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ORIGINAL PAPER

Poly(aryl imino sulfone)s as new high-performance engineering plastics

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Abstract Poly(aryl imino sulfone)s (PAISs) as novel high-performance polymers have been obtained by the condensation polymerization of 4,4′-dibromodiphenyl sulfone with different primary aromatic diamines via Palladium-catalyzed aryl amination reaction. The influence of the halogen-containing monomers, solvent, concentration, and temperature on the polycondensation reaction was investigated. The structure of polymers synthesized was characterized by means of FT–IR, NMR spectroscopy, and elemental analysis, the results showed an agreement with the proposed structure. Differential scanning calorimetry and thermal analysis measurements showed that polymers possessed high glass transition temperature ($T_g > 145$ °C) and good thermal stability with high decomposition temperatures ($T_D > 450$ °C). These novel polymers also exhibited good mechanical behaviors and good solubility.

Keywords Poly(aryl imino sulfone) · Palladium-catalyzed · High-performance polymer · 4,4′-dibromodiphenyl sulfone

Introduction

The synthetic polymers containing the C–N bond has been attracting a great deal of interest due to the importance of such polymers in fields as diverse as natural

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products, photography, and high-performance polymers [1–4]. An example of C–N containing polymer is poly(arylene amide)s, which are materials with high thermal stability, good chemical resistance, and high tensile properties. However, their high glass transition temperatures (T_g) and insolubility in organic solvents seriously limit their processability [5–8]. Another example of aromatic polymers are polyimides (PI). Much research effort has been dedicated to the structural variation of PIs to control and improve their properties. Owing to their excellent mechanical dielectric, thermal, and chemical properties, PIs have been widely used in microelectronics, sleeve bearings, and valve seatings, and as the matrix component of graphite composites for compressor vanes in jet engines and other aerospace applications [9–11]. In recent years, PIs have also been explored for applications in organic electronics, such as light-emitting diodes, photovoltaics, and xerography [12–14]. Due to their outstanding physical and chemical properties, the polymers containing the C–N bond were considered the most promising class of materials for special applications in automotive, aircraft, and spacecraft industry.

It is well-known to all of us that the polymers containing sulfone group exhibit good comprehensive properties. Poly(ether sulfone) (PES) is a typical example, which shows good thermal stability for extended periods at high temperature, fracture toughness, water and steam resistance, and high glass transition temperature (T_g) [15]. Other characteristics such as good electrical properties and transparency, as well as ease of molding, are also desirable [16]. In addition, for composite applications, these amorphous polymers that have the advantage of being solvent soluble can be readily prepregged from low cost solvents [17, 18].

Although a number of traditional methods exist for aryl C–N 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, and regiochemical ambiguities [19–21]. From the standpoint of directness and atom economy, a transition metal-catalyzed approach to C–N bond construction is appealing because it entails simply the cross-coupling of an amine with an aryl halide and has many potential applications for the synthesis of aniline derivatives [20, 22–26]. In the past few years, 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 [27–36]. The Pd-catalyzed aryl amination has also been successfully applied to polycondensation reactions to give various polyamines and its related poly(iminoarylene)s with no or scarcely cross-linked structures [37–39]. The combination of $Pd_2(dba)_3$ and BINAP was considered one of the most important catalyst system, by which the poly(imino ketone)s were successfully obtained [40–42].

Herein, our aim is to use this method for synthesizing poly(aryl imino sulfone)s (PAISs) with the C–N bond and sulfone group as new high-performance polymers. We expect the polycondensation of 4,4′-dibromodiphenyl sulfone with primary aromatic diamines to produce a new type of polymers with good thermal, soluble, and dynamic mechanical properties.

Experimental section

Material

4,4′-dibromodiphenyl sulfone and 4,4′-diiododiphenyl sulfone were synthesized in our laboratory; 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 Company in USA. Other dihalides and primary aromatic diamines were purchased from Daikin Fine Chemical Laboratory, Ltd, Toshima, Kita-ku, Tokyo, Japan; The rest materials and reagents were obtained from different commercial sources and used without further purification.

Measurements

FT–IR spectra were recorded on a Nicolt 6700 FT–IR 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 dimethylsulfoxide (DMSO)-d_6. The molecular weight and molecular weight distributions were measured by GPC. The glass transition temperature was obtained by differential scanning calorimetry (DSC) curves at a rate of 10 °C/min under flowing nitrogen gas. Thermo gravimetric analysis was performed on a Mettler TC 10A at a heating rate of 10 °C/min under nitrogen. Dynamic mechanical thermal analysis (DMA) was performed on dynamic mechanical thermal analyzer V in tension mode at a heating rate of 3 °C/min and a frequency of 1 Hz.

Modified synthesis of 4,4′-dihaloiddiphenyl sulfone

An three-neck flask (250 mL), into which chlorosulfonic acid (36.8 g, 13.7 mmol) and chloroform (50 mL) were added, stirred at -20 to -15 °C for 1 h, in this case, bromobenzene or iodobenzene was dropwisely added. After this procedure, the flask was increased up to 50 °C during 2 h of reflux with continuous stirring. After the reaction, the ice water was added to the mixture with fully stirring, then filtered and the collected organic horizon was washed with water several times. The solids were dried with anhydrous $MgSO_4$ under reduced pressure distillation to give yellow crude products, which were recrystallized from benzene to give white needle-like crystals.

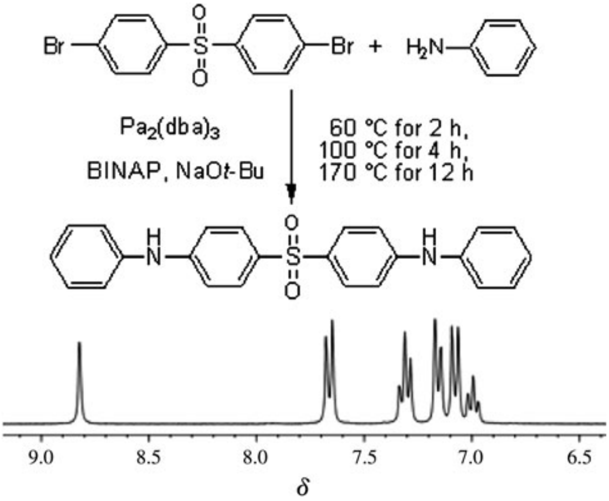
4,4′-dibromodiphenyl sulfone. Yield: 15.31 g, 81.5%; mp 172–173 °C. IR spectra (KBr pellet): 3087 cm^{-1} (m, νAr–H), 1570, 1469 cm^{-1} (m, νC=C), 1329 cm^{-1} (m, νS=O), 813, 821 cm^{-1} (s, δAr–H), 564 cm^{-1} (m, νC–Br). ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 7.75$ (d, 4H, J = 7.0 Hz, 2,2′, 6,6′-H), 7.90 (d, 4H, J = 7.0 Hz, 3,3′, 5,5′-H). MS (EI): 375.86. UV recorded in CHC_{13} λmax at 268 nm. Anal. Calcd for $C_{12}H_8Br_2O_2S$ (376.06): C, 38.30; H, 2.13; S, 8.51. Found: C, 38.26; H, 2.16; S, 8.49.

4,4′-diiododiphenyl sulfone. Yield: 18.54 g, 79.0%; mp 206–207 °C. IR spectra (KBr pellet): 3075 cm^{-1} (m, νAr–H), 1564, 1472 cm^{-1} (m, νC=C), 1323 cm^{-1} (m, νS=O), 815, 824 cm^{-1} (s, δAr–H), 560 cm^{-1} (m, νC–I). ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 7.60$ (d, 4H, J = 8.6 Hz, 2,2′, 6,6′-H), 7.85 (d, 4H, J = 8.6 Hz, 3,3′, 5,5′-H). MS (EI): 469.72. UV recorded in CHC_{13} λmax at 276 nm. Anal. Calcd for $C_{12}H_8I_2O_2S$ (469.83): C, 30.65; H, 1.72; S, 6.80. Found: C, 30.63; H, 1.74; S, 6.79.

Synthesis of *N*,*N*′-diphenyl-4,4′-diaminodiphenyl sulfone as a model compound (Scheme 1)

An oven-dried resealable two-neck 50-mL flask equipped with magnetic stirrer, a nitrogen outlet, inlet, and water-cooled condenser, added to which were tris(dibenzylideneacetone)dipalladium(0) $Pd_2(dba)_3$ (0.05 mmol), BINAP (0.15 mmol), 4,4′-dibromodiphenyl sulfone (5.0 mmol), and dimethylacetamide (8 mL). The reaction mixture was flushed with high purity nitrogen. This procedure was repeated three times. The flask was immersed in a 60 °C oil bath for 2 h. Then, aniline (12.0 mmol) and sodium *tert*-butoxide (NaO*t*-Bu) (14.0 mmol) were added and the reaction mixture was heated to 100 °C for 4 h and then to 170 °C for 12 h with continuous stirring. The resulting solution was allowed to slowly cool to room temperature and subsequently poured into cold water, filtered through Celite, and dried. The crude material was purified by recrystallized from dimethyl sulfoxide/ethanol to afford *N*,*N*′-diphenyl-4,4′-diaminodiphenyl sulfone as gray crystals.

Yield: 1.92 g, 96.0%; mp: 225–226 °C. IR spectra (KBr pellet): 3364 cm^{-1} (m, νN–H), 3079 cm^{-1} (m, νAr–H), 1610, 1452 cm^{-1} (m, νC=C), 1311 cm^{-1} (m, νS=O), 808, 816 cm^{-1} (s, δAr–H). MS (EI): 400.10. Anal. Calcd for $C_{24}H_{20}N_2O_2S$ (400.12): C, 72.00; H, 5.00; N, 7.00; S, 8.00. Found: C, 71.95; H, 5.01; N, 6.98; S, 7.99. As an example, the ^{1}H NMR spectra of model compound is shown in Scheme 1 (DMSO-d_6).



Scheme 1 Synthesis of model compound

Synthesis of PAISs

An oven-dried resealable two-neck 50-mL flask equipped with magnetic stirrer, a nitrogen outlet, inlet and water-cooled condenser, added to which are tris(dibenzylideneacetone)dipalladium(0) $Pd_2(dba)_3$ (0.05 mmol), BINAP (0.15 mmol), 4,4′-dibromodiphenyl sulfone (5.0 mmol), and dimethylacetamide (6–9 mL). The reaction mixture was flushed with high purity nitrogen. This procedure was repeated three times. The flask was immersed in a 60 °C oil bath for 2 h. Then, primary aromatic diamines (5.0 mmol) and sodium *tert*-butoxide (NaO*t*-Bu) (14.0 mmol) were added and the reaction mixture was heated to 100 °C for 4 h and then to 170 °C for 12 h with continuous stirring. The resulting polymer solution was allowed to slowly cool to room temperature and precipitated into methanol/water (80:20), this procedure was repeated three times, filtered, and then dried at 100 °C under vacuum.

Synthesis of PAIS-1

Yield: 1.44 g, 89%; FT–IR spectrum (KBr pellet): γ NH at 3357 cm^{-1}; γ SO_2 at 1326, 1143 cm^{-1}; γ C–N at 1303 cm^{-1}; UV recorded in dimethylacetamide (DMAc) λ_{max} at 311 nm. ^1H NMR (500 MHz, DMSO-d_6): $\delta = 8.72$ (s, NH); 6.93–7.82 (m, C_6H_4). ^{13}C NMR: $\delta = 120.0$, 129.1, 129.9, 130.9, 139.3, 146.6. Anal.Calcd for $C_{18}H_{14}N_2SO_2$ (322.08): C, 67.08; H, 4.35; N, 8.69; S, 9.94. Found: C, 66.93; H, 4.47; N, 8.72; S, 9.94.

Synthesis of PAIS-2

Yield: 1.38 g, 86%; FT–IR spectrum (KBr pellet): γ NH at 3353 cm^{-1}; γ SO_2 at 1323, 1144 cm^{-1}; γ C–N at 1297 cm^{-1}; UV recorded in DMAc λ_{max} at 305 nm; ^1H NMR (500 MHz, DMSO-d_6): $\delta = 8.57$ (s, NH); 6.76–7.80 (m, C_6H_4). ^{13}C NMR: $\delta = 108.6$, 120.1, 129.7, 130.6, 139.2, 140.5, 146.7. Anal.Calcd for $C_{18}H_{14}N_2SO_2$ (322.08): C, 67.08; H, 4.35; N, 8.69; S, 9.94. Found: C, 66.98; H, 4.50; N, 8.78; S, 9.89.

Synthesis of PAIS-3

Yield: 2.45 g, 90%; FT–IR spectrum (KBr pellet): γ NH at 3355 cm^{-1}; γ SO_2 at 1330, 1147 cm^{-1}; γ C–N at 1298 cm^{-1}; UV recorded in DMAc λ_{max} at 362 nm. ^1H NMR (500 MHz, DMSO-d_6): $\delta = 9.00$ (s, NH); 6.65–8.10 (m,C_6H_4). ^{13}C NMR: $\delta = 66.3$, 109.2, 116.8, 119.6, 129.2, 135.3, 147.3, 144.6. Anal.Calcd for $C_{27}H_{18}F_6N_2O_2S$ (548.05): C, 59.12; H, 3.28; N, 5.11; S, 5.84. Found: C, 59.09; H, 3.31; N, 5.08; S, 5.81.

Synthesis of PAIS-4

Yield: 2.27 g, 84%; FT–IR spectrum (KBr pellet): γ NH at 3349 cm^{-1}; γ SO_2 at 1321, 1153 cm^{-1}; γ C–N at 1304 cm^{-1}. UV recorded in DMAc λ_{max} at 345 nm; ^1H

NMR (500 MHz, DMSO-d_6): $\delta = 8.40$ (s, NH); 7.23–7.80 (m, C_6H_4). ^{13}C NMR: $\delta = 110.4$, 119.2, 120.8, 130.4, 143.7, 147.5. Anal.Calcd for $C_{24}H_{10}F_8N_2O_2S$ (542.03): C, 53.14; H, 1.85; N, 5.17; S, 5.90. Found: C, 53.04; H, 1.88; N, 5.11; S, 5.83.

Synthesis of PAIS-5

Yield: 2.40 g, 95%; FT–IR spectrum (KBr pellet): γ NH at 3366 cm^{-1}; γ SO_2 at 1590, 1497 cm^{-1}; γ C–N at 1300 cm^{-1}; γ C–O at 1110 cm^{-1}. UV recorded in DMAc λ_{max} at 321 nm; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.95$ (s, NH); 6.30–8.10 (m, C_6H_4). ^{13}C NMR: $\delta = 117.0$, 120.2, 129.5, 139.2, 141.6, 146.0. Anal.Calcd for $C_{30}H_{22}N_2O_4S$ (506.13): C, 71.15; H, 4.35; N, 5.53; S, 6.32. Found: C, 71.09; H, 4.38; N, 5.50; S, 6.30.

Synthesis of PAIS-6

Yield: 3.02 g, 97%; FT–IR spectrum (KBr pellet): γ NH at 3362 cm^{-1}; γ SO_2 at 1588, 1494 cm^{-1}; γ C–N at 1303 cm^{-1}; γ C–O at 1110 cm^{-1}. UV recorded in DMAc λ_{max} at 318 nm; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.75$ (s, NH); 6.50–7.75 (m, C_6H_4); 1.60 (CH_3). ^{13}C NMR: $\delta = 42.7$, 54.7, 118.0, 120.5, 129.4, 139.3, 144.5. Anal.Calcd for $C_{39}H_{32}N_2O_4S$ (624.48): C, 75.00; H, 5.16; N, 4.49; S, 5.14. Found: C, 74.79; H, 5.37; N, 4.52; S, 4.98.

Synthesis of PAIS-7

Yield: 2.64 g, 94%; FT–IR spectrum (KBr pellet): γ NH at 3400 cm^{-1}; γ SO_2 at 1327, 1147 cm^{-1}; γ C–N at 1300 cm^{-1}. UV recorded in DMAc λ_{max} at 374 nm; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.70$ (s, NH); 6.50–8.40 (m, C_6H_4). ^{13}C NMR: $\delta = 54.9$, 116.8, 120.3, 130.5, 139.0, 141.7. Anal.Calcd for $C_{37}H_{27}N_2O_2S$ (563.18): C, 78.86; H, 4.80; N, 4.97; S, 5.68. Found: C, 78.74; H, 4.83; N, 4.95; S, 5.66.

Synthesis of PAIS-8

Yield: 2.87 g, 96%; FT–IR spectrum (KBr pellet): γ NH at 3404 cm^{-1}; γ SO_2 at 1319, 1139 cm^{-1}; γ C–N at 1305 cm^{-1}. UV recorded in DMAc λ_{max} at 368 nm; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.73$ (s, NH); 6.55–8.45 (m, C_6H_4). ^{13}C NMR: $\delta = 54.7$, 120.2, 128.6, 138.5, 141.1, 161.3. Anal.Calcd for $C_{37}H_{25}F_2N_2O_2S$ (599.16): C, 74.12; H, 4.17; N, 4.67; S, 5.34. Found: C, 74.04; H, 4.20; N, 4.65; S, 5.30.

Synthesis of PAIS-9

Yield: 2.74 g, 93%; FT–IR spectrum (KBr pellet): γ NH at 3402 cm^{-1}; γ SO_2 at 1317, 1137 cm^{-1}; γ C–N at 1303 cm^{-1}. UV recorded in DMAc λ_{max} at 365 nm; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 8.68$ (s, NH); 6.35–8.15 (m, C_6H_4); 1.55 (CH_3). ^{13}C NMR: $\delta = 15.9$, 55.7, 120.1, 129.7, 139.1, 146.5. Anal.Calcd for $C_{39}H_{31}N_2O_2S$

(591.21): C, 79.19; H, 5.25; N, 4.74; S, 5.41. Found: C, 79.09; H, 5.29; N, 4.69; S, 5.37.

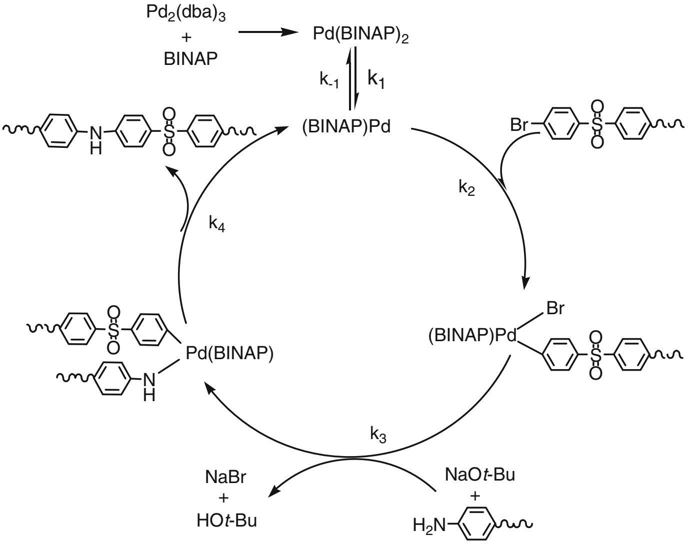
Results and discussion

Through iterative cycles of ligand design, methodological studies, and mechanistic investigations, highly active and broadly useful catalyst systems have been developed [43]. The combination of $Pd_2(dba)_3$ and BINAP (BINAP/$Pd_2(dba)_3$ ratio = 3:1) was used as an efficient catalyst for the synthesis of poly(aryl imino sulphone)s proved by experiments. The mechanism of the Pd-catalyzed amination involves oxidative addition of the sulfonate by Pd (0). The palladium (II) aryl amide can be formed by direct displacement of sulfonate by the amide (Scheme 2).

To investigate the potential of amination reaction for a polycondensation process, *N*,*N*′-diphenyl-4,4′-diaminodiphenyl sulfone was synthesized as model compound by the Pd-catalyzed amination of 4,4′-dibromodiphenyl sulfone with aniline using $Pd_2(dba)_3$ as the main catalyst and BINAP as the ligand. Through FT–IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis studies, no minor undesired products were detected.

Polymer synthesis

Reactions of electron-poor aromatic halides and electron-rich amines give high yields in the amination protocol [41]. Thus, we attempted to do polycondensation of



Scheme 2 Proposed Pd-BINAP catalytic cycle of amination of 4,4′-dibromodiphenyl sulfone with primary diamines

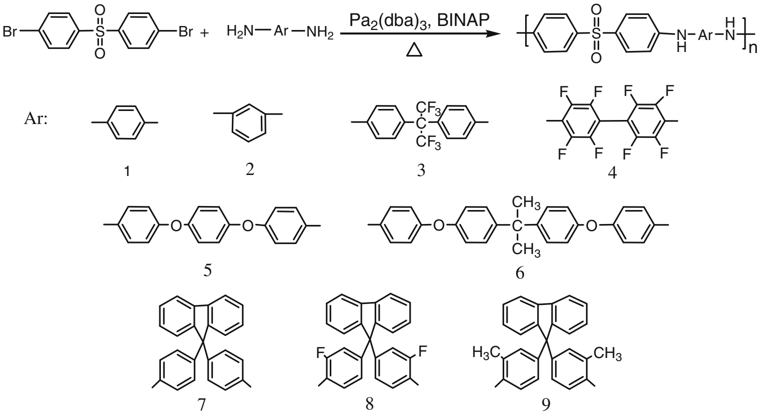
4,4′-dibromodiphenyl sulfone as electron-poor arylene halides with different electron-rich primary aromatic diamines (Scheme 3).

PAIS is a kind of copolymer constructed by the repeated units of sulfone segment and imino segment. Figure 1 shows the chemical structure and three-dimensional stereostructure of PAIS repeated unit created by chemical office software.

The structures of polymers synthesized were confirmed by FT–IR, NMR spectroscopy, and Elemental analysis. The results showed good agreement with the proposed structure. As an example, the ^{1}H NMR spectrogram of PAIS-3 was shown in Fig. 2 (DMSO-d_6). From the ^{1}H NMR spectrogram, however, we could conclude that polymer PAIS-3 contained a low concentration of amino end groups (resonances at 5.4 ppm). The concentration corresponded to less than 5 mol% end groups per repeat unit, which meant the concentration of end groups in PAIS-3 was very low. Bromine end groups were not detectable. Remarkably, in the case of the higher molecular weight PAIS, no end groups were detected.

The molecular weights of the reprecipitated polymers were measured by GPC (calibrated by polystyrene standards). The M_n values are in the range of 11000–46100 and the M_w values in the range of 35100–238700. The polydispersity index (PDI) varies from 1.68 up to 5.17 (Table 1). In order to get more information about the molecular weight of the polymer obtained, their intrinsic viscosities [η] have been determined and compared. All viscosity measurements are carried out in *N*,*N*-dimethyformamide (DMF) at 25 °C. The determined [η] are in the range of 0.130–0.458 g/dL. From Table 1, it can be seen that the intrinsic viscosity of polymer increases with the increasing molecular weight of polymer determined from GPC measurements. In comparison, the intrinsic viscosity [η] of PAISs are lower than those of the higher molecular weight poly(ether ketone)s (PEK) and those of the aromatic polyamides.

To test which solvent would be most suitable material for the polycondensation process to form PAISs, we attempted the amination of 4,4′-dibromodiphenyl sulfone with *p*-phenylenediamine in different solvents (Table 2). It appeared that DMAc gave the better yields, higher molecular weight, and lower polydispersity of the



Scheme 3 Synthesis of PAISs via Pd-catalyzed aryl amination

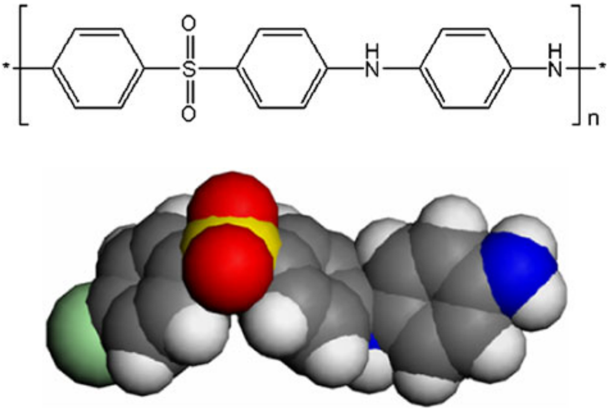


Fig. 1 Repeated unit for the chemical structure and three-dimensional stereostructure of PAIS

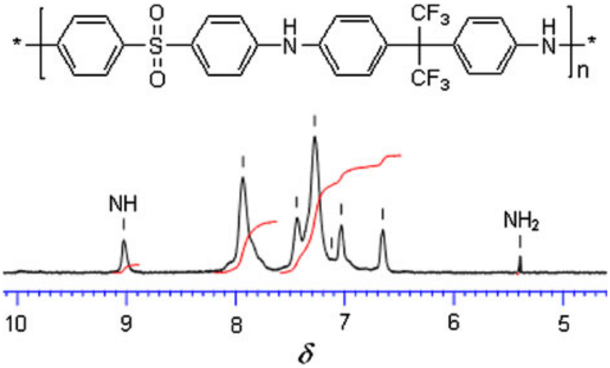


Fig. 2 ^{1}H NMR (500 MHz) spectrum of PAIS-3 recorded in DMSO-d_6

Table 1 Characterization of PAISs (GPC and intrinsic viscosity)

Polymer code	M_n	M_w	PDI	[η], g/dL (25 °C in DMF)
PAIS-1	11000	35100	3.19	0.130
PAIS-2	20200	69400	3.44	0.170
PAIS-3	15400	45700	2.97	0.150
PAIS-4	20800	85300	4.10	0.180
PAIS-5	40700	128200	3.14	0.304
PAIS-6	46100	238700	5.17	0.458
PAIS-7	32200	57700	1.79	0.206
PAIS-8	40800	67800	1.68	0.247
PAIS-9	36700	65500	1.78	0.225

Table 2 Different solvents for PAIS-1

	DMAc	Sulfolane	DMSO	Diphenyl sulfone	DMF	THF
M_n	11000	9800	9100	9400	5600	4300
M_w	35000	33000	27000	30400	26300	9700
PDI	3.19	3.37	2.97	3.23	4.70	2.26
Yield (%)	89	90	73	82	80	61

polymer than sulfolane and that both were superior to diphenyl sulfone, DMF, and DMSO as a suitable material for polycondensation process to form PAISs.

During the synthesis of PAIS, the effect of temperature and concentration on the molecular weight and the PDI of the PAIS could be followed. Upon increasing the temperature from 60 to 190 °C, M_n and M_w both increased. When the reaction was operated under 190 °C, the combination of $Pd_2(dba)_3$ and BINAP can change from sable to unstable, M_n and M_w both decreased. While upon increasing the concentration from 15 to 35% at temperature 170 °C, M_n and M_w both increased too. Because of poor solubility of 4,4′-dibromodiphenyl sulfone, the concentration higher than 35% cannot be detected. In addition, the PDI increased with the increasing temperature and increasing concentration. On the basis of all factors into consideration, a temperature of 100–170 °C and a concentration of 35%, comprehensive concerned, are more suitable for the palladium-catalyzed polycondensation to produce theses polymers with higher molecular weight (Table 3).

The reactivity of the halogen-containing monomers (**a**–**d**) was studied during the polycondensation process to form polymer PAIS-1(Table 4). It is known that for aryl amination the reactivity decreases significantly with higher electronegativity of the halogen atoms, and oxidative addition is rate-limiting. 4,4′-dibromodiphenyl sulfone (**c**) and 4,4′-diiododiphenyl sulfone (**d**) gave PAISs in higher yield and molecular weight than 4,4′-dichlorophenyl sulfone (**b**), while 4,4′-difluorodiphenyl sulfone (**a**) is totally unreactive. Because of 4,4′-diiododiphenyl sulfone's high production cost and low yield, the 4,4′-dibromodiphenyl sulfone is considered the ideal monomer in preparation of PAISs.

Table 3 Different temperatures and concentration monomers for PAIS-1

Run	Temperature (°C)	Concentration of monomers (%)	M_n	M_w	PDI	Yield (%)
1	60	15	3200	6700	2.09	23
2	60	25	3800	8900	2.34	26
3	100	25	6300	18800	2.98	72
4	150	30	8100	24900	3.07	80
5	170	35	7100	38600	5.44	86
6	190	35	4200	30100	7.17	68
7	100–170	35	11000	35100	3.19	89

Table 4 Synthesis of PAIS-1 using different halogen-containing monomers

Run	Polymer code	X	M_n	M_w	PDI	Yield (%)
1	PAIS-1a	F	–	–	–	0
2	PAIS-1b	Cl	4300	13600	3.16	73
3	PAIS-1c	Br	11000	35100	3.19	89
4	PAIS-1d	I	11300	30400	2.69	80

Thermal behaviors

Figure 3 shows the primary thermogravimetric curves obtained by dynamic TGA of PAISs. Thermal analysis (TG) curves reveal that the polymers are thermally stable up to 380–520 °C and show a single stage thermal degradation at temperatures lower than 600 °C. In addition, From Fig. 3, the temperature difference between T_5 (the temperature for 5% weight loss) and T_p (the temperature corresponding to maximum degradation rate) is about 60 °C in PAIS-5, which can be taken as a measure of the rate of degradation. This shows that though chain scission starts at a lower degradation temperature (380 °C) in PAIS-5, the degradation and loss of volatile products is very slow.

However, the thermal stability of the polymers synthesized is reduced in air environment. For example, by comparing the TG thermograms of PAIS-1 in air and nitrogen (the inset in Fig. 3), it was observed that in air a 50% weight loss of PAIS-1 took place at 470 °C, but in nitrogen the 50% weight loss was not observed up to 650 °C. In air the char yield at 600 °C was 0%, but in nitrogen the char yield at 600 °C was 57%.

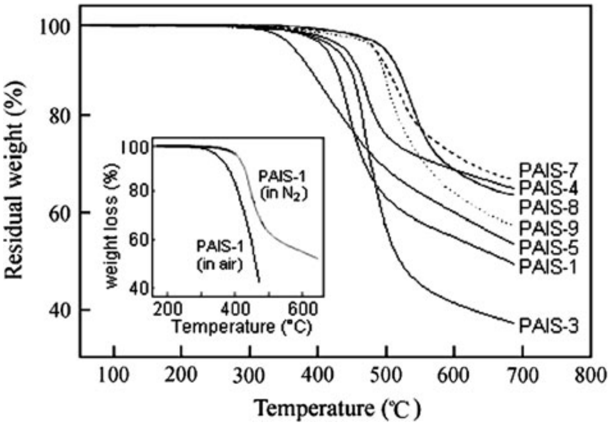


Fig. 3 TG of PAISs

The glass transition temperatures (T_g) of PAISs were determined using the DSC method. The T_g was defined as the midpoint of the maximum baseline shift from the second run. As shown in Fig. 4, all of the polymers synthesized exhibited a single T_g ranging from 144.6 to 332.0 °C, the absence of the melting temperature suggested a homogeneous amorphous polymer structure. Being comparable with the T_gs of PEKs, only PAIS-5 with flexible backbone (ether bone) gave a lower T_g at 144.6 °C, while PAIS-4 with rigid backbone (biphenyl group) gave a higher T_g at 332.0 °C. In addition, T_g of PAIS-7 was 221.0 °C being lower than that of the corresponding polymer PAIS-9 which was 269.0 °C. It could be suggested that the introduction of the bulky side methyl groups leaded to a decrease of free volume of the polymers, and restricted the free rotation along the polymer chain.

Wide-angle X-ray diffraction

The wide-angle X-ray diffraction patterns of PAISs over the 2θ range of 5°–70° were shown in Fig. 5. PAIS-1 and PAIS-5 showed amorphous patterns, but more than one amorphous peaks were present, indicating that more than one type of chain packing arrangements co-exist in the polymer matrix. PAIS-3 and PAIS-7 had a similar diffraction pattern at 25.2 °C, but the patterns for PAIS-3 and PAIS-7 were broadened considerably, suggesting that the packing regularity of the polymers decreased greatly. Despite the presence of the rigid secondary amine ring they revealed essentially amorphous patterns. Obviously, the sulfonyl, methyl and fluorene 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. We could conclude that insertion of butyl groups into the repeating units of the polymers resulted in a significant increase of the amorphous nature of the polymer. However, the diffraction arising from the crystallites was observed which showed crystalline pattern of PAIS-4 at 26.2 and 47.4 °C, this may be attributed to the existence of the

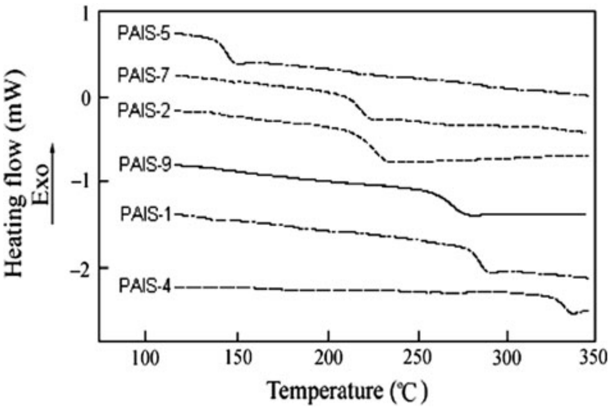


Fig. 4 Differential scanning calorimetry of PAISs

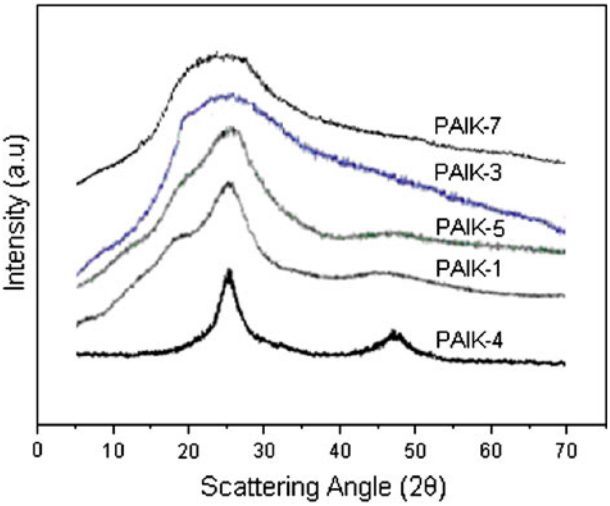


Fig. 5 WAXD diffractograms intensity versus Bragg angle graph for powders of PAIS

rigid biphenyl and secondary amino segments in their polymer backbones and at the same time the absence of bulky groups, leading to a better packing of the polymer chains. But the crystallization property was not detected by DSC.

Dynamic mechanical behaviors

DMA was employed to investigate the mechanical behavior of the synthesized polymers as well as to obtain information about the molecular relaxations and interactions taking place in these materials. Figure 6 shows the temperature dependence of the storage modulus (E') and loss modulus (E'') of PAIS and the different derivatives at the frequency of 1 Hz. The results indicate that the polymer exhibits a spectrum of viscoelastic properties characteristic for linear amorphous entangled polymers. The storage modulus (E') of PAIS decreases progressively with increasing temperature, and the reduction of E' over the entire temperature range measured can be divided into two steps. Below the glass transition temperature (T_g), there is a slow reduction in E' associated with gentle chain segmental motion of PAIS molecules, and for the range of 140 and 350 °C, which belongs to a part of the glass transition region, the sharp reduction in E' is observed because of acceleration of the chain segmental motion which is inevitable. In the loss-modulus plot, there is a major secondary-relaxation process (the γ peek) showing a broad maximum around −87 °C. It is believed that this low-temperature transition reflects short-range mobility of PAIS main chain including flips of phenylene rings. In addition to the low-temperature transition, an intense peak at 140–350 °C, α relaxation, which corresponds to the glass transition of PAIS.

It is obvious that addition of butyl or/and ether groups into the repeating units of PAIS can decrease the level of the storage modulus (E') in the whole glassy region.

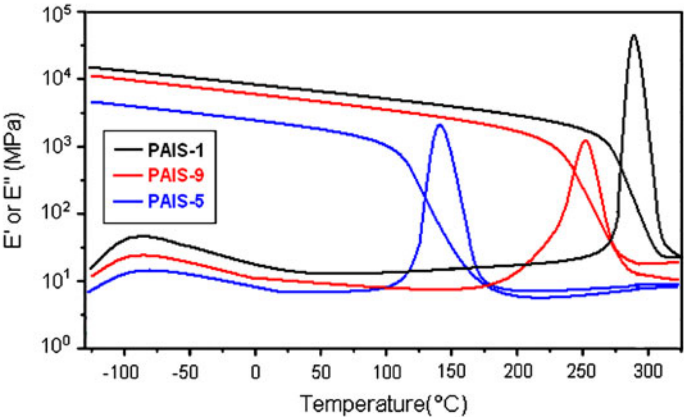


Fig. 6 Dynamic-mechanical spectrum of PAISs

In a word, all the polymers synthesized showed high E' values, even after their broad glass transitions.

Solubility

Poly(aryl imino sulfone)s 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 5). PAIS could be easily soluble in high polar solvents, such as DMAc, DMSO, DMF, tetrahydrofuran (THF), and chloroform ($CHCl_3$), while it was partially soluble in common organic solvents, such as toluene and acetone. Due to the particular structure of PAIS (showed in Fig. 1), all polymers showed greatly improved solubility compared with PI and PEK.

Table 5 Solubility of PAISs

Polymer code	DMAc	DMSO	DMF	THF	$CHCl_3$	Toluene	Acetone
PAIS-1	+ +	+ +	+ +	+ +	+ −	− −	− −
PAIS-2	+ +	+ +	+ +	+ +	+ +	− −	− −
PAIS-3	+ +	+ +	+ +	+ +	+ +	+ −	− −
PAIS-4	+ +	+ +	+ +	− −	− −	− −	− −
PAIS-5	+ +	+ +	+ +	+ +	+ +	− −	− −
PAIS-6	+ +	+ +	+ +	+ +	+ +	+ −	+ −
PAIS-7	+ +	+ +	+ +	+ +	+ +	+ −	− −
PAIS-8	+ +	+ +	+ +	+ +	+ +	+ −	− −
PAIS-9	+ +	+ +	+ +	+ +	+ +	− −	− −

+ + solid polymer was completely dissolved at room temperature, + − solid polymer was completely dissolved at 50 °C, − − solid polymer could swell at 50 °C

Conclusions

A series of PAISs have been obtained by a Pd-catalyzed polycondensation of 4,4′-dibromodiphenyl sulfone with different primary aromatic amines. These novel polymers can be considered as a new class of high-performance polymers with high thermal stability ($T_g > 145$ °C, $T_D > 450$ °C), good mechanical behaviors and good solubility. The unique molecular structure gives the PAIS good comprehensive properties. The combination of $Pd_2(dba)_3$ and BINAP was used as an efficient catalyst for the synthesis of PAIS. In comparison to the established PEK and PES, although molecular weights and yields of polymers are not high in this study, the polycondensation could provide a variety of PAIS by changing the structure of diamines. One major advantage of PAIS is that these novel polymers can use cheaper monomers, e.g., bromo-functionalized dibromoarenes, instead of the corresponding difluoro structures. Furthermore, PAIS exhibit good solubility in organic solvents, which establishes theory and experiment foundation for its extensive application. Further studies for processing and applications of PAIS are now in progress.

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