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Syntheses and Properties of Soluble Biphenyl-Based Polyimides from Asymmetric Bis(chlorophthalimide)s

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ABSTRACT: A novel synthesis of asymmetric bis(chlorophthalimide)s (3,4-BCPIs) has been established. The polymerizations of them produced higher molecular weight (0.38−0.51 dL/g) polyimides containing biphenyl units than those of isomeric polymers derived from symmetric bis(chlorophthalimide)s (4,4′-BCPIs) and 3,3′-BCPIs. The distribution of the formed biphenyl units of head to tail, head to head, and tail to tail in the chain of the polymers was about 58.0:21.0:21.0, determined by ^{13}C NMR spectra of the polymers. The composition of model compounds, determined by HPLC, was well consistent with the ^{13}C NMR spectrum result. Comparing with polymers derived from 4,4′-BCPIs and 3,3′-BCPIs, the polymers derived from 3,4-BCPIs showed better solubilities in *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and *N*-methylpyrrolinone (NMP). Flexible films could be cast from the polymer solution with the inherent viscosities of above 0.35 dL/g. The polymer derived from asymmetric bis(chlorophthimide)s gave the highest T_g among the isomeric polymers. The 10% weight loss of these polyimides was above 549 °C.

Introduction

Aromatic polyimides (PIs) are a class of advanced materials known for their high-temperature stability, excellent electrical and mechanical properties, and good chemical resistance.[1] Most PIs are often insoluble and intractable in their fully imidized form, thus showing severe difficulties in processing.[2] Therefore, significant synthetic efforts have been carried out to improve processability and solubility of PIs with compromising their attractive properties by the incorporation of flexible bridging links and/or bulky units into the rigid PI backbone or by attachment of bulky side groups.[3] It has been demonstrated that the polymerization of isomeric dianhydrides and diamines produced polymers with broad processing windows and good solubilities without loss of thermal properties.[4] Step polymerizations via Ni- and Pd-catalyzed carbon−carbon bond formation were developed to synthesize a series of polymers.[5] The polymerization of 4,4′- or 3,3′-BCPIs (Figure 1), easily prepared from chlorophthalic anhydrides and stiff diamines, via nickel-catalyzed coupling reaction produced low molecular weight polymers due to the formation of crystalline polymers and cyclic oligomers, respectively.[5b]

According to our best knowledge, there have been no reports on the syntheses and polymerizations of 3,4-BCPIs, and the properties of the polymers therefrom prior to this work. In this paper, we would like to report a novel method for the synthesis of 3,4-BCPIs using 3- and 4-chlorophthalic anhydrides and diamines in xylene as well as the properties of the polymers resulted from the polymerization of 3,4-BCPIs (Scheme 1). The composition of the biphenyl units in polymer was also investigated by the ^{13}C NMR spectrum.

Experimental Section

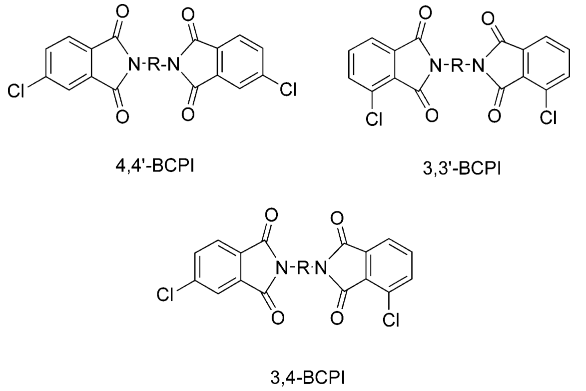

Figure 1. Isomers of BCPIs.

Materials. Anhydrous $NiCl_2$, triphenylphosphine (PPh_3), powdered (100 mesh) zinc, chlorophthalic anhydrides, and *N*,*N*-dimethylacetamide (DMAc) were purified as described in the literature.[5b] 4,4′-Oxydianiline (**a**), 1,3-bis(4-aminophenyloxy)benzene (**b**), and 4,4′-methylenedianiline (**c**) were used as received. 2,3,2′,3′-Biphenyltetracarboxylic dianhydride (*iso*-BPDA), 2,3,3′,4′-biphenyltetracarboxylic dianhydride (*a*-BPDA), and 3,4,3′,4′-biphenyltetracarboxylic dianhydride (*s*-BPDA) were prepared as reported in the literature (Figure 2).[6a−c]

Instrumentation. The ^{1}H and ^{13}C NMR spectra were measured at 400 MHz on a AV400 spectrometer, and acquisition parameters of ^{13}C NMR spectra were as follows: pulprog, zgig; ns, 1000; swh, 25062.0 Hz; d1, 8.0 s; and p1, 5.5 μs. The HPLC analysis was carried out on a Gilson-117 spectrometer with a Hypersil CN (5 μm) column, and hexane and 2-propanol (98/2, v/v) were used as mobile phase. The X-ray diffrction (WAXD) measurements were undertaken on a Philos X-ray diffractometer with Cu K radiation (40 kV, 30 mA). The scanning rate was 2°/min. The FTIR spectra, the elemental analyses data, the inherent viscosities, the thermogravimetric analyses (TGA) curves, the differential scanning calorimetry (DSC) curves, the MALDI−TOF mass spectra, and the dynamic mechanical property of PI film were obtained as described in the literature.[5b] The X-ray diffraction data of *a*-BPDA were collected on a SiemensP4 4-circle diffractometer at 293 K under monochromatized MoKα radiation (λ = 0.710 73 Å). 2,3,3′4-BPDA crystallized in a triclinic system with space group *P*-1, M_r = 294.20, *a* = 7.0366(4) Å, *b* =

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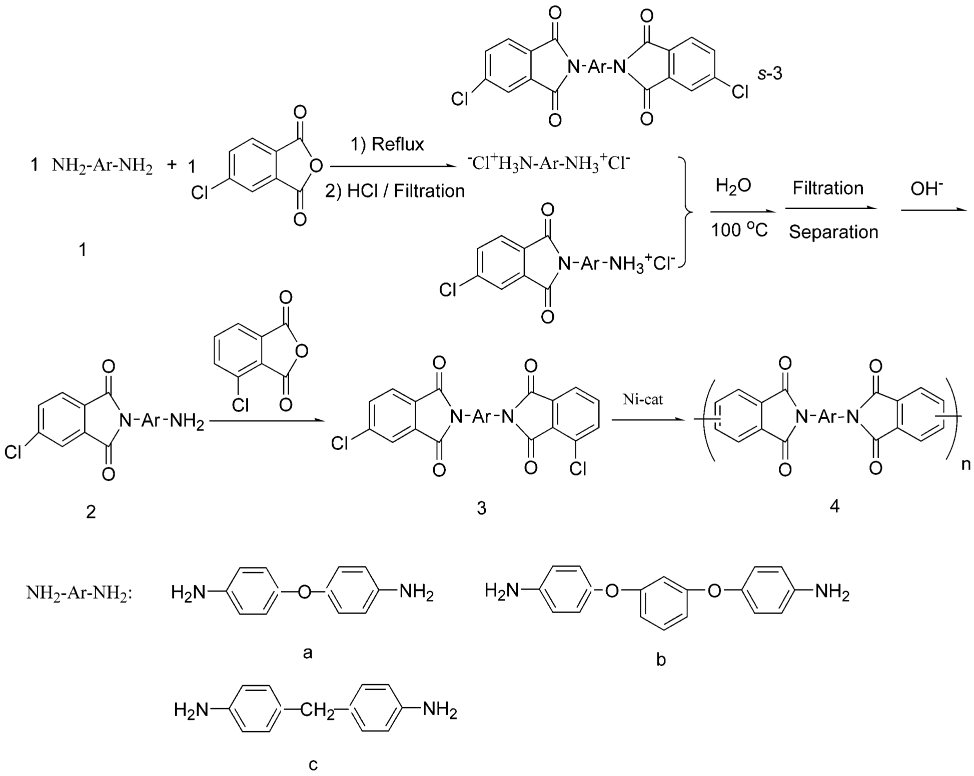
Scheme 1. Synthesis of PIs from 3,4-BCPIs



15.1679(8) Å, c = 18.4629(12) Å, β = 83.296(2)°, and V = 1859.54(4) Å^3 with Z = 4 for D_{calcd} = 1.576 mg/m^3. Least-squares refinement based on 7954 independent reflections converged to final R_1 = 0.0397 and R_w = 0.0806. The structure of *a*-BPDA was solved by direct methods using the SHELXTL revision 5.1 program. The single crystal of *a*-BPDA was prepared by sublimation at 200 °C.

Monomer Synthesis. 2-[4-(4-Aminophenoxy)phenyl]-5-chloro-isoindole-1,3-dione (2a). In a 500 mL three-necked round-bottomed flask, 10.01 g (0.05 mol) of **a** was dissolved in 200 mL of xylene at ca. 100 °C under a nitrogen atmosphere, 9.13 g (0.05 mol) of 4-chlorophthalic anhydride was added in portion into the system and stirred for 2 h at 95 °C, and then the resulted suspension was refluxed until the generated water was removed via a Dean−Stark trap. The resulted soluble mixture was cooled to 100 °C, and dry hydrochloride was sparged into the system until **2a** was not detected by TLC (hexane:ethyl acetate = 2:1, v/v). The resulting suspensions (hydrochloric salts of **2a** and the unreacted **a**) were filtered while hot, washed with hot xylene, and dried under vacuum at 100 °C for 10 h. Then the mixture of hydrochloric salts was stirred in boiling water for 1 h, then filtered, and washed with water. The resulting hydrochloric salt of **2a** was dissolved in 20 mL of DMAc, poured slowly into 100 mL of 15% Na_2CO_3 solution, stirred, filtered, and washed with ethanol until pH = 7. The product was recrystallized from DMAC and ethanol (1:1, v/v) to afford **2a** in a yield of 56.5% (10.30 g, based on **a**); mp 172−174 °C. ^{1}H NMR ($CDCl_3$): 7.92 (1H, s), 7.90−7.77 (2H, d d), 7.34−7.03 (4H, d d), 6.95−6.70 (4H, d d), 3.53 (2H, s) ppm. IR (paraffin): 3453 and 3370 cm^{-1} (NH_2 of aryl), 1778 and 1706 cm^{-1} (C=O of imide), 1388 cm^{-1}(C−N stretching), 742 cm^{-1} (C=O bending). Anal. Calcd for $C_{20}H_{13}O_3N_2Cl$: C, 65.85%; H, 3.59%; N, 7.68%. Found: C, 65.68%; H, 3.50%; N, 7.50%. Meanwhile, the filtrate containing hydrochloric salts of **a** was poured slowly into another 50 mL of 15% Na_2CO_3 solution, stirred, and filtered, and then the unreacted **a** was recovered, sublimated in vacuo at 200 °C (1.80 g); mp 189−191 °C. On the other hand, when the xylene solution was cooled, symmetric 4,4′-bis(4-chlorophthalimido)diphenyl ether (*s*-**3a**), was collected, recrystallized from xylene, and obtained in the yield of 17.1% (4.52 g, based on **a**); mp 238−240 °C (lit.[5b] mp 238−240 °C).

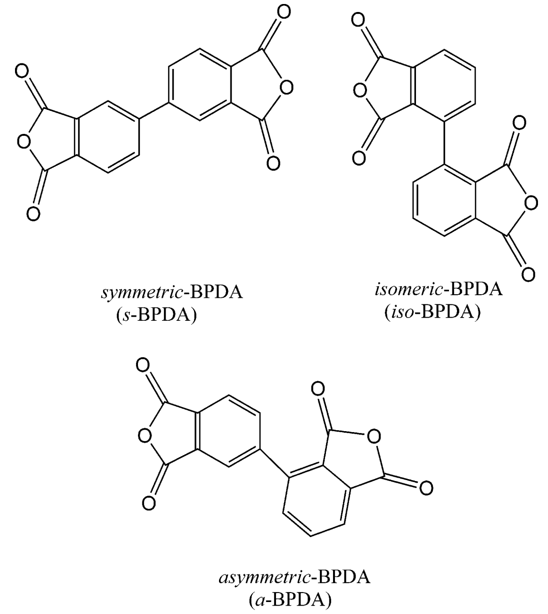

symmetric-BPDA (*s*-BPDA)
isomeric-BPDA (*iso*-BPDA)
asymmetric-BPDA (*a*-BPDA)

Figure 2. Isomers ofBPDAs.

2-{4-[3-(4-Aminophenoxy)phenoxy]phenyl}-5-chloro-isoindole-1,3-dione (2b). This compound was prepared from 4-chlorophthalic anhydride and **b** using the same procedure as described above and recrystallized from xylene. The product was obtained as a white solid in the yield of 58.6% (13.4 g, based on **b**); mp 160−162 °C. ^{1}H NMR (DMSO-d_6): 8.03 (1H, s), 7.98−7.93 (2H, d d), 7.76−7.44 (2H, d), 7.35−7.30 (1H, t), 7.17−7.15 (2H, d), 6.84−6.82 (2H, d), 6.70−6.63 (4H, m), 6.58 (1H, s) and 5.35 ppm (2H, s). IR (paraffin): 3454 and 3372 cm^{-1} (NH_2 of aryl), 1778 and 1706 cm^{-1} (C=O of imide), 1387 cm^{-1} (C−N stretching), 740 cm^{-1} (C=O bending). Anal. Calcd for $C_{26}H_{17}O_4N_2Cl$: C, 68.35%; H, 3.75%; N, 6.13%. Found: C, 68.47%; H, 3.86%; N, 5.95%. Symmetric 1,3-bis[4-(4-chlorophthalimido)phenoxy]benzene (*s*-**3b**), as a white solid, recrys-

Table 1. Preparation of PIs Containing Biphenyl Units

	polymerization via Ni−Cat coupling			polymerization of BPDAs and **a**			
monomer	**3a**	**3b**	**3c**	*s*-BPDA	*iso*-BPDA	*a*-BPDA	*m*-BPDA[a]
polymer	**4a**	**4b**	**4c**	*s*-**PI**	*iso*-**PI**	*a*-**PI**	*m*-**PI**
yield (%)	95	96	94	99	97	98	98
η_{inh} (dL g^{-1})	0.51	0.40	0.38	0.58[b]	0.25	0.41	0.56
film appearance	flexible	flexible	flexible	flexible	brittle	flexible	flexible

[a] *s*-BPDA:*a*-BPDA:*iso*-BPDA = 21:58:21 (mol/mol/mol). [b] (1) *s*-BPDA:phthalic anhydride:**a** = 0.98:0.04:1 (mol/mol/mol); (2) determined in *p*-chlorophennol/*m*-cresol (1:1, w/w).

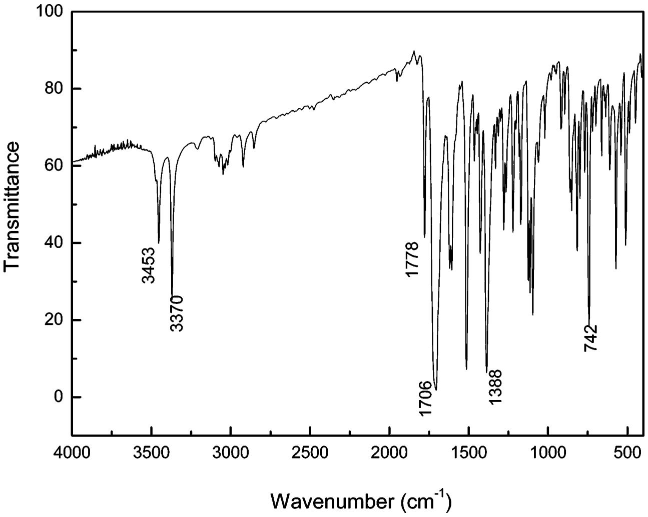


Figure 3. IR spectrum of **2c**.

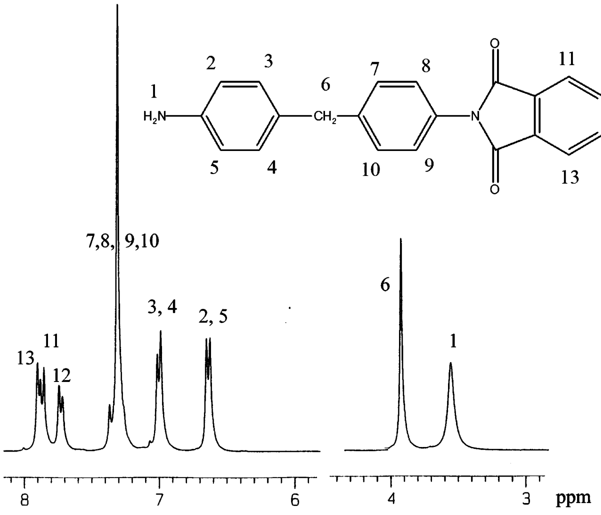


Figure 4. ^{1}H NMR spectrum of **2c**.

tallized from xylene, was obtained in the yield of 15.7% (4.87 g, based on **b**); mp 257−259 °C. ^{1}H NMR (DMSO-d_6): 8.03 (2H, s), 7.98−7.93 (4H, d d), 7.48−7.44 (5H, m), 7.23−7.21 (4H, t), 6.90−6.87 (2H, d d) and 6.80−6.79 ppm (1H, t). IR (paraffin): 1778 and 1706 cm^{-1} (C=O of imide), 1387 cm^{-1} (C−N stretching), 740 cm^{-1} (C=O bending). Anal. Calcd for $C_{34}H_{18}O_6N_2Cl_2$: C, 65.71%; H, 2.92%; N, 4.51%. Found: C, 65.57%; H, 2.86%; N, 4.53%. In the meantime, 2.4 g of **b** was recovered.

2-[4-(4-Aminobenzyl)phenyl]-5-chloroisoindole-1,3-dione (2c). This compound was prepared from 4-chlorophthalic anhydride and **c** using the same procedure as described above and recrystallized from xylene. The product was as a yellow solid (53.3%, 9.66 g, based on **c**); mp 182−184 °C. ^{1}H NMR (DMSO-d_6): 7.93 (1H, s), 7.88−7.90 (2H, d d), 7.34−7.39 (4H, d), 7.01−7.04 (2H, d), 6.65−6.67 (2H, d), 3.95 (2H, s) and 3.58 ppm (2H, s). IR (paraffin): 3454 and 3372 cm^{-1} (NH$_2$ of aryl), 1778 and 1706 cm^{-1} (C=O of imide), 1387 cm^{-1}(C−N stretching), 740 cm^{-1} (C=O bending). Anal. Calcd for $C_{26}H_{17}O_4N_2Cl$: C, 68.35%; H, 3.75%; N, 6.13%. Found: C, 68.47%; H, 3.86%; N, 5.95%. 4,4-Bis(4-chlorophthalimido)diphenylmethane, *s*-**3c**, recrystallized from xylene, was obtained in the yield of 18.1% (4.78 g, based on **c**); mp 239−241 °C (lit.[7] mp 239−241 °C). In the meantime, 1.9 g of **c** was recovered.

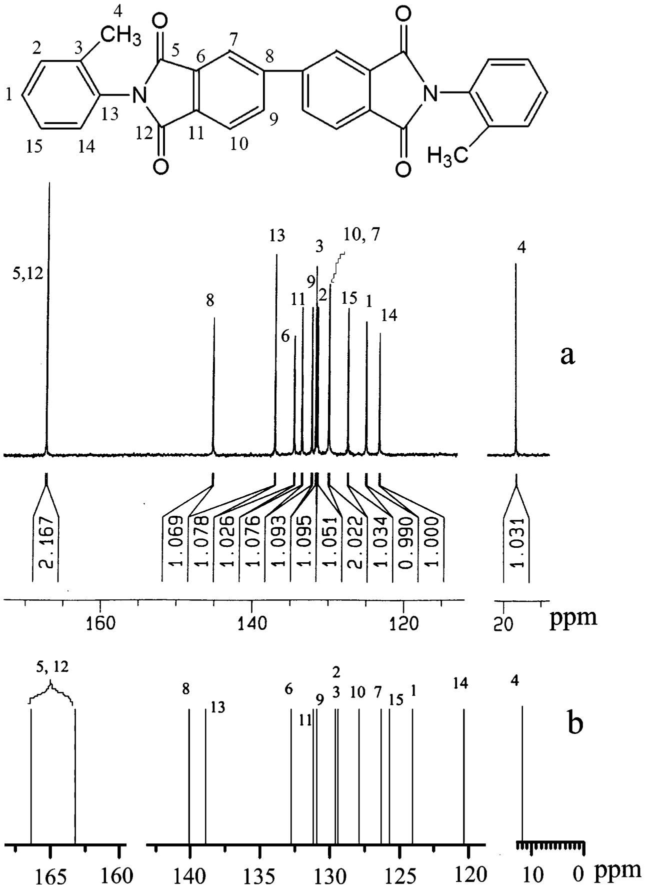
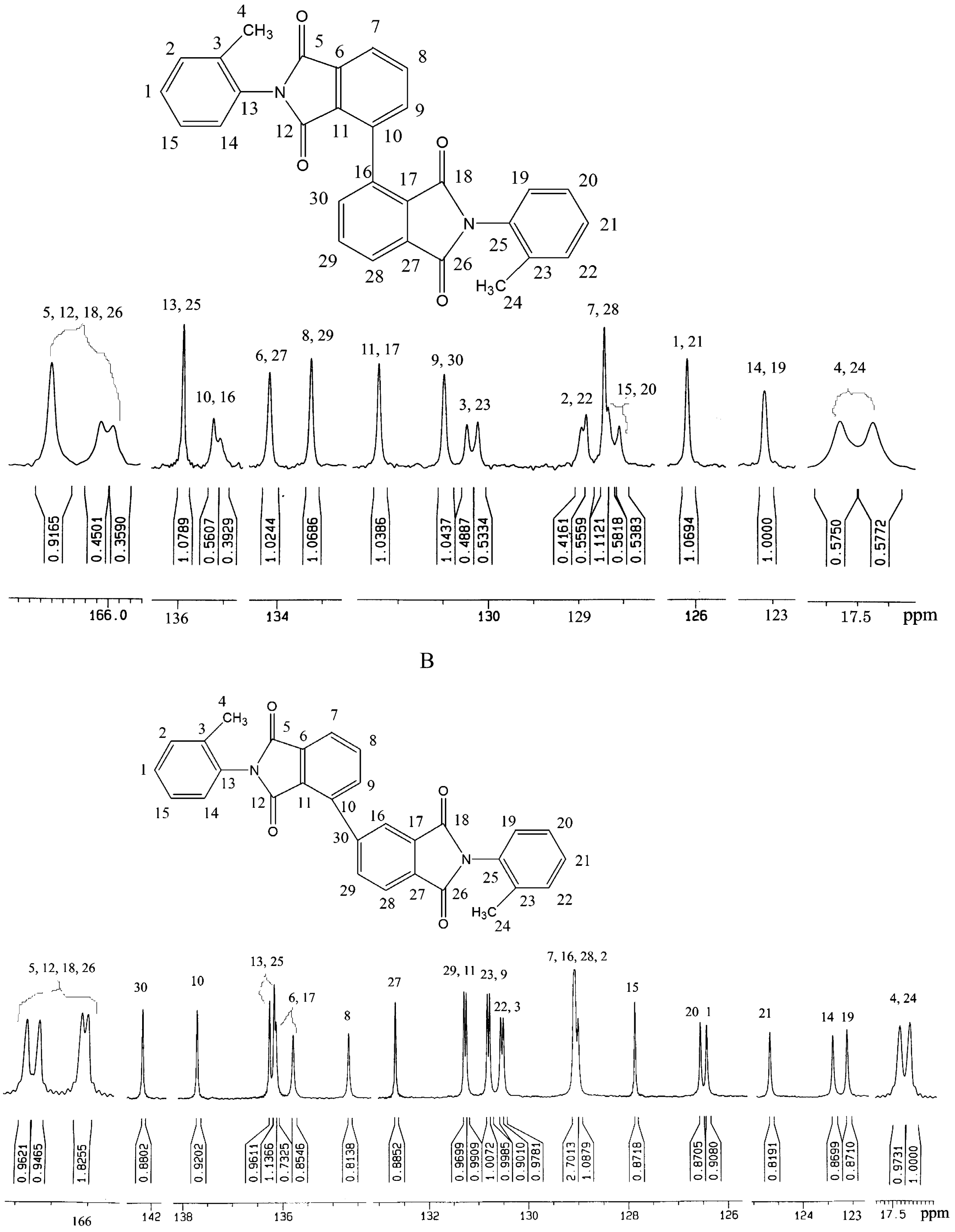


Figure 8. ^{13}C NMR spectrum of compound **A** (a, measured in DMSO-d_6; b, estimated by calculation.)

4-(4-Chlorophthalimido)phenyl-4-(3-chlorophthalimido)phenyl Ether (3a). In a 100 mL three-necked round-bottomed flask, 3.65 g (0.01 mol) of **2a**, 1.83 g (0.01 mol) of 3-chlorophthalic anhydride, and 50 mL of xylene were added and refluxed for 24 h in nitrogen until the generated water was removed via a Dean−Stark trap. The system was cooled, and a yellow participate was collected by filtration. The product, **3a**, recrystallized from xylene, was obtained in a yield of 90% (4.76 g); mp 230−232 °C. ^{1}H NMR (DMSO-d_6): 8.02 (1H, s), 7.84−7.99 (5H, m), 7.50−7.53 (4H, d), 7.24−7.27 ppm (4H, d). 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 $C_{28}H_{14}O_5N_2Cl_2$: C, 63.53%; H, 2.67%; N, 5.29%. Found **A**: C, 63.56%; H, 2.72%; N, 5.26%.

1-[4-(3-Chlorophthalimido)phenoxy]-3-[4-(4-chlorophthalimido)phenoxy]benzene (3b). This compound was prepared from **2b** and 3-chlorophthalic anhydride using the same procedure as described above. The product, **3b**, as a white solid, recrystallized from xylene, was obtained in the yield of 86% (5.34 g); mp 235−237 °C. ^{1}H NMR (DMSO-d_6): 8.02 (1H,



B

C

Figure 9. ^{13}C NMR spectra of compounds **B** and **C** (DMSO-d_6).

s), 7.85−7.98 (5H, m), 7.45−7.49 (5H, t), 7.20−7.23 (4H, d d), 6.87−6.90(2H, d d) and 6.80−6.81 ppm (1H, t). IR: 1774 and 1727 cm^{-1} (C=O of imide), 1375 cm^{-1} (C−N stretching), 740 cm^{-1} (C=O bending). Anal. Calcd for $C_{34}H_{18}O_6N_2Cl_2$: C, 65.71%; H, 2.92%; N, 4.51%. Found: C, 65.67%; H, 2.96%; N, 4.50%.

4-(3-Chlorophthalimido)phenyl-(4-chlorophthalimido)-phenylmethane (3c). This compound was prepared from **2c** and 3-chlorophthalic anhydride using the same procedure as described above. The product, **3c**, as a yellow solid, recrystallized from xylene, was obtained in the yield of 84% (4.43 g); mp 254−256 °C. ^{1}H NMR (DMSO-d_6): 8.02 (1H, s), 7.84−7.98 (5H, m), 7.38−7.45 (8H, d d) and 4.10 ppm (1H, s). IR: 1778 and 1727 cm^{-1} (C=O of imide), 1378 cm^{-1} (C−N stretching), 745 cm^{-1} (C=O bending). Anal. Calcd for $C_{29}H_{16}O_4N_2Cl_2$: C, 66.05%; H, 3.06%; N, 5.31%. Found: C, 65.97%; H, 2.96%; N, 5.40%.

Syntheses of Calibration Compounds A, B, C, D, and E for HPLC Analysis. 4,4′-Bis[*N*-(2-methylphenyl)phthalimide] (A) and 3,3′-Bis[*N*-(2-methylphenyl)phthalimide] (B). Compounds **A** and **B** were prepared as reported in the literature.[5b] The characteristic data were well consistent with the results in the literature.[5b]

3,4-Bis[*N*-(2-methylphenyl)phthalimide] (C). The compound **C** was prepared from 2,3,3′,4-BPDA and toluidine using the similar procedure as reported in the literature.[8] The yield of product was 85% (3.78 g); mp 224−226 °C. ^{1}H NMR (CDCl$_3$): 8.15 (1H, s), 8.06−8.07 (1H, d), 8.03 (2H, s), 7.90−

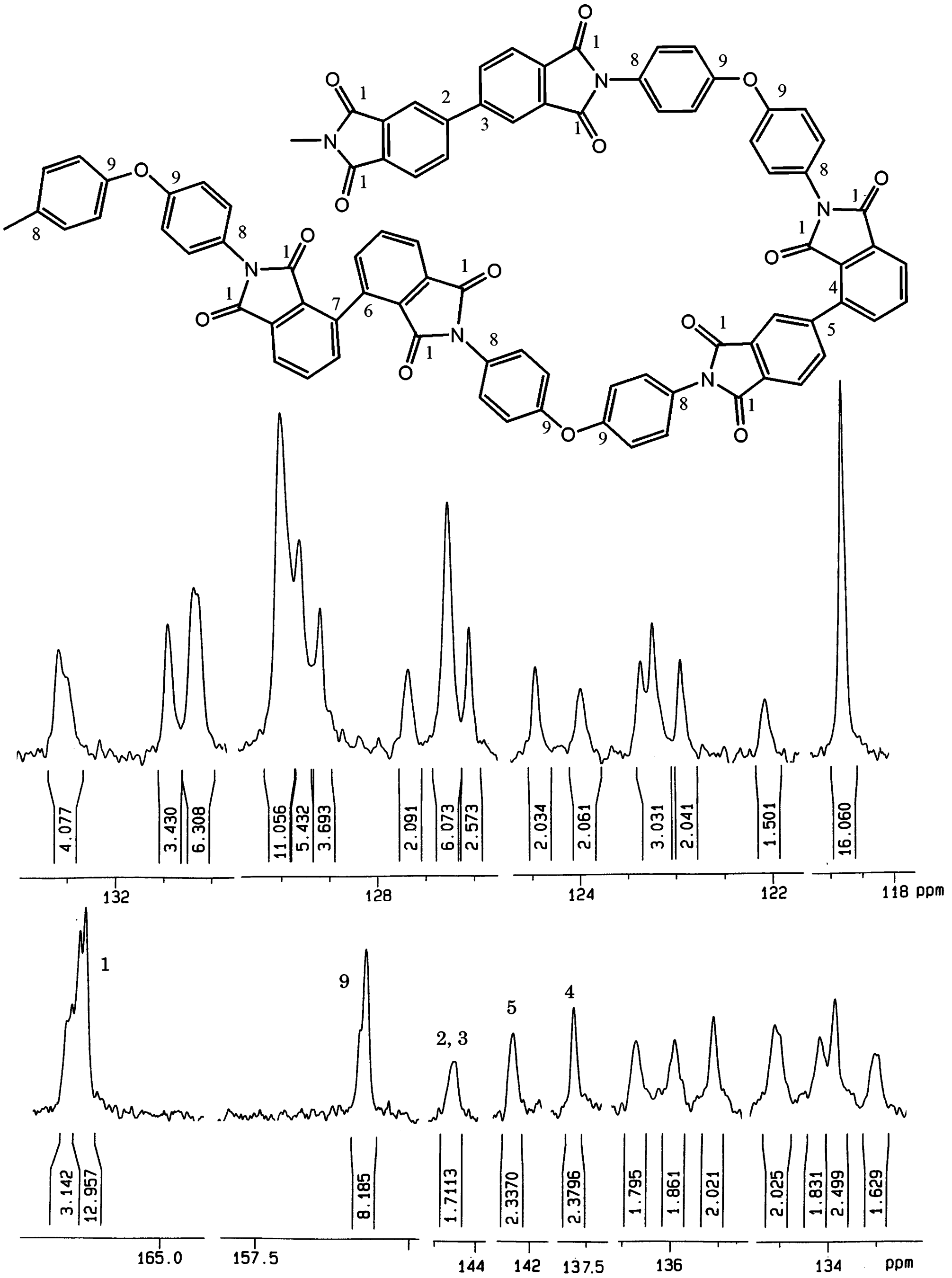


Figure 10. ^{13}C NMR spectrum of polymer **4a** (DMSO-d_6, 100 °C).

7.93 (1H, t), 7.77–7.78 (1H, d), 7.30–7.39 (6H, m), 7.19–7.21 (1H, d d), and 2.22 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, 76.15%; H, 4.39%; N, 5.88%.

***N*-(2-Methylphenyl)-4-chlorophthalimide (D).** Compound **D** was prepared from 4-chlorophthalic anhydride and *o*-toluidine using the similar procedure as reported in the literature.[6a] The product was obtained in the yield of 90%; mp 156–158 °C. ^{1}H NMR (CDCl$_3$): 7.96 (1H, d), 7.91–7.93 (1H, d), 7.77–7.80 (1H, d d), 7.20–7.44 (5H, m), and 2.22 ppm (3H, s). Anal. Calcd for $C_{15}H_{10}O_2NCl$: C, 66.31%; H, 3.71%; N, 5.16%. Found: C, 66.47%; H, 3.96%; N, 4.98%.

***N*-(2-Methylphenyl)-3-chlorophthalimide (E).** This compound was prepared as described above from 3-chlorophthalic anhydride and *o*-toluidine. The yield was 88%; mp 165.5–167 °C. ^{1}H NMR (CDCl$_3$): 7.87–7.92 (1H, m), 7.71–7.77 (2H, m), 7.28–7.41 (5H, m), and 2.24 ppm (3H, s). Anal. Calcd for $C_{15}H_{10}O_2NCl$: C, 66.31%; H, 3.71%; N, 5.16%. Found: C, 66.19%; H, 3.85%; N, 5.20%.

Model Reaction for Determing the Isomeric Biphenyl Distribution. 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), *N*-(2-methylphenyl)-3-chlorophthalimide (0.54 g, 2 mmol), and *N*-(2-methylphenyl)-4-chlorophthalimide (0.54 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 resulted mixture was poured into 100 mL of 10% hydrochloric acid solution, extracted with 30 mL of chloroform. The chloroform solution was dried with anhydrous magnesium sulfate and analyzed by HPLC analysis to determine the composition of products. The model compounds **A**, **B**, and **C** were used as external standards.

Table 3. Solubilities of PIs[a]

polymer	η_{inh} (dL g^{-1})	solvents[b] DMAc	*p*-CPhol	*m*-cresol	NMP	DMF	DMSO
4a	0.51	+	+	+	+	+	+
4b	0.40	+	+	+	+	+	+
4c	0.38	+	+	+	+	+	+
iso-PI	0.25	+	+	+	+	+	+
m-PI	0.56	+	+	+ −	+ −	+ −	+ −
a-PI	0.41	+	+	+ −	+ −	+ −	−
s-PI	0.58	+	+ −	−	−	−	−

[a] Solubility: +, soluble; + −, partially soluble; −, insoluble. [b] *p*-CPhol = *p*-chlorophenol; DMSO = dimethyl sulfone.

Table 4. Thermal Properties of Biphenyl PIs

polymer	η_{inh} (dL g^{-1})	T_g (°C) (DSC)	T_g (°C) (DMTA)	$T_{5\%}$ (°C) (TGA)	$T_{10\%}$ (°C) (TGA)
4a	0.51	313	313	534	585
4b	0.40	258	262	532	570
4c	0.38	302	303	530	565
s-PI	0.58	270	270	529	576
iso-PI	0.25	310		520	560
a-PI	0.41	306	304	523	557
m-PI	0.56	289	295	502	549

Polymer Synthesis. Representative examples of the polymerizations are given below.

Preparation of Polymer 4a via Nickel-Catalyzed Coupling Polymerization of 3a. The polymerization of **3a** was carried out as reported in the literature.[5b] The yield was 95% (0.87 g). The inherent viscosity of the polymer in cresol was 0.51 dL g^{-1}, measured at a concentration of 0.5 g dL^{-1} at 30 °C. IR: 1775 and 1725 cm^{-1} (C=O of imide), 1377 cm^{-1}(C−N stretching), 743 cm^{-1} (C=O bending).

Preparation of Polymer *a*-PI from *a*-BPDA and a. The polymer *a*-**PI** was prepared from *a*-BPDA and **a** using the similar procedure as reported in the literature.[4a] The inherent viscosity of the polymer in cresol was 0.41 dL g^{-1}. IR: 1776 and 1725 cm^{-1} (C=O of imide), 1376 cm^{-1} (C−N stretching), 742 cm^{-1} (C=O bending).

Results and Discussion

Monomer Synthesis. Three asymmetric aryl bis(chlorophthalimide)s were prepared from 3- and 4-chlorophthalic anhydrides and three diamines, **a**, **b**, and **c**, in xylene; other solvents, such as chlorobenzene, anisole, and dichlorobenzene, were also suitable as the solvents for the reaction. The diamines reacted with chlorophthalic anhydrides in xylene at low temperature (95 °C) to give insoluble amic acids. The reaction was completed within 2 h, and upon refluxing, the amic acids dehydrated to give soluble imides. Upon purging the reaction with dry hydrochloric acid, monochlorophthalimides **2** and unreacted diamines were converted into insoluble hydrochloric salts in xylene and separated from *s*-**3** by filtration. The hydrochloric acid salt of compound **2** was insoluble in water and, therefore, easily separated from the soluble diamine salt. Neutralization of the salt of compound **2** using Na_2CO_3 gave the neutral monochlorophthalimides **2**. Figure 3 shows the representative IR spectrum of **2c**, which shows strong absorptions at 3453 and 3370 cm^{-1} (NH_2) and at 1776, 1717,1373, 1103, and 742 cm^{-1} (consistent with the imide group). As shown in Figure 4, the ^1H NMR spectrum of **2c** is consistent with the proposed structure. The 3,4-BCPIs were easily synthesized from **2** and 3-chlorophthalic anhydride in good yields, and the representative ^1H NMR and IR spectra of monomer **3c** are shown in Figures 5 and 6, respectively.[9] The spectra are consistent with the proposed structures and the amino structure was not found.

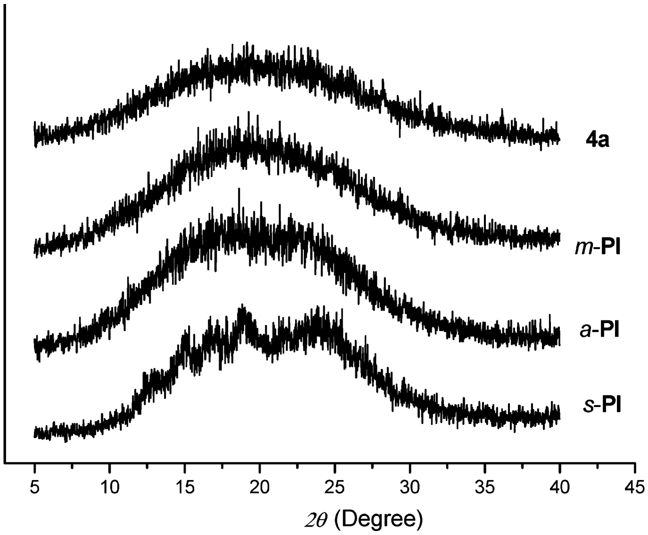


Figure 13. Reflection mode WAXD patterns of polymer **4a** and its isomers.

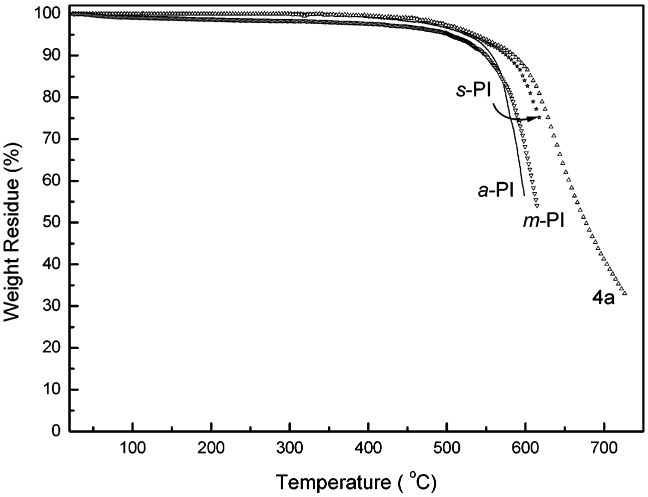


Figure 14. TGA curves of polymer **4a** and its isomers.

Syntheses of Polymers. The Ni-catalyzed coupling polymerization was performed with 1 mmol of monomer in DMAc in the presence of zinc and triphenylphosphine at 95 °C as reported in our previous work.[5b] In contrast, PIs from BPDAs and **a** (*iso*-PI from *iso*-BPDA and **a**; *s*-PI from *s*-BPDA and **a**) were prepared via the conventional method.[4] The results are shown in Table 1. The Ni-catalyzed coupling polymerization of **3a**−**3c** produced the soluble polymers with inherent viscosities of 0.38−0.51 dL g^{-1}. Because the syn conformation of *iso*-BPDA facilitated the formation of cyclic oligmers,[5b,10] the polymerization of *iso*-BPDA and **a** gave low molecular weight polymer. In comparison, the conformation of *a*-BPDA (Figure 7) was confirmed to be anti, and the two phenyl rings of *a*-BPDA are also noncoplanar with dihedral angles of 44.3° (1), 45.8° (2), and 41.09° (3);[9] in the meantime, the conformation of *s*-BPDA was confirmed to be anti and coplanar.[10] Assuming that the similar conformations in the chain of polymers from *a*-BPDA or *s*-BPDA were adopted, the formation of cyclic oligomers would not occur. This presumption was supported by the MALDI−TOF mass spectra of polymer **4** and *a*-**PI** that no peak was associated with cyclic oligomers. Therefore, the polymerizations of *a*-BPDA, *s*-BPDA with **a** gave higher molecular weight polymers

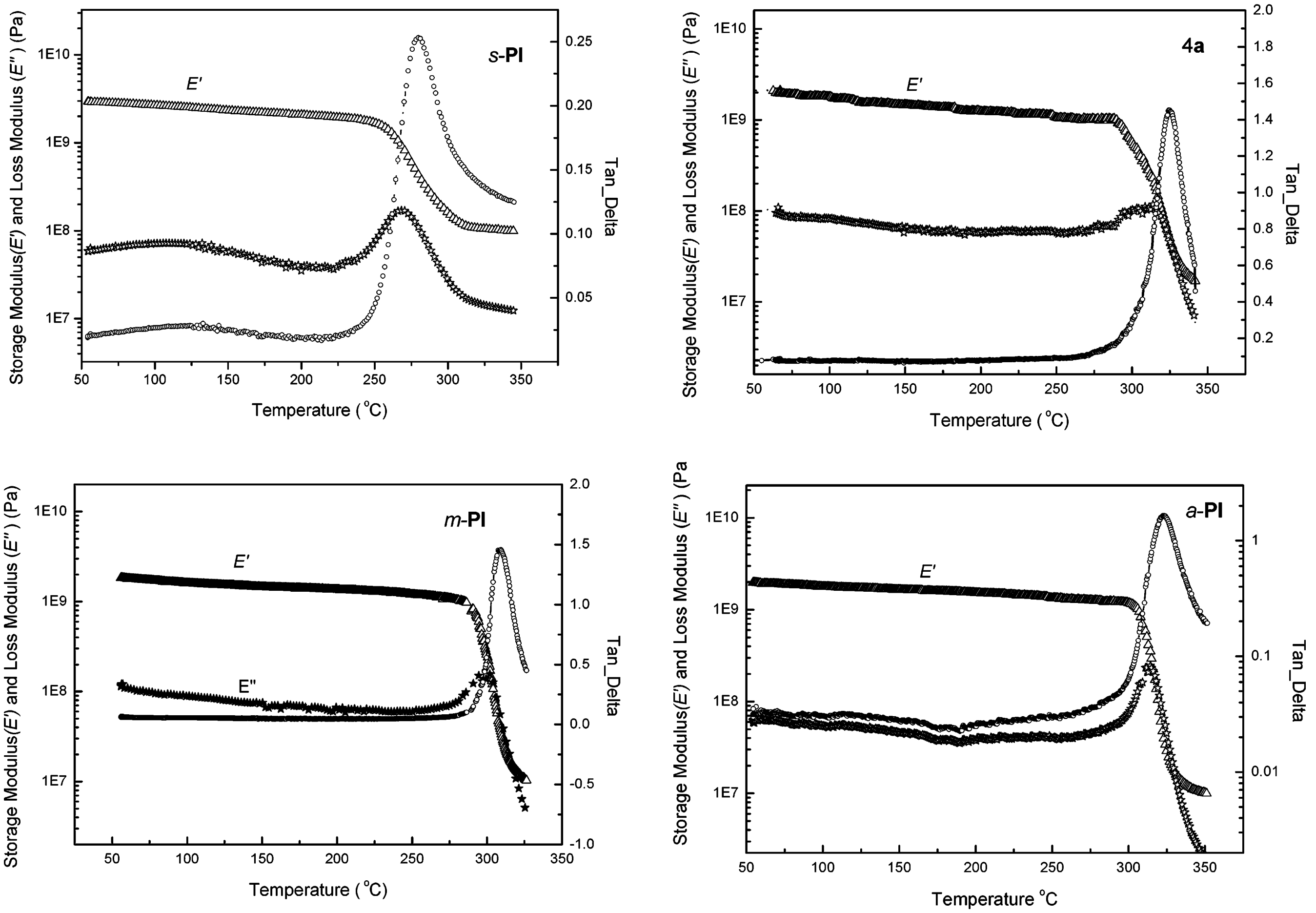


Figure 15. Dynamic modulus as a function of temperature for PI Films of polymer **4a** and its isomers (*s*-PI, $\eta_{inh} = 0.58$ dL g^{-1}, 35.4 μm thick; *m*-PI, $\eta_{inh} = 0.56$ dL g^{-1}, 31.5 μm thick; **4a**, $\eta_{inh} = 0.51$ dL g^{-1}, 33.3 μm thick; *a*-PI, $\eta_{inh} = 0.41$ dL g^{-1}, 31.2 μm thick).

(0.41 and 0.58 dL g^{-1}, respectively). The inherent viscosity of model polymer *m*-**PI**, prepared from the mixture of BPDAs (*a*-BPDA:*s*-BPDA:*iso*-BPDA = 58:21:21) and **a**, was 0.56 dL g^{-1}.

Determination of Isomeric Biphenyl Distribution. The Ni-catalyzed coupling reactions of 3,4-BCPIs may produce three isomeric biphenyl units in the PIs, such as head to head, head to tail, and tail to tail. The composition of three isomeric biphenyl units would have effect on the polymer properties. To determine the ratio of three isomeric biphenyl arrangements, a model reaction was carried out by coupling equimolar amounts of *N*-(2-methylphenyl)-3-chlorophthalimide and *N*-(2-methylphenyl)-4-chlorophthalimide using the procedure described above. Three bisimides (**A**, **B**, **C**) was obtained in the ratio of 21.2: 20.8: 57.9, as determined by HPLC.

Polymer Characterization. The phenyl groups of polymer **4** could not be resolved by ^{1}H NMR specroscopy. The ^{13}C NMR spectrum is a useful tool to quantitatively determine compound structure. Figures 8 and 9 show the ^{13}C NMR spectra of compounds **A**, **B**, and **C**. The ^{13}C NMR spectrum of compound **A** shows C_8 at 144.5 ppm, as determined by calculation, while those of C_{10} and C_{16} of compound **B** are at 135.6 ppm and C_{10} and C_{30} of compound **C** are found at 137.8 and 142.3 ppm, respectively. The resolution of these peaks made it possible to determine the composition of three biphenyl units. Figure 10 presents the ^{13}C NMR of polymer **4a**, and the ^{13}C NMR shows C_2-C_3 at 144.4 ppm and those of C_4-C_5 are at 142.0 and 137.5 ppm, respectively, but that of C_6-C_7 overlaps with those of other carbons. It has been recognized that the coupling reaction of aryl chlorides, especially those with electron-withdrawing substituents, can be carried out quantitatively.[11] So it could be presumed that the amount of C_6-C_7 is equal to that of C_2-C_3. Then the proposition of C_2-C_3, C_4-C_5, and C_6-C_7 could be estimated as 21.0:58.0:21.0. This result is in good agreement with that of model reaction.

The elemental analyses of the polymers are reported in Table 2,[9] and these are in agreement with calculated values for the proposed structure. Figure 11 presents a typical FT-IR spectrum of polymer **4a**, which exhibited absorptions at 1780, 1720, 1380, and 742 cm^{-1} associated with the imide structure.[9] As shown in Figure 12, the ^{1}H NMR (DMSO-d_6, 100 °C) spectrum of polymer **4a** is consistent with the proposed structure.[9]

Polymer Properties. The solubilities of the polymers are shown in Table 3. The polymers **4a**–**4c** and *iso*-PI are soluble in phenolic and amide solvents, polymers *m*-PI and *a*-PI are partially soluble in amide solvents, and *s*-PI is only soluble in *p*-chlorophenol. This fact may be explained by the coplanar of the two phenyl rings in biphenyl units and the crystalline generated from the stiff diamines for *s*-PI. In contrast, the biphenyl unit of *iso*-BPDA, twisted with a dihedral angle of 62.9° and adopting a syn conformation, was suitable for the formation of a large amount of cyclic oligomers.[5b] As shown in Figure 7,[9] the *a*-BPDA includes three isomers, in which the biphenyl groups are nonplanar and adopted anti conformations. So the solubility of *a*-PI was better than that of *s*-PI. On the other hand, the crystallinities of the PIs were evaluated by wide-angle X-ray diffraction measurements. As shown in Figure 13, the diffraction patterns indicate that the order of the crystallinities is *s*-PI > *a*-PI > *m*-PI > **4a**, suggesting that polymer **4a** was the most soluble among them. The polymers with inherent viscosities of above 0.35 dL g^{-1} from 3,4-BCPIs were easily made into flexible films (Table 1). In contrast, the film of *s*-PI must be made from poly(amide acid), followed by thermal imidization because of its poor solubility for the imidized form, and polymer *iso*-PI was difficult to be made into the film.[6a,10]

The thermal stability of the polymers was examined by TGA. As shown in Figure 14 and Table 4, PIs showed 10% weight loss at above 549 °C. The T_g's from DSC are summarized in Table 4. Polymers **4** give the T_g's in the range of 258−313 °C. Figure 15 displays the dynamic storage modulus (E') and loss modulus (E'') as a function of temperature for polymer 4**a** and its isomers. The T_g's of *s*-PI, *m*-PI, *a*-PI, and **4a** are observed at 270, 295, 304, and 313 °C, respectively, as determined by the peak temperature in the E'' curves. So the T_g of PI from 3,4-BCPIs was higher than that from *m*-PI, *a*-PI, and *s*-PI. PI film of **4a** shows higher modulus (E') preservation than that of PI film from *s*-PI and similar to those from *a*-PI and *m*-PI before 288 °C.

Conclusions

A facile method for synthesis of 3,4-BCPIs was established. The nickel-catalyzed coupling polymerization of 3,4-BCPIs produced soluble biphenyl PIs with high molecular weight. The proposition of the biphenyl units, head to tail, head to head, and tail to tail, in the polymer chain was 58.0:21.0:21.0, determined by model reaction and the ^{13}C NMR spectrum. The polymers from 3,4-BCPIs were more soluble and had higher T_g than the other related polymers.

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Supporting Information Available: Elemental analyses of polymers (Table 2), ^{1}H NMR and IR spectra of monomer **3c** (Figures 5 and 6), molecular structure of *a*-BPDA (Figure 7), and IR and and ^{1}H NMR spectra of polymer **4a** (Figures 11 and 12).This material is available free of charge via the Internet at http://pubs.acs.org.

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