Synthesis of Novel High-Performance Polymers via Pd-Catalyzed Amination of Dibromoarenes with Primary Aromatic Diamines

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ABSTRACT: A series of novel polymers have been obtained by the condensation polymerization of different dibromoarenes with different primary aromatic diamines via palladium-catalyzed aryl amination reaction. The structures of polymers are characterized by means of FT-IR, ^{1}H NMR spectroscopy, and elemental analysis; the results show an agreement with the proposed structure. DSC and TG measurements show that polymers possess high glass transition temperature ($T_g > 170$ °C) and good thermal stability with high decomposition temperatures ($T_D > 450$ °C). Thesis novel polymers also exhibit good mechanical behavior and good solubility.

1. Introduction

The synthesis of compounds containing the N-aryl moiety has attracted a great deal of interest recently due to the importance of such compounds in fields as diverse as natural products, photography, and materials.[1−5] Although a number of traditional methods exist for aryl carbon−nitrogen bond construction, they typically suffer from problems such as limited generality, harsh conditions, the need to employ stoichiometric quantities of valuable reagents, numerous synthetic steps, or regiochemical ambiguities.[6−11] From the standpoint of directness and atom economy, transition-metal-catalyzed approaches to C−N bond construction are appealing because they entail simply the cross-coupling of an amine with an aryl halide. In the past few years, Hartwig[12−19] and Buchwald[20−31] have progressively and independently contributed to the development of a general, reliable, and practical methodology for the formation of aromatic carbon−nitrogen bonds.

The catalytic amination reaction of arylene halides with primary amines using palladium complexes has become an important synthetic procedure for a variety of arylene amines including pharmaceuticals, electronic materials, and ligands for metal catalysts. This reaction has become a widely used practical synthetic method for C−N bond formation. The interest in the synthesis of oligoanilines was an inspiration for Buchwald's group to develop Pd-catalyzed couplings of primary anilines with aryl bromides. Using standard condition [$Pd_2(dba)_3$ and BINAP], they found that anilines were effectively coupled with a variety of aryl bromides.[32−34] Reactions of electron-poor aromatic halides and electron-rich amines give high yields in the amination protocol.[35,36]

The Pd-catalyzed aryl amination has also been applied to polycondensation reactions to give various polyamines, poly(imino arylene)s, and poly(imino ketone)s with no or scarcely cross-linked structures.[37−43] Herein the idea is to use Pd-catalyzed aryl amination to synthesize new types of polymers. This approach has aimed at developing new conditions for Hartwig−Buchwald reactions[44−52] and to apply them to obtain new polymer structures. In this paper, a series of novel polymers have been obtained by the polycondensation of different dibromoarenes with primary aromatic diamines using the catalytic system generated from tris(dibenzylideneacetone)-dipalladium(0) ($Pd_2(dba)_3$) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP). The use of inexpensive monomers with bromine leaving groups instead of expensive fluorine-containing monomers is, as has already been shown for PEEKKs (poly(ether ether ketone ketone)s), very attractive for obtaining aromatic polymers.

2. Experimental Section

2.1. Materials. Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) were purchased from Alfa Aesar, a Johnson Matthey Co. 3,6-Diaminoacridine, di(4-bromophenyl) ketone, and 4,4′-diaminoazobenzene were synthesized in our laboratory; other dibromoarenes and primary aromatic diamines were purchased from Daikin Fine Chemical Laboratory, Ltd., Toshima, Kita-ku, Tokyo, Japan. The rest of the materials and reagents were obtained from different commercial sources and used without further purification.

2.2. Measurements. FT-IR spectra were recorded on a Nicolt 320 FTIR spectrometer. Elemental analysis was measured on a Vario EL III. ^{1}H NMR and ^{13}C NMR were performed on AVANCE 500 MHz NMR spectrometers in DMSO-d_6. The molecular weights and molecular weight distributions were measured by GPC. The glass transition temperature was obtained by DSC curves at a rate of 10 °C/min under flowing nitrogen gas. Thermogravimetric analysis was performed on a Mettler TC 10A at a heating rate of 10 °C/min under air or nitrogen. Dynamic mechanical thermal analysis (DMTA) was performed on dymamic mechanical thermal analyzer V in tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz.

2.3. Synthesis of Novel Polymers. An oven-dried resealable Schlenk flask (50 mL) equipped with magnetic stirrer, a nitrogen outlet, inlet, and water-cooled condenser, into which were added dibromoarenes (5.0 mmol), primary aromatic diamines (5.0 mmol), sodium *tert*-butoxide (1.350 g, 14.0 mmol), $Pd_2(dba)_3$ (45.75 mg, 0.05 mmol), BINAP (94.0 mg, 0.15 mmol), and dimethylacetamide (8−15 mL) (Scheme 1). The reaction mixture was flushed with high-purity nitrogen. This procedure was repeated several times. The flask was immersed in a 100 °C oil bath for 2−8 h and then in a 165 °C oil bath for 10−14 h with continuous stirring. The resulting polymer solution was allowed to slowly cool to room temperature, then filtered and subsequently poured into methanol,

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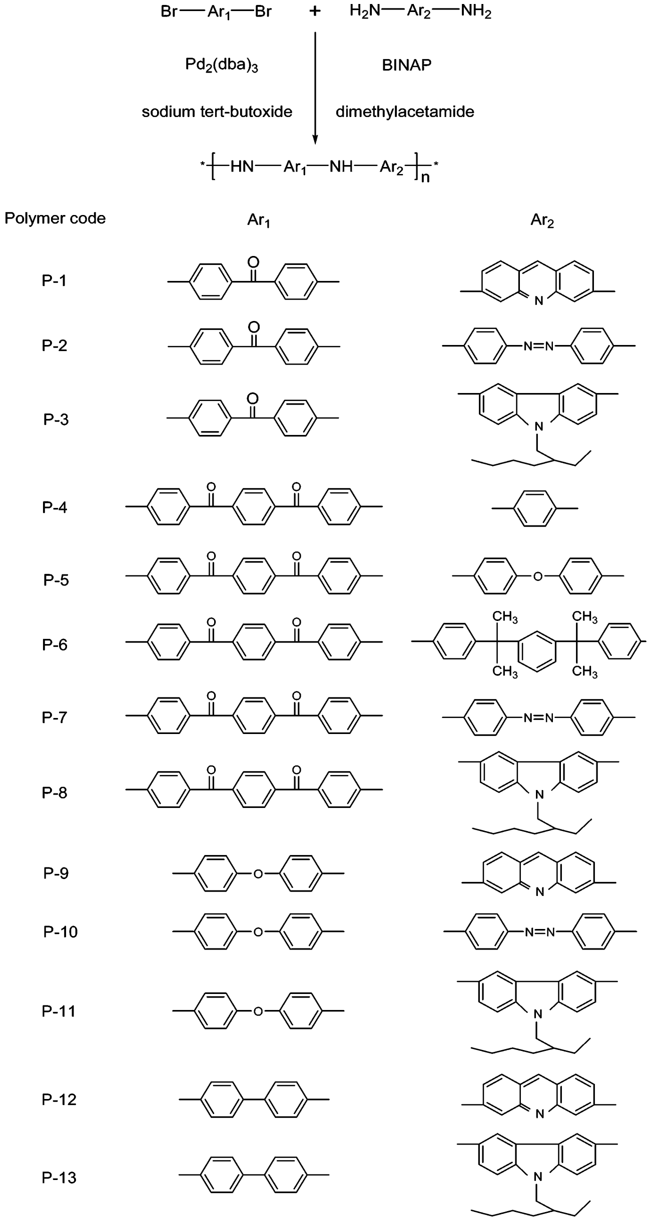
Scheme 1. Synthesis of Novel Polymers via Pd-Catalyzed Aryl Amination



filtered, washed with methanol several times, and then dried at 100 °C under vacuum.

Synthesis of P-1. Yield: 1.68 g, 86%; FT-IR spectrum (KBr pellet): γ NH at 3330 cm^{-1}; γ C=O at 1620 cm^{-1}; γ C−N at 1311 cm^{-1}. ^{1}H NMR: $\delta = 9.34$ (s, NH); 8.58 (s, H-1); 7.49 (d, H-2). ^{13}C NMR: $\delta = 196.3$, 150.5, 148.1, 146.3, 142.1, 139.5, 136.7, 131.1, 126.5, 122.5, 116.0, 111.9, 88.4. Anal. Calcd for $C_{26}H_{17}N_3O$ (387.44): C, 80.62; H, 4.38; N,10.88. Found: C, 80.04; H, 4.39; N, 10.77.

Synthesis of P-2. Yield: 1.70 g, 87%; FT-IR spectrum (KBr pellet): γ NH at 3383 cm^{-1} ; γ C=O at 1664 cm^{-1}; γ C− N at 1308 cm^{-1}. ^{1}H NMR: $\delta = 9.28$ (s, NH); 7.71 (s, H-1); 7.25 (s, H-2); 6.64 (s, H-3). ^{13}C NMR: $\delta = 196.1$, 149.8, 143.3, 136.7, 130.2, 128.8, 123.9, 118.8, 113.8. Anal. Calcd for $C_{25}H_{18}N_4O$ (390.43): C, 76.90; H, 4.65; N, 14.35. Found: C, 75.93; H, 4.68; N, 14.17.

Synthesis of P-3. Yield: 1.10 g, 91%; FT-IR (KBr pellet): γ NH at 3405 cm^{-1}; γ C=O at 1630 cm^{-1}, γ C−H aromatic at 3029 cm^{-1} and C−N at 1312 cm^{-1}; UV recorded in DMAc λ_{max} at 370 nm. ^{1}H NMR: $\delta = 8.24$ (s, NH); 7.93 (s, H-1); 7.59 (s, H-2); 7.32 (s, H-3); 6.96 (s, H-4); 4.19 (s, CH$_2$, H-5); 2.03 (s, CH, H-6); 1.23 (d, CH$_2$, H-7); 0.82 (d, CH$_3$, H-8). ^{13}C NMR: $\delta = 196.2$, 145.1, 142.1, 136.7, 130.2, 125.6, 118.8, 112.3, 40.9, 28.3, 14.1, 11.9. Anal. Calcd for $C_{33}H_{33}N_3O$ (487.64): C,81.28; H,6.80; N,8.64. Found: C,80.31; H,6.82; N,8.52.

Synthesis of P-4. Yield: 925 mg, 95%; FT-IR (KBr pellet): γ NH at 3318 cm^{-1}; γ C=O at 1631 cm^{-1}, γ C−H aromatic at 3049 cm^{-1} and C−N at 1312 cm^{-1}. Anal. Calcd for $C_{26}H_{18}N_2O_2$ (390.44): C, 80.12; H, 4.65; N, 7.16. Found: C, 79.05; H, 4.68; N, 7.09. ^{1}H NMR and were not recorded due to the poor solubility.

Synthesis of P-5. Yield: 1.11 mg, 92%; FT-IR (KBr pellet): γ NH at 3320 cm^{-1}; γ C=O at 1638 cm^{-1}, γ C−H aromatic at 3049 cm^{-1} and C−N at 1316 cm^{-1}. ^{1}H NMR: $\delta = 8.93$ (s, NH); 7.69 (d, H-1); 7.14 (s, H-2). ^{13}C NMR: $\delta = 196.0$, 146.5, 140.7, 136.7, 132.7, 131.2, 128.7, 118.3, 113.1. Anal. Calcd for $C_{32}H_{22}N_2O_3$ (482.54): C, 79.65; H, 4.60; N, 5.81. Found: C, 78.94; H, 4.61; N, 5.76.

Synthesis of P-6. Yield: 1.39 g, 89%; FT-IR (KBr pellet): γ NH at 3360 cm^{-1}; γ C=O at 1644 cm^{-1}, γ C−H aromatic at 3028 cm^{-1}; γ C−H aliphatic at 2961 cm^{-1} and C−N at 1307 cm^{-1}. ^{1}H NMR: $\delta = 8.78$ (s, NH); 7.94 (d, H-1′); 7.66 (d, H-1 + 2′); 7.05 (d, H-2 + 3′); 6.80 (s, H-4′); 6.44 (d, H-5′); 4.71 (s, NH$_2$); 1.55 (s, H-6, CH$_3$); and 1.48 (s, H-6′, CH$_3$). ^{13}C NMR: $\delta = 196.4$, 146.6, 143.0, 136.5, 130.0, 124.9, 118.5, 114.0, 42.7, 31.0. Anal. Calcd for $C_{44}H_{38}N_2O_2$ (626.79): C, 84.31; H, 6.06; N, 4.47. Found: C, 83.96; H, 6.08; N, 4.45.

Synthesis of P-7. Yield: 1.98 g, 81%; FT-IR spectrum (KBr pellet): γ NH at 3352 cm^{-1}; γ C=O at 1646 cm^{-1}; γ C− N at 1316 cm^{-1}; ^{1}H NMR: $\delta = 9.42$ (s, NH); 7.80 (d, H-1); 7.62 (t, H-2); 7.37−7.27 (m, H-2). ^{13}C NMR: $\delta = 195.9$, 149.5, 141.8, 136.6, 131.3, 130.1, 123.8, 118.6, 113.8. Anal. Calcd for $C_{32}H_{22}N_4O_2$ (494.55): C, 77.72; H, 4.48; N, 11.33. Found: C, 77.01; H, 4.50; N, 11.23.

Synthesis of P-8. Yield: 1.30 g, 88%; FT-IR (KBr pellet): γ NH at 3415 cm^{-1}; γ C=O at 1630 cm^{-1}, γ C−H aromatic at 3049 cm^{-1} and C−N at 1310 cm^{-1}; UV recorded in DMAc λ_{max} at 380 nm. ^{1}H NMR: $\delta = 7.94$ (s, NH); 7.80 (s, H-1); 7.37 (s, H-2); 7.22 (s, H-3); 6.99 (s, H-4,5); 4.14 (s, CH$_2$, H-6); 1.94 (s, CH, H-7); 1.21 (d, CH$_2$, H-8); 0.77 (d, CH$_3$, H-9). ^{13}C NMR: $\delta = 196.1$, 145.1, 143.3, 136.9, 131.5, 130.6, 124.5, 118.5, 110.8, 40.7, 28.3, 29.6, 14.1, 11.0. Anal. Calcd for $C_{40}H_{37}N_3O_2$ (591.75): C, 81.19; H, 6.25; N, 7.10. Found: C, 80.85; H, 6.28; N, 7.08.

Synthesis of P-9. Yield: 1.70 g, 90%; FT-IR spectrum (KBr pellet): γ NH at 3384 cm^{-1}; γ C− N at 1307 cm^{-1}. ^{1}H NMR: $\delta = 8.78$ (s, NH), 8.48 (s, H-1) , 7.81 (s, H-2), 7.19 (d, H-3), 6.68 (s, H-4). ^{13}C NMR: $\delta = 154.0$, 149.6, 146.4, 141.0, 131.5, 123.9, 118.4, 113.6. Anal. Calcd for $C_{25}H_{17}N_3O$ (375.43): C, 79.96; H, 4.55; N, 11.20. Found: C, 79.33; H, 4.57; N, 11.06.

Synthesis of P-10. Yield: 1.64 g, 83%; FT-IR spectrum (KBr pellet): γ NH at 3389 cm^{-1}; γ C− N at 1312 cm^{-1}. ^{1}H NMR: $\delta = 8.72$ (s, NH), 7.72 (d, H-1), 7.58−7.46 (m, H-2), 7.21−7.02 (m, H-3). ^{13}C NMR: $\delta = 153.8$, 148.9, 146.1, 140.3, 130.6, 123.4, 117.8, 113.2. Anal. Calcd for $C_{24}H_{18}N_4O$ (378.43): C, 76.24; H, 4.75; N, 14.83. Found: C, 75.83; H, 4.78; N, 14.74.

Synthesis of P-11. Yield: 1.04 g, 87%; FT-IR (KBr pellet): γ NH at 3385 cm^{-1}, γ C−H aromatic at 3029 cm^{-1} and C−N at 1305 cm^{-1}. ^{1}H NMR: $\delta = 7.71$ (s, NH), 7.37 (s, H-1); 7.20 (s, H-2), 6.91 (d, H-3,4,5), 4.14 (s, CH$_2$, H-6), 2.01 (s, CH, H-7), 1.25 (d, CH$_2$, H-8), 0.82 (d, CH$_3$; H-9). ^{13}C NMR: $\delta = 154.6$, 146.5, 140.0, 137.1, 132.1, 125.6, 117.9, 112.0, 41.2, 28.0, 23.1, 14.6, 12.3. UV recorded in DMAc λ_{max} at 280, 310, and 400 nm. Anal. Calcd for $C_{32}H_{33}N_3O$ (475.63): C, 80.90; H, 6.94; N, 8.83. Found: C, 79.93; H, 6.98; N, 8.74.

Synthesis of P-12. Yield: 1.98 g, 81%; FT-IR spectrum (KBr pellet): γ NH at 3391 cm^{-1}; γ C− N at 1312 cm^{-1}. ^{1}H NMR: $\delta = 9.09$ (s, NH); 8.52 (s, H-1); 7.82 (s, H-2); 7.39 (d, H-3); 6.85 (s, H-4). ^{13}C NMR: $\delta = 150.5$, 146.3, 143.1, 139.5, 133.5, 128.7, 116.8, 110.4, 88.3. Anal. Calcd for $C_{25}H_{17}N_3$ (359.43): C, 83.54; H, 4.77; N, 11.69. Found: C, 82.88; H, 4.89; N, 10.94.

Synthesis of P-13. Yield: 1.18 mg, 87%; FT-IR (KBr pellet): γ NH at 3389 cm^{-1}; γ C−H aromatic at 3023 cm^{-1} and C−N at 1294 cm^{-1}. UV recorded in DMAc λ_{max} at 350 nm. ^{1}H NMR: $\delta =$ 7.79 (s, NH); 7.53 (s, H-1); 7.26 (s, H-3 + 4); 7.01 (s, H-5); 4.15

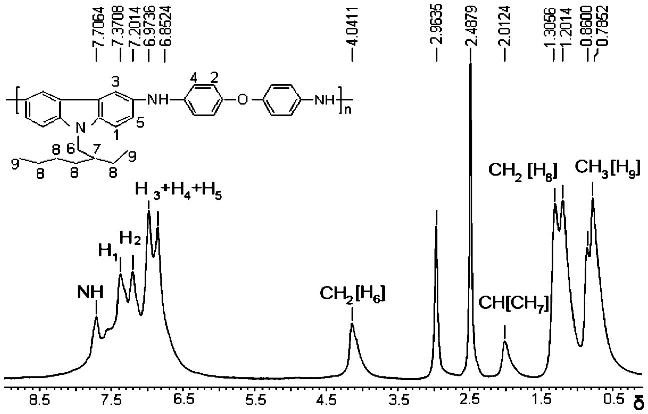


Figure 1. ^{1}H NMR (500 MHz) spectrum of **P-11** recorded in DMSO.

Table 1. Characterization of Polymers[a]

polymer code	M_n	M_w	M_w/M_n	yield (%)
P-1	–	–	–	86
P-2	11 700	45 700	3.90	87
P-3	16 000	64 000	4.00	91
P-4	–	–	–	95
P-5	13 000	26 300	2.02	92
P-6	12 800	21 000	1.64	89
P-7	8500	34 000	4.00	81
P-8	9900	58 000	5.86	88
P-9	4 500	8 200	1.82	90
P-10	11 900	55 700	4.68	83
P-11	11 000	78 000	7.09	87
P-12	–	–	–	81
P-13	17 500	123 000	7.02	87

[a] The soluble fraction in DMF calibrated by GPC polystyrene standards; –, not measured due to poor solubility.

(s, CH_2, H-6); 2.02 (s, CH, H-7); 1.26 (d, CH_2, H-8); 0.82 (d, CH_3; H-9). ^{13}C NMR: $\delta = 145.1$, 140.0, 137.1, 133.0, 125.6, 119.6, 112.3, 110.9. Anal. Calcd for $C_{32}H_{33}N_3$ (459.63): C, 83.55; H, 7.18; N, 9.14. Found: C, 82.95; H, 7.20; N, 9.07.

3. Results and Discussion

3.1. Polymer Synthesis. The mechanism of the Pd-catalyzed amination involves oxidative addition of the aromatic halides to a palladium species to form an arylene palladium halide. By inductive effect or by resonance, this step should be favored for an arylene bromide substituted with an electron-withdrawing group in the para position. Reactions of electron-poor aromatic halides and electron-rich amines give high yields in the amination protocol. Thus, we attempted to do polycondensation of different dibromoarenes as electron-poor arylene halides with different electron-rich primary aromatic diamines.

All of the polymers was characterized by FT-IR, ^{1}H NMR, and elemental analysis. The results showed good agreement with the proposed structure. As an example, the ^{1}H NMR spectra of **P-11** is shown in Figure 1 (DMSO-d_6).

The molecular weights of the reprecipitated polymers were measured by GPC (calibrated by polystyrene standards). The M_n values are in the range of 4500–17 500 and the M_w values in the range of 8200–123 000. The polydispersity index (PDI) varies from 1.64 up to 7.09. Especially with increasing molecular weights, the polydispersity increases drastically (Table 1).

The elemental analysis of the polymers showed that in all cases the determined carbon and nitrogen content were lower than the calculated ones. This can be explained by the hygroscopic nature of the imino groups of these polymers. The intake of water was in the range of 2.0–8.0% as measured from the weight increase of the vacuum-dried polymer samples after exposure to air at room temperature for 12 h. Therefore, the measured elemental analysis value should be corrected by elimination of the amount of absorbed water. Similar to the study performed on hygroscopic polyaramides, the experimental data were then in good agreement with the calculated ones.

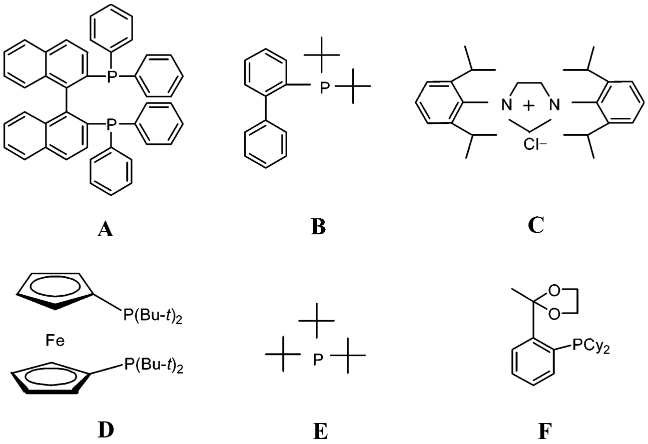


Figure 2. Complex ligands of amination for polymers.

Table 2. Different Experimental Conditions for P-5

run	temp (°C)	concn of monomers (%)	M_n	M_w	M_w/M_n	yield (%)
1	60	15	4500	8200	1.82	48
2	60	25	6900	11700	1.70	64
3	100	25	9700	18800	1.94	73
4	150	30	11500	20400	1.78	82
5	165	35	13000	26300	2.02	92

Table 3. Synthesis of P-2 Using Different Ligands

run	polymer code	ligand	M_n	M_w	M_w/M_n	yield (%)
1	**P-2A**	A	11700	45700	3.90	87
2	**P-2B**	B	10200	23500	2.30	79
3	**P-2C**	C	6500	26000	4.00	63
4	**P-2D**	D	3200	16500	5.16	36
5	**P-2E**	E	9200	18700	2.04	71
6	**P-2F**	F	2800	9800	3.50	32

Table 4. Synthesis of P-3 Using Different Halogen-containing Monomers

run	polymer code	X	M_n	M_w	M_w/M_n	yield (%)
1	**P-3a**	F				0
2	**P-3b**	Cl	11100	19500	1.76	83
3	**P-3c**	Br	16000	64000	4.00	95
4	**P-3d**	I	15800	55200	3.49	92

During the synthesis of polymers, the effect of concentration and temperature on the molecular weight could be followed. Upon increasing the temperature from 100 to 165 °C, both M_n and M_w increased, while upon increasing the concentration form 20% to 35% at temperature 165 °C, both M_n and M_w increased, too. A temperature of 165 °C and a concentration of 35% are more suitable for the palladium-catalyzed polycondensation to produce theses polymers with higher molecular weight (Table 2).

In order to test which ligand would be most suitable for the polycondensation process to form polymers, we attempted the amination to form **P-2** using different ligands from **A** to **F** (Figure 2, Table 3). It appears that ligand **A** (BINAP) gives polymers with higher yields and molecular weight and lower polydispersity index than those produced with other ligands.

The reactivity of the halogen-containing monomers (**1**–**4**) was studied during the polycondensation process to form polymer **P-3** (Table 4). 1,4-Bis(4-bromobenzoyl)benzene gave polymer in higher yield and molecular weight than other halogen-containing monomers, while 1,4-bis(4-fluorobenzoyl)-

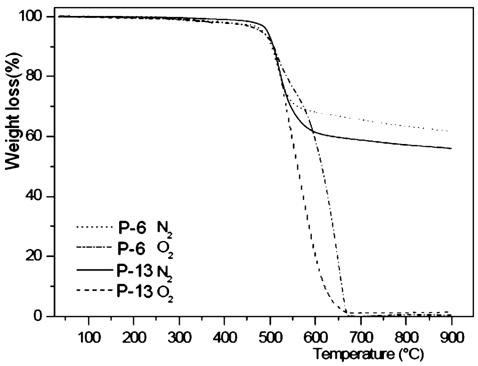


Figure 3. TG of polymers in air and nitrogen.

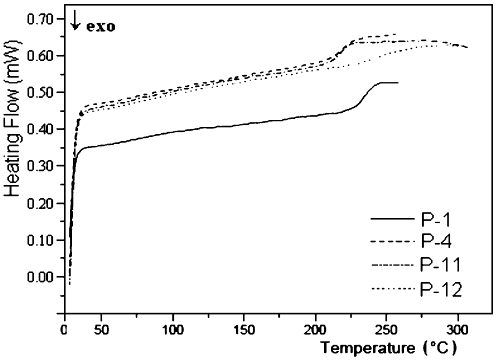


Figure 4. DSC of polymers in nitrogen.

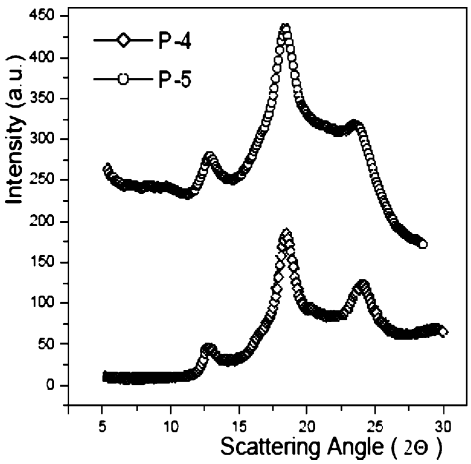


Figure 5. WAXD diffractograms intensity vs Bragg angle graph for powders of **P-4** and **P-5**.

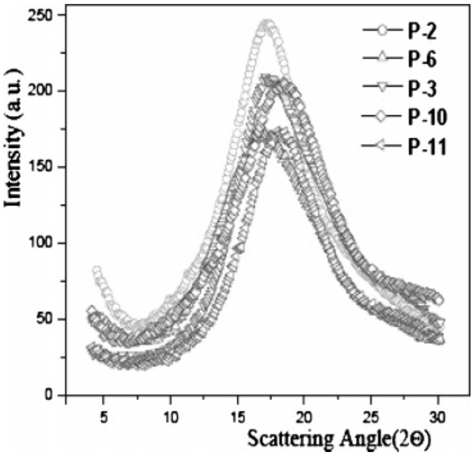


Figure 6. WAXD diffractograms intensity vs Bragg angle graph for **P-2** , **P-6** , **P-3**, **P-10**, and **P-11**.

benzene is totally unreactive. It is known that for aryl amination the reactivity decreases significantly with higher electronegativity of the halogen atoms, and oxidative addition is rate-limiting.

3.2. Thermal Behaviors. All the polymers synthesized showed high thermal stability and a high char yield in nitrogen at 500 °C. Typical TG traces in air and nitrogen are shown in Figure 3 for polymers **P-6** and **P-13**. TG curves revealed that the polymers were thermally stable at up to 450−500 °C. The 50% weight losses took place at over 900 °C in nitrogen. Char yield is an easy and important measurement which correlates to the ability to sustain combustion. For these polymers the char yield in nitrogen at 600 °C was up to 60%.

Differential scanning calorimetry (DSC) of these polymers up to 200 °C showed a single T_g. Four representative DSC thermograms of the polymers are shown in Figure 4. All polymers show high T_gs ranging from 169 to 249 °C, being comparable with the T_gs of modified polyterephthalamides bearing pendent groups connected to the polymer backbone with ester linkages. Only **P-10** gave a lower T_g at 169 °C. The T_gs are higher than those of the related PEKs which range from 129 to 167 °C and lower than those of aromatic polyamides which amount to 292−319 °C.

3.3. Wide-Angle X-ray Diffraction. The wide-angle X-ray diffraction patterns of all the polymers over the 2θ range of 5°−30° are shown in Figure 5. The diffraction arising from the crystallites is observed which showed crystalline pattern of **P-4** and **P-5** at 12.6°, 18.7°, 24.3°, 29.3°, 12.8°, 17.8°, and 23.2° (Figure 5). This may be attributed to the existence of the rigid *p*-diiminophenylene or *p*-diiminodiphenyl ether segments in their polymer backbones and at the same time the absence of bulky groups such as *tert*-butyl or isopropylidene groups, leading to a better packing of the polymer chains. However, only the broad halo arising from the amorphous region of polymers (**P-2**, **P-6**, **P-3**, **P-10**, and **P-11**) is observed at 17.8°, 18.1°, 17.2°, 18.4°, 16.8°, and 17.2° (Figure 6). Despite the presence of the rigid secondary amine ring, all polymers revealed essentially amorphous patterns. Obviously, the bulky *tert*-butyl and/or isopropylidene groups hindered chain packing and reduced the level of ordering, thus leading to the amorphous nature of the polymer. The amorphous nature of these polymers was also reflected in their good solubility. On comparing WAXD of these polymers with poly(ether ketone)s (PEKs), the latter polymers exhibited semicrystalline behavior, and no amorphous behavior was detected.[53−55] We can conclude that insertion of *tert*-butyl group and/or isopropylidene groups into the repeating units of the polymers resulted in a significant increase of the amorphous nature of the polymer. However, the absence of these groups and at the same time the presence of the rigid secondary amine rings in the backbone of polymers showed a significant increase of the crystalline nature. This is despite the presence of a kinked ether group which is known to induce loose chain packing.

3.4. Mechanical Behaviors. The mechanical behavior of these novel polymers has been examined by means of dynamic mechanical testing performed at various temperatures and various frequencies with a small-amplitude sinusoidal deformation. An example of the mechanical behavior determined for **P-6** is shown in Figure 7. The results indicate that the polymer exhibits a spectrum of viscoelastic properties characteristic for linear amorphous entangled polymers. The two relaxation

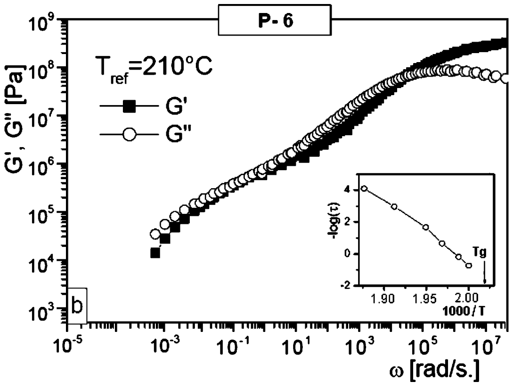


Figure 7. Mechanical behavior of **P-6**.

Table 5. Thermal Behavior of Polymers

polymer code	O_2/N_2	T_5[a]	T_{50}[b]	char yield at 500 °C	T_g (°C)
P-1	O_2	482	620	59	233
	N_2	489	>900	79	
P-2	O_2	471	568	58	202
	N_2	478	>900	79	
P-3	O_2	486	659	66	219
	N_2	492	>900	81	
P-4	O_2	494	663	69	220
	N_2	498	>900	81	
P-5	O_2	469	596	54	215
	N_2	475	>900	76	
P-6	O_2	476	612	58	177
	N_2	484	>900	77	
P-7	O_2	468	603	61	203
	N_2	474	>900	81	
P-8	O_2	489	645	68	213
	N_2	498	>900	89	
P-9	O_2	414	562	53	206
	N_2	432	889	77	
P-10	O_2	384	494	48	169
	N_2	402	854	68	
P-11	O_2	436	589	67	220
	N_2	448	>900	87	
P-12	O_2	501	692	74	249
	N_2	506	>900	95	
P-13	O_2	486	588	68	231
	N_2	495	>900	92	

[a] T_5: temperature of 5% weight loss. [b] T_{50}: temperature of 50% weight loss.

processes—(1) segmental relaxation at high frequencies detected as the cross points of the storage (G') and loss (G'') modular on the frequency scale and (2) chain relaxation at low frequencies—are controlling the behavior.

Summarizing the first results from Figure 7, one can see that these polymrs show good mechanical properties (storage (G') and loss (G'') modular $<10^8$ and extended rubber plateau) comparable to polyaramides or poly(arylene ether ketone)s.

The inset in Figure 7 shows the temperature dependence of the segmental relaxation time, which indicates that the relaxation time slows down to nearly 100 s when the polymer is approaching the glass transition temperature (T_g) from higher temperatures.

3.5. Solubility. These novel polymers showed different solubility behavior in different organic solvents. Polymer solubility was qualitatively determined by the dissolution of 5 mg of solid polymers in 1 mL of organic solvent at room temperature and 50 °C (Table 6). The polymers could be easily soluble in high polar solvents, such as dimethylacetamide (DMAc) , dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), while it is partially soluble in common organic solvents, such as toluene and chloroform. All polymers showed improved solubility compared with polyimide (PI).

Table 6. Solubility of Polymers[a]

polymer code	DMAc	DMSO	DMF	THF	$CHCl_3$
P-1	++	++	+−	−−	−−
P-2	++	++	++	++	+−
P-3	++	++	++	++	+−
P-4	++	+−	+−	−−	−−
P-5	++	++	++	+−	−−
P-6	++	++	++	++	+−
P-7	++	++	++	+−	−−
P-8	++	++	++	+−	−−
P-9	++	++	++	+−	−−
P-10	++	++	++	++	++
P-11	++	++	++	++	+−
P-12	++	++	+−	−−	−−
P-13	++	++	++	+−	−−

[a] ++: Solid polymer was completely dissolved at room temperature. +−: Solid polymer was completely dissolved at 50 °C. −−: Solid polymer could swell at 50 °C.

4. Conclusions

A series of novel polymers have been obtained by a Pd-catalyzed polycondensation (Buchwald−Hartwig reaction) of different dibromoarene ketones or dibromoarene ethers with different primary aromatic amines. These novel polymers can be considered as a new class of high-performance polymers with high thermal stability (T_g > 170 °C, T_D > 450 °C), good mechanical behaviors, and good solubility. One major advantage in comparison to the established PEKs is obvious; that is, these novel polymers can use cheaper monomers, e.g., bromo-functionalized dibromoarenes, instead of the corresponding difluoro structures. Furthermore, dibromoarenes and many primary aromatic diamines are either readily available or can be easily to synthesized giving a fast access to numerous new polymers with optimal properties.

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Supporting Information Available: DMA data for part of the other polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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