

Synthesis and Properties of Novel Aromatic Copolyamides Containing Chloro-substituted Phthalazinone Moiety in the Main Chain

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ABSTRACT: A series of novel copolyamides were synthesized by the direct polycondensation of 1,2-dihydro-2-(4-carboxyphenyl)-4-[3-chloro-4-(4-carboxyphenoxy)phenyl]-phthalazinone (**1**), terephthalic acid (TPA) with three commercial diamines. The inherent viscosities of the polyamides were between 0.82 and 1.86 dL/g. When the molar ratios of **1** and TPA were higher than 1 : 1, the polymers were soluble in some polar aprotic solvents such as *N*-methyl-pyrrolidone and *N,N*-dimethyl acetamide etc. These polymers were amorphous with 10% weight loss temperatures in N₂ above

490°C and their glass transition temperatures were above 269°C. Some films of the polymers were pale yellow and transparent with tensile strengths up to 147.8 MPa, initial modulus up to 2.56 GPa and elongations at break values up to 9.8%, which depended on the repeating unit structures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2807–2811, 2007

Key words: polyamides; phthalazinone; solubility; mechanical properties; thermal properties

INTRODUCTION

Wholly aromatic polyamides are thermal stable polymers with an attractive combination of chemical, physical, and mechanical properties.¹ However, in many cases, they are insoluble and do not melt below their decomposition temperatures. So, processing in melt or solution is extremely difficult.^{2,3} Therefore, the preparation of soluble or thermoplastic polyamides without obviously lowering the high thermal properties has been a major research interest. Many attempts^{4–8} have been made through copolymerization, incorporating twisted noncoplanar structures or flexible links into the main chain, introducing bulky pendant groups into the polymer backbones or destroying the molecular symmetry by *meta*- or *ortho*-catenated aromatic or heterocyclic units etc.

In previous articles, we have described the synthesis of a series of poly(aromatic ether amide)s containing phthalazinone (DHPZ) moiety in the main

chain.^{9–11} The diamines and dicarboxylic acids derived from the DHPZ structure contain both twisted noncoplanar architecture and flexible ether linkages, both serve to disrupt the polymers' symmetry and regularity, and improve the solubility of the polyamides. In addition, because of the aromatic heterocyclic structure of the DHPZ, the polyamides show acceptable thermal properties with 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 chemical structure/property relationships and search for polyamides with unique combination properties for special applications. As part of our interest in preparing high-performance polyamides containing DHPZ moieties, 2-(4-carboxyphenyl)-4-[3-chloro-4-(4-carboxyphenoxy)phenyl]-phthalazinone (**1**) was used to synthesize aromatic copolyamides. To relate the structures with properties and study the contribution of chloro-substituted DHPZ structure to the properties of the polyamides, a series of three 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.

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EXPERIMENTAL

Reagents and solvents

4,4'-Oxydianiline and 4,4'-methylenedianiline were recrystallized from ethanol and toluene, respectively. *p*-Phenylenediamine was purified by vacuum sublimation. TPA was used as received. *N*-methyl-pyrrolidone (NMP) was distilled under reduced pressure over CaH₂. Pyridine (Py) was refluxed over KOH pellets and distilled. Triphenyl phosphite (TPP) was distilled under vacuum. Anhydrous calcium chloride (CaCl₂) was dried for 3 h at 180°C under vacuum just before use.

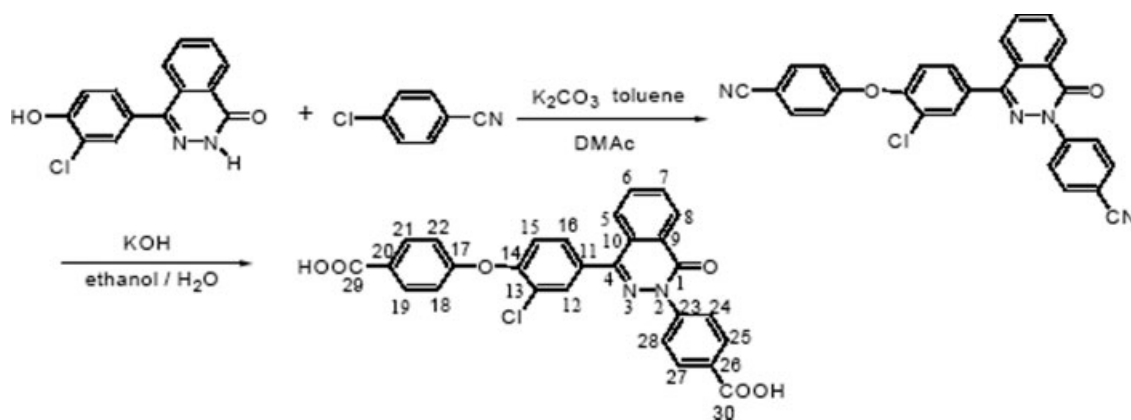
According to a well-established procedure,¹¹ 2-(4-carboxyphenyl)-4-[3-chloro-4-(4-carboxyphenoxy)phenyl]-phthalazinone (**1**) was prepared by the aromatic nucleophilic substitution reaction of 1,2-dihydro-4-(3-chloro-4-hydroxyphenyl)-phthalazinone¹² with *p*-chlorobenzonitrile followed by alkaline hydrolysis. Our previous study provided a detailed procedure for preparing **1** (Scheme 1). A mixture of 1,2-dihydro-4-(3-chloro-4-hydroxyphenyl)-phthalazinone (0.1 mol), *p*-chlorobenzonitrile (0.2 mol), K₂CO₃ (0.22 mol), DMAc, and toluene was placed in a 500 mL three-necked flask fitted with a mechanical stirring bar, a thermometer, a reflux condenser, and a N₂ inlet and outlet. The mixture was gradually heated to reflux for 4–5 h to remove all water by means of azeotropic distillation with toluene under N₂. The temperature was then increased to 155°C to remove toluene for 1 h and then cooled. The mixture then poured into an ethanol–water mixture (1 : 1, v/v, 500 mL). The precipitate was collected on a filter and crystallized from DMAc and ethanol to give white solid of dinitrile compound (yield 73.5%, mp 226–227°C). A suspension of the dinitrile (0.1 mol) in 400 mL of water and ethanol (1 : 1, v/v) containing KOH (0.1 mol) was heated to reflux for 48 h. The resulting clear solution was acidified to pH = 2–3 by hydrochloric acid. The yellow precipitate was filtered off, washed with water to neutral and dried to give diacid **1**.

Its properties are as follows: mp 316°C; FTIR (KBr): 2800–3460 cm⁻¹ (s, O–H), 1680 cm⁻¹ (s, C=O), 1600 cm⁻¹ (m, C=N), 1500 cm⁻¹ (m, C=C), 1250 cm⁻¹ (m, C–O–C); MS(EI) *m/z* 511[C₂₈H₁₇ClN₂O₆–H]⁻; ¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.12 (2H, H-18, 22), 7.42 (1H, H-13), 7.73 (1H, H-12), 7.84 (1H, H-5), 7.90 (2H, H-24, 28), 7.96 (1H, H-16), 7.99 (1H, H-7), 8.00 (3H, H-6, 19, 21), 8.10 (2H, H-25, 27), 8.47 (1H, H-8), 13.02 (2H, H-29, 30); ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 116.62 (C-18, 22), 122.12 (C-13), 125.43 (C-11), 125.75 (C-20), 126.68 (C-5), 126.98 (C-8), 127.88 (C-10), 128.14 (C-9), 129.47 (C-24, 26, 28), 129.53 (C-25, 27), 130.10 (C-12), 131.61 (C-16, 19, 21), 132.46 (C-15), 134.04 (C-6), 144.91 (C-23), 145.37 (C-4), 151.02 (C-14), 157.82 (C-1), 159.85 (C-17), 166.44 (C-29), 166.51 (C-30).

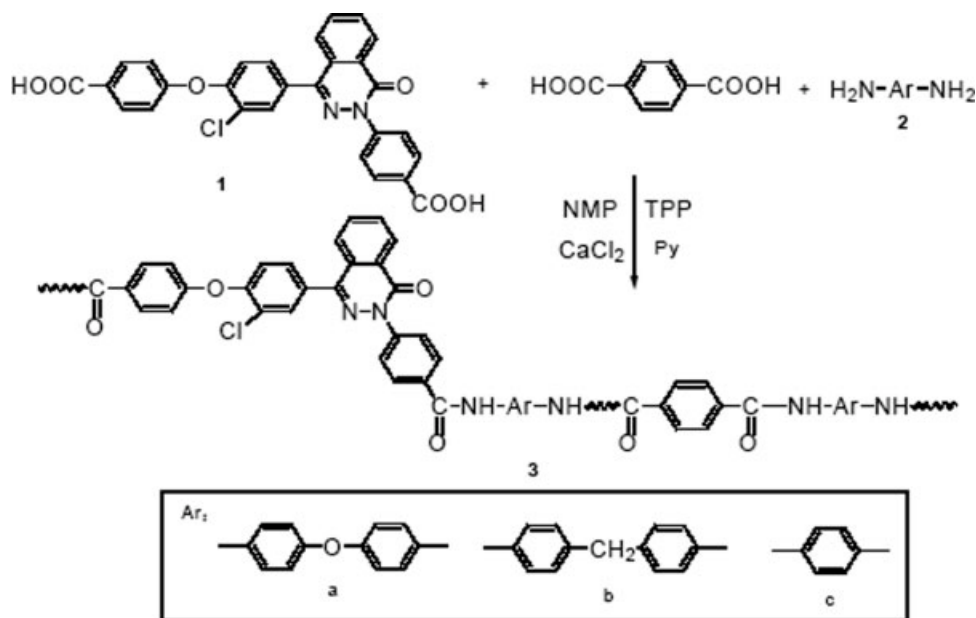
Polymer synthesis and film casting

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. **1** (1.2310 g, 2.4 mmol), TPA (0.0997 g, 0.6 mmol), **2a** (0.6007 g, 3 mmol), CaCl₂ (1.20 g) and TPP (1.3 mL, 6 mmol) were mixed into 8 mL NMP and 2.5 mL Py, and the mixture was maintained with stirring under N₂ atmosphere at 110°C for 5 h. After cooling, it was poured into 200 mL ethanol/water (1 : 1, v/v) and the precipitated polymer was washed thoroughly with hot water and dried. Then the polymers were 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 of 60°C. Then the semidried films were stripped from the glass surface and further dried in a vacuum oven at 120°C for 12 h. The obtained films showed about 0.04 mm in thickness and they were used for X-ray diffraction measurements and tensile tests.



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



Scheme 2 Synthesis route of copolyamides.

Characterization methods

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. ^1H NMR spectra were obtained using a Varian INOVA 400 M nuclear magnetic resonance. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Netzsch 204 DSC and Netzsch 209 TG instruments, 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. Mechanical clamps were used, and an extension rate of 100 mm/min was applied. The wide-angle X-ray diffraction measurements were performed on a Rigaku D/max 2400 automatic X-ray diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation (40 V, 100 mA).

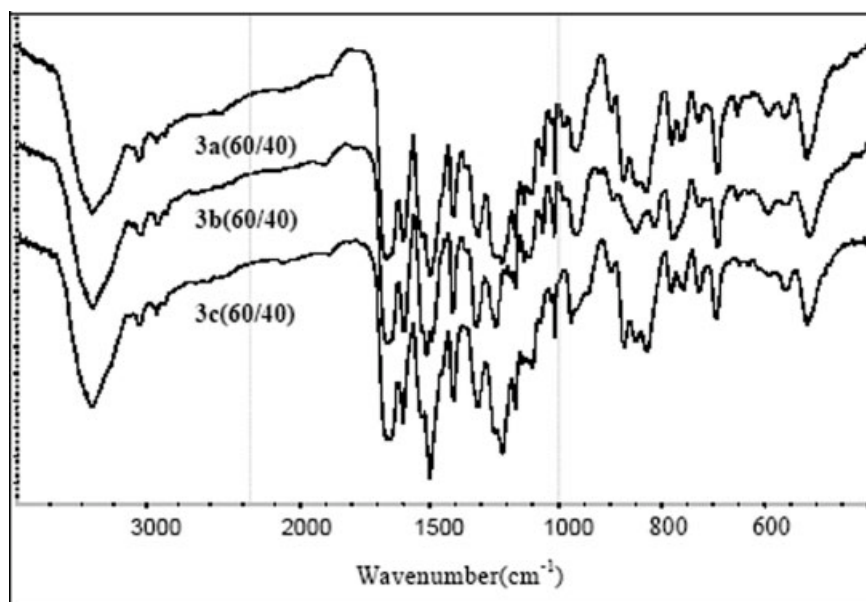


Figure 1 FTIR spectra of copolyamides.

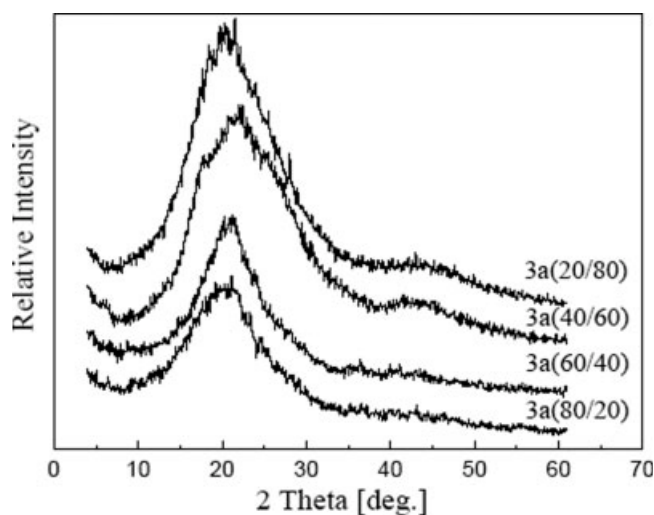


Figure 2 Wide-angle X-ray diffraction curves of copolyamides.

RESULTS AND DISCUSSION

Polymer synthesis and characterization

A new class of copolyamides was prepared by direct polycondensation method¹³ via the phosphorylation route described by Yamazaki et al. in the presence of CaCl_2 . Most of the polymerizations proceeded in homogeneous solutions and the viscosity of the solutions were high at the end. But low viscosity polymer of **3c(20/80)** was precipitated at the middle time due to its low solubility in the polymerization system. All the polymers were obtained in almost quantitative yield with inherent viscosities (η_{inh}) in the range of 0.82–1.86 dL/g. The η_{inh} of the series of **3a** were higher than those of the corresponding **3b** because the activity of 4,4'-oxydianiline is higher than 4,4'-methylenedianiline. Though *p*-phenylenediamine is more active, the rigid structure results in not very high η_{inh} of **3c**.

The structures were analyzed by FTIR and ^1H NMR. As representative examples, the spectra of **3a(60/40)**, **3b(60/40)**, and **3c(60/40)** are shown in Figure 1. IR spectra showed the absorption bands at 3400 cm^{-1} due to N—H stretch, at 1660 cm^{-1} due to amide C=O stretch, at 1600 cm^{-1} due to phthalazinone C=N stretch, at 1498 cm^{-1} due to aromatic C=C stretch and at 1248 cm^{-1} due to Ph—O—Ph stretch. Solution ^1H NMR spectra in $\text{DMSO-}d_6$ confirmed the chemical structures of the polymers with amide proton chemical shifts observed at 10.2–10.4 ppm.

Representative wide-angle X-ray diffractograms of copolyamides **3a** are given in Figure 2. The curves had wide peaks that are characteristic of amorphous polymers. No polymers showed any characteristic peaks of well-defined long-range order structure or crystallinity but with the decrease of **1** in the diacid monomers, the peaks became sharper. The curves of polymer **3b** and **3c** had the same pattern. This was attributed to the twisted, noncoplanar phthalazinone structure, which significantly increased the disorder of the main chain.

Polymer properties

The solubility of these copolyamides was determined at concentration of 2% (w/v) in several solvents and the results are listed in Table I. 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 even in *m*-cresol. This is attributed to the fact that the polyamides containing more of the twisted, noncoplanar phthalazinone moieties and flexible ether linkages, which reduce the chain–chain interaction and do not allow the macromolecules to pack closely through hydrogen bonds between amides groups. This facilitates the penetra-

TABLE I
The Inherent Viscosities and Solubility of Copolyamides

Copolyamide	η_{inh} (dL/g)	Solvent						
		NMP	DMAc	DMF	DMSO	Py	<i>m</i> -cresol	Chloroform
3a(80/20)	1.56	++	++	+	+	++	++	–
3a(60/40)	1.86	++	+	–	+	+	+	–
3a(40/60)	1.46	+	–	–	–	–	–	–
3a(20/80)	1.02	–	–	–	–	–	–	–
3b(80/20)	1.23	++	++	–	+	+	+	–
3b(60/40)	1.27	++	+	–	+	–	+	–
3b(40/60)	1.36	+	–	–	–	–	–	–
3b(20/80)	0.97	–	–	–	–	–	–	–
3c(80/20)	1.41	++	+	–	+	–	+	–
3c(60/40)	1.52	+	–	–	–	–	+	–
3c(40/60)	1.37	–	–	–	–	–	–	–
3c(20/80)	0.82	–	–	–	–	–	–	–

Solubility: (++) soluble at room temperature, (+) soluble on heating, (–) insoluble. DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethyl formamide; DMSO, dimethyl sulfoxide.

tion of the small solvent molecules between the polymer chains. Polymers **3c** were less soluble than the others owing to the more rigid structure of the corresponding diamine.

Thermal analysis was performed with DSC and TGA and Table II summarized these results. The glass transition temperatures (T_g 's), as shown by DSC analysis, were in the range of 269–308°C. The T_g 's of the polymers did not vary obviously when the molar ratio of diacid **1** and TPA changed. Though the introduction of phthalazinone moiety decreases the tight arrangement of the polymer chain, it is a wholly aromatic structure that increases the segment size in the polyamide molecular chain and thus retains the heat-resistance property of aromatic polyamides. T_g 's of the polyamides **3c** were higher than the others because of the rigidity of *p*-phenylenediamine. TG curves of the polyamides showed more or less similar patterns of decomposition. The temperatures of polyamides at 10% weight loss ranged from 490 to 514°C in N_2 atmosphere. It can be seen from the original curves that the heat resistance temperature of polyamides varies between 380 and 410°C (taking drops in the TG curve as the onset of decomposition), thus indicating good thermal stability of phthalazinone-containing polyamides.

Some transparent films of the polyamides were obtained by casting from their NMP solutions. However, the other polyamide films were not obtained because of their poor solubility. The tensile properties of the films are shown in Table III and the introduction of phthalazinone moiety retained the excellent mechanical properties of polyamide. These films had tensile strengths of 83.2–147.8 MPa, elongations to break of 6.5–9.8% and initial moduli of 1.60–2.56 GPa. The tensile strength of **3c** was higher because of the more regular and closer of hydrogen bond in the main chains. The reason for the lower tensile strengths of **3b** is the existence of the aliphatic carbons in the main chain. It is well known that the sp^3 -hybridized carbon in a main molecular chain usually results in poor me-

TABLE II
Thermal Properties of Copolyamides

Copolyamide	T_g (°C)	T_d (5%, °C)	T_d (10%, °C)
3a(80/20)	301	483	507
3a(60/40)	296	487	512
3a(40/60)	303	482	502
3a(20/80)	295	490	509
3b(80/20)	275	472	497
3b(60/40)	269	461	490
3b(40/60)	273	468	492
3b(20/80)	277	470	495
3c(80/20)	307	490	512
3c(60/40)	308	488	511
3c(40/60)	302	487	509
3c(20/80)	304	491	514

TABLE III
Tensile Properties of Copolyamide Films

Copolyamide	Tensile strength (MPa)	Initial modulus (GPa)	Break elongation (%)
3a(80/20)	107.1	2.29	8.8
3a(60/40)	108.9	1.91	9.5
3b(80/20)	83.2	1.75	6.5
3b(60/40)	87.6	1.60	7.1
3c(80/20)	139.9	2.56	9.8
3c(60/40)	147.8	2.49	8.2

chanical properties. 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-[3-chloro-4-(4-carboxyphenoxy)phenyl]-phthalazinone, TPA and three kind of commercial aromatic diamines through direction polymerization method. The introduction of chloro-substituted phthalazinone moiety into the main chain of aromatic polyamides 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. Wholly aromatic structure of phthalazinone moiety contained the excellent thermal properties of polyamides.

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