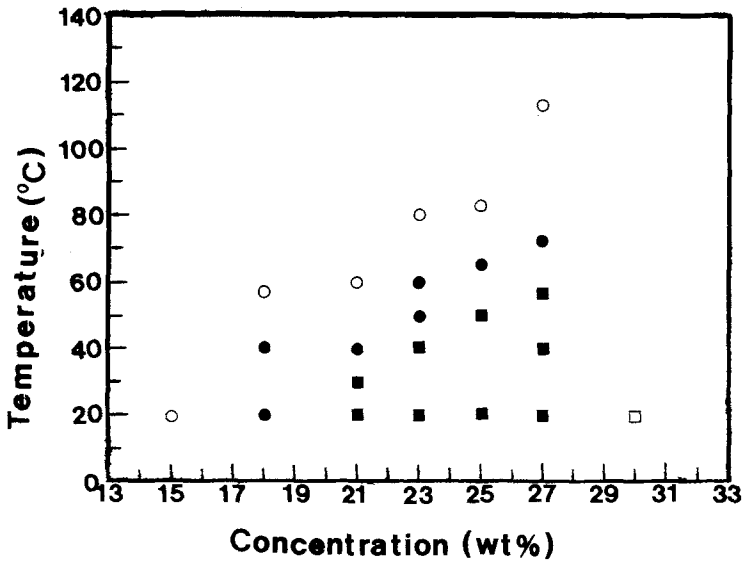


Figure 2. Phase diagram of HQ10 Polymer in 100% sulfuric acid.
 ○ :isotropic state ● :Biphasic state
 ■ :anisotropic state □ :anisotropic state + solid

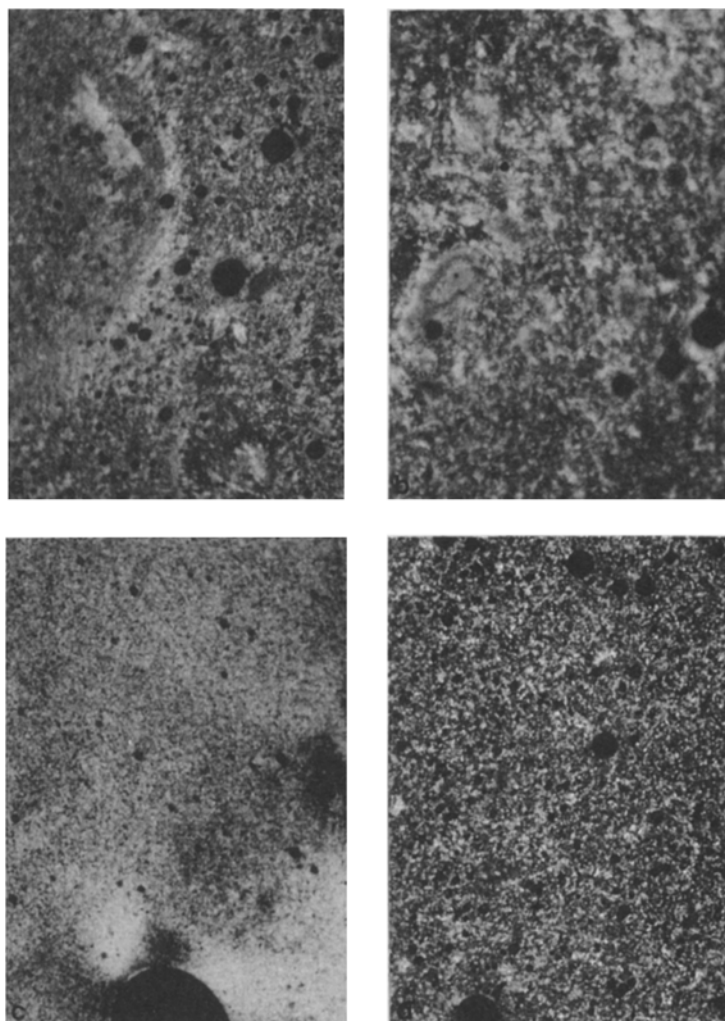


Figure 3. Photographs of HQ Polymers in 100% Sulfuric Acid by using a Cross Polarized Light Microscope.
(a) 25 wt% HQ5 Polymer Solution (132X, at 20°C)
(b) 25 wt% HQ3 Polymer Solution (132X, at 20°C)
(c) 30 wt% HQ2 Polymer Solution (132X, at 20°C)
(d) 35 wt% HQ1 Polymer Solution (132X, at 20°C)

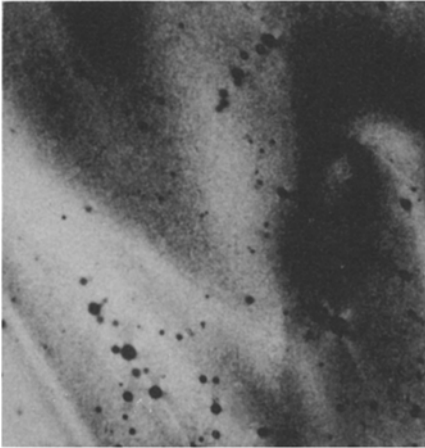


Figure 4. Photograph of 35 wt% M6 Polymer Solution in 100% Sulfuric Acid by using a Cross Polarized Light Microscope.

As shown in Figure 4, 35 wt% M6 polymer solution in 100% sulfuric acid shows the shear-induced liquid crystalline phase, which disappears within 2 minutes after cessation. This texture is similar to that of biphasic state of PPTA solution. M6 polymer is too flexible to form an anisotropic phase by itself. It indicates that the polyesteramide is losing an anisotropy with increasing flexible units in a main chain. Generally the critical concentration increases but the potentiality to form an anisotropy decreases with the chain rigidity(1). Although the polyesteramide contains the p-phenylene group between two ester groups, the polymer with methylene units between amide groups does not show a lyotropic liquid crystalline phase. That is, P6 polymer in 100% sulfuric acid is incapable of forming an anisotropic phase with or without shear. This seems that polyesteramide with p-phenylene rings between ester groups and methylene units between amide groups does not form a liquid crystalline phase in a solvent system because P6 is more flexible than M6.

Conclusions

The lyotropic liquid crystalline phases for three kinds of copolyesteramides with the different ratio of amide and ester groups are observed by using a cross polarized light microscope.

HQ polymer solutions in 100% sulfuric acid show a typical nematic phase. The range of liquid crystalline phase of polyesteramide becomes wider with increasing the portion of amide groups in a main chain because a mesophase is formed due to not only the chain rigidity but also the polymer-solvent hydrogen bondings.

M6 polymer solution with flexible units between ester groups is capable of forming an anisotropic phase but P6 with p-phenylene group between ester groups and six methylene units between amide groups does not show an anisotropy. The liquid crystalline phase of polyesteramide appears at higher concentration and gradually disappears when more flexible spacers are added into a main chain.

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