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Pengtao Liu[a]; Cheng Liu[a]; Xigao Jian[a]
[a] Department of Polymer Science and Materials, Liaoning Research Center of High-performance Resin Engineering and Technology, Dalian University of Technology, Dalian, P.R. China

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Synthesis and Properties of Novel Aromatic Copolyamides Containing Phthalazinone Moiety

PENGTAO LIU, CHENG LIU, AND XIGAO JIAN

Department of Polymer Science and Materials, Liaoning Research Center of High-performance Resin Engineering and Technology, Dalian University of Technology, Dalian, P.R. China

*A series of novel aromatic copolyamides were synthesized by the direct polycondensation of 2-(4-carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone (**1**), terephthalic acid (TPA), and four commercial diamines. The inherent viscosities of the polyamides were between 0.79 ~ 1.56 dL/g. Introduction of the non-coplanar phthalazinone segments into the main chains remarkably decreased the crystallinity and improved the solubility of the copolyamides. When the percentage of **1** in the diacid monomers was above 50%, the copolymers were soluble in aprotic polar solvents, such as N-methyl-pyrrolidinone and N,N-dimethylacetamide. The copolyamides showed high thermal properties associated with the glass transition temperatures in the range of 276 ~ 337°C and 10% wt loss temperatures in nitrogen over 496°C. Some polymer films cast from NMP solution had tensile strengths up to 123.4 MPa, initial moduli up to 2.10 GPa, and elongation at break values up to 9.6%.*

Keywords copolyamides, phthalazinone, solubility, thermal properties, tensile properties

Introduction

Wholly aromatic polyamides have received much attention since they possess many desirable characteristics such as excellent thermal stability, chemical resistance, mechanical properties and low flammability (1, 2). These properties make them suitable for a wide variety of applications. However, a large number have extremely high glass transition temperatures and poor solubility in organic solvents, thus making them difficult to process (3). Therefore, research has been directed towards the synthesis of high-temperature polymers which are melt processible or soluble in common or environmental-acceptable solvents without any of the other mechanical and thermal properties being compromised. Many attempts have been made through copolymerization, incorporating twisted non-coplanar structures or flexible links into the main chain, or introducing bulky pendant groups into the polymer backbones (4–7). It has been demonstrated that polyamides containing the phthalazinone (DHPZ) moiety and ether linkages have enhanced solubility and acceptable thermal properties (8–10). The improved solubility was attributed to the twisted non-coplanar structure and flexible aryl ether bond, which

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Address correspondence to Xigao Jian, Department of Polymer Science and Materials, Dalian University of Technology, Dalian 116012, P.R. China. E-mail: jian4616@dl.cn

interrupt close chain packing and thus decrease chain-chain interactions. In addition, due to the aromatic heterocyclic structure of the DHPZ, the polyamides show T_g's up to 340°C.

Although many excellent polyamides are known and commercially available, new polyamides are continuing to appear as researchers continue to conduct fundamental studies on the relationships of chemical structure and property and search for polyamides with unique combination properties for special applications. As part of our interest in preparing high-performance polyamides containing DHPZ moieties, we used 2-(4-carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone (**1**), to synthesize aromatic copolyamides. In order to relate the structures with properties and study the contribution of DHPZ structure to the properties of the polyamides, a series of copolyamides were prepared using **1**, terephthalic acid (TPA) and commercial diamines. The solubility, crystallinity, thermal and tensile properties of the copolymers were investigated. It was determined that the properties of these copolyamides can be tailored by changing the monomer molar ratios of **1** to TPA.

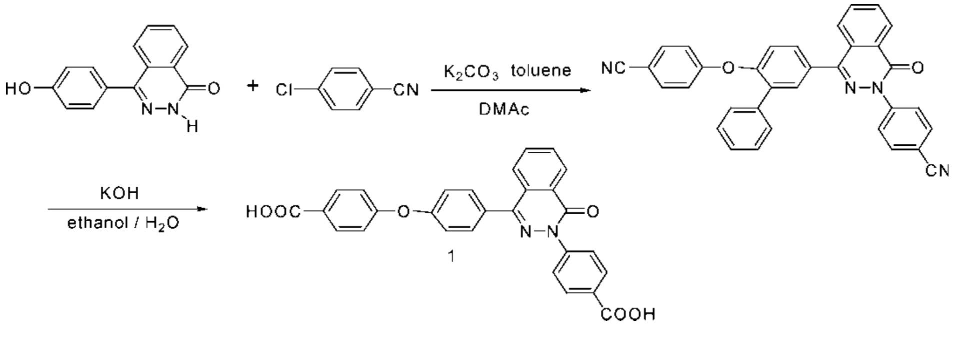
Experimental

Materials

4,4′-Oxydianiline, 4,4′-methylenedianiline and 4,4′-sulphonyldianiline were recrystallized from ethanol and toluene, respectively. *p*-Phenylenediamine was purified by vacuum sublimation. Terephthalic acid (TPA) was used as received. *N*-methyl-pyrrolidinone (NMP) was distilled under reduced pressure over CaH_2. Pyridine (Py) was refluxed over KOH pellets and distilled. Triphenyl phosphite (TPP) was distilled under vacuum. Anhydrous calcium chloride ($CaCl_2$) was dried for 3 h at 180°C under vacuum just before use.

2-(4-Carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone (**1**) is an excellent dicarboxylic acid monomer that was synthesized by the aromatic nucleophilic substitution reaction shown in Scheme 1 using 1,2-dihydro-4-hydroxylphenyl-phthalazinone and *p*-chlorobenzonitrile to obtain the dinitrile compound; then followed by alkaline hydrolysis to obtain **1**.

Its properties are as follows: (11) mp 334°C; FT-IR (KBr): 2800–3420 cm^{-1} (s, O–H), 1663 cm^{-1} (s, C=O), 1596 cm^{-1} (m, C=N), 150 cm^{-1} (m, C=C), 1250 cm^{-1} (m, C–O–C); MS(EI) m/z 477 $[C_{28}H_{18}N_2O_6]^-$; ^{1}H-NMR (400 MHz, DMSO-d_6) $\delta = 7.16$ (2H, H-18, 22), 7.29 (2H, H-13,15), 7.75 (2H, H-12,16), 7.82 (1H, H-5), 7.87 (2H, H-24, 28), 7.98 (4H, H-6, 7, 19, 21), 8.07 (2H, H-25, 27), 8.46



Scheme 1. Synthesis route of diacid **1**.

(1H, H-8), 12.95 (2H, H-29, 30); ^{13}C-NMR (100 MHz, DMSO-d_6) $\delta = 117.83$ (C-18, 22), 119.62 (C-13, 15), 125.67 (C-24, 28), 125.80 (C-20), 126.91 (C-5), 127.10 (C-8), 128.09 (C-9), 128.45 (C-10), 129.52 (C-26), 129.64 (C-25, 27), 130.53 (C-11), 131.53 (C-12, 16), 131.71 (C-19, 21), 134.09 (C-6), 145.18 (C-23), 146.68 (C-4), 156.25 (C-14), 157.99 (C-1), 160.34 (C-17), 166.65 (C-29), 166.68 (C-30).

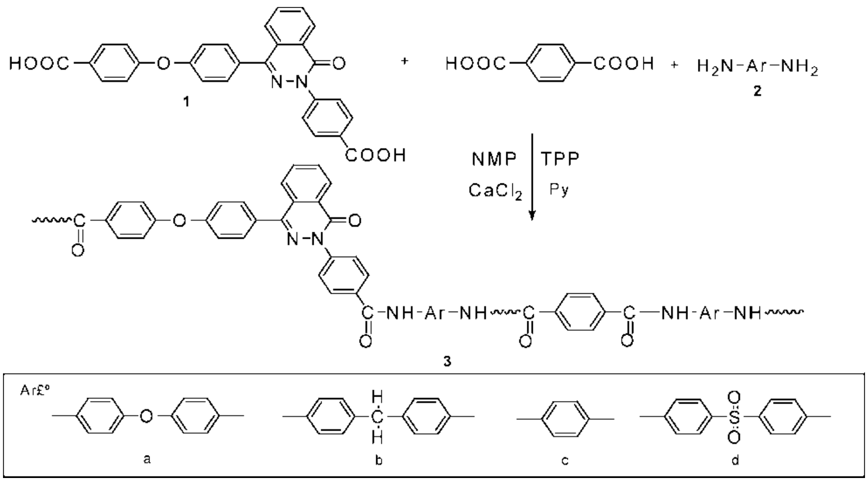
Polymer Synthesis and Film Casting

The copolyamide containing 80 mol% **1**, 20 mol% TPA and diamine **2a** is written as **3a(80/20)** and the designation for the other copolymers follow the same pattern. A typical example of the synthesis of **3a(80/20)** is shown as follows. A flask was charged with 1.1483 g (2.4 mmol) of **1**, 0.0997 g (0.6 mmol) of TPA, 0.6007 g (3 mmol) of **2a**, 1.20 g of $CaCl_2$, 1.3 mL of TPP, 2.5 mL of Py and 8 mL of NMP. The mixture was heated with stirring under N_2 atmosphere at 110°C for 5 h. As polycondensation proceeded, the solution gradually became viscous. The solution was then poured slowly into ethanol and the precipitated polymer was washed thoroughly with hot water and dried. The polymers were then extracted with acetone for 8 h and dried under vacuum overnight at 100°C. The synthesis route of the copolyamides is shown in Scheme 2.

The polyamide films were cast from their NMP solutions (8% w/v) on a glass plate in an oven at 60°C. Then, the semi-dried films were stripped from the glass surface and further dried in a vacuum oven at 140°C for 12 h. The obtained films were about 0.04 mm in thickness and they were used for X-ray diffraction measurements and tensile tests.

Measurements

Inherent viscosities were measured at 0.5 g/dL at 25°C using an Ubbelohde viscosimeter. FT-IR spectra were recorded on a Nicolet 20DXB FT-IR spectrometer with KBr pellets. ^{1}H-NMR spectra were obtained using a Varian INOVA 400M nuclear magnetic resonance instrument. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on NetzSch 204 DSC and NstzSch 209 TG instruments,



Scheme 2. Synthesis route of copolyamides.

respectively. All samples were tested under N_2 at a heating rate of 10°C/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 an average of at least five individual determinations were used. The wide-angle X-ray diffraction measurements were performed on a Rigaku D/max 2400 automatic X-ray diffractometer using Ni-filtered Cu-Kα radiation (40 V, 100 mA).

Results and Discussion

Polymer Synthesis and Characterization

A new class of copolyamides was synthesized using the Yamazaki-Higashi phosphorylation polyamidation procedure (12, 13) from dicarboxylic acid **1**, TPA and diamines **2a–d**. Most of the polymerizations proceeded in homogeneous solutions, except for polyamide **3c(20/80),** which precipitated from the reaction medium when the system became viscous due to its low solubility in the reaction mixture. As shown in Table 1, inherent viscosities (η_{inh}) of the polymers ranged from 0.79 to 1.56 dL/g in NMP or NMP containing 1 wt% LiCl. The η_{inh} of the series of **3a** were higher than those of the corresponding **3b** and **3d** because the activity of 4,4′-oxydianiline is higher than 4,4′-methylenedianiline and 4,4′-sulphonyldianiline. Although *p*-phenylenediamine is more active, the rigid structure results in a not very high η_{inh} of **3c**.

The FT-IR spectra of the polyamides exhibited a characteristic absorption band at 1650 cm^{-1}, amide **I** band, resulting from the amide C=O vibration. A strong amide **II** band which arises from the coupling of N–H bending and C=N stretching of C–N–H group, was observed at 1510 cm^{-1}. Strong absorption bands at 3400 cm^{-1} were due to N–H stretch. The absorption bands at 1600 cm^{-1} and 1248 cm^{-1}, characteristic of phthalazinone C=O stretching and Ph–O–Ph stretching were also observed. As representative examples, the FT-IR spectra of **3a(60/40)**, **3b(60/40)**, and **3c(60/40)** are shown in Figure 1. Solution ^{1}H-NMR spectra in DMSO-d_6 confirmed the chemical structures of the polymers with amide proton chemical shifts observed at 10.2 ~ 10.5 ppm.

The crystallinity of the polyamides was examined by wide-angle X-ray diffraction and the representative diagrams of copolyamides **3a** are given in Figure 2. All the polymers showed amorphous characteristics and exhibited no sharp peak in the testing range, but with the decrease of **1** in the diacid monomers, the peaks became sharper. This was attributed to the twisted, non-coplanar phthalazinone structure, which significantly increased the disorder of the main chain.

Polymer Properties

The qualitative solubility of the copolyamides was tested in various solvents at a concentration of approximately 1 wt%. The results are shown in Table 1. The solubility was remarkably enhanced with the increasing percentage of phthalazinone moiety in the copolymers. When the percentage of **1** in the diacid monomers was above 50%, the polymers were soluble in polar aprotic solvents such as NMP, DMAc and DMF. This is attributed to the fact that the polyamides containing more of the twisted, non-coplanar phthalazinone moieties and flexible ether linkages, which reduce the chain-to-chain interaction and do not allow the macromolecules to pack closely through hydrogen bonds between amides groups. This facilitates the penetration of the small solvent molecules between the

Table 1
The inherent viscosities and solubility of copolyamides

Copolyamide	η_{inh} dL/g$^{\circ}$	Solvent						
		NMP	DMAc	DMF	DMSO	Py	*m*-Cresol	Chloroform
3a(80/20)	0.91	++	+	+	+	++	++	−
3a(60/40)	1.56	++	+	−	+	+	+	−
3a(40/60)	1.51	++	+	−	−	−	−	−
3a(20/80)	1.40	−	−	−	−	−	−	−
3b(80/20)	0.80	++	++	−	+	+	+	−
3b(60/40)	0.83	++	++	−	+	−	+	−
3b(40/60)	0.76	+	++	−	−	−	−	−
3b(20/80)	0.87	−	−	−	−	−	−	−
3c(80/20)	0.97	+	+	−	+	−	+	−
3c(60/40)	1.22	+	−	−	−	−	+	−
3c(40/60)	0.82	−	−	−	−	−	−	−
3c(20/80)	0.79	−	−	−	−	−	−	−
3d(80/20)	1.03	+	+	+	+	+	+	−
3d(60/40)	0.98	+	+	−	+	−	−	−
3d(40/60)	0.83	−	−	−	−	−	−	−
3d(20/80)	0.63	−	−	−	−	−	−	−

Note: ++ soluble at room temperature; + soluble on heating; − insoluble.

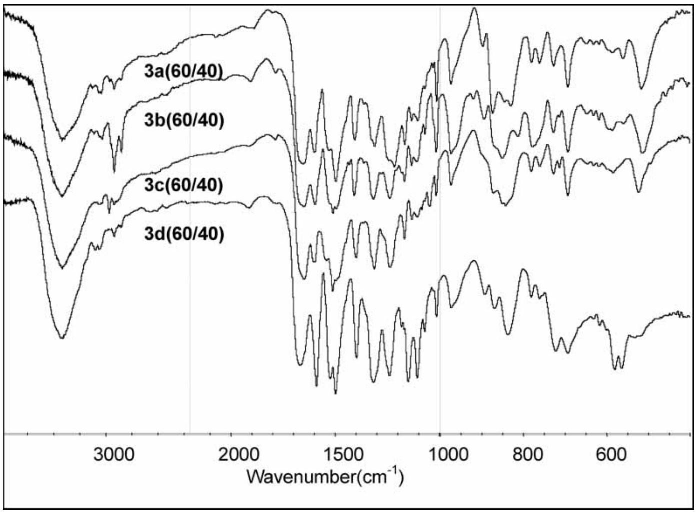


Figure 1. FT-IR spectra of copolyamides.

polymer chains. Polymers **3c** showed relatively lower solubility, possibly due to the rigid structure.

Thermal properties of the copolyamides were determined by DSC and TGA and Table 2 summarizes these results. The glass transition temperatures (T_g's), as shown by DSC analysis, were in the range of 276°C ~ 337°C. However, for all the polymers, no melting endotherm was detected which is primarily due to the melting temperature being higher than the thermal decomposition temperature. The T_g's of the polymers didn't vary significantly when the proportion of diacid **1** and TPA changed. Although the introduction of phthalazinone moiety decreased, the tight arrangement of the polymer chain, the wholly aromatic structure increases the segment size in the polyamide molecular chain and retained the heat-resistance property of aromatic polyamides. T_g's of the polyamides **3c** were higher than the others because of the

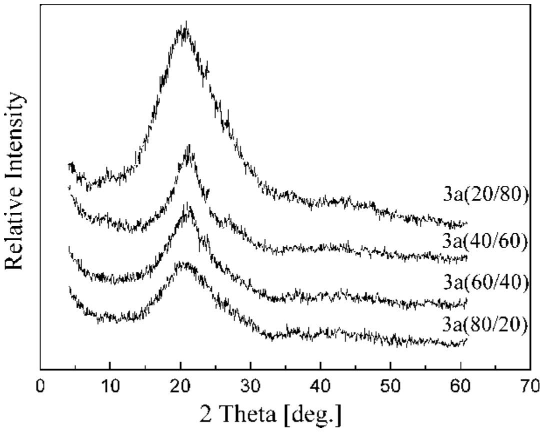


Figure 2. Wide-angle X-ray diffraction curves of copolyamides.

Table 2
Thermal properties of copolyamides

Corpolyamide	T_g (°C)	T_d (5%,°C)	T_d (10%,°C)
3a(80/20)	301	489	510
3a(60/40)	305	495	514
3a(40/60)	307	491	509
3a(20/80)	299	492	511
3b(80/20)	276	477	498
3b(60/40)	284	473	496
3b(40/60)	278	479	501
3b(20/80)	281	480	502
3c(80/20)	326	489	510
3c(60/40)	337	498	521
3c(40/60)	323	491	517
3c(20/80)	330	493	519
3d(80/20)	320	490	512
3d(60/40)	314	489	507
3d(40/60)	318	494	514
3d(20/80)	313	486	508

[a] Could not be measured (to be deleted).

rigidity of *p*-phenylenediamine. TG curves of the polyamides showed more or less similar patterns of decomposition. The temperatures of polyamides at 10% wt loss ranged from 496°C–521°C in N_2 atmosphere, which indicated good thermal stability of phthalazinone-containing polyamides.

Some of the polymers afforded transparent and flexible films prepared from their NMP solutions. However, the other polyamides film was not obtained because of their poor solubility. Table 3 summarizes the tensile properties of the films. The films had tensile strengths of 89.4 ~ 123.4 MPa, elongations to break of 5.5 ~ 9.6%, initial moduli of 1.66 ~ 2.10 GPa, which indicated that the introduction of phthalazinone

Table 3
Tensile properties of polyamide films

Copolyamide	Tensile strength (MPa)	Initial modulus (GPa)	Break elongation (%)
3a(80/20)	97.8	2.10	7.9
3a(60/40)	94.5	2.00	9.2
3b(80/20)	89.4	1.83.	8.2
3b(60/40)	90.2	1.72	9.6
3c(80/20)	123.4	2.08	6.5
3c(60/40)	120.8	1.71	7.7
3d(80/20)	101.1	2.04	6.2
3d(60/40)	103.8	1.66	5.5

moiety retained the excellent mechanical properties of polyamide. The tensile strength of **3c** was higher because of the more regular and closer of hydrogen bond in the main chains. The structure of **3b** was similar with that of **3a**, and the inherent viscosity of **3b** was lower than that of **3a.** From this, we can partly deduce that the molecular weight of **3b** was lower than that of **3a**, so the mechanical properties of **3b** were less than that of **3a**. Additional work is required to relate the tensile properties to the internal structure of the phthalazinone-containing copolyamides.

Conclusions

A series of copolyamides were prepared from 1,2-dihydro-2-(4-carboxyphenyl)-4-[4-(4-carboxyphenoxyl)phenyl]-phthalazinone, terephthalic acid and some commercial aromatic diamines by the direction polymerization method. The introduction of the phthalazinone moiety into the main chain of the polymers led to remarkable improved solubility and easy processability of such polymers from their solutions in appropriate organic solvents. The polymers were amorphous as evidenced by WAXD and some thin films obtained showed high tensile properties. The rigid phthalazinone moiety maintained the excellent thermal properties of polyamides.

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