6860 *Macromolecules* **1999,** *32,* 6860−6863

Synthesis and Properties of New Soluble Polyamides Derived from 2,2′-Dimethyl-4,4′-bis(4-carboxyphenoxy)biphenyl

Der-Jang Liaw,* Been-Yang Liaw, Jun-Rong Chen, and Chao-Min Yang

Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan 106, Republic of China

Received March 1, 1999
Revised Manuscript Received June 28, 1999

Introduction

High-performance aromatic polyamides have been used in applications demanding service at high temperatures, while maintaining their combination of excellent chemical, physical, and mechanical properties. However, these polyamides encounter processing difficulties due to their infusibility and poor solubility in organic solvents. The reasons for these characteristics are strong interchain forces, inherent macromolecular rigidity, or semicrystallinity.[1,2] Many investigations have attempted to enhance the solubility and processability of polyamides by introducing flexible segments[3−7] or bulky side groups[8−12] into the polyamide backbone. Similarly, noncoplanar diamines are remarkably effective in improving solubility.[13−15]

Incorporating 2,2′-disubstituted biphenylylene in a para-linked polymer chain does not initially change the polymer backbone's rodlike structure, but it does reduce the interactions of polymer chains. The phenyl rings are forced by the 2,2′-disubstitution into a noncoplanar conformation, decreasing the intermolecular forces between the polymer chains. The crystallization tendency and transition temperatures are markedly lowered, and the solubilities are significantly enhanced.[16−19] In addition, aryl ether linkages inserted in aromatic main chains provide a significantly lower energy of internal rotation, leading to a lower glass transition temperature and crystalline melting temperature, as well as significantly improving solubility and other process characteristics of the polymers without greatly sacrificing thermal stability. Therefore, the introduction of both noncoplanar 2,2′-disubstituted biphenylylene and flexible aryl ether units into a polymer backbone would be expected to be potentially beneficial structural modifications to the rodlike polymer. This work primarily concentrates on synthesizing new polyamides with good processability and excellent combinations of thermal and mechanical properties, which can potentially be used as high-performance materials.

Experimental Section

Materials. 1,4-Phenylenediamine (**4a**, from Merck) and 1,3-phenylenediamine (**4b**, from Merck) were purified by vacuum sublimation. 9,9-Bis(4-aminophenyl)fluorene (**4c**, from TCI) and 1,4-bis(4-aminophenoxy)benzene (**4f**, from Wakayama Seika Co. Ltd) were recrystallized from ethanol. 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane[20] (**4d**), 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane[7] (**4e**), 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene[8] (**4g**), 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene[9] (**4h**), and 8,8-bis[4-(4-aminophenoxy)phenyl]tricyclo[5.2.1.0^{2,6}]decane[21] (**4i**) were synthesized and purified according to the method previously reported.[7−9,20,21]

Monomer Synthesis. *2,2′-Dimethylbiphenyl-4,4′-diol (**1**).* A flask (1 L) equipped with a mechanical stirrer, addition funnel, and reflux condenser was charged with 2,2′-dimethyl-4,4′-diaminobiphenyl dihydrochloride (28.5 g, 0.1 mol), 20 mL of hydrochloride (37 wt %) solution, and water (250 mL) below 5 °C. The aqueous solution of $NaNO_2$ (17.3 g, 0.25 mol) in 40 mL of water was added dropwise into the flask. After the whole quantity was added to the flask, the reaction mixture was allowed to warm to room temperature, and then toluene (400 mL) and water (400 mL) were subsequently added. After addition of toluene, the reaction mixture was heated to 50 °C for 4 h. The oil layer was separated and collected. Then, the solution was concentrated by a rotary evaporator. The crude red product was obtained and recrystallized from benzene twice: mp 121−123 °C; yield 41%. IR (KBr): 3280 cm^{-1} (O−H). ^{1}H NMR (DMSO-d_6) δ (ppm): 9.2 (s, 2H, OH), 6.6−6.8 (m, 6H, Ar−H), 1.9 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6) δ (ppm): 156.2, 136.9, 132.1, 130.7, 116.5, 112.6, 19.9.

Anal. calcd for $C_{14}H_{14}O_2$: C, 78.50%; H, 6.54%. Found: C, 79.10%; H, 6.78%.

*2,2′-Dimethyl-4,4′-bis(4-cyanophenoxy)biphenyl (**2**).* Into a three-neck flask equipped with a nitrogen inlet, a Dean−Stark trap, and a condenser were placed 5.0 g (23.4 mmol) of **1** and 6.54 g (47.4 mmol) of potassium carbonate with 40 mL of dry *N*,*N*-dimethylformamide (DMF) and 10 mL of toluene. The mixture was heated with stirring at 140 °C for 2 h under nitrogen to remove the water azeotropically. After the toluene had been completely removed, 5.88 g (48.6 mmol) of *p*-fluorobenzonitrile was added. The mixture was heated at 150 °C for 6 h, then allowed to cool, and poured into cool water. The crude product was filtered and recrystallized from acetonitrile to afford the dinitrile compound (**2**): mp 163−165 °C; yield 85%. IR (KBr): 2216 cm^{-1} (C≡N str), 1239 cm^{-1} (C−O str). ^{1}H NMR (DMSO-d_6) δ (ppm): 7.9 (d, 4H, Ar−H), 7.2−7.1 (m, 8H, Ar−H), 7.0 (dd, 2H, Ar−H), 2.02 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6) δ (ppm): 160.8, 153.3, 137.9, 136.8, 134.4, 130.8, 121.1, 118.5, 117.9, 117.2, 104.9, 19.7.

Anal. calcd for $C_{28}H_{20}O_2N_2$: C, 80.75%; H, 4.84%; N, 6.73%. Found: C, 80.60%; H, 4.96%; N, 6.46%.

The procedure mentioned above for the compound **2** preparation is also repeated, except that *p*-chlorobenzonitrile is used to replace *p*-fluorobenzonitrile under the same condition (yield 79%).

*2,2′-Dimethyl-4,4′-bis(4-carboxyphenoxy)biphenyl (**3**).* A mixture of 2.08 g (5 mmol) of dinitrile compound **2**, 5.61 g of potassium hydroxide in 30 mL of 2-propanol, and 30 mL of distilled water was stirred at 120 °C. Hydrogen peroxide (10 mL) was added dropwise over a period of 0.5 h to the suspension solution. After 3 days, the solution became clear and then was cooled, and the pH value was adjusted by hydrochloric acid to near 2. The white precipitate that formed was collected by filtration, washed with water and ethanol several times, and dried under vacuum at 100 °C for 24 h; mp 306 °C (by DSC), yield 99%. IR (KBr): 2500−3600 cm^{-1} (C(O)O−H str), 1673 cm^{-1} (C=O str), 1235 (C−O str). ^{1}H NMR (DMSO-d_6) δ (ppm): 12.8 (s, 2H, COOH), 7.9 (d, 4H, Ar−H), 7.1−7.0 (m, 8H, Ar−H), 6.9 (dd, 2H, Ar−H), 2.0 (s, 6H, CH_3). ^{13}C NMR (DMSO-d_6) δ (ppm): 168.6, 162.6, 156.0, 139.5, 137.9, 133.1, 132.3, 126.6, 122.1, 118.6, 118.1, 19.6.

Anal. calcd for $C_{28}H_{22}O_6$: C, 73.99%; H, 4.88%. Found: C, 73.64%; H, 4.80%.

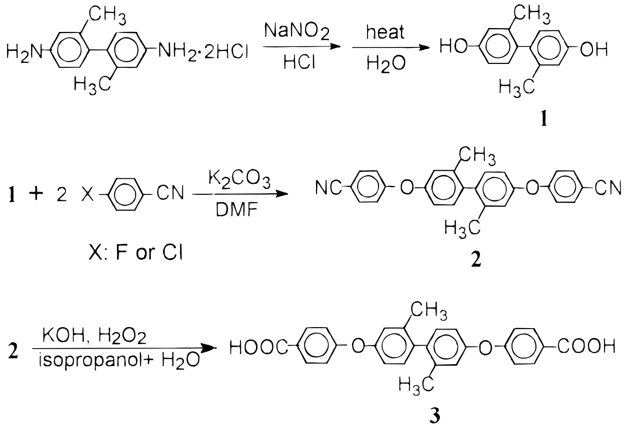
Polymerization. *Polyamide **5b** from **3** and **4b**.* A mixture of 0.668 g (1.25 mmol) of dicarboxylic acid **3**, 0.208 g (1.25 mmol) of diamine **4b**, 0.35 g of calcium chloride, 0.8 mL of triphenyl phosphite, 0.8 mL of pyridine, and 3.5 mL of NMP was heated with stirring at 100 °C for 3 h. After cooling, the

---

* To whom correspondence should be addressed. Phone 886-2-27376638, 886-2-27335050; FAX 886-2-23781441 or 886-2-27376644; e-mail liaw@ch.ntust.edu.tw.

10.1021/ma9903198 CCC: $18.00

Scheme 1. Synthesis of 2,2′-Dimethyl-4,4′-bis(4-carboxyphenoxy)biphenyl (3)

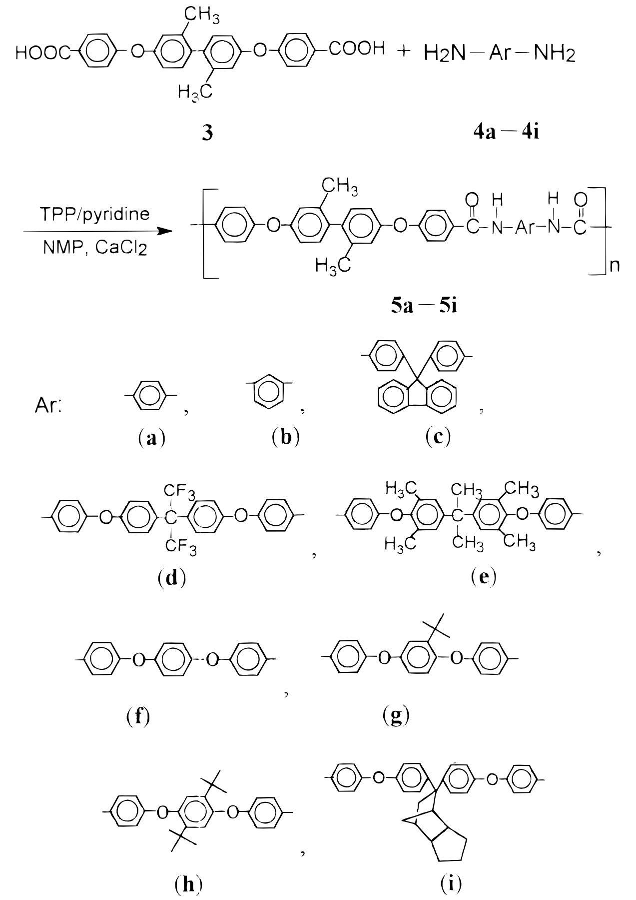


reaction mixture was poured into methanol, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100 °C under vacuum. The inherent viscosity of the polymer in DMAc was 0.81 dL g^{-1}, measured at a concentration 0.5 g dL^{-1} at 30 °C. IR (film): 3284 cm^{-1} (N−H), 1647 cm^{-1} (C═O). ^1H NMR (DMSO-d_6) δ (ppm): 10.3 (s, 2H, C(O)N−H), 8.3 (s, 1H, Ar−H), 8.0 (d, 4H, Ar−H), 7.5 (d, 2H, Ar−H), 7.3−6.9 (m, 11H, Ar−H). All other polyamides were prepared using a similar procedure.

Results and Discussion

Monomer Synthesis. As shown in Scheme 1, 2,2′-dimethyl-biphenyl-4,4′-diol (**1**) was synthesized from 2,2′-dimethyl-4,4′-diaminobiphenyl dihydrochloride. The nitrosation of amine (−Ar−NH_2) with sodium nitrite and dilute acid led to the formation of the aromatic diazonium cation (−Ar−N^+≡N). After applying heat, nitrogen was eliminated, and aromatic carbocation (−Ar^+) was formed which reacted with water. The aromatic nucleophilic substitution reaction of **1** with *p*-fluorobenzonitrile or *p*-chlorobenzonitrile under the same conditions in the presence of K_2CO_3 yielded a dinitrile compound (**2**). The yield of **2** varied from 85 to 79%, depending upon the leaving group (F or Cl) of halogenbenzonitrile. The hydrolysis of the dinitrile compound **2** to the dicarboxylic acid **3** was accomplished by means of potassium hydroxide as well as hydrogen peroxide in the mixture of 2-propanol (IPA) and water. It was worth noting that nitriles can be hydrolyzed to give either amides or carboxylic acids. The amide is formed initially, but since amides are also hydrolyzed with acid or base, carboxylic acid is the more common product. When the carboxylic acid is desired, the reagent of choice is aqueous KOH containing about 6−12% hydrogen peroxide, though acid-catalyzed hydrolysis is also frequently carried out.[22] The structures of these synthesized compounds were confirmed by elemental analysis, IR, and NMR spectroscopy. The cyano group (C≡N) of compound **2** was evident from the peak at 2216 cm^{-1} in the IR spectrum. In the IR spectrum of **3**, the cyano stretching vibration was absent, but a broad C(O)O−H absorption appeared in the region of 2500−3600 cm^{-1} and a C═O stretching absorption appeared at 1673 cm^{-1}. The ^{13}C NMR spectrum of **3** revealed that the carbon of the carboxyl group has a resonance at 168.6 ppm. A broad peak attributed to the carboxylic acid proton of **3** was observed at 12.8 ppm in the ^1H NMR spectrum.

Scheme 2. Preparation of Polyamides



Preparation of Polyamides. Polyamides were prepared by the direct polycondensation of the dicarboxylic acid **3** with various diamines in NMP containing dissolved $CaCl_2$ using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The obtained polyamides had inherent viscosities between 0.81 and 1.70 dL g^{-1} (Table 1). The polymers **5d**, **5e**, **5g**, and **5i** exhibited number-average molecular weights ($\bar{M}_n$) and weight-average molecular weights ($\bar{M}_w$) in the ranges 37 900−54 700 and 81 400−113 000, respectively. Except for polymer **5a**, tough and flexible polymer films could be obtained by solution casting from DMAc solutions.

The formation of polyamides was confirmed by IR and ^1H NMR spectroscopy. The IR spectra of the polymers showed that the characteristic absorptions of amide groups occurred around 3284−3316 and 1636−1659 cm^{-1}, indicating N−H and carbonyl stretching, respectively. The ^1H NMR spectral data of polyamide **5b** are listed in the Experimental Section. Each proton of **5b** was assigned, and the integration values were in accordance with the expected structure.

Polymer Characterization. The crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams. All of the polymers, except polymer **5a**, showed amorphous patterns. This observation is reasonable since the presence of noncoplanar conformation of 2,2′-dimethyl-substituted biphenylylene unit decreases the intermolecular forces between the polymer chains, causing a decrease in crystallinity.[13] In addition, the presence of the flexible ether unit also reduced the rigidity of the polymer chain. The polyamide **5a** was the only one to show a crystalline pattern, possibly due to the presence of the rigid and symmetric *p*-phenylene structure. The more ordered nature of polyamide **5a** film is reflected in its brittle nature.

Table 1. Inherent Viscosity, Molecular Weight, and Solubility of Various Polyamides

				solubility[e]					
polymer code	η_{inh}[a] (dL g^{-1})	$\bar{M}_n \times 10^{-4}$ [c]	$\bar{M}_w \times 10^{-4}$ [c]	NMP	DMAc	DMSO	cyclohexanone	γ-butyrolactone	THF
5a	1.70[b]	*d*	*d*	++	+−	+−	+−	−	−
5b	0.81	*d*	*d*	++	++	++	+	++	−
5c	1.38	*d*	*d*	++	++	++	++	++	+−
5d	1.05	5.46	11.3	++	++	++	++	++	++
5e	0.99	4.67	9.30	++	++	++	++	++	++
5f	1.16	*d*	*d*	++	++	++	+	++	+−
5g	1.28	5.47	8.89	++	++	++	++	+	++
5h	1.48	*d*	*d*	++	++	++	++	+	+−
5i	0.95	3.79	8.14	++	++	+−	++	+−	++

[a] Measured in DMAc at a concentration of 0.5 g dL^{-1} at 30 °C. [b] Measured in NMP at a concentration of 0.5 g dL^{-1} at 30 °C. [c] Measured by GPC in THF, polystyrene was used as standard. [d] Polymer was not soluble in THF. [e] ++, soluble at room temperature; +, soluble on heating at 70 °C; +−, partial soluble; −, insoluble.

Table 2. Thermal and Tensile Properties of Various Polyamides

polymer code	T_m[a] (°C)	T_g[b] (°C)	Td_{10}[c] (°C) in nitrogen	Td_{10}[c] (°C) in air	tensile strength (MPa)	elongation at break (%)	tensile modulus (GPa)
5a	400	*d*	528	500	*e*	*e*	*e*
5b	*d*	269	487	530	110	6	2.4
5c	*d*	354	514	535	107	10	2.4
5d	*d*	279	511	530	90	7	2.3
5e	*d*	252	483	511	95	7	2.0
5f	*d*	282	513	530	87	9	2.2
5g	*d*	290	500	511	90	8	2.4
5h	*d*	354	501	524	84	7	2.0
5i	*d*	346	500	537	102	8	2.0

[a] From the first heating traces of DSC measurements conducted at a heating rate of 20 °C min^{-1}. [b] From the second heating traces of DSC measurements conducted at a heating rate of 20 °C min^{-1}. [c] Temperature at 10% weight loss determined by TGA in nitrogen at a heating rate of 20 °C min^{-1}. [d] Could not be detected by DSC. [e] Polymer film was too brittle to measure.

The solubility characteristics of the polyamides are shown in Table 1. It was found that most dissolved readily in polar solvents such as NMP, DMAc, and dimethyl sulfoxide (DMSO), as well as less polar solvents such as γ-butyrolactone, cyclohexanone, and tetrahydrofuran. Polyamide **5a** was less soluble, possibly due to the rigid nature of its diamine moiety, and entirely soluble in NMP. All noncoplanar polyamides were readily processed from NMP solutions into films. The excellent solubility of the polyamides is attributed to the presence of noncoplanar biphenylylene and flexible aryl ether moieties which reduced the polymer chain interaction and rigidity, respectively.

The thermal behavior data of the polyamides are summarized in Table 2. All had glass transition temperatures (T_g's) in the range 252−354 °C, depending on the diamine component's structure. However, polyamide **5a** displayed no discernible glass transition by DSC but did exhibit an endothermic peak around 400 °C during the first heating cycle. The T_g order was comparable to the decreasing order of stiffness of the polymer backbones. The lowest T_g was observed for the polyamide derived from **4e,** containing flexible isopropylidene units. The polymers **5g** and **5h**, with rigid and bulky *tert*-butyl substituents, had higher glass transition temperatures compared to that of polymer **5f** without this substituent. Notably, polymer **5h** with symmetric di-*tert*-butyl substituents gives a higher T_g value than **5g** having only one *tert*-butyl substituent. This is due to the molecular symmetry in polymer **5h** which allows better packing, while polymer **5g** with an unsymmetric mono *tert*-butyl substituent packs quite loosely.[7,8] It was observed that cardo polymers **5c** and **5i** exhibited T_g values above 340 °C. In general, chain rigidity of the polymer was increased due to the bulky pendent group, which restricted the free rotation of the polymer chain.[23]

The TGA curves of most polymers indicated they were stable up to around 450 °C. The temperatures for 10% weight loss (Td_{10}) (given in Table 2) were in the ranges 483−528 and 500−537 °C for nitrogen and air, respectively. It is interesting to find that most of the polymers showed higher Td_{10} in air than in nitrogen. The higher Td_{10} value in air may reflects CH_3 oxidation of the polymer chain, which forms carbonyl (C═O) and hydroxy (O−H) groups and then causes weight gain.

Table 2 also lists the tensile properties of the polyamide films. The films had tensile strengths in the range 84−110 MPa, elongation at break values in the range 6−10%, and tensile moduli of 2.0−2.4 GPa. Thus, these polymer films can be considered strong materials in comparison with other literature reported.[24−28]

Acknowledgment. The authors thank the National Science Council of the Republic of China for support of this work.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymer*; Dekker: New York, 1980.
(2) Frazer, A. H. *High-Temperature Resistant Polymers*; Wiley: New York, 1968.
(3) Yamashita, M.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1513.
(4) Lucas, M.; Brock, P.; Hedrich, J. L. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2179.
(5) Bellomo, M. R.; Pasquale, G. Di.; La Rosa, A.; Pollicino, A.; Siracusa, G. *Polymer* **1996**, *37*, 2877.
(6) Liaw, D. J.; Liaw, B. Y.; Tsai, M. Y. *Polym. J.* **1997**, *29*, 474.
(7) Liaw, D. J.; Liaw, B. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1075.
(8) Liaw, D. J.; Liaw, B. Y. *Macromol. Symp.* **1997**, *122*, 343.
(9) Liaw, D. J.; Liaw, B. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1069.
(10) Jeong, H. J.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 3293.

(11) Sakaguchi, Y.; Harris, F. W. *Polym. J.* **1992**, *24*, 1147.
(12) Spiliopoulos, I. K.; Mikroyannidis, J. *Macromolecules* **1998**, *31*, 515.
(13) Liaw, D. J.; Liaw, B. Y.; Jeng, M. Q. *Polymer* **1998**, *39*, 1597.
(14) Hatke, W.; Schmidt, H. W. *Polym. Prepr.* **1992**, *33* (2), 321.
(15) Liou, G. S.; Maruyama, M.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2029.
(16) Hatke, W.; Schmidt, H. W.; Heitz, W. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1387.
(17) Schmidt, H. W.; Guo, D. *Makromol. Chem.* **1988**, *189*, 2029.
(18) Sinta, R.; Minns, R. A.; Gaudiana, R. A.; Rogers, H. G. *Macromolecules* **1987**, *20*, 2374.
(19) Becker, K. H.; Schmidt, H. W. *Macromolecules* **1992**, *25*, 6784.
(20) Liaw, D. J.; Wang, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1209.
(21) Liaw, D. J.; Liaw, B. Y.; Chung, C. Y. *Macromol. Chem. Phys.* **1999**, *200*, 1023.
(22) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992; pp 887−888.
(23) Liaw, D. J.; Liaw, B. Y.; Li, L. J.; Sillion, B.; Mercier, R.; Thiria, R.; Sekiguchi, H. *Chem. Mater.* **1998**, *10*, 734.
(24) Yang, C. P.; Chen, W. T. *Macromol. Chem.* **1993**, *194*, 1603.
(25) Hsiao, S. H.; Chang, H. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 1428.
(26) Chern, Y. T.; Wang, W. C. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1257.
(27) Lozano, A. E.; la Campa, J. G.; de Abajo, J.; Preston, J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1383.
(28) Liaw, D. J.; Liaw, B. Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2301.

MA9903198