

Synthesis and Characterization of Wholly Aromatic Polyamides Containing Halogen-Substituted Triphenylamine Moiety

NSC 96-2221-E-036-004

Hui-Min Wang (王惠民), Yi-Chun Kung (龔義群), Sheng-Huei Hsiao (蕭勝輝)*
 Department of Chemical Engineering Tatung University (大同大學化學工程學系)
 Tel: +886-2-25925252 ext. 2977 re-ext. 119; Fax: +886-2-25861939
 E-mail: shhsiao@ttu.edu.tw



ABSTRACT

A new family of wholly aromatic polyamides containing halogen-substituted triphenylamine units were synthesized by the phosphorylation polyamidation reactions of 4,4'-diamino-4'-halo-triphenylamines with terephthalic acid (TPA) and isophthalic acid (IPA), respectively, in *N*-methyl-2-pyrrolidone using triphenyl phosphite and pyridine as condensing agents, where the halogen atoms included F, Cl, Br and I. All polyamides were readily soluble in polar organic solvents. These polymers were amorphous and most of them could afford flexible and tough films. They had useful levels of thermal stability associated with high glass-transition temperatures (255–330°C), 10% weight-loss temperatures in excess of 442°C in nitrogen, and char yields at 800°C in nitrogen higher than 66%. Cyclic voltammograms of the polyamide films on an indium-tin oxide (ITO)-coated glass substrate exhibited one reversible redox couple at around 0.83–0.90 V versus Ag/AgCl in acetonitrile solution. The polymer films revealed excellent stability of electrochromic characteristics, with coloration change from a pale yellowish neutral state to a green oxidized state.

INTRODUCTION

Wholly aromatic polyamides (aramids) are characterized as high-performance polymers with a favorable balance of thermal and mechanical properties. However, rigidity of the backbone and strong interchain interactions result in high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their wide-spread applications. To overcome such a difficulty, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of aramids without much impairing their thermal and mechanical properties is the incorporation of bulky, packing-disruptive groups into the polymer backbone.¹ We have demonstrated that aromatic polyamides containing bulky, propeller-shaped triphenylamine unit are amorphous, have good solubility in organic solvents, and exhibit excellent thin-film-forming capability and high thermal stability.² Furthermore, many triphenylamine-based polymers also show interesting light-emitting and electrochromic behavior.³⁻⁷

It has been demonstrated that the introduction of halogen substituents into the polyamide backbones generally led to an increase in solubility and T_g because of the great volume of halogen atoms and the polarity of carbon-halogen bonds.^{8,9} To understand the effect of halogen substitution on the properties of triphenylamine-containing aramids, we prepare four 4,4'-diamino-4'-halotriphenylamines and their derived triphenylamine-based polyterephthalamides and polyisophthalamides. The solubility, thermal, electrochemical, and electrochromic properties of these halogen-substituted polyamides were compared with those of the parent polyamides without the halogen substitution.

EXPERIMENTAL SECTION

Monomer Synthesis

Synthesis of 4-Halo-4',4'-dinitrotriphenylamine (1)

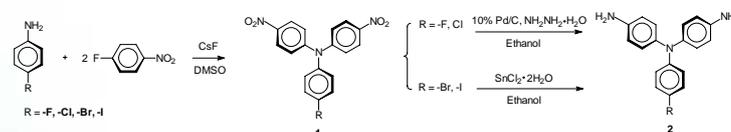
A typical example of the synthesis of 4-fluoro-4',4'-dinitrotriphenylamine (1-F) is described as follows: A mixture of 11.1 g (0.1 mol) of 4-fluoroaniline, 28.5 g (0.2 mol) of 4-fluorobenzene, and 30.4 g (0.2 mol) of cesium fluoride (CsF) in 100 mL of dimethyl sulfoxide (DMSO) was heated with stirring at 140 °C for 12 h. After cooling, the mixture was poured into 500 mL mixed solution of ethanol/water (1:1), and the olive precipitate was collected by filtration and washed thoroughly with water. Recrystallization from DMF/methanol yielded 26.5 g of the desired dinitro compound 1-F as yellow crystals in 75% yield [mp = 295–296 °C, measured by differential scanning calorimetry (DSC) at a scan rate of 2°C/min]. IR (KBr): 1321, 1551 cm⁻¹ (NO₂ stretch). ANAL. Calcd for C₁₄H₁₀N₂O₄F (333.30): C, 61.19%; H, 3.42%; N, 11.89%. Found: C, 60.79%; H, 3.49%; N, 11.73%.

Synthesis of 4,4'-Diamino-4'-fluorotriphenylamine (2-F)

In a 300 mL, round-bottom flask, 17.7 g (0.05 mol) of dinitro compound 1-F, 0.2 g of 10 wt% Pd/C, 10 mL hydrazine monohydrate and 100 mL of ethanol was heated in nitrogen flow at a reflux temperature for 12 h. The solution was filtered hot to remove Pd/C and then allowed to cool to room temperature to afford 11.7 g (80% yield) of diamine 2-F as colorless needles; mp = 175–177 °C (DSC, 2°C/min). IR (KBr): 3407, 3234 cm⁻¹ (NH₂ stretch). ANAL. Calcd for C₁₄H₁₂N₄F (292.34): C, 73.70%; H, 5.50%; N, 14.32%. Found: C, 74.11%; H, 5.93%; N, 14.72%. ¹H NMR (500 MHz, DMSO-*d*₆): δ, ppm: 4.95 (s, 4H, -NH₂), 6.55 (d, J = 8.6 Hz, 4H, H_a), 6.64 (dd, J_{H_aH_b} = 9.0 Hz, J_{H_aH_c} = 4.7 Hz, 2H, H_b), 6.78 (d, J = 8.6 Hz, 4H, H_c), 6.90 (t, overlapped dd, J = 8.9 Hz, 2H, H_d). ¹³C NMR (125 MHz, DMSO-*d*₆): δ, ppm: 114.82 (C¹), 115.05 (d, J_{C-F} = 22.6 Hz, C²), 118.64 (d, J_{C-F} = 7.5 Hz, C³), 126.69 (C⁴), 136.38 (C⁵), 145.19 (C⁶), 155.30 (d, J_{C-F} = 23.4 Hz, C⁷).

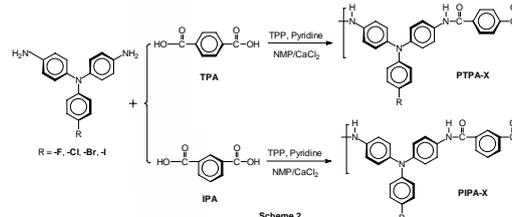
Synthesis of 4,4'-Diamino-4'-iodotriphenylamine (2-I)

In a 1000 mL, round-bottom flask, 23 g (0.05 mol) of nitro compound 1-I, 90.3 g (0.05 mol) of SnCl₄ · 2H₂O and 400 mL of ethanol was heated in nitrogen flow at a reflux temperature for 4 h. After cooling to room temperature, the solution was filtered to remove the impurities. The filtrate was evaporated under reduced pressure to remove the ethanol. The pH is made slightly basic (pH 7–8) by addition of 1M aqueous sodium hydroxide before being extracted with ethyl acetate. The organic phase is thoroughly washed with brine, treated with charcoal and dried over anhydrous magnesium sulfate. Evaporation of the solvent leaves 17.7 g (88.2% yield) of diamine 2-I as gray powders; mp = 147–149 °C (DSC, 2°C/min). IR (KBr): 3399, 3309 cm⁻¹ (NH₂ stretch). ¹H NMR (500 MHz, DMSO-*d*₆): δ, ppm: 4.99 (s, 4H, -NH₂), 6.41 (d, J = 8.9 Hz, 2H, H_a), 6.56 (d, J = 8.6 Hz, 4H, H_b), 6.82 (d, J = 8.6 Hz, 4H, H_c), 7.32 (d, J = 8.9 Hz, 2H, H_d). ¹³C NMR (125 MHz, δ, ppm, DMSO-*d*₆): 78.43 (C¹), 114.77 (C²), 118.45 (C³), 127.39 (C⁴), 135.07 (C⁵), 136.82 (C⁶), 145.86 (C⁷), 149.39 (C⁸).



Polymer Synthesis

The preparation of polyamide PTPA-F was used as an example to illustrate the general synthetic procedure to produce the polyamides. A 50 mL, round-bottom flask equipped with a magnetic stirrer was charged with 0.4400 g (1.50 mmol) of diamine monomer 2-F, 0.2492 g (1.50 mmol) of terephthalic acid (TPA), 1.5 mL of triphenyl phosphite (TPP), 3 mL of NMP, 0.8 mL of pyridine, and 0.2 g of calcium chloride (CaCl₂). The reaction mixture was heated with stirring at 110 °C for 3 h. The resulting polymer solution was poured slowly into excess of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. The other polyamides were prepared by an analogous procedure.



RESULTS AND DISCUSSION

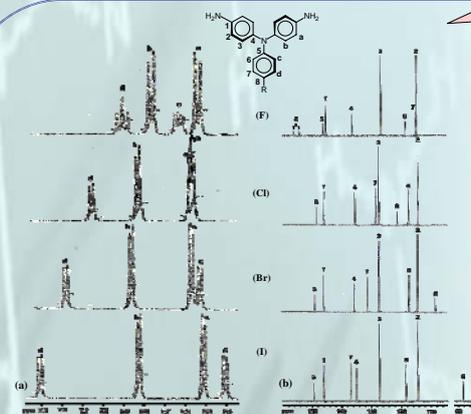


Figure 1. (a) ¹H NMR and (b) ¹³C NMR spectra of 4,4'-diamino-4'-halotriphenylamines in DMSO-*d*₆.

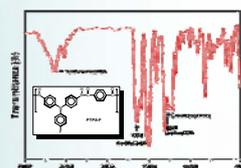


Figure 2. Typical IR spectrum of the poly(amine amide) PTPA-F.

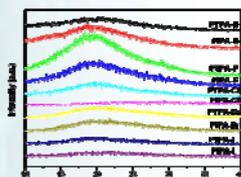


Figure 3. WAXD patterns of the poly(amine amide) thin films.

Table 2. Optical and electrochemical properties of the polyamides

Polymer code	Solution (nm)		Film (nm)		$E_{1/2}$ (V) ^b (vs. Ag/AgCl)	E_g (eV)	HOMO/ LUMO ^c (eV)
	Abs	PL	Abs	Abs			
PTPA-H	316	365	325	407	0.84	3.05	5.20/2.15
PTPA-F	354	435	359	424	0.83	2.92	5.19/2.27
PTPA-Cl	347	426	349	433	0.89	2.86	5.25/2.39
PTPA-Br	334	438	345	430	0.88	2.88	5.24/2.36
PTPA-I	349	427	351	473	0.88	2.62	5.24/2.62
PIPA-H	338	409	342	448	0.85	2.77	5.21/2.44
PIPA-F	338	418	341	431	0.86	2.88	5.22/2.34
PIPA-Cl	334	419	334	400	0.89	3.10	5.25/2.15
PIPA-Br	335	453	332	400	0.90	3.10	5.26/2.16
PIPA-I	337	404	341	425	0.88	2.92	5.24/2.32

^a UV-vis absorption measured in NMP (1 × 10⁻⁴ mol/L) at room temperature.
^b E_{1/2} spectra measurements in NMP (1 × 10⁻⁴ mol/L) at room temperature.
^c Oxidation half-wave potentials from cyclic voltammograms.
^d Energy gap = |E_{HOMO} - E_{LUMO}| of polymer films.
^e The HOMO energy levels were calculated from E_{1/2} and were referenced to ferrocene (4.8 eV); LUMO = HOMO - E_g.

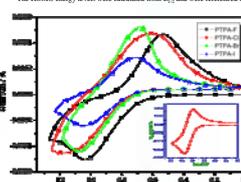


Figure 5. Cyclic voltammograms of the cast films of polyamides PTPA-X on the ITO-glass in CH₂CN containing 0.1 M TBAP at a sweep rate of 100 mV/s. The inset shows the CV curve of ferrocene as the standard.

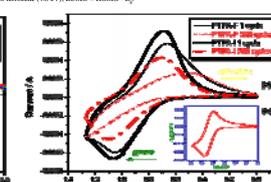


Figure 6. Cyclic voltammograms of (a) polyamides PTPA-F and (b) polyamide PIPA-F film on the ITO-coated glass substrate over 500 cyclic scans (b) ferrocene in CH₂CN containing 0.1 M TBAP at scan rate = 100 mV/s.

Table 1. Inherent viscosity, solubility behavior and thermal properties of the polyamides

Polymer code	η_{inh}^a (dL/g)	Solubility in various solvents ^b							T_g (°C)	$T_d^{10\%}$ (°C)	$T_d^{50\%}$ (°C)	Char yield ^c (%)
		NMP	DMAc	DMF	DMSO	m-Cresol	THF	THP				
PTPA-H	1.04	+	+	+	+	+	+	264	250	545	455	74
PTPA-F	0.86	+	+	+	+	+	+	281	270	506	490	71
PTPA-Cl	0.74	+	+	+	+	+	+	282	274	518	501	70
PTPA-Br	0.52	+	+	+	+	+	+	279	282	442	452	62
PTPA-I	0.71	+	+	+	+	+	+	306	281	444	441	65
PIPA-H	0.61	+	+	+	+	+	+	267	257	515	475	72
PIPA-F	0.67	+	+	+	+	+	+	255	253	502	511	69
PIPA-Cl	0.49	+	+	+	+	+	+	280	251	525	509	71
PIPA-Br	0.26	+	+	+	+	+	+	289	289	444	440	66
PIPA-I	0.66	+	+	+	+	+	+	330	289	442	439	69

^a Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc-5 wt % LiCl at 30 °C.
^b Solubility: +, soluble at room temperature; +h, soluble on heating; -, insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.
^c The film samples were heated at 300 °C for 1 h prior to all thermal analysis. The midpoint temperature of baseline shift on the DSC heating trace (scan rate 20 °C/min) was defined as T_g .
^d Softening temperature measured by TMA (scan rate 10 °C/min) using a penetration method.
^e Softening temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.
^f Decomposition temperature at 300 °C for 1 h prior to all thermal analysis. The midpoint temperature of baseline shift on the DSC heating trace (scan rate 20 °C/min) was defined as T_g .
^g Residual weight percentages at 800 °C under nitrogen flow.

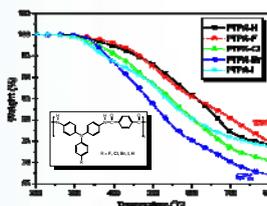


Figure 4. TGA thermograms of polyamides PTPA-X in nitrogen at a scan rate of 20 °C/min.

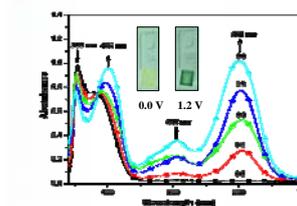


Figure 7. Spectroelectrochromic behavior of the cast film of polyamide PTPA-F on the ITO-glass in CH₂CN with 0.1 M TBAP as supporting electrolyte at various applied voltages: (a) 0.0, (b) 0.3, (c) 0.6, (d) 0.9, (e) 1.2 V.

REFERENCES

- Myung, B. Y.; Ahn, C. J.; Yoon, T. H. *Polymer* **2004**, *45*, 3185.
- Hsiao, S.-H.; Chen, C.-W.; Liou, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3302.
- Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, *38*, 307.
- Liou, G.-S.; Hsiao, S.-H.; Fang, Y.-K. *Eur. Polym. J.* **2006**, *42*, 1533.
- Liou, G.-S.; Hsiao, S.-H.; Huang, N.-K.; Yang, Y.-L. *Macromolecules* **2006**, *39*, 5337.
- Liou, G.-S.; Chen, H.-W.; Yen, H.-Z. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4108.
- Hsiao, S.-H.; Chang, Y.-M.; Chen, H.-W.; Liou, G.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4579.
- Alvarez, J. C.; de la Campa J.G.; Lozano A. E.; de Abajo J. *Macromol. Chem. Phys.* **2001**, *202*, 3142.
- Kakimoto, M.; Yoneyama M.; Imai Y. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3911.
- Yamazaki, N.; Matsumoto, M.; Higashi, F. *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 1373.