

LIQUID CRYSTALLINE BEHAVIOR OF AROMATIC COPOLYAMIDE IN CONCENTRATED SULPHURIC ACID

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ABSTRACT

The liquid crystalline behavior of anisotropic solutions in 100% sulphuric acid of aromatic copolyamide obtained by low-temperature solution copolycondensation of terephthalic acid chloride (TPC), p-phenylene diamine (PPD) and 4, 4'-diamino-diphenylether (DAPE) has been studied by optical microscopy and X-ray diffraction. The effects of inherent viscosity, concentration of copolyamide in sulphuric acid, the content of the third monomer (DAPE) and sequence distribution of copolyamide on the critical concentration, isotropic temperature, phase diagram and texture of liquid crystal were investigated. The schlieren texture was observed and the results of X-ray diffraction indicate that the concentrated solutions of copolyamide exhibit nematic liquid crystalline behavior.

INTRODUCTION

Poly(1, 4-benzamide) (PBA) and poly(p-phenyleneterephthalamide) (PPTA) can be synthesized from the hydrochloride salt of p-aminobenzoyl chloride^[1], PPD and TPC^[2,3] by low-temperature solution polycondensation, respectively. The anisotropic solutions of PBA in N, N-dimethylacetamide/LiCl^[1,4], N, N, N', N'-tetramethylurea/LiCl^[1] and 100% sulphuric acid^[5], and PPTA in 100% sulphuric acid^[6] have been studied. The oriented fibers with high strength and high modulus can be prepared from the liquid crystalline solutions of PBA by dry or wet spinning^[7], as well as from the liquid crystalline solutions of PPTA by dry-jet wet spinning^[6]. But some of the fiber properties (such as strength, modulus et al.) are disappointed to the

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users, while the most efficient method to improve these properties is to add a third monomer into the polycondensation system. However, the liquid crystalline behavior of the obtained copolymers is necessary to be examined.

In recent years, the modification of PPTA by copolycondensation has attracted special attention^[8-9], but only a few of the modified copolyamides were studied on their liquid crystalline behavior^[9].

In this paper, the critical concentration, isotropic temperature and phase diagram of liquid crystalline solutions of aromatic copolyamides synthesized from TPC, PPD and DAPE were studied and discussed in detail.

EXPERIMENTAL

1. *Synthesis of copolyamides*

The copolyamides were prepared from TPC, PPD and DAPE in N-methylpyrrolidone/LiCl/pyridine solvent system by low-temperature solution copolycondensation. Under the guidance of molecular design, the aromatic copolyamides with two types of chain segment structure^[9] were synthesized. The monomers feeding sequences of copolymer F and G were PPD+TPC₁ (an half mole of the PPD) + DAPE + TPC₂ (the residual TPC) and PPD+DAPE+TPC, respectively. The amount of DAPE used (f_{DAPE}) and inherent viscosity (η_{inh}) of the copolyamides are listed in Table 1.

2. *Measurement of the liquid crystalline critical concentration and phase diagram*

Copolyamides 6—20 wt% were swelled and dissolved in 100% H₂SO₄ for 3—4 h at 50°C. The critical concentration was determined using polarizing microscope, and the liquid crystalline phase diagram was measured by a set of depolarization instrument with hot stage whose principle and scheme was illustrated as follows:

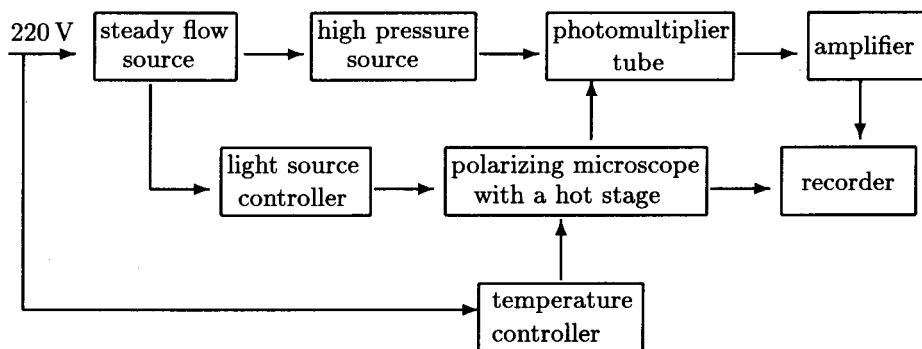


Table 1 f_{DAPE} and η_{inh} of copolymers

Sample	f_{DAPE} (mol/mol)	η_{inh}^* (l/g)	Sample	f_{DAPE} (mol/mol)	η_{inh} (l/g)	Sample	f_{DAPE} (mol/mol)	η_{inh} (l/g)
E	0.0	0.0660	F-2	0.2	0.0355	G-2	0.2	0.0626
		0.0605	F-3	0.3	0.0542			0.0554
		0.0505	F-4	0.4	0.0637			0.0421
		0.0409			0.0574	G-3	0.3	0.0496
		0.0309			0.0508	G-4	0.4	0.0650
F-1	0.1	0.0546			0.0450			0.0538
F-2	0.2	0.0657	F-5	0.6	0.0508			0.0448
		0.0554	F-6	0.8	0.0435	G-5	0.6	0.0384
		0.0455	G-1	0.1	0.0534	G-6	0.8	0.0356

* Different η_{inh} can be obtained depending on the amount of LiCl used during copolycondensation

RESULTS AND DISCUSSION

All of the critical concentration, the isotropic temperature, the range of liquid crystal phase and the texture of liquid crystal can be regarded as the suitable criteria of liquid crystal behavior. They will change with the variation of the content of third monomer, inherent viscosity and sequence distribution of copolyamides and their concentration in 100% sulphuric acid.

1. Critical concentration

The critical concentration at which the liquid crystal formed is one of the parameters characterizing liquid crystal behavior. The lower is the critical concentration, the easier the liquid crystal forms.

According to the theory proposed by Flory and Ronca^[10-11], the critical concentration of liquid crystal is decreased by increasing of the axial ratio, so that the critical concentration for a given copolymer in solution may be expected to vary with molecular weight and chain segment structure.

In Fig. 1 and Fig. 2, the effects of inherent viscosity of copolyamides on critical concentration in 100% sulphuric acid were shown. When the molecular weight of copolyamide decreased, a higher concentration or volume fraction of copolymer was needed to induce the formation of anisotropic phase at the same content of third monomer unit. The critical concentration of copolyamide F was slightly lower than that of copolyamide G at room temperature, and the slopes of the plot of critical concentration vs. inherent viscosity, $d[C^*]/d[\eta_{\text{inh}}]$, were different. For instance, it

was -159 for copolyamide F and -197 for copolyamide G, when the third monomer unit content of copolymer was 20%.

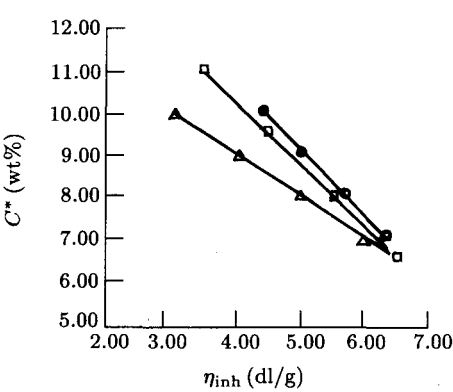


Fig. 1 Effect of η_{inh} of copolyamide F on critical concentration in 100% sulphuric acid

○ $f_{DAPE} = 0.4$; □ $f_{DAPE} = 0.2$; △ $f_{DAPE} = 0.0$

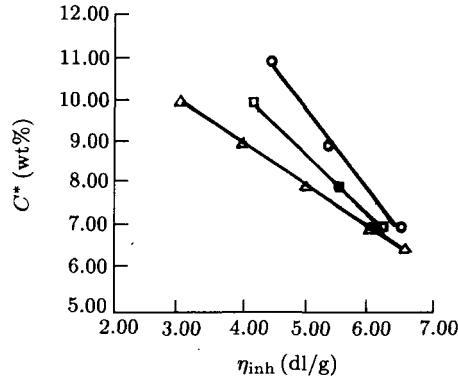


Fig. 2 Effect of η_{inh} of copolyamide G on critical concentration in 100% sulphuric acid

The critical concentration also varied with the content of third monomer unit in copolymer. The results are listed in Table 2. Adding DAPE could enhance the flexibility of molecular chain, decrease the axial ratio and increase the critical concentration of copolyamides.

Table 2 Critical concentration of copolyamides

Sample	η_{inh} (l/g)	C^* (wt%)	Sample	η_{inh} (l/g)	C^* (wt%)
E	0.0505	8	E	0.0505	8
F-1	0.0546	8	G-1	0.0534	8
F-2	0.0554	8	G-2	0.0554	8
F-3	0.0542	8.5	G-3	0.0496	10
F-4	0.0508	9	G-4	0.0448	11
F-5	0.0508	10	G-5	0.0384	13
F-6	0.0435	11	G-6	0.0356	14

2. Isotropic temperature

The isotropic temperature at which the liquid crystal phase completely disappears is another important parameter of characterizing liquid crystal behavior. The higher is the isotropic temperature, the more stable the liquid crystal phase is.

The liquid crystal has a high degree of long range orientational order of the molecular chain. First of all, it is the segment motion, then, the chain of polymer slips. Both the higher molecular weight and the longer segment structure enhance the potential energy which the motion of segment and chain must consume, so

that the isotropic temperature increase with increasing of the inherent viscosity of copolyamide (see Fig. 3 and 4).

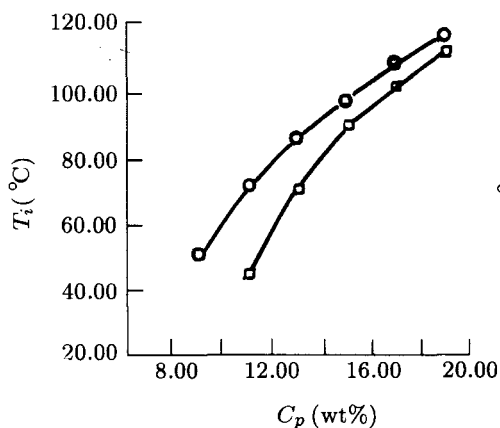


Fig. 3 The isotropic temperature versus the inherent viscosity and the concentration of copolyamide F-4

○ $\eta_{inh} = 0.0650$ l/g; □ $\eta_{inh} = 0.0448$ l/g

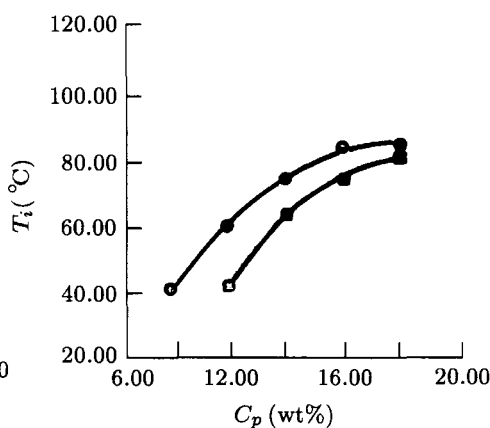
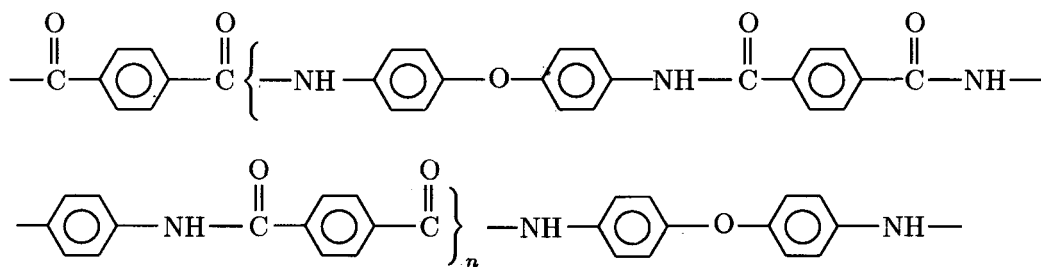


Fig. 4 The isotropic temperature versus the inherent viscosity and the concentration of copolyamide G-4

○ $\eta_{inh} = 0.0637$ l/g; □ $\eta_{inh} = 0.0508$ l/g

The orientational degree changes with the content of the third monomer unit, thus, barrier energy and isotropic temperature altered (see Fig. 5 and 6). By using the parameters of bond length and bond angle, the axial ratio of $\{\dots\dots\}$ segment in the molecular chain, which was illustrated as follows, was 6.67. It shows that the



copolyamide prepared with DAPE, TPC and a few of PPD could form liquid crystal phase in the 100% sulphuric acid at a suitable copolymer concentration. This result was demonstrated in their schlieren texture. In Fig. 3 to Fig. 6, the isotropic temperature of copolyamide F was higher than that of copolyamide G. It was most

probable that the length of $\text{---NH---C}_6\text{H}_4\text{---NH---C(=O)---C}_6\text{H}_4\text{---C(=O)---}$ segment in copolyamide F is longer than that in copolyamide G.

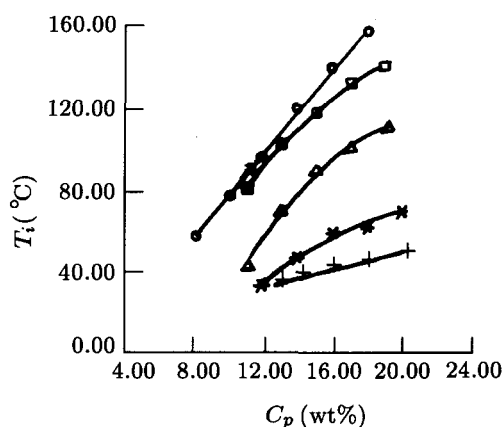


Fig. 5 The isotropic temperature versus the content of third monomer unit and the concentration of copolyamide F

○ $f_{\text{DAPE}} = 0.0$; □ $f_{\text{DAPE}} = 0.2$; △ $f_{\text{DAPE}} = 0.4$; * $f_{\text{DAPE}} = 0.6$; + $f_{\text{DAPE}} = 0.8$

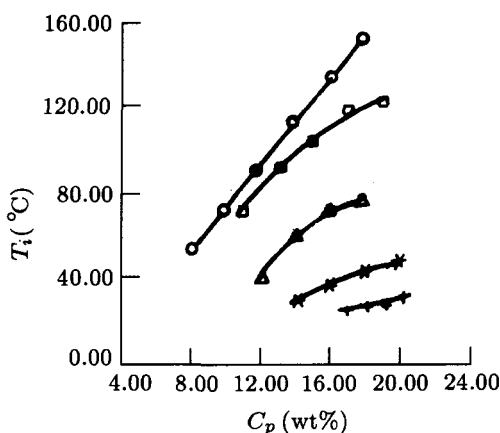


Fig. 6 The isotropic temperature versus the content of third monomer unit and the concentration of copolyamide G

3. Liquid crystal phase diagrams and range of liquid crystal phase

The curves of copolyamide solution temperature and depolarization, which varied with the inherent viscosity, the content of third monomer, sequence distribution of copolyamide and its solution concentration were plotted. Figs. 7 and 8 presented the plots of various transition temperatures versus the solution concentration of copolyamides. Not only the copolyamides ($f_{\text{DAPE}} = 0.4$) were studied, but also the others were investigated.

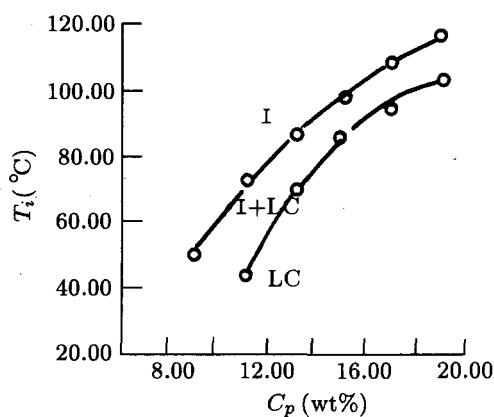


Fig. 7 The phase diagram of copolyamide F-4 ($\eta_{\text{inh}} = 0.0637$ l/g) in 100% sulphuric acid

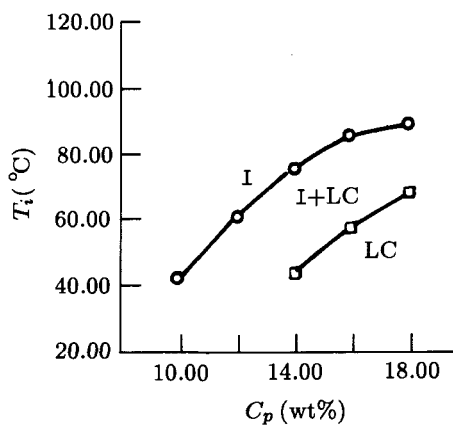


Fig. 8 The phase diagram of copolyamide G-4 ($\eta_{\text{inh}} = 0.0650$ l/g) in 100% sulphuric acid

Several important conclusions can be drawn from these results:

① The phase transition temperatures varies with the changes of concentrations and inherent viscosities of copolyamides.

② The phase transition temperatures decrease rapidly with increasing of the content of third monomer unit. The decreasing degree of copolyamide G is larger than that of copolyamide F at the same condition.

③ The solutions of copolyamides F or G form liquid crystal at room temperature when the content of third monomer is not lower than 0.2, but the solution of PPTA forms a gel phase.

The temperature range of liquid crystal phase were listed in Table 3.

Table 3 Temperature range of liquid crystal phase

Sample	η_{inh} (l/g)	$\Delta T(^{\circ}\text{C})$	Sample	η_{inh} (l/g)	$\Delta T(^{\circ}\text{C})$
E	0.0505	40	E	0.0505	40
F-1	0.0546	66			
F-2	0.0554	99	G-2	0.0554	73
F-3	0.0580	103			
F-4	0.0508	71	G-4	0.0650	41

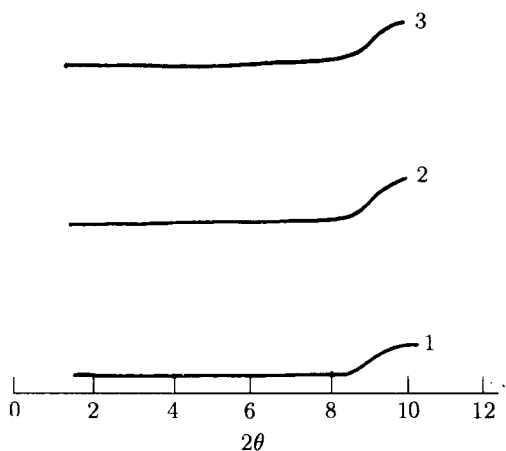


Fig. 9 Small-angle X-ray diffraction of copolyamide solutions in 100% sulphuric acid

$C_p = 16\%$; 1— F-2, $\eta_{inh} = 0.0554$ l/g; 2— F-6, $\eta_{inh} = 0.0435$ l/g; 3— G-2, $\eta_{inh} = 0.0554$ l/g

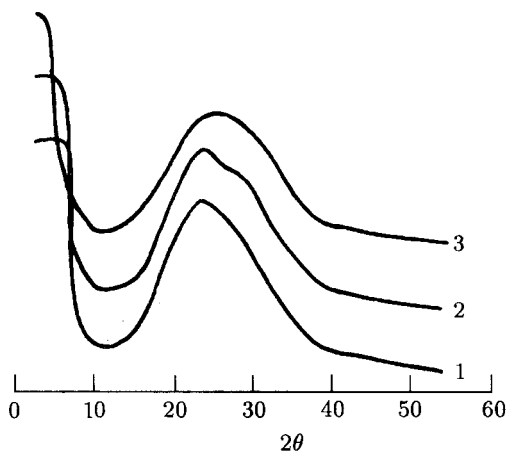


Fig. 10 Wide-angle X-ray diffraction of copolyamide solutions in 100% sulphuric acid

4. X-ray diffraction of liquid crystalline solution

The textures of liquid crystal solutions varied considerably with the preparation procedure of the sample. When a thin layer of solution was held between two glass plates and magnified between crossed polarizers in a microscope, colour domains

which changed with the copolymer concentration, content of third monomer unit and inherent viscosity were observed. At room temperature, a typical threaded schlieren texture can be observed from photos.

The liquid crystal texture became more obvious and brighter with the change of copolymer concentration, molecular weight, and the content of third monomer unit.

The type of liquid crystal was determined directly by X-ray diffraction. The results of small-angle X-ray diffraction indicated that there were no diffraction peaks in the region from 1.5—8° (Fig. 9), while the wide-angle X-ray diffraction evinced a diffusive peak (Fig. 10), so, the liquid crystal type of copolyamides contained various contents of third monomer unit and sequence distribution is nematic liquid crystal in 100% sulphuric acid.

Keywords:

Liquid crystalline behavior; Aromatic copolyamide

NOMENCLATURE

C^* : the critical concentration at which the liquid crystal phase starts forming. (wt %)

C_p : the concentration of copolyamide in 100% sulphuric acid. (wt %)

f_{DAPE} : the ratio of third monomer (DAPE) to diamines (DAPE+PPD). (mol/mol)

T : the temperature of studying liquid crystal behavior of copolyamide. (°C)

T_i : the isotropic temperature. (°C)

X : the enlargement factor of the polarizing microscope. (times)

ΔT : the phase transition temperature range from liquid crystal phase to isotropic phase. (°C)

η_{inh} : the inherent viscosity of copolyamide (5 g/l, the solvent is 96—98 wt% concentrated sulphuric acid, measured at 30.00±0.05°C). (l/g)

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