Synthesis, characterization and properties of novel thermally stable copoly(amide-imide)s containing dimethylsilane moieties

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Abstract: New type of poly(amide-imide)s were prepared based on novel diacid monomer containing softening siloxane groups. Bis(*p*-aminophenoxy) dimethyl silane (**3**) was prepared by the reaction of dimethyl dichlorosilane with *p*-aminophenol in toluene. *N,N'*-Bis(4-trimellitimidophenoxy) dimethylsilane (**5**) as a novel aromatic dicarboxylic acid containing silicone moiety was synthesized by condensation of bis(*p*-aminophenoxy) dimethylsilane with trimellitic anhydride in acetic acid. The structure of diacid **5** was confirmed using various spectroscopy methods. The direct polycondensation technique was used for the polyamidation of monomer **5** with several aromatic diamines using pyridine / 2-methylpyrrolidone / triphenyl phosphite / CaCl₂ as condensing agent. The resulting novel poly(amide-imide-siloxane)s were obtained in high yields and inherent viscosities. These polymers were characterized using FT-IR, ¹H-NMR, thermogravimetric and elemental analysis techniques. The results show that silicone modified poly(amide-imide)s show high solubility and excellent thermal stability.

Key words: poly(amide-imide); silicone; polycondensation; inherent viscosity; thermally stable polymers

Introduction

Organic polymers are one of the most versatile groups of materials that combine light weight, cost-effectiveness, and processability. Among the various heterocyclic polymers investigated for high-performance applications, aromatic polyimides are used widely in the semiconductor and electronic-packaging industries because of their outstanding thermal stability, good insulation properties with a low dielectric constant, good adhesion to common substrates, and superior chemical stability [1, 2]. Aromatic polyamides are hydrophilic polymers that can absorb water because of their amide linkages. Therefore, these polymers are good candidates for semipermeable membranes, particularly for the filtration of aqueous solutions and for water purification [3]. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting or glass-transition temperatures (*T_g*'s) and their limited solubility in organic solvents [4].

Much effort has been made to create structurally modified aromatic polymers having better characterization in terms of both solubility and processability with retention of their high thermal stability. Introduction of flexible chains into the polyamide backbone [5, 6], the use of meta-oriented monomers [7,8], synthesis of polymers with

noncoplaner unit in the polymer chains [9], preparation of copolymers such as poly(ester amide)s [10], poly(amide-ester-imide)s [11,12] and cardo copolymers [13] resulted in a number of modified polyamides. A further strategy is based on the introduction of bulky side groups into the polymer chains [14–20]. A limitation for the preparation of polyarylate with pendant functional groups on the accurate sites is that most of wholly aromatic polymers are insoluble and infusible by virtue of their dense rigid structures [21].

Another way for improving solubility and lowering the T_g of aromatic polymers is the introduction of silane moieties in the main chain [22, 23]. Organosilicon chemistry plays an increasingly important role in organic synthesis. Since the silicon can serve as an important bridge between the organic and inorganic materials, recently, the silicon-containing polymers have received considerable attention [24]. In addition, these polymers are biocompatible and can be used in different applications such as controlled drug delivery systems [25, 26].

The solubility and melting processability of the polyoxadiazoles, polyesters, polyamides and polyimides containing silicone group in the main chain polymer were improved [27-30]. Meanwhile, the ionic characteristic of Si–C bond and the lower electronegativity of the silicon with respect to the carbon atom increased the thermal stability of the polymer. On the other hand, the silicon having aromatic neighbors is able to give s–p conjugation, which is advantageous for the electron and hole transport along the polymer chain so that silicon-containing polymers show the potential applications in the field of optoelectronic materials [31].

In this article, *N,N'*-bis(4-trimellitimidophenoxy) dimethylsilane as a novel diacid monomer containing siloxane and imide linkage was prepared. Direct polyamidation of this diacid with different aromatic diamines were carried out using phosphorylation reaction. Softening siloxane group were incorporated within the main chain of resulting poly(amide-imide-siloxane)s (PAISs). Thereby, the polymers showed good solubility and thermal stability.

Results and discussion

Monomer synthesis

The diamine **3** was synthesized by the condensation reaction of *p*-aminophenol (**1**) and dichlorodimethylsilane (**2**) in dry toluene in the presence of triethylamine (Scheme 1). Chemical structure and purity of the compound **3** was proven by using TLC, using *n*-hexan:tetrahydrofurane (60:40) as eluent and FT-IR spectroscopy technique. In FT-IR spectrum of this diamine the peak at 3400 cm^{-1} shows amino groups and peaks at 1260 , 2950 cm^{-1} are attributed to Si-CH₃ groups. In addition strong peaks at 1077 cm^{-1} and 933 cm^{-1} confirms Si-O and Si-O-Ph linkages, respectively.

Scheme 1. Synthesis of bis-(*p*-aminophenoxy) dimethylsilane (**3**).

The diamine **3** was reacted with trimellitic anhydride (**4**) in glacial acetic acid (Scheme 2) to yield novel diacid monomer **5** containing imide and siloxane groups. The structure and chemical purity of this novel compound was confirmed using TLC, elemental analysis, FT-IR (Figure 1), $^1\text{H-NMR}$ (Figure 2) and $^{13}\text{C-NMR}$ spectroscopy methods. TLC shows one spot for this diacid using n-hexan:tetrahydrofuran (50:50) as eluent. Elemental analysis shows good agreement between calculated and found value for carbon, hydrogen and nitrogen contents. In Figure 1 broad peak around $2600\text{--}3500\text{ cm}^{-1}$ show OH of carboxylic acid group, two peaks at 1705 and 1782 cm^{-1} are attributed to the symmetry and asymmetry stretching C=O of imide groups. Two other peaks at 723 and 1390 cm^{-1} confirms imide heterocyclic ring. Si-CH_3 peaks appeared at 1211 cm^{-1} . Other peaks at 1092 cm^{-1} and 932 cm^{-1} prove the existence of Si-O and Si-O-Ph connections, respectively.

The $^1\text{H-NMR}$ of this monomer (Figure 2) shows the characteristic absorption of CH_3 at 0 ppm, aromatic hydrogen between 6.8–8.3 ppm and acidic hydrogen at 13.8 ppm. The $^{13}\text{C-NMR}$ of diacid **5** (Figure 3) shows twelve different carbons from 116–167 ppm and one type of carbon near 0 ppm.

Scheme 2. Synthesis of *N,N'*-bis-(4-trimellitimidophenoxy) dimethylsilane (**5**).

Fig. 1. FT-IR spectrum of *N,N'*-bis-(4-trimellitimidophenoxy) dimethylsilane (**5**).

Fig. 2. ¹H-NMR (500MHz) spectrum of *N,N'*-bis-(4-trimellitimidophenoxy) dimethylsilane (5) in DMSO-d₆ at RT.

Fig. 3. ¹³C-NMR (500MHz) spectrum of *N,N'*-bis-(4-trimellitimidophenoxy) dimethylsilane (5) in DMSO-d₆ at RT.

Polymer syntheses

Direct polycondensation of a dicarboxylic acid with a diamine using TPP and Py as condensing agent to form amide bonds is an efficient way to obtain polyamides of moderate to high degree of polymerization on a laboratory scale. This method was successfully applied for the preparation of PAIS(7a-7h) from novel dicarboxylic acid **5** with various aromatic diamines (**6a–6g**) (Scheme 3). All of polymerization reactions in NMP in the presence of CaCl_2 proceeded homogeneously.

Scheme 3. Polymerization reactions of monomer **5** with aromatic diamines.

Fig. 4. The effect of reaction temperature on PAIS-7a yield and inherent viscosity (inherent viscosity were measured at concentration of 0.5 g/dL in DMF, reaction conditions: NMP/Py=2:1, CaCl_2 /diacid=2:1, reaction time= 6 h).

Fig. 5. The effect of reaction time on PAIS-7a yield and inherent viscosity (inherent viscosity were measured at concentration of 0.5 g/dL in DMF, reaction conditions: NMP/Py=2:1, $\text{CaCl}_2/\text{diacid}$ =2:1, reaction temperature= 130 °C).

Tab. 1. The optimum conditions for the preparation of PAISs using TPP/NMP/Py/ CaCl_2 as a condensing agent.

Parameter	Optimum condition
Reaction Temperature (°C)	130
Reaction Time (h)	6
NMP/Py (mL:mL)	10:3
$\text{CaCl}_2/\text{diacid}$ (mole:mole)	5:1

Fig. 6. The effect of NMP/Py ratio on PAIS-7a yield and inherent viscosity (inherent viscosity were measured at concentration of 0.5 g/dL in DMF, reaction conditions: $\text{CaCl}_2/\text{diacid}$ =2:1, reaction time= 6h, reaction temperature= 130 °C).

Different parameters such as reaction time, reaction temperature, NMP/Py ratio and $\text{CaCl}_2/\text{diacid}$ ratio have critical effect on polymerization reaction using phosphorylation reaction [32], so this parameters were modified with different reactions (Figures 4-7) and the best results were carefully chosen for direct polymerization reactions (Table 1). All of these parameters had acute effect on the polymer chain growth.

Fig. 7. The effect of $\text{CaCl}_2/\text{diacid}$ ratio on PAIS-7a yield and inherent viscosity (inherent viscosity were measured at concentration of 0.5 g/dL in DMF, reaction conditions: NMP/Py=10:3, reaction time= 6 h, reaction temperature= 130 °C).

Tab. 2. Synthesis and some physical properties of **PAIS(7a-7h)** prepared using TPP/NMP/Py^a.

Diamine	Polymer		
	Polymer code	$\eta_{\text{inh}}(\text{dL/g})$	Yield (%)
6a	PAIS-7a	0.51 ^b	97
6b	PAIS-7b	0.35 ^b	98
6c	PAIS-7c	0.31 ^b	74
6d	PAIS-7d	0.44 ^b	87
6e	PAIS-7e	0.24 ^b	98
6f	PAIS-7f	0.27 ^b	94
6g	PAIS-7g	0.27 ^c	98
6h	PAIS-7h	0.24 ^b	96

^a Reaction conditions: reaction temperature=130 °C, reaction time= 6 h, NMP/Py=10:3 and $\text{CaCl}_2/\text{diacid}$ =5:1.

^b Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

^c Measured at a concentration of 0.5 g/dL in DMF with 1% LiCl (w/w) at 25 °C.

The synthesis and some physical properties of these poly(amide-imide)s containing siloxane group in the main chain are listed in Table 2. The inherent viscosities of the

resulting polymers under optimized conditions were in a range of 0.24-0.51 dL/g and the yields were 74-98%.

FT-IR study

The structures of these polymers were confirmed as **PAISs** by means of FT-IR spectroscopy. The FT-IR spectra data of **PAIS(7a-7h)** are reported in Table 3. The FT-IR spectra of all polymers showed absorptions around 3300-3400 cm^{-1} (N-H). Two absorptions (symmetry and asymmetry imide C=O) appeared around 1720, 1780 cm^{-1} . Imide heterocyclic ring are confirmed using two other peaks approximately at 730, 1385 cm^{-1} . All of these **PAISs** exhibited absorption at 1649-1657 cm^{-1} that shows the presence of the amide groups in these polymers. Si-CH₃ peaks appeared in the region of 1250 cm^{-1} . Other peak around 1100 cm^{-1} proves the existence of Si-O starching. The **PAIS-7a** showed characteristic absorptions at 1315, 1154 cm^{-1} due to SO₂ group in polymer chain.

Tab. 3. FT-IR spectra of PAIS(7a-7h).

Polymer code	Wavenumber (cm^{-1})
PAIS-7a	3336(b), 1784(w), 1721(s), 1651(m), 1595(m), 1518(s), 1385(m), 1315(w), 1238(sh), 1154(w), 1106(m), 1101(w), 910(w), 819(m), 735(m), 693(w), 525(w).
PAIS-7b	3409 (b), 1787 (w), 1727(s), 1653(m), 1513(s), 1393(m), 1239(m), 1099(m), 825(m), 732 (w).
PAIS-7c	3320(b), 1774(w), 1725(s), 1656(m), 1594(m), 1511(s), 1394(m), 1318(m), 1242(m), 1159(m), 1118(m), 1014(w), 11(w), 814(m), 730(m), 524(w).
PAIS-7d	3327(b), 1781(w), 1718(s), 1649(m), 1587(m), 1511(s), 1387(m), 1332(w), 1242(m), 1173(w), 1125(sh), 1001(w), 821(s), 725(m), 662(w), 524(w).
PAIS-7e	3253(b), 1786(w), 1711(s), 1657(s), 1521(s), 1385(m), 1385(m), 1269(m), 1100(s), 780(w), 721 (sh).
PAIS-7f	3424(b), 1784(w), 1719(s), 1658(s), 1517(m), 1393(m), 1250(m), 1126(sh), 931(w), 735(m)
PAIS-7g	3320(b), 1785(w), 1718(s), 1649(m), 1553(w), 1511(m), 1394(m), 1235(m), 1118(m), 814(m), 732(m), 669(w), 524(m).
PAIS-7h	3442(b), 1779(w), 1721 (s), 1654(m), 1522(m), 1386(m), 1292(w), 1170(m), 1168(m), 1106(m), 835(w), 728 (m).

¹H NMR Study and elemental analysis

Figure 8 shows the ¹H NMR (500 MHz) spectrum of **PAIS-7a** as a typical of **PAISs**. In the ¹H NMR spectrum of this polymer, appearance of the N-H proton of amide groups around 10.8 ppm indicate amide group in the polymer's chain. The absorption of aromatic protons appeared at a range of 6.6-8.3 ppm. The proton of CH₃ appeared at around 0.0 ppm as a singlet peak.

Fig. 8. ^1H -NMR (500MHz) Spectrum of **PAIS-7a** in DMSO-d_6 at RT.

Elemental analysis data of **PAISs** are listed in Table 4. The chemical structures of these newly synthesized polymers were confirmed by the good agreement of the elemental analysis values with those of the calculated values.

Tab. 4. Elemental Analysis of typical PAISs.

Polymer code	Formula		Elemental Analysis (%)			
			C	H	N	S
PAIS-7a	$(\text{C}_{44}\text{H}_{30}\text{N}_4\text{O}_{10}\text{SSi})_n$	Calcd	63.30	3.62	6.71	3.84
	$(843.88)_n$	Found	62.86	3.98	6.51	3.64
PAIS-7b	$(\text{C}_{44}\text{H}_{31}\text{N}_4\text{O}_9\text{Si})_n$	Calcd	67.08	3.97	7.11	0.00
	$(787.82)_n$	Found	65.92	4.21	6.89	0.15

Solubility and Thermal properties

Because of flexible siloxane group in polymer's main chains these polymers are expected to have good solubility. The solubility of **PAISs** was tested quantitatively in various solvents. All of the **PAISs** are soluble in organic polar aprotic solvents such as DMF, DMAc, NMP and polar protic solvent such as H_2SO_4 at room temperature. The solubility of the polymers in other solvents such as methanol, ethanol, chloroform, dichloromethane and ethylacetate are varied and depends on the structure of diamines segment in polymer chain, although these polymers are partial; soluble in these solvents (Table 5).

The thermal properties of **PAIS-7a**, **PAIS-7c**, **PAIS-7d** and **PAIS-7g** were evaluated by means of TGA/DTG in a nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The temperature of 5% and 10% weight loss together with char yield at $600\text{ }^\circ\text{C}$ have been

calculated by means of thermograms (Table 6). The Figures 9-12 shows the TGA thermograms of these polymers respectively.

Tab. 5. The solubility test result of PAISs^a.

Polymer	NMP	DMAc	DMF	H ₂ SO ₄	EtOAc	CH ₃ OH	CH ₃ CH ₂ OH	CH ₂ Cl ₂	CHCl ₃
PAIS-7a	++	++	++	++	+-	+-	+-	+-	+-
PAIS-7b	++	++	++	++	+-	-	-	+-	+-
PAIS-7c	++	++	++	++	+	+	+	+	+
PAIS-7d	++	++	++	++	-	+-	+-	-	-
PAIS-7e	++	++	++	++	-	+-	+-	-	-
PAIS-7f	++	++	++	++	+	+	+	+	+
PAIS-7g	++	++	++	++	-	+-	-	-	-
PAIS-7h	++	++	++	++	+	+	+	+	+

^a Soluble at room temperature: ++, Soluble at boiling point of solvent: +, Partial soluble: +-, Insoluble: -

These novel polymers are stable up to around 450 °C and show excellent thermal stability. The thermoanalysis data of these polymers are summarized in Table 6. The TGA measurement of the polymers revealed that these new polymers exhibited good thermal stability, especially in term of char yields, in compare with other poly(amide-imide)s contains analogous diacid without siloxane group [33].

Fig. 9. TGA thermograms of **PAIS-7a** under N₂ atmosphere and a heating rate of 10 °C/min.

Fig. 10. TGA thermograms of **PAIS-7c** under N₂ atmosphere and a heating rate of 10 °C/min.

Fig. 11. TGA thermograms of **PAIS-7d** under N₂ atmosphere and a heating rate of 10 °C/min.

DSC spectra of **PAIS-7a**, **PAIS-7c**, **PAIS-7d** and **PAIS-7g** show that T_g of these polymers are in a range of 170-290 °C (Table 6). So in spite of high thermal stability of these new class polymers, they can be processable. The reason of this observation is attributed to the existence softening of siloxane moieties in the polymers main chains.

Fig. 12. TGA thermograms of **PAIS-7g** under N₂ atmosphere and a heating rate of 10 °C/min.

Tab. 6. Thermal behavior of some PAISs prepared using TPP/NMP/Py as a condensing agent.

Polymer Code	T ₅ ^a (°C)	T ₁₀ ^b (°C)	Char Yield(%) ^c	T _g (°C)
PAIS-7a	420	495	76	190
PAIS-7c	460	525	81	255
PAIS-7d	445	525	82	290
PAIS-7g	335	435	76	175

^a Temperature at which 5% weight loss was recorded by TGA at heating rate of 10 °C/min under N₂ atmosphere.

^b Temperature at which 10% weight loss was recorded by TGA at heating rate of 10 °C/min under N₂ atmosphere.

^c Weight percent of the material left undecomposed after TGA at maximum temperature 600 °C in a N₂ atmosphere.

Conclusions

In this study we have successfully synthesized a novel aromatic dicarboxylic acid (**5**), containing siloxane group. A series of novel aromatic **PAISs** were prepared by the direct polycondensation from the compound **5** with various aromatic diamines using TPP/NMP/Py as a condensing agent in the presence of CaCl₂. The main advantages of this polycondensation reaction are that in this procedure we do not need to prepare diacid chloride, therefore saves time and energy. The resulting polymers were obtained in high yields and inherent viscosities.

The results presented herein demonstrate clearly that incorporating of imide heterocyclic rings into the polymer chain as well as combination of wholly aromatic backbone, together with existence of polarizable dimethyl siloxane group (in compare with carbon analogous) in the presence of amide functional groups remarkably enhanced the thermal stability of the new polymers.

Flexible siloxane groups in the main chain of **PAISs** polymers disturbed the strong interchain forces and inherent macromolecular rigidity and cause these novel polymers to be soluble in most polar organic solvents. These polymers show moderate T_g . This property together with high solubility of these polymers makes these polymers processable.

From the chemical point of view the siloxane group imparts the polymer's main chain increased sensibility to hydrolysis that can cause chain breaking. So these polymers are expected to be biodegradable and therefore are classified under environmentally friendly polymers.

Experimental

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. *p*-Aminophenol (**1**) (from Merck), dichlorodimethylsilane (**2**) (from Aldrich), and triphenyl phosphite (from Riedel de Haen) were used as received. 4,4'-Diaminodiphenylsulfone (**6a**) was used as obtained without further purification. Benzidine (**6d**) and 4,4'-diaminodiphenyl methane (**6c**) was purified by recrystallization from ethanol and water, respectively. 4,4'- Diaminodiphenylether (**6b**), *p*-phenylenediamine (**6g**), *m*-phenylenediamine (**6h**) and 2,5-diaminotoluene (**6f**) were purified by sublimation.

Techniques

Proton nuclear magnetic resonance ($^1\text{H-NMR}$, 500 MHz) spectra were recorded in DMSO-d_6 solution using a **Bruker** (Germany) Avance 500 instrument at Sharif University of Technology, Tehran, Iran. FT-IR spectra were recorded on Nicolet Impact 400 spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by using a Cannon-Fenske Routine Viscometer (Germany) at concentration of 0.5 g/dL at 25 °C. Thermal gravimetric analysis (TGA) data for polymers were taken on Perkin Elmer in nitrogen atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Iran Polymer and Petrochemical Research Institute, Tehran, Iran.

Synthesis of bis-(*p*-aminophenoxy) dimethylsilane (**3**)

Bis-(*p*-aminophenoxy) dimethylsilane (**3**) was prepared by some modification of reported procedure [29].

A mixture of *p*-aminophenol (**1**) (2.18 g, 0.02 mol), anhydrous triethylamine (3 mL), and 40 mL toluene in a 100 mL three-necked flask was stirred with magnetic stirrer for 1 h at room temperature. The reaction was cooled with an ice bath and purged with nitrogen atmosphere, and then dichlorodimethylsilane (**2**) (1.2 mL, 0.01mol) was

added dropwise. This mixture was stirred for 3 h in ice bath and for 24 h in gentle reflux condition. After cooling the reaction mixture was filtered and solvent was removed. The crude product was then dissolved in chloroform and filtered. The solvent of the filtrate was removed and the residue was finally dried in vacuum at 50 °C. The final product was viscous brown oil. Yield = 2.24 g, 81%.

FT-IR: 3400(br), 2950(s), 1730(s), 1620(w), 1510(s), 1460(m), 1390(w), 1260(s), 1125(m), 1077(s), 933(s), 809(s), 768(s), 535(w).

Synthesis of N,N'-bis-(4-trimellitimidophenoxy) dimethylsilane (5)

In a round bottom flask equipped with a condenser and magnetic stirrer, bis(*p*-aminophenoxy)dimethyl silane (**3**) (2.47g, 10 mmol) and trimellitic anhydride (**4**) (3.84g, 20 mmol) were suspended in glacial acetic acid (50mL) and refluxed for 15 h. The solvent was removed under reduced pressure and the residue was poured in 50 mL of a cold mixture of water and 5 mL concentrated hydrochloric acid. The white precipitate was formed, filtered off and dried under vacuum to give 5.72 g (yield 92%) of diacid **5**.

FT-IR (KBr): 2500-3500 (br), 1782 (w), 1705 (s), 1608 (m), 1510 (s), 1454 (m), 1390 (s), 1211 (s,sh), 1176 (m), 1092 (s,sh), 1016 (w), 932 (m), 828 (m,sh), 723 (m,sh), 654 (w), 598 (w) cm⁻¹.

¹H NMR (500 MHz, DMSO-*d*₆): δ= 0.0 (S,3H), 6.8 (d,2H), 7.2 (d,2H), 8(d, 1H), 8.2 (s,1H), 8.3 (d,1H).13.8 (s,1H) ppm.

¹³C NMR (500 MHz, DMSO-*d*₆): δ= 1, 116.3, 123.5, 124.1, 124.4, 129.5, 132.9, 135.7, 136.2, 137.2, 158.2, 166.7, 167.4, 167.5 ppm.

Elemental analysis: (C₃₂H₂₂N₂O₁₀Si) (622.61): calcd. C= 61.73%, H= 3.56%, N= 4.50%; Found: C= 61.28%, H= 3.65%, N= 4.42%.

Polymer syntheses

Polymerization reactions were carried out using triphenyl phosphite (TPP) and pyridine (Py) as a condensing agent in the presence of calcium chloride and *N*-methyl-2-pyrrolidone (NMP) as a solvent. Different parameters such as reaction time, reaction temperature, NMP/Py ratio and amount of CaCl₂ have influence on polymers yield and inherent viscosities. In a typical procedure for preparation of PAIS-7a, a mixture of 0.2000 g (3×10⁻⁴ mol) of dicarboxylic acid **5**, 0.0744 g (3×10⁻⁴ mol) of diamine **6a**, 0.14 mL of TPP, 0.14 mL of pyridine, 0.0714 g of calcium chloride and 0.46 mL of NMP was heated at 130 °C for 6 h. After cooling, the viscous reaction mixture was poured into 30 mL of methanol with constant stirring. The precipitate was collected on a filter and washed thoroughly with methanol and water. The solid was dried under vacuum to give 0.2714 g of PAIS-7a (97% yield). The inherent viscosity of the resulting polyamide measured at a concentration of 0.5 g/dL at 25 °C in DMF was 0.51 dLg⁻¹,

FT-IR (KBr): 3336 (b), 1784 (w), 1721 (s), 1651 (m), 1595 (m), 1518 (s), 1385 (m), 1315 (w), 1238 (sh), 1154 (w), 1106 (m), 101 (w), 910 (w), 819 (m), 735 (m), 693 (w), 525 (w) cm⁻¹.

All of the polymers were prepared using a similar procedure.

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