Macromolecules **2003,** *36,* 5559−5565

Syntheses of Biphenyl Polyimides via Nickel-Catalyzed Coupling Polymerization of Bis(chlorophthalimide)s

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Received January 10, 2003; Revised Manuscript Received April 29, 2003

ABSTRACT: A facile method for the synthesis of biphenyl polyimides, which involves the nickel-catalyzed coupling of aromatic dichlorides containing imide structure in the presence of zinc and triphenylphosphine, has been developed. The polymerizations proceeded smoothly under mild conditions and produced biphenyl polyimides with inherent viscosities of 0.13−0.98 dL/g. The polymerizations of bis(4-chlorophthalimide)s with bulky side substituents gave high molecular weight polymers. Low molecular weight polymers from bis(4-chlorophthalimide)s containing rigid diamine moieties and bis(3-chlorophthalimide)s were obtained because of the formations of polymer precipitate and cyclic oligoimides, respectively. The effects of various factors, such as amount of catalyst, solvent volume, ligand, reaction temperature, and time, on the polymerization were studied. The random copolymerization of two bis(chlorophthalimide)s in varying proportions produced medium molecular weight material. The T_gs of prepared polyimides were observed at 245−311 °C, and the thermogravimetry of polymers showed 10% weight loss in nitrogen at 470−530 °C.

Introduction

Polyimides (PIs) are high-performance polymers which exhibit several technologically interesting characteristics, such as excellent mechanical properties, electric insulation, and good chemical resistance and thermal stability. Incorporation of biphenyl linkages can lead to improve mechanical properties, low moisture absorption, and thermal expansion.[1] Biphenyl PIs are exclusively prepared by reacting biphenyltetracarboxylic dianhydrides (BPDAs) with diamines in solution to give polyamic acids or polyimides.[2] BPDAs are synthesized by nickel-,[2a,3] copper-,[2b] or palladium[4,5]-catalyzed coupling of phthalic acid derivatives (Scheme 1). Step polymerization reactions via Ni- or Pd-catalyzed carbon−carbon bond formation in polymers prompt us to develop a simple route to synthesizing biphenyl PIs.

The synthesis of biphenyls via the nickel-catalyzed coupling of chlorobenzene in the presence of zinc and triphenylphosphine under mild reaction conditions was first reported by Colon and Kelsey.[7] Since 1990, the Ni- or Pd-catalyzed coupling reactions have been utilized in the syntheses of poly(ether ether sulfone)s,[8] poly(arylene ether ketone)s,[9] poly(aryl amide)s,[10] and poly(3-phenyl-2,5-thiophene).[11] Moreover, an extensive number of poly(phenylene)s via metal-catalyzed coupling reactions were reported.[12]

To our best knowledge, there have been no reports on the Ni(0)-catalyzed coupling polymerization for biphenyl PIs based on bis(chlorophthalimide)s, available fully imidized monomers. In this paper, we report the syntheses of biphenyl PIs by coupling bis(chlorophthalimide)s using nickel catalyst generated in situ from a nickel salt and an excess reducing agent (Scheme 2). The properties of the prepared PIs were also characterized.

Experimental Section

Materials. Reagent grade anhydrous $NiCl_2$ was dried at 220 °C under vacuum. Triphenylphosphine (PPh_3) was recrystallization from hexane. Powdered (100 mesh) zinc was stirred with acetic acid, filtrated, washed thoroughly with diethyl ether, and dried under vacuum. 4-Chlorophthalic anhydride (99.2%) and 3-chlorophthalic anhydride (99.0%) were purified by distillation. 4,4′-Oxydianiline, 3,3′-dimethyl-4,4′-methylenedianiline, 2,2′,3,3′-tetramethyl-4,4′-methylenedianiline, and 4,4′-(9-fluoroenylidene)dianiline were used as received from Aldrich. *N*,*N*-Dimethylacetamide (DMAc) was stirred over phosphorus pentoxide for 5 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves.

Instrumentation. The ^{1}H NMR spectra were measured at 300 MHz on a AV300 spectrometer. The FTIR spectra were obtained with a Bio-Rad digilab Division FTS-80 spectrometer. The elemental analyses were performed on an elemental analysis FLASH-EA-1112 series. The inherent viscosities were determined at a 0.5% concentration of polymer in *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer, and the experiments were carried out with 10 ± 2 mg samples at a heating rate of 10 °C/min. The differential scanning calorimetry (DSC) experiments were carried out on a Perkin-Elemer DSC-7 system at a heating rate of 20 °C/min under a nitrogen atmosphere. The dynamic mechanical property of PI film was measured on a dynamic mechanical thermal analyzer (DMTA). The MALDI−TOF mass spectra were recorded on a LDI-1700 mass spectrometer with the instrument set in the positive reflection mode. 1,8,9-Anthracemetriol (dithranol) was used as the matrix and $CHCl_3$ was used as the solvent. The X-ray diffraction data were collected on a SiemensP4 4-circle diffractometer at 293 K. The UV−vis spectra were obtained on a Varian Cray 50 spectrophotometer.

Monomer Synthesis. 2,2′-Bis[4-(4′-aminophenyloxy)phenyl]propane (b). The compound was prepared as reported in the literature;[13] mp 126−127 °C (lit.[13] mp 127 °C).

1,1′-Bis(3-methyl-4-aminophenyl)cyclohexane (e). In a three-necked round-bottomed flask, a mixture of 30 mL of H_2O, 30 mL of concentrated HCl (0.36 mol), and 9.8 g (0.1 mol) of cyclohexanone was stirred in an ice bath, and 23.5 g (0.22 mol) of *o*-toluidine was dropped within 20 min under nitrogen and then refluxed for 24 h. The mixture was poured slowly into

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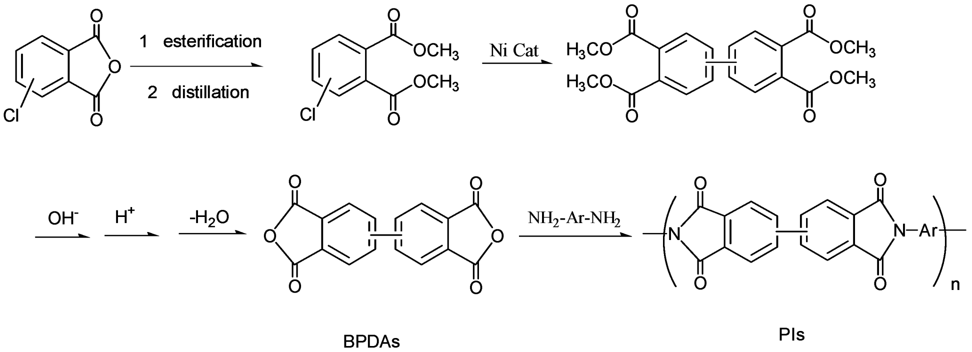
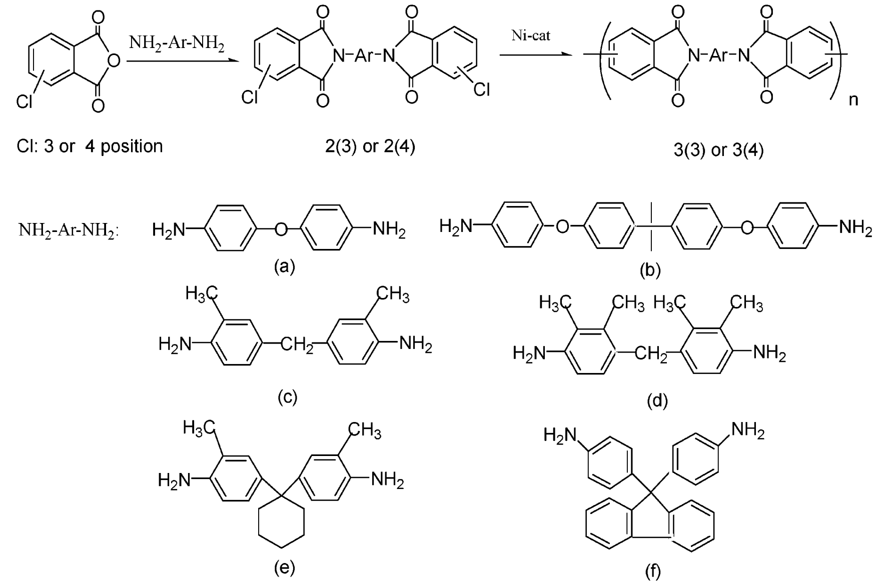
10.1021/ma034036y CCC: $25.00

Scheme 1. Typically Conventional Preparation of Biphenyl PIs



Scheme 2. Syntheses of Biphenyl PIs from Chlorophthalic Anhydrides and Diamines



300 mL of 15% Na_2CO_3 solution; the white precipitate formed was filtered and washed with water until a neutral pH was obtained. The residual crude product was recrystallized from isopropyl alcohol. The yield of **e** was 22.0 g (75%); mp 162−163 °C. ^{1}H NMR ($CDCl_3$): 6.94−7.98 (4H, m), 6.60−6.63 (2H, d), 3.35 (4H, s), 2.19−2.22 (4H, t), 2.16 (6H, s), 1.49−1.57 ppm (6H, m). Anal. Calcd for $C_{20}H_{26}N_2$: C, 81.58%; H, 8.90%; N, 9.51%. Found: C, 81.46%; H, 8.81%; N, 9.70%.

4,4′-Bis(3-chlorophthalimido)diphenyl Ether 2(3a). In a 500 mL round-bottomed flask, a mixture of 18.25 g (0.1 mol) of 3-chlorophthalic anhydride, 10.01 g (0.05 mol) of **a**, and 200 mL of acetic acid was stirred at ca. 40 °C for 30 min. The suspension was refluxed for 24 h, and 50 mL of acetic acid was distilled off. The hot mixture was filtered, washed with acetic acid, and dried under vacuum at 130 °C for 24 h. The product was recrystallized from toluene and DMAc (2:1, v/v), obtained in the yield of 90% (23.8 g); mp 259−260 °C. ^{1}H NMR ($CDCl_3$): 7.95−7.89 (6H, m), 7.50−7.53 (4H, d d), 7.24−7.27 ppm (4H, d d). IR (KBr): 1774 and 1718 cm^{-1} (C=O of imide), 1387 cm^{-1}(C−N stretching), 737 cm^{-1} (C=O bending). Anal. Calcd for $C_{28}H_{14}O_5N_2Cl_2$: C, 63.53%; H, 2.66%; N, 5.29%. Found: C, 63.38%; H, 2.50%; N, 5.33%.

4,4′-Bis(4-chlorophthalimido)diphenyl Ether 2(4a).[14] This compound was prepared from 4-chlorophthalic anhydride and **a** using the same procedure as described above and recrystallized from toluene and DMAc (2:1, v/v). The product was as a yellow solid (88%, 23.3 g); mp 238−240 °C (lit.[14] mp 238−240 °C). ^{1}H NMR ($CDCl_3$): 7.94 (2H, d), 7.91 (2H, d), 7.78−7.76 (2H, d d), 7.43−7.41 (4H, d d), 7.2−7.18 ppm (4H, d d). IR: 1777 and 1718 cm^{-1} (C=O of imide), 1393 cm^{-1}(C−N stretching), 736 cm^{-1} (C=O bending). Anal. Calcd for $C_{28}H_{14}O_5N_2Cl_2$: C, 63.53%; H, 2.66%; N, 5.29%. Found: C, 63.33%; H, 2.76%; N, 5.13%.

2,2′-Bis[4-(4′-(3-chlorophthalimido)phenyloxy)phenyl]-propane 2(3b). This compound was prepared from 3-chlorophthalic anhydride and **b** using the same procedure as described above and recrystallized from toluene and DMAc (2.5:1, v/v). The product was as a white solid (85%, 31.4 g); mp 227−229 °C. ^{1}H NMR ($CDCl_3$): 7.89 (2H, m), 7.74 (4H, m), 7.39 (2H, d d), 7.28 (2H, d d), 7.14 (2H, d d), 7.02 (2H, d d), 1.73 ppm (6H, s). IR: 1778 and 1722 cm^{-1} (C=O of imide), 1375 cm^{-1}(C−N stretching), 739 cm^{-1} (C=O bending). Anal. Calcd for $C_{43}H_{28}O_6N_2Cl_2$: C, 69.83%; H, 3.82%; N, 3.79%. Found: C, 69.63%; H, 3.76%; N, 3.90%.

2,2′-Bis[4-(4′-(4-chlorophthalimido)phenyloxy)phenyl]-propane 2(4b). This compound was prepared from 4-chlorophthalic anhydride and **b** using the same procedure as described above and recrystallized from toluene and DMAc (2.5:1, v/v). The product was as a yellow solid (83%, 30.7 g); mp 218−220 °C. ^{1}H NMR ($CDCl_3$): 7.95 (2H, d), 7.92 (2H, d), 7.78 (2H, d d), 7.38 (2H, d d), 7.27 (2H, d d), 7.14 (2H, d d), 7.01 (2H, d d), 1.73 ppm (6H, s). IR: 1779 and 1721 cm^{-1} (C=O of imide), 1384 cm^{-1}(C−N stretching), 738 cm^{-1} (C=O bending). Anal. Calcd for $C_{43}H_{28}O_6N_2Cl_2$: C, 69.83%; H, 3.82%; N, 3.79%. Found: C, 69.77%; H, 3.86%; N, 3.85%.

4,4′-Bis(3-chlorophthalimido)-3,3′-dimethyldiphenyl-methane 2(3c). This compound was prepared from 3-chlorophthalic anhydride and **c** using the same procedure as described above and recrystallized from toluene and DMAc (4:1, v/v). The product was as a white solid (80%, 22.2 g); mp 258−260 °C. ^{1}H NMR ($CDCl_3$): 7.91 (2H, m), 7.74 (4H, m), 7.24 (2H, d), 7.21 (2H, d), 7.18−7.15 (2H, d d), 4.06 (2H, s), 2.22 ppm (6H, s). IR: 1780 and 1718 cm^{-1} (C=O of imide), 1378 cm^{-1}(C−N stretching), 740 cm^{-1} (C=O bending). Anal. Calcd for $C_{31}H_{20}O_4N_2Cl_2$: C, 67.04%; H, 3.63%; N, 5.04%. Found: C, 66.97%; H, 3.46%; N, 5.22%.

4,4′-Bis(4-chlorophthalimido)-3,3′-dimethyldiphenylmethane 2(4c). This compound was prepared from 4-chlorophthalic anhydride and **c** using the same procedure as described above and recrystallized from toluene and DMAc (4:1, v/v). The product was as a white solid (82%, 22.7 g); mp 207−209 °C.^{1}H NMR (CDCl$_3$): 7.96 (2H, d), 7.92 (2H, d) 7.8−7.7 (2H, d d), 7.24 (2H, s), 7.18 (4H, q), 4.05 (2H, s), 2.20 ppm (6H, s). IR: 1776 and 1717 cm^{-1} (C═O of imide), 1374 cm^{-1}(C−N stretching), 741 cm^{-1} (C═O bending). Anal. Calcd for $C_{31}H_{20}O_4N_2Cl_2$: C, 67.04%; H, 3.63%; N, 5.04%. Found: C, 66.90%; H, 3.55%; N, 5.05%.

4,4′-Bis(3-chlorophthalimido)-2,2′,3,3′-tetramethyldiphenylmethane 2(3d). This compound was prepared from 3-chlorophthalic anhydride and **d** using the same procedure as described above and recrystallized from toluene and DMAc (5:1, v/v). The product was as a white solid (83%, 24.2 g); mp 172−175 °C. ^{1}H NMR (CDCl$_3$): 7.91 (2H, m), 7.75 (4H, m), 7.00 (2H, d), 6.92 (2H, d), 4.07 (2H, s), 2.29 (6H, s), 2.17 ppm (6H, s). IR: 1777 and 1723 cm^{-1} (C═O of imide), 1378 cm^{-1} (C−N stretching), 743 cm^{-1} (C═O bending). Anal. Calcd for $C_{33}H_{24}O_4N_2Cl_2$: C, 67.93%; H, 4.15%; N, 4.80%. Found: C, 67.74%; H, 4.13%; N, 4.98%.

4,4′-Bis(4-chlorophthalimido)-2,2′,3,3′-tetramethyldiphenylmethane 2(4d). This compound was prepared from 4-chlorophthalic anhydride and **d** using the same procedure as described above and recrystallized from toluene and DMAc (6:1, v/v). The product was as a white solid (81%, 23.6 g); mp 236−238 °C. ^{1}H NMR (CDCl$_3$): 7.97 (2H, d), 7.93 (2H, d), 7.78 (2H, d d), 7.01 (2H, d), 4.06 (2H, s), 2.29 (6H, s), 2.15 ppm (6H, s). IR: 1777 and 1726 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{33}H_{24}O_4N_2Cl_2$: C, 67.93%; H, 4.15%; N, 4.80%. Found: C, 67.75%; H, 4.08%; N, 4.56%.

4,4′-Bis(3-chlorophthalimido)-3,3′-dimethyldiphenyl-1,1′-cyclohexane 2(3e). This compound was prepared from 3-chlorophthalic anhydride and **e** using the same procedure as described above and recrystallized from toluene and DMAc (6:1, v/v). The product was as a white solid (76%, 23.4 g); mp 275−277 °C. ^{1}H NMR (CDCl$_3$): 7.85−7.89 (2H, m), 7.68−7.72 (4H, m), 7.27 (2H, d), 7.25−7.22 (2H, d d), 7.10 (2H, d), 2.30 (4H, m), 2.18 (6H, s), 1.60−1.52 ppm (6H, m). IR: 1777 and 1726 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{36}H_{28}O_4N_2Cl_2$: C, 69.35%; H, 4.53%; N, 4.49%. Found: C, 69.50%; H, 4.48%; N, 4.43%.

4,4′-Bis(4-chlorophthalimido)-3,3′-dimethyldiphenyl-1,1′-cyclohexane 2(4e). This compound was prepared from 4-chlorophthalic anhydride and **e** using the same procedure as described above and recrystallized from toluene and DMAc (6:1, v/v). The product was as a white solid (85%, 26.3 g); mp 303−304 °C. ^{1}H NMR (CDCl$_3$): 7.92 (2H, d), 7.88−7.90 (2H, d), 7.73−7.76 (2H, d d), 7.26 (2H, d), 7.25−7.23 (2H, d d), 7.10 (2H, d), 2.31 (4H, t), 2.15 (6H, s), 1.59−1.53 ppm (6H, m). IR: 1776 and 1725 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{36}H_{22}O_4N_2Cl_2$: C, 69.35%; H, 4.53%; N, 4.49%. Found: C, 69.50%; H, 4.44%; N, 4.60%.

4,4′-Bis(3-chlorophthalimido)diphenyl-9-fluoroenylidene 2(3f). This compound was prepared from 3-chlorophthalic anhydride and **f** using the same procedure as described above and recrystallized from toluene and DMAc (5:1, v/v). The product was as a white solid (82%, 27.78 g); mp 339.5 °C (based on DSC, 5 °C/ min). ^{1}H NMR (CDCl$_3$): 7.85−7.88 (2H, m), 7.79 (2H, d), 7.66−7.71 (4H, m), 7.30−7.45 ppm (14H, m). IR: 1776 and 1725 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{41}H_{22}O_4N_2Cl_2$: C, 72.68%; H, 3.27%; N, 4.13%. Found: C, 72.46%; H, 3.31%; N, 4.06%.

4,4′-Bis(4-chlorophthalimido)diphenyl-9-fluoroenylidene 2(4f). This compound was prepared from 4-chlorophthalic anhydride and **f** using the same procedure as described above and recrystallized from toluene and DMAc (5:1, v/v). The product was as a white solid (83%, 28.11 g); mp 328 °C (based on DSC, 5 °C/ min). ^{1}H NMR (CDCl$_3$): 7.90 (2H, d), 7.86 (2H, d), 7.79 (2H, d), 7.71−7.74 (2H, d d), 7.28−7.45 ppm (14H, m). IR: 1776 and 1725 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{41}H_{22}O_4N_2Cl_2$: C, 72.68%; H, 3.27%; N, 4.13%. Found: C, 72.46%; H, 3.21%; N, 4.16%.

4,4′-Bis(2-methyl-*N*-phenylphthalimide) (A). Compound **A** was prepared from 4-chlorophthalic anhydride and *o*-toluidine using a similar procedure as reported in the literature.[2a] The yield of **A** was 80%; mp 302−303 °C. ^{1}H NMR (CDCl$_3$): 8.01−8.04 (2H, d d), 7.84−7.90 (2H, t), 7.75−7.78 (2H, d d), 7.11−7.34 (8H, m), 2.14 ppm (6H, s). IR: 1776 and 1725 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{30}H_{20}O_4N_2$: C, 76.26%; H, 4.27%; N, 5.93%. Found: C, 76.40%; H, 4.21%; N, 5.76%.

3,3′-Bis(2-methyl-*N*-phenylphthalimide) (B). This compound was prepared from 3-chlorophthalic anhydride and *o*-toluidine using the same procedure as **A**. The yield of **B** was 71.0%; mp 290−291 °C. ^{1}H NMR (CDCl$_3$): 8.26 (2H, s), 8.08−8.14 (4H, m), 7.22−7.41 (8H, m), 2.25 ppm (6H, s). IR: 1776 and 1725 cm^{-1} (C═O of imide), 1375 cm^{-1}(C−N stretching), 742 cm^{-1} (C═O bending). Anal. Calcd for $C_{30}H_{20}O_4N_2$: C, 76.26%; H, 4.27%; N, 5.93%. Found: C, 76.20%; H, 4.29%; N, 5.98%. The single crystals of **A** and **B** for X-ray diffraction analysis were obtained by the slow sublimation of the powdered samples at 300 °C under vacuum.

X-ray Structure Determination. The X-ray diffraction data were collected on a SiemensP4 4-circle diffractometer at 293 K under monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Compound **A** crystallized in a triclinic system with space group *P*-1, $M_r = 472.48$, $a = 8.349(2)$ Å, $b = 10.0926(17)$ Å, $c = 13.7891(18)$ Å, $\beta = 80.826(15)°$, and $V = 1137.5(4)$ Å^3 with $Z = 2$ for $D_{calcd} = 1.380$ mg/m^3. Least-squares refinement based on 4478 independent reflections converged to final $R_1 = 0.0456$ and $R_w = 0.0526$. Compound **B** formed in a monoclinic system with space group *C*2/*c*, $M_r = 472.48$, $a = 29.010(2)$ Å, $b = 8.5518(19)$ Å, $c = 24.000(4)$ Å, $\beta = 126.520(9)°$, and $V = 4785.1(14)$ Å^3 with $Z = 8$ for $D_{calcd} = 1.312$ g/cm^3. Least-squares refinement based on 4715 independent reflections converged to final $R_1 = 0.0452$ and $R_w = 0.0826$. The structures of compounds **A** and **B** were solved by direct methods using SHELXTL revision 5.1 program.

Polymer Synthesis. Representative examples of the nickel-catalyzed polymerization are given below.

Homopolyimides from 2(4c). In a 50 mL two-necked round-bottomed flask were placed NiCl$_2$ (0.0182 g, 0.140 mmol), PPh$_3$ (0.2566 g, 0.980 mmol), zinc (0.52 g, 8.0 mmol), and **2(4c)** (1.11 g, 2 mmol). The flask was evacuated and filled with nitrogen three times. Then, dry DMAc (10 mL) was added via syringe through the serum cap. The mixture became red-brown in 20 min and was stirred at 95 °C for 8 h. The resulting viscous mixture was diluted with 10 mL of cresol, filtered, and then poured into 100 mL of methanol. The polymer was collected by filtration, washed with methanol, and dried in vacuo at 200 °C for 24 h. The yield was 98% (0.95 g). The inherent viscosity of the polymer in cresol was 0.98 dL g $^{-1}$, measured at a concentration of 0.5 g dL^{-1} at 30 °C.

Copolymerization of 2(3c) and 2(4c). The copolyimide was prepared via the similar procedure as described above using **2(3c)** (0.555 g, 1 mmol) and **2(4c)** (0.555 g, 1 mmol). The yield was 97% (0.94 g). The inherent viscosity of the polymer in cresol was 0.48 dL g $^{-1}$.

Preparation of Polymer 3(4c) from Dianhydride and Diamine. This polymer was synthesized as reported in the literature.[3] The yield was 99%. The inherent viscosity in cresol was 0.70 dL g $^{-1}$.

Results and Discussion

Monomer Synthesis. Twelve aryl dichlorides **2-(3a)−2(4f)** containing bisimide structure were prepared from 3- or 4-chlorophthalic anhydrides and six diamines in high yields. The structures of the monomers were confirmed by elemental analyses, IR, and NMR spectroscopies.

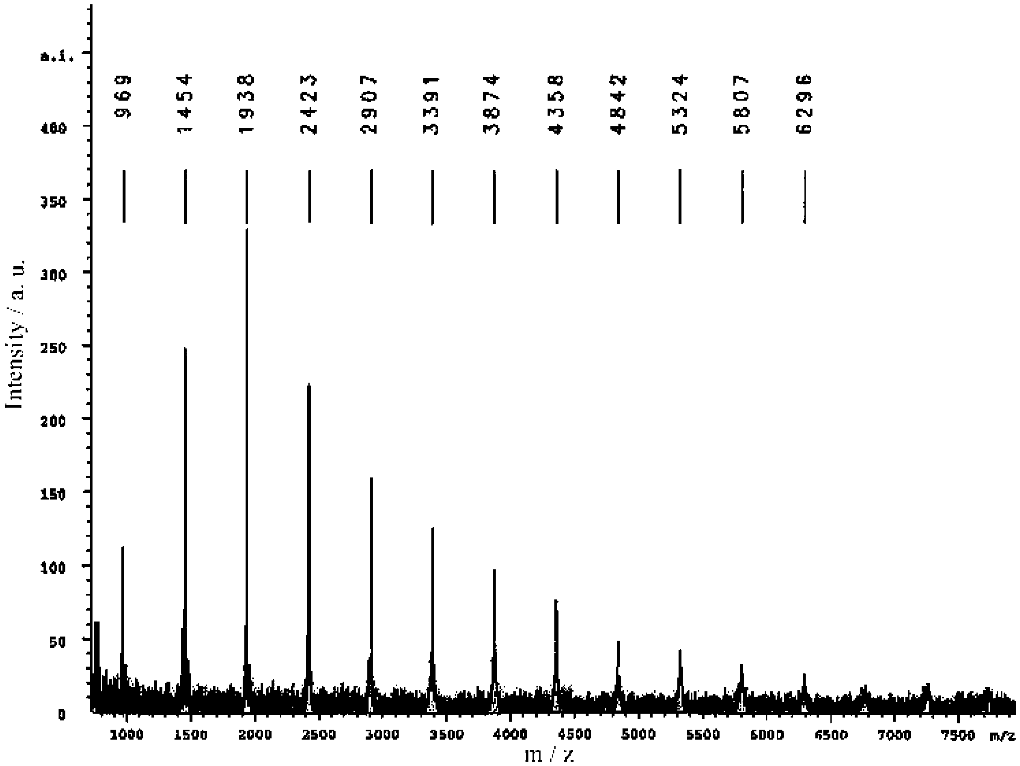


Figure 1. Cycle distribution of oligoimide **3(3c)** (molecular weight: 484.51*n*, $n = 2, 3, 4$, etc.).

Synthesis of Polymers. The nickel-catalyzed polymerization was performed with 2 mmol of monomer in DMAc in the presence of zinc and triphenylphosphine. The effects of temperature, solvent volume, nickel catalyst, and 2,2-bipyridine on molecular weight were studied by following the polymerization of monomer **2(4c)**, which gave soluble polymer in DMAc. Figure S1 shows that the optimal amount of solvent for a 1 mmoL scale reaction was 4−6 mL,[15] and the highest inherent viscosity was observed with a 7 mol % concentration of nickel catalyst (Figure S2).[15] An increase in nickel catalyst leads to the formation of long-lived nickel species at polymer ends,[7] leading to lower molecular weight materials.[9a]

The inherent viscosity of the polymer from **2(4c)** is shown in Figure S3.[15] The polycondensation at 95 °C gave the highest value. Raising the temperature to above 105 °C gave inferior results because higher temperature would favor the formation of the highly coordinated bis complex [Ni(PPh_3)$_2$], and then the oxidative addition of triphenylphosphine can occur.[7] The effect of the ratio of zinc to nickel catalyst on the polymerization was examined.[15] As shown in Figure S4, a great deal of excess zinc was needed to obtain higher molecular weight polymer.[15] Since 2,2-bipyridine could force diarylnickel(II) complex into a cis-aryl geometry which would facilitate reductive elimination due to the proximity of the phenyl groups,[7] the influences of the amount of bipyridine on the polymerization are also investigated. Figure S5 shows that the optimal amount of bipyridine in the polymerization was 25 mol % in relation to $NiCl_2$.[15] Upon further addition of bipyridine, the inherent viscosity of the polymer decreased because of the formation of a stable Ni(0)−bipyridine complex, which retarded the oxidative addition of aryl chlorides.[7] Figure S6 shows the progress of the polymerization as a function of inherent viscosity. Rapid polymerization proceeded within 60 min, followed by a very slow increase in inherent viscosity.[15] When polymerization was carried out for longer than 8 h, some insoluble gelation was observed.

Table 1. Preparation of Biphenyl PIs[a]

monomer	DMAc (mL)	time (h)	polymer	yield (%)	η_{inh} (dL g^{-1})
2(3a)	3	8	**3(3a)**	97	0.25
2(4a)	5	8	**3(4a)**	97	0.20
2(3b)	3	8	**3(3b)**	98	0.36
2(4b)	5	8	**3(4b)**	96	0.24
2(3c)	3	8	**3(3c)**	96	0.21
2(4c)	5	8	**3(4c)**	98	0.98
2(3d)	3	8	**3(3d)**	97	0.23
2(4d)	5	8	**3(4d)**	98	0.77
2(3e)	3	8	**3(3e)**	96	0.18
2(4e)	5	8	**3(4e)**	98	0.40
2(3f)	3	8	**3(3f)**	96	0.13
2(4f)	5	8	**3(4f)**	98	0.30
			3(4c)[b]	99	0.70

[a] Monomer (1 mmoL), $NiCl_2$ (0.07 mol), PPh_3 (0.49 mmol), Zn (4 mmol), 95 °C. [b] Prepared by the conventional method.

The main side reactions in the nickel-catalyzed coupling of aryl chlorides were minimized by using thoroughly dried solvents in which water content was less than 30 ppm and by using excess amounts of triphenylphosphine with respect to $NiCl_2$.

The inherent viscosities and results of thermal studies are summarized in Table 1. The polymerizations of **2(4a)** and **2(4b)** proceeded rapidly with the polymer precipitation because of crystalline polymers and gave low molecular weight materials, and those of **2(3a)**−**2(3f)** and **2(4c)**−**2(4f)** took place homogeneously. The polymerizations of monomers **2(4c)**−**2(4e)** with diamines moieties containing side pendants gave polymers with high inherent viscosities up to 0.98 dL g $^{-1}$. In contrast, the polymerizations of bis(3-chlorophthalimide)s gave polymers with lower molecular weights, though these polymers had good solubilities. Low inher-

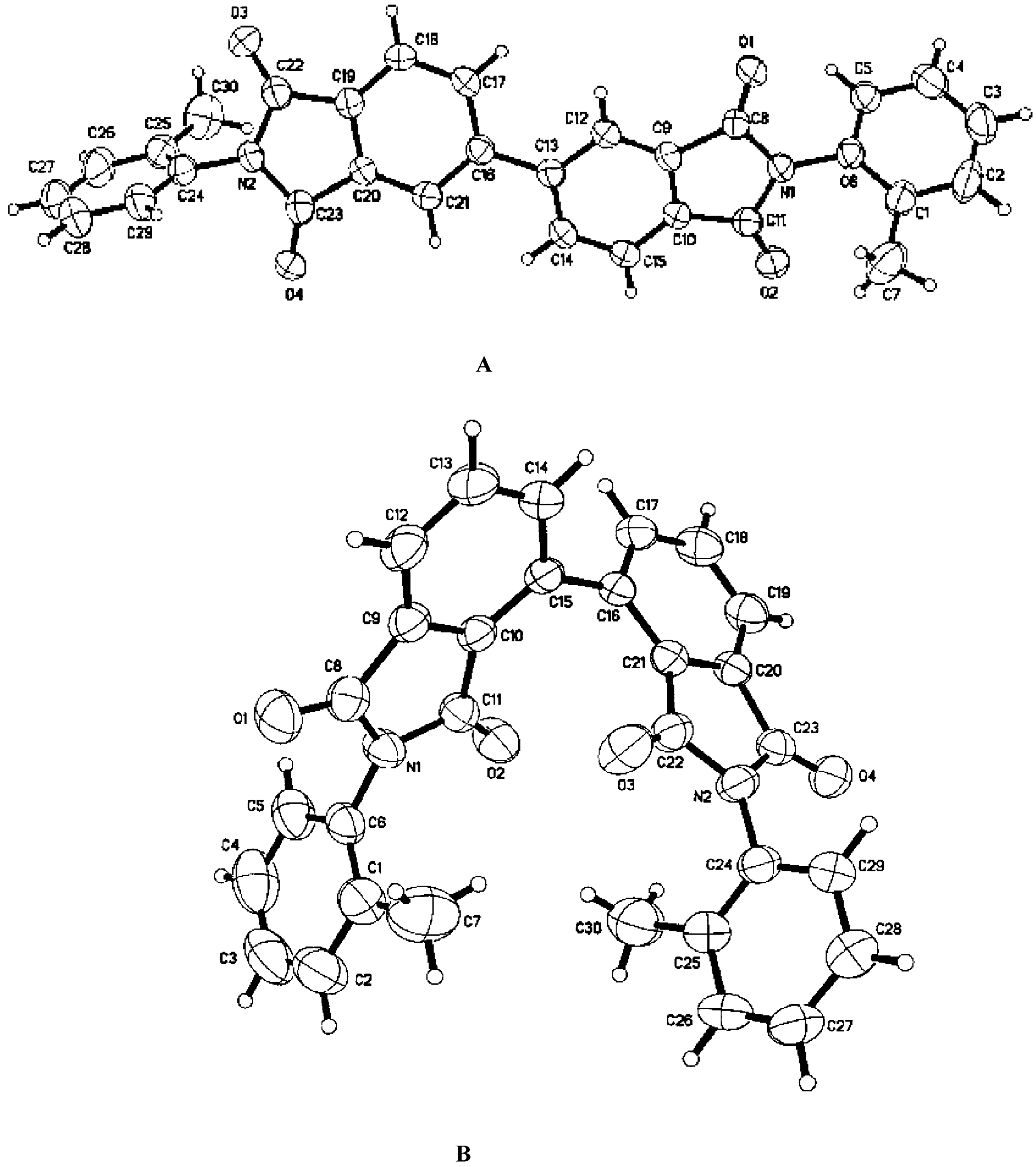


Figure 2. Molecular structures of compounds **A** and **B**.

ent viscosities of the polymers from bis(3-chloropthalimide)s would indicate the peculiarities of molecular shapes which favor the formation of oligomers. Figure 1 shows the MALDI−TOF mass spectrum of polymer **3(3c)**. As expected, the polymerization of bis(3-chloropthalimide)s produced a large amount of cyclic oligoimides (MW = $(C_{31}H_{20}O_4N_2/484.51)_n$: 969; 1454; 1983; 2423, etc.).

Rozhanskii et al.[2a] reported the single-crystal structure of 4,4′-bis(*N*-phenylphthalimide) (**A′**). The biphenyl unit of **A′** was confirmed to be coplanar; the stiffness of its structure directly decreased its solubility in common solvents. It could be explained that the polymerizations of **2(4a)** and **2(4b)** did not give high molecular weight polymers because of the formation of crystalline polymers. For comparison, compounds **A** and **B** were synthesized from 2-methyl-*N*-phenylchlorophthalimides by Ni-catalyzed coupling, and the structures were determined by X-ray diffraction methods (see Figure 2). As expected, steric hindrance forced the phthalimide planes and the 2-methylphenyl rings in compound **A** to twist with dihedral angles of 59.3° and 71°, respectively. The two phenyl rings of the biphenyl unit are also noncoplanar with a dihedral angle of 24.8°. The phthalimide planes in compound **B** formed a 57.1° dihedral angle, and the dihedral angles between the phthalimides and the 2-methylphenyl rings were 94.1° and 80.4°, respectively. The ultraviolet−visible absorption spectra of biphenyl derivatives provide qualitative information on the phenyl conformation in solution. As shown in Figure S9, the UV spectra of compounds **A** and **B** indicated a lower degree of conjugation for **B**, as may be concluded from the different intensities of their $\pi-\pi^*$ bands.[15] It has been recognized that the noncoplanar moieties or flexible links or bulky side substituents in the main chain of polymers could improve the solubility of the polymers because of the reduction of their intermolecular interaction.[16] Assuming a similar configuration of repeating units in polymers, the solubility of the polymers in DMAc, in the order of **3(3d)** > **3(3c)** > **3(3b)** > **3(3a)** and **3(4d)** > **3(4c)** > **3(4b)** > **3(4a)**, could be anticipated (see Table S2).[15]

Table 2. Thermal Properties of Biphenyl PIs

polymer	η_{inh}, dL g^{-1}	T_g (°C) (DSC)	$T_{5\%}$ (°C) (TGA)	$T_{10\%}$ (°C) (TGA)
3(3a)	0.25	296	500	520
3(4a)	0.20	306	498	530
3(3b)	0.36	260	450	470
3(4b)	0.24	245	480	510
3(3c)	0.21	300	460	470
3(4c)	0.98	299	458	480
3(3d)	0.23		440	493
3(4d)	0.77	297	442	471
3(3e)	0.18	300	445	486
3(4e)	0.40	305	450	480
3(3f)	0.13	315	500	550
3(4f)	0.30	311	480	520
3(4c)[a]	0.70	301	462	490

[a] Prepared by the conventional method.

On the other hand, the trend of bis-imide **B** to adopt syn conformations may indicate a facile formation of undesired cyclic oligomers. The experimental results are in good agreement with the conformation of **B**. In contrast, the structure features of **A** to adopt anti conformation predict the formation of linear polymers instead of cyclic oligomers. In fact, the MALDI−TOF mass spectrum of polymer **3(4d)** did not show any peak value of cyclic oligomers. In our study, the high concentrated system did not suppress the cyclization of the polymerization of the bis(3-chlorophthimide)s. It was presumed that both intramolecular and intermolecular cyclizations of polymerization might occur. It has been recognized that incorporation of long chain diamines (e.g., **b**) could reduce the formation of cyclic oligomers in the polymerization.[17] As shown in Table 1, the polymerization of monomer **2(3b)**, compared with those of other **2(3)**s, gave higher inherent viscosity polymer ($\eta = 0.36$ dL/g).

Copolymerization was attempted to obtain higher molecular weight polymers, and aryl dichlorides, **2(4c)** and **2(3c)**, were copolymerized in varying proportions. The results are shown in Table S3; it is observed that slightly higher molecular weight materials are obtained when monomer **2(4c)** is greater than 66 mol %.[15]

Polymer Characterization. Structural characterization of polymers was accomplished by elemental analyses, IR (KBr), and NMR. The elemental analysis values of polymers in Table S4 were in agreement with the calculated values for the proposed structure.[15] Figure S10 presents a typical FT-IR spectrum of PI **3(4c)**, which exhibited absorptions at 1776, 1717,1373, 1103, and 742 cm^{-1} associated with the imide structure, and no amic acid peaks were found, showing that the imide rings are intact.[15] As shown in Figure S11, the ^{1}H NMR (DMSO-d_6, 70 °C) spectrum of PI **3(4c)** is consistent with the proposed structure. Peak assignments are given in the figure.[15]

Polymer Properties. The thermal stability of the polymers was examined by TGA. For comparison, polymer **3(4c)** was prepared via the conventional method. Typical traces for polymer **3(4c)** are shown in Figure S12.[15] The PIs prepared via the two methods almost have the same TGA trace and show 10% weight loss at about 480 °C. The T_gs from DSC are summarized in Table 2. Polymers **3(3b)** and **3(4b)** give the lower T_gs because they contained long chain diamine moiety. Other PIs give the T_gs at about 300 °C. Figure 3 displays the dynamic storage modulus (E') and loss modulus (E'') as a function of temperature for polymer **3(4c)**. The T_g of polymer **3(4c)** was observed at 305 °C, as determined by the peak temperature in the E'' curve and consistent with DSC results. PI films of **3(4c)** prepared via two methods also show a good modulus (E') preservation before 280 °C.

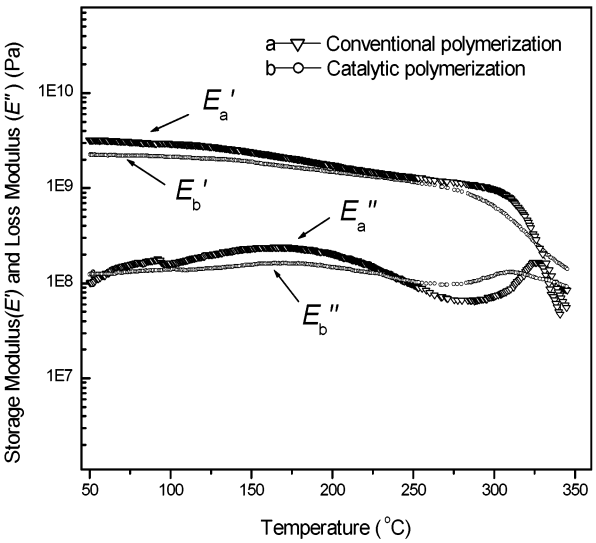


Figure 3. Dynamic modulus as a function of temperature for PI films of polymer **3(4c)** (○: $\eta_{inh} = 0.72$ dL g^{-1}, 16.7 μm thick; ▽: $\eta_{inh} = 0.70$ dL g^{-1}, 18.5 μm thick).

Conclusions

Our studies indicate that biphenyl PIs can readily be prepared by the nickel-catalyzed coupling polymerization of bis(chlorophthalimide)s. The polymerization of bis(4-chlorophthalimide)s containing the diamines moieties with bulky side substituents gave polymers with high inherent viscosities, but the crystalline PIs with high molecular weights from bis(4-chlorophthalimide)s cannot be prepared because of the limited solubility of the polymers. The polymerization of bis(3-chlorophthalimide)s produced undesired cyclic oligoimides which decreased the molecular weights of the polymers. The cyclization of the polymerization of bis(3-chlorophthalimide) was partially suppressed by copolymerization with bis(4-chlorophthalimide).

Acknowledgment. The authors express their thanks to the National Science Foundation of China for financial support (No. 20174040; No. 50033010).

Supporting Information Available: Tables of solubilities of PIs, preparation of copolyimides, and elemental analysis of polymers; figures of effects of amounts of solvent, catalyst, reaction temperature, ratio of zinc to nickel catalyst, and amount of bipyridine, course of polymerization, UV−vis absorption spectra of compounds **A** and **B**, FT-IR spectrum of PI **3(4c)**, ^{1}H NMR spectrum of PI **3(4c)**, and TG curves of polymer **3(4c)**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Itatani, H. U.S. Patent 4,568,715, 1986. (b) Itatani, H. U.S. Patent 4,247,443, 1981. (c) Sasaki. U.S. Patent 4,290,-936, 1981. (d) Sasaki. U.S. Patent 4,473,523, 1984. (e) Kaneda, T.; Katsura, T.; Nakagawa, K.; Makino, H. *J. Appl. Polym. Sci.* **1986**, *32*, 3151.

(2) (a) Rozhanskii, I.; Okuyama, K.; Goto, K. *Polymer* **2000**, *41*, 7057. (b) Tong, Y.; Huang, W.; Luo, J.; Ding, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1425. (c) Hasegawa, M.; Sensui, N.; Shindo, Y.; Yokota, R. *Macromolecules* **1999**, *32*, 387.

(3) Ding, M.; Wang, X.; Yang, Z.; Zhang, J. U.S. Patent 5,081,281, 1992.

(4) (a) Itatani, H.; Kashima, M.; Matsuda, M.; Yoshimoto, H.; Yamamoto, H. U.S. Patent 3,940,426, 1976. (b) Kitai, M.; Katsuro, Y.; Kawamura, S.; Hino, M.; Sato, K. U.S. Patent 4,900,843, 1990. (c) Itatani, H.; Shiotani, A.; Fujimoto, M. U.S. Patent 4,581,469, 1986. (d) Freudenberger, J. H. U.S. Patent 5,081,291 1992. (e) Becker, A.; Ewenson, A. A.; Croitoru_ B. U.S. Patent 5,117,258, 1993. (f) Katsuro, Y.; Matsuda, H. U.S. Patent 5,258,530, 1993.

(5) Iataaki, H.; Yoshimoto, H. *J. Org. Chem.* **1973**, *38*, 76.

(6) Percec, V.; Hill, D. H. In *Step Growth Polymers for High-Performance Materials, New Synthetic Methods*; Labadie, J. W., Hedrick, J. L., Eds.; ACS Symposium Series Vol. 624; American Chemical Society: Washington, DC, 1996; p 2.

(7) Colon, I.; Keley, D. R. *J. Org. Chem.* **1986**, *51*, 2627.

(8) (a) Colon, I.; Kwiatkowski, G. T. *J. Polym. Sci., Part A* **1990**, *28*, 367. (b) Ueda, M.; Ito, T. *Polym. J.* **1991**, *23*, 297. (c) Ueda, M.; Yokoo, T.; Nakamura, T. *J. Polym. Sci., Part A* **1994**, *32*, 2989.

(9) (a) Ueda, M.; Ichikawa, F. *Macromolecules* **1990**, *23*, 926. (b) Ueda, M.; Seino, Y.; Haneda, Y.; Yoneda, M.; Sugiyama, J.-I. *J. Polym. Sci., Part A* **1994**, *32*, 675. (d) Ueda, M.; Yokoo, T. *J. Polym. Sci., Part A* **1994**, *32*, 2065.

(10) Ueda, M.; Ito, T.; Seino, Y. *J. Polym. Sci., Part A* **1994**, *30*, 1567.

(11) Ueda, M.; Miyaji, Y.; Ito, T.; Oba, Y.; Sone, T. *Macromolecules* **1991**, *24*, 2694.

(12) (a) Gagne, R. R.; Marrocco, M. L., III; Trimmer, M. S.; Hendricks, N. H. U.S. Patent 5,824,744, 1998. (b) Gagne, R. R.; Marrocco, M. L., III; Trimmer, M. S.; Hendricks, N. H. U.S. Patent 5,973,075, 1999. (c) Gagne, R. R.; Marrocco, M. L., III; Trimmer, M. S.; Hendricks, N. H. U.S. Patent 5,869,592, 1999. (d) Pettit, G. R.; Singh, S. B. U.S. Patent 5,569,786, 1996. Gagne, R. R. (e) Wang, Y.; Ouirk, R. P. *Macromolecules* **1995**, *28*, 3495. (f) Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. *Polymer* **1989**, *30*, 1054. (g) Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. *Polymer* **1989**, *30*, 1060.

(13) Genies, C.; Mercier, R.; Sillion, B.; Cornert, N.; Gebel, G.; Pineri, M. *Polymer* **2001**, *42*, 359.

(14) Wirth, J. G.; Heath, D. R. U.S. Patent 3,787,364, 1974.

(15) See the Supporting Information.

(16) (a) Harris, F. W.; Hsu, S. L. C. *High Perform. Polym.* **1989**, *1*, 3. (b) Matsumoto, T.; Hasuda, Y.; Nishi, S.; Yamada, N. *Macromolecules* **1991**, *24*, 5001. (c) Falcigno, P. A.; Jasne, S.; King, M. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 1433. (d) Oishi, Y.; Isshida, M.; Kakimoto, M.; Imal, Y. *J. Polym. Sci., Polym. Chem.* **1992**, *30*, 1027. (e) Kim, W. G.; Hay, A. S. *Macromolecules* **1993**, *26*, 5275. (F) Eastmond, G. C.; Paprotny, J. *Macromolecules* **1995**, *28*, 2140.

(17) Fang, X.; Yang, Zh.; Zhang, S.; Gao, L.; Ding, M. *Macromolecules* **2002**, *35*, 8708.

MA034036Y