

Preparation and Characterization of Lyotropic Liquid Crystalline Aromatic Copolyamides Containing Twisty and Non-coplanar Moiety

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ABSTRACT: A series of aromatic rigid-chain copolyamides were prepared from 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-(aminophenoxy)phenyl)](2H)phthalazin-1-one (DHPZ-DA), *p*-phenylenediamine (PPD), 1,4-bis(4-aminophenoxy)benzene (BAPOB) and terephthaloyl dichloride (TPC) by low temperature solution polycondensation. The polymers were produced with high yields and relatively high inherent viscosities, ranging from 1.74 to 4.31 dL/g. The introducing of phthalazinone moiety and ether linkages into the main chain improved the solubility in some polar solvents. The T_g values of the polymers were in the range of 291–351 °C and the 5 and 10% weight loss temperatures in nitrogen were in the range of 486–518 and 509–538 °C, respectively, indicating their good thermal stability. WAXD measures indicated that these copolyamides were semicrystalline in nature. Most of the polymers exhibited nematic lyotropic liquid crystalline characteristics in concentrated H₂SO₄, NMP (1 wt % LiCl) and DMAc (1 wt % LiCl) solutions, as evidenced by polarizing light microscopy. [doi:10.1295/polymj.38.477]

KEY WORDS Lyotropic Liquid Crystalline / Copolyamides / Phthalazinone / Nematic /

Since the discovery of liquid crystalline, anisotropic ordering behaviors of liquid crystals (LCs) have been of considerable interest to academe and industry.^{1–4} Liquid crystalline polymers (LCPs) can be found in a number of commercial applications ranging from high strength engineering plastics to optical display devices. Polymers that exhibit liquid crystallinity, either in the melt or in their solutions, usually consist of comparatively rigid structures that confer high extension on the molecular chains.^{3–6} The structure of rigid chain polymers always contains aromatic rings together with functional groups, hydrogen bonding, and molecular symmetry. These structural factors, promoting strong intermolecular interaction and hence liquid crystallinity, unavoidably led to high melting temperatures and poor solubility of the resulting polymers which prevent their process or use in many applications. For example, poly(*p*-phenylene terephthalamide) (PPTA) which is the chemical structure of Kevlar[®] is a lyotropic LCP and exhibits outstanding mechanical properties, good thermal stability, and excellent chemical resistance, but this polyamide fiber can only be spun from its conc. H₂SO₄ solution.⁷

In an attempt to improve the solubility of rigid chain liquid crystalline polymers especially PPTA, many efforts have been made to modify the polymer chain structure. Some of these approaches include the incorporation of twist and non-planar moiety and flexible links into the polymer chain.^{8–10} It has been

found that aromatic polyamides containing phthalazinone moiety and ether linkages in the polymer backbone exhibit excellent properties including being soluble in some polar aprotic solvents such as NMP, DMAc etc.^{11–14} But studying of the liquid crystalline behavior of these polyamides is only at the beginning.

It has been demonstrated that one of the prerequisites for a polymer to exhibit liquid crystallinity is the straightness and rigidity of the polymer chain, which can be related to persistence length.^{15–17} Flory predicted that for a rigid rod polymer chain to exhibit liquid crystallinity, the aspect ratio of the rodlike molecule should be larger than 6.¹⁷ It will be interesting to see rigid chain polymers containing a high percentage of twist non-planar moiety and ether linkages still exhibiting liquid crystallinity.

In the present article, 1,2-dihydro-2-(4-aminophenyl)-4-[4-(4-(aminophenoxy)phenyl)](2H)phthalazin-1-one (DHPZ-DA) and 1,4-bis(4-aminophenoxy)benzene (BAPOB) were introduced into the main chain of PPTA by low temperature solution polymerization method.¹⁸ Thus a series of copolyamides containing varying ratios of twist non-planar moiety and ether linkages were obtained. The ability of the polymers to form LC solutions was tested. The structures of the copolyamides were characterized and their inherent viscosity, solubility, thermal properties, and crystallinity were also investigated.

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EXPERIMENTAL

Materials

1,2-Dihydro-2-(4-aminophenyl)-4-[4-(4-(aminophenoxy)phenyl)](2H)phthalazin-1-one (**DHPZ-DA**, mp: 260–261 °C) was prepared according to the reported method.¹¹ *p*-Phenylenediamine (**PPD**) was purified by vacuum sublimation. 1,4-Bis(4-aminophenoxy)benzene (**BAPOB**, mp: 174–175 °C) was prepared by the aromatic substitution reaction of hydroquinone and *p*-chloronitrobenzene and by the subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compound.¹⁹ Terephthaloyl dichloride (**TPC**) was purified by vacuum distillation. Reagent grade LiCl was dried under vacuum at 180 °C just before use. *N*-methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over CaH₂ and stored over 4 Å molecular sieves. Pyridine (Py) was refluxed over KOH pellets and distilled.

Polymer Synthesis

The copolyamide containing 10 mol % **DHPZ-DA**, 30 mol % **BAPOB** and 60 mol % **PPD** is nominated as **P-103060** and the other denomination of the polymers are the same. A typical example of the synthesis of **P-103060** is shown as follows. A mixture of 0.4205 g (1.0 mmol) **DHPZ-DA**, 0.8770 g (3.0 mmol) **BAPOB**, 0.6489 g (6.0 mmol) **PPD** and 0.40 g LiCl were charged into a three-neck flask containing 30 mL NMP and 1.0 mL Py at 0 °C. After all the diamines and salt were dissolved, 2.0423 g (10.0 mmol) **TPC** were added into the mixture. Then the system were maintained with stirring under N₂ atmosphere for about 6 h at 0 °C. The resulting copolyamide was crushed and poured into 400 mL ethanol/water (1:1, v/v). The pale yellow massive copolymer was washed thoroughly with hot water and dried then extracted with acetone for 8 h and dried under vacuum overnight at 100 °C. The yield was 99%. *Anal.* calcd for **P-103060**: C, 72.50%;

H, 4.1%; N, 9.49%. Found: C, 70.52%; H, 4.23%; N, 9.30%.

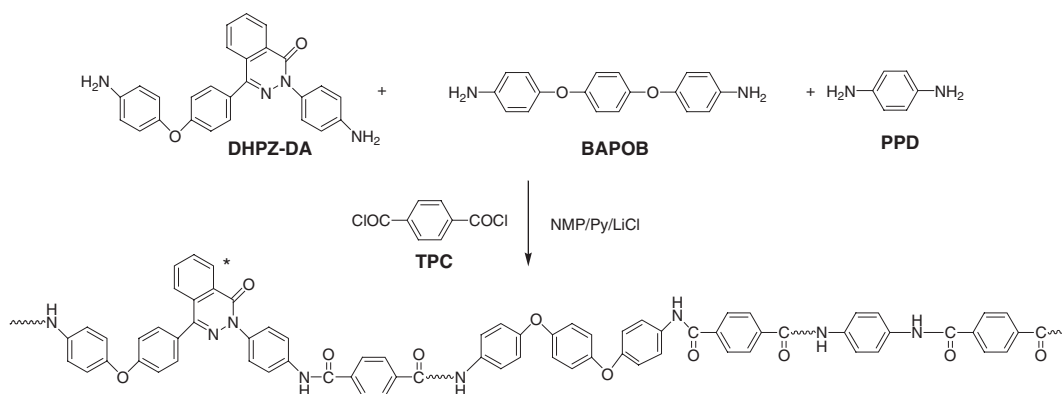
Measurements

Inherent viscosities (η_{inh}) were measured by Ubbelohde viscometer at a concentration of 0.5 g/dL. FT-IR spectra were recorded by reflection method with a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. ¹H NMR spectra were obtained using a Varian INOVA 400M nuclear magnetic resonance. Elemental analysis was performed on Carl'd Erba1106 CHN elemental analyzer. Differential scanning calorimetry (DSC) analysis and thermogravimetric analysis (TGA) were performed on Netzsch 204 DSC and Nstzsch 209 TG instruments, respectively. All samples were tested in flowing N₂ at a heating rate of 20 °C/min. The wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku D/max 2400 automatic X-ray diffractometer using Ni-filtered Cu K α radiation (40 V, 100 mA) at room temperature. The rotated velocity of the goniometry was 4°/min. Tensile properties of the thin polymer film specimens (about 8 mm wide and 60 mm long) were evaluated at room temperature on a Shimadzu AG-2000A tester and the extension rate was 100 mm/min. The textures of the copolyamides were identified with an Olympus BH-2 polarizing light microscope (PLM).

RESULTS AND DISCUSSION

Polymer Synthesis

Although Yamazaki-Higashi phosphorylation method starting from dicarboxylic acid and diamine is the widely used procedure in the laboratory, it is difficult to get high molecular weight polyamide.^{19–21} The low temperature solution polycondensation of diacidchloride with diamines is a convenient method for the preparation of high molecular weight polyamide. The synthesis route is shown in Scheme 1. By chang-



Scheme 1. The synthesis route of the copolyamides.

ing the molar ratios of the diamines and optimizing the reaction parameters, we have successfully got a series of novel copolyamides with the inherent viscosity (η_{inh}) values ranged from 1.74 to 4.31 dL/g measured in NMP (1 wt % LiCl) or conc. sulfuric acid according to their solubilities. Obvious rod climbing phenomena and stir opalescence were observed during the starting period of polymerization. When the percentages of PPD were more than 60%, such as **P-101080** and **P-102070**, the reaction systems changed into gel state quickly, the dry of the solutions appeared, and the polymers were splitted into small particles with the intensively stirring within 20 min. When the percentages of PPD were in the range of 40–60%, the polymer were in jelly state and did not drop when they were attached to the wall of the flask, so just static placing was needed in the later reaction process and the color of these products were pale yellow. While the percentages of PPD were less than 40%, such as **P-404020** and **P-206020**, the systems were very viscous liquid and stirring could go on until the reaction was stopped and the polymers were white (Table I).

The structures of these resulting copolyamides were characterized by FT-IR and ^1H NMR. The representative FT-IR spectra of the polymers are shown in Figure 1. It showed the characteristic absorption bands near 3300 cm^{-1} due to N–H stretch, 1653 cm^{-1} due to C=O stretch, 1600 cm^{-1} due to C=N stretch, 1516 cm^{-1} due to combined N–H bend and C–N stretch, 1248 cm^{-1} due to Ph–O–Ph stretch and 1112 cm^{-1} due to N–N stretch. The representative ^1H NMR spectrum of **P-404020** is shown as Figure 2. In the spectrum the resonance of N–H proton appeared at

Table I. Physical properties and solubility of the copolyamides

Copolymer	η_{inh}^a (dL/g)	Color	Solubility ^c				
			NMP	NMP /LiCl ^d	DMAC	DMAC /LiCl ^d	Conc. H ₂ SO ₄
P-101080	2.59 ^b	Yellow	–	+–	–	+–	+
P-102070	3.63	Yellow	+–	+–	–	+–	+
P-103060	4.31	Yellow	+–	+	+–	+	+
P-202060	2.75	Yellow	+–	+	+–	+	+
P-203050	2.82	Yellow	+–	+	+–	+	+
P-206020	2.95	White	+ ^e	+	+–	+	+
P-301060	3.94	Yellow	+–	+	+–	+	+
P-303040	2.38	Yellow	+–	+	+–	+	+
P-402040	2.17	Yellow	+–	+	+–	+	+
P-404020	1.74	White	+ ^e	+	+–	+	+

^adetermined at a concentration of 0.5 g/dL in NMP (1 wt % LiCl) at 25 °C. ^bdetermined at a concentration of 0.5 g/dL in concentrated sulfuric acid at 25 °C. ^cTested with 0.02 g of the polymers in 1 ml of solvent: +: soluble at room temperature; +–: partially soluble; –: insoluble. ^dSolvent containing 1 wt % LiCl. ^eGood films were casted from their NMP solutions. The tensile strength, initial modulus, and break elongation for **P-206020** film were 141.2 Mpa, 2.18 Gpa, and 6.2%; for **P-404020** film were 157.8 Mpa, 2.42 Gpa, and 6.7%, respectively.

the chemical shift of 10.32–10.62 ppm and the resonance of C–H of aromatic rings appeared at 7.12–8.46 ppm. The peak at 8.46 ppm corresponded to the C*–H protons which is a special shift of phthalazine. The ratio of integral area of the peaks of N–H: C*–H: C–H (except C*–H) was 5.08:1:38.79 which is very near the theoretical ratio of 5:1:39. Therefore the structure of the obtained copolymer was coincident with our design.

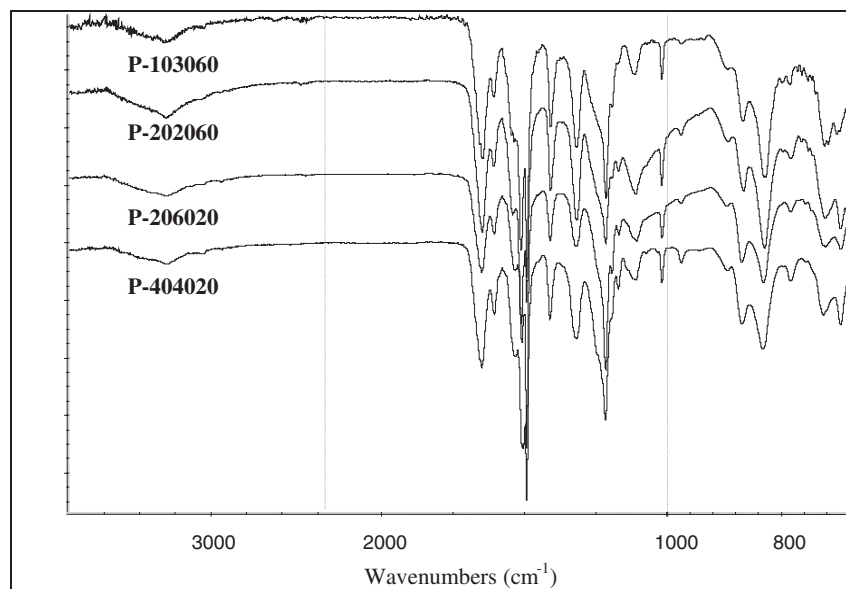


Figure 1. FT-IR spectra of copolyamides.

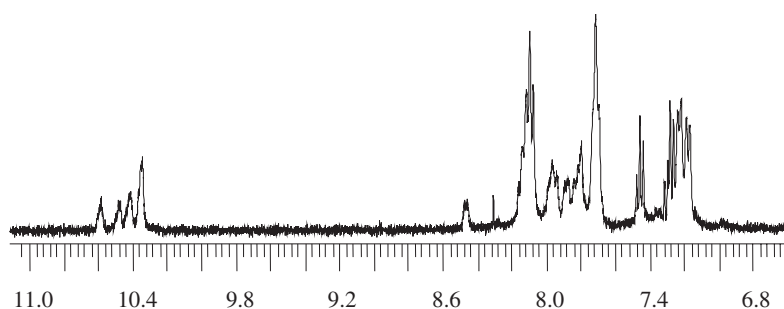


Figure 2. ^1H NMR spectrum of **P-404020**.

Polymer Solubility

The solubility of the copolyamides was qualitatively tested in some typical organic solvents, and the results are reported in Table I. They showed improved solubility with the content of phthalazinone moieties and ether linkages increase, which was coincide with the phenomenon of polymerization. The more percentages of PPD in the action systems resulted in poor solubility and thus the time of homogeneous reaction was shortened. This is attribute to the fact that twist and non-coplanar phthalazinone moiety and ether linkages reduce the tight packing of the polymer chains and do not allow the macromolecules to pack closely through hydrogen bonds between amides groups, thus they facilitate the penetration of the small molecules of solvent into the polymer chains. Almost all the polymers were soluble in NMP or DMAc both containing few LiCl. When the ratio of PPD is less than 40%, the polymers were soluble in NMP. These make it possible for the polymers to form lyotropic LC in the polar solvents and to apply in spinning or casting processes.

Thermal Properties

To study the thermal behavior of the polymers, differential scanning calorimetry (DSC) test was performed between 50–400 °C in flowing N_2 at a heating rate of 20 °C/min. No transition due to softening or melting was observed. The glass transition temperatures (T_g , taken as the midpoint of the change in slope of the baseline) of polyamides were found in the range of 291–351 °C and the obtained results are collected in Table II. The thermal decomposition temperatures of the polymers were evaluated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis at a heating rate of 20 °C/min in flowing N_2 . All of these polymers showed similar decomposition behavior and the representative curves are shown in Figure 3. Most of the polymers showed no significant weight loss up to 400 °C. But there were more ether linkages in **P-206020** and **P-404020** which were easy to decomposition, the initial weight loss temperature was low. The temperatures

Table II. Thermal properties of the copolyamides

Copolymer	T_g (°C) ^a	$T_{5\%}$ (°C) ^b	$T_{10\%}$ (°C) ^c	T_{\max} (°C) ^d	C_y (%) ^f
P-101080	— ^g	504	538	582	55
P-102070	—	518	536	578	56
P-103060	351	504	521	552	56
P-202060	340	496	514	557, 562 ^e	53
P-203050	324	511	526	571	54
P-206020	314	486	509	518	62
P-301060	328	499	516	563	57
P-303040	319	506	526	530, 570 ^e	60
P-402040	303	499	518	529, 573 ^e	55
P-404020	291	491	509	519	57

^aFrom DSC measurements conducted at a rate of 20 °C/min in nitrogen. ^bTemperature for 5% weight loss in N_2 , heating rate of 20 °C/min. ^cTemperature for 10% weight loss in N_2 , heating rate of 20 °C/min. ^dTemperature for the maximum in N_2 , heating rate of 20 °C/min. ^eTwo peaks in the DTG curves. ^fChar yield calculated as the percentage of solid residue after heating from 200 to 800 °C in N_2 . ^gnot detected.

for 10% gravimetric loss ($T_{10\%}$), which are important evidence for thermal stability, were in the range of 509–538 °C. The temperatures for 5% weight loss ($T_{5\%}$) and for the maximum weight loss rate (T_{\max}) were in the range of 486–518 and 518–582 °C, respectively. In addition, char yield (C_y) at 800 °C for the polymers were about 53–62% (Table II). These resultant data suggested that the introduction of the aromatic heterocyclic phthalazinone moiety into the polymer backbone retains the excellent thermal stability of Kevlar.

Polymer Crystallinity

The crystallinity of the copolyamides was examined by wide angle X-ray diffractions obtained on slice samples. All of the polymers exhibited amorphous patterns before being annealed. As shown in Figure 4, the representative polyamides exhibited broad dispersive peaks of diffraction at around $2\theta = 20$ –22°. This observation is quite reasonable because the presence of twist non-coplanar conformation of the phthalazinone moiety decrease the intermolecular force be-

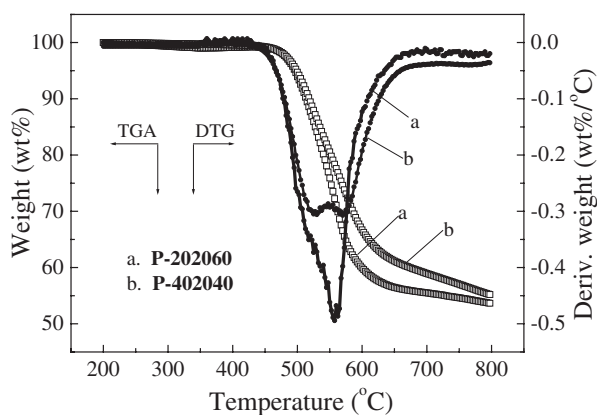
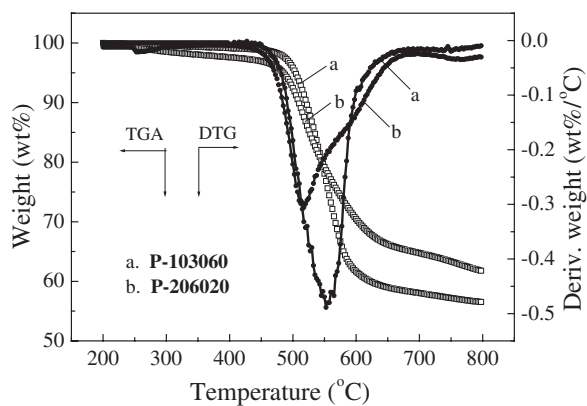


Figure 3. TGA (\square) and DTG (\bullet) curves of copolyamides in nitrogen, heating rate of $20^\circ\text{C}/\text{min}$.

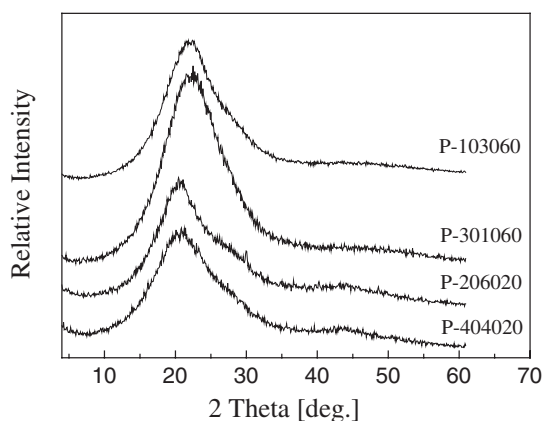


Figure 4. X-Ray diffraction patterns of copolyamides before annealing.

tween the polymer chains, subsequently cause a decrease in crystallinity. However, when the samples were heated up to 360°C , which is slightly above their T_g s, and kept at this temperature for 2 h, the polymer chains could receive enough energy to overcome the hindrance and rearrange in the more regular form. Then the samples were cooled gradually and the rearranged main chain structures were remained, which imparted the samples with the semicrystalline character. As shown in Figure 5, several obvious diffraction

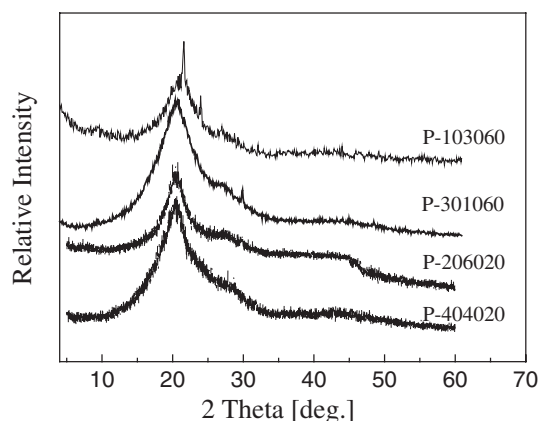


Figure 5. X-Ray diffraction patterns of copolyamides after annealing.

peaks in their X-ray diffraction pattern were observed after being annealed. The angle peaks of the spectrum were at $2\theta = 20\text{--}23^\circ$ corresponding to the intermolecular layer thickness of $4.01\text{--}4.38\text{ \AA}$. Additionally, when the percentages of PPD decreased from 60 to 20%, the thickness increased from ~ 4.05 to $\sim 4.35\text{ \AA}$. These data also indicate that the kink non-planar phthalazinone moiety and ether linkages in the polymer chains increase the disordered state and thus increase the distance of the polymer chains.

Lyotropic Behavior

For the formation and examination of prospective lyotropic systems, the polymers are dissolved in conc. H_2SO_4 , NMP (1 wt % LiCl), DMAc (1 wt % LiCl) or pure NMP, respectively, to form a class of solutions with different concentration in the range of 4–30 wt %. Concentrations higher than 30 wt % were not investigated since the polymers were not soluble thoroughly in the system. Then the homogeneous polymer solutions were placed on a glass slide and covered with a cover glass and observed on a polarizing light microscope (PLM) under crossed polarizer. The critical concentration C^* values in different solvents at room temperature are listed in Table III. Most of these copolyamides formed anisotropic phase in their conc. H_2SO_4 , NMP (1 wt % LiCl) and DMAc (1 wt % LiCl) solutions, with C^* values in the range of 20–28, 5–16 and 4–13 wt %, respectively. The C^* of different copolymer in the same solvent varied evidently. With the molar ratio of PPD in the diamines decreased, the density of hydrogen bonds between interchains decreased and the polymer chain became disorder because of the twisted non-coplanar phthalazinone structure and flexible ether linkages. So it needed higher concentration to form LC and thus the C^* increased. Table III also shown that the C^* values in NMP/LiCl or DMAc/LiCl are lower than the corresponding values in conc. H_2SO_4 . This can be understood as ex-

Table III. Critical concentration values of the copolyamides

Copolymer	C^* (wt %) ^a			
	Conc. H ₂ SO ₄	NMP /1% wt LiCl	NMP	DMAc /1% wt LiCl
P-101080	22	ND ^b	ND	—
P-102070	20	6	ND	—
P-103060	21	5	ND	5
P-202060	22	5	ND	4
P-203050	23	5	ND	5
P-206020	— ^c	13	12	12
P-301060	23	6	ND	6
P-303040	26	8	ND	6
P-402040	28	8	7	6
P-404020	—	16	14	13

^aThe critical concentration C^* (wt %) values at which the lyotropic phase appears at room temperature. ^bNot determined for the limited solubility. ^cLyotropic phase was not available under the test condition.

plained by Aharoni that the onset of anisotropy and attainment of full anisotropy are dependent on the magnitude and sign of the polymer–solvent interaction parameter,²² the smaller the interaction parameter, the lower the values of the critical concentrations. As representative examples, four photographs of different copolyamides in different solutions at room temperature are shown in Figure 6. Droplet texture, threaded texture, schlieren texture and marbled texture

can be separated from these photos, which are the typical texture of nematic liquid crystals.

It is exciting to discover that polyamide containing twist and non-planar moiety and ether linkages in the polymer backbone also exhibit lyotropic liquid crystallinity. The formation of the liquid crystalline solutions of aromatic polyamides is complex and influenced by a combination of factors.^{15,16} In solution the polyamide chains must have an extended rigid chain character including a trans configuration of the amide linkages. The solubility must be sufficiently high to exceed the critical concentration at which the formation of a biphasic solution (liquid crystalline phase coexisting with isotropic phase) occurs. Solubility and chain stiffness are affected by polymer structure, polymer–solvent interactions, aggregation, molecular weight, and temperature. Although the introduction of phthalazinone moiety and ether linkages destroy the tightness of the polymer chains, it improved the solubility and polymer–polar solvent interaction obviously and it is possible to form lyotropic phase in polar organic solvent.

When the solutions were placed under PLM with hot stage, we could observe that the C^* values were gradually increased with the temperature. Take **P-103060** in NMP/LiCl solution for example, the C^* value at room temperature (20 °C) was 5% and when the temperature is 180 °C, the C^* value increased to 8.1%.

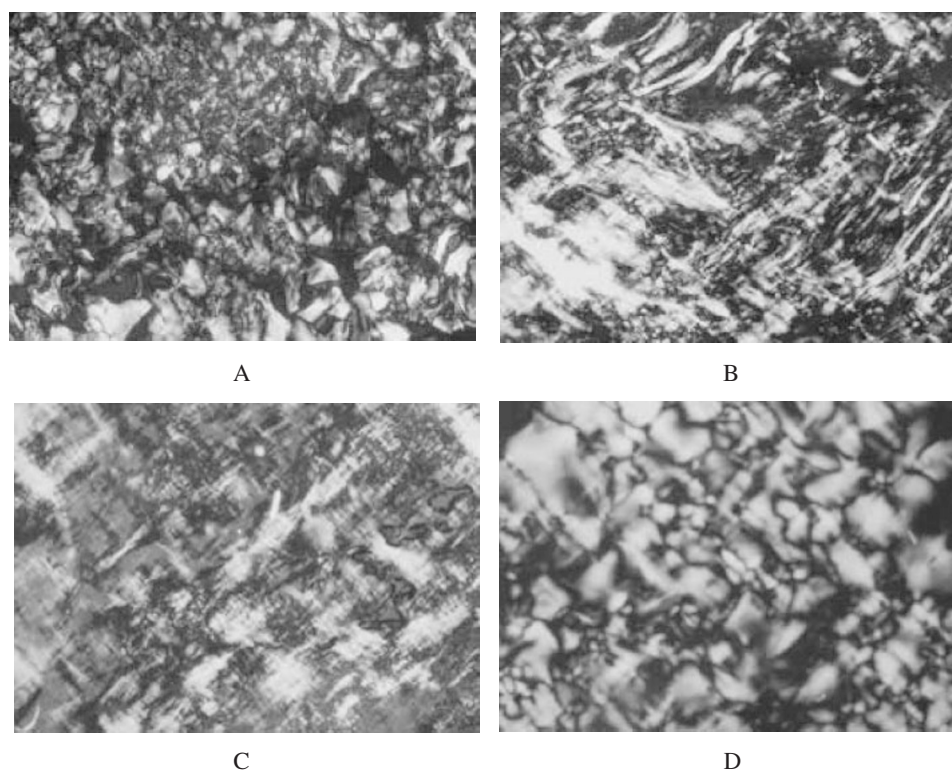


Figure 6. Optical micrographs of copolyamide solutions (magnification 40×): (A) **P-103060** at 9 wt % in NMP/LiCl (1% w/v) solution (droplet texture); (B) **P-303040** at 8 wt % in DMAc/LiCl (1% w/v) solution (schlieren texture); (C) **P-404020** at 16 wt % in NMP (threaded texture); (D) **P-301060** at 25 wt % in conc. H₂SO₄ (marbled texture).

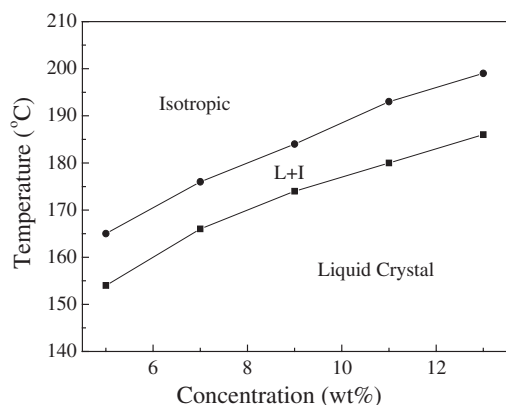


Figure 7. Phase diagram derived from optical microscopy of **P-103060** in NMP/LiCl (1% w/v) solution; The lower curve is the appearance of isotropic inclusions in the LC phase and the upper curve is the disappearance of the birefringence at the nematic–isotropic transition temperatures.

The temperature–concentration behavior of the solutions was also observed. When a glass slide with solution was placed on a hot stage between crossed polar, a birefringent (bright) nematic texture was appeared. Upon heating, the LC texture melted and dark areas corresponding to the isotropic phase appeared. Continued heating increased the size of dark areas until they finally coalesced to give a completely isotropic field of view at a temperature T_{NI} , which we defined as the nematic–isotropic transition temperature. The representative phase diagram of **P-103060** in NMP/LiCl (1% w/v) solution is shown as Figure 7 and all the other copolymers had the similar diagram in different solutions.

CONCLUSIONS

A series of aromatic copolyamides containing phthalazinone moiety and ether linkages were synthesized. The polymers exhibit improved solubility in polar aprotic solvents with or without the addition of LiCl because the introduction of twisted non-coplanar phthalazinone moiety and flexible linkages. The polymers possessed high T_g values and excellent thermal stability. WAXD measures indicated that the polymers were semicrystalline after being annealed. Observations under PLM demonstrated that the texture of the polymers solutions were nematic lyotropic liquid crystalline in conc. H_2SO_4 , NMP (1 wt % LiCl) and DMAc (1 wt % LiCl). The polyamides with excellent properties made it possible for the different proc-

essing and applications such as dry-wet spinning of fibers or the preparation of films, membranes and coatings.

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