

Polyamides Obtained by Direct Polycondensation of 4-[4-[9-[4-(4-Aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline with Dicarboxylic Acids Based on a Diphenyl-Silane Moiety

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ABSTRACT: Polyamides (PAs) containing fluorene, ether, and diphenyl-silane moieties in the repeating unit were synthesized in > 85% yield by direct polycondensation between a diamine and four dicarboxylic acids. Alternatively, one PA was synthesized from an acid dichloride. The diamine 4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline (**3**) was obtained from the corresponding dinitro compound, which was synthesized by nucleophilic aromatic halogen displacement from *p*-chloronitrobenzene and 9,9-bis(4-hydroxy-3-methyl-phenyl)fluorene (**1**). Monomers and polymers were characterized by FTIR and ¹H, ¹³C, and ²⁹Si-NMR spectroscopy and the results were in agreement with the proposed structures. PAs showed inherent viscos-

ity values between 0.14 and 0.43 dL/g, indicative of low molecular weight species, probably of oligomeric nature. The glass transition temperature (T_g) values were observed in the 188–211°C range by DSC analysis. Thermal decomposition temperature (TDT_{10%}) values were above 400°C due to the presence of the aromatic rings in the diamine. All PAs showed good transparency in the visible region (>88% at 400 nm) due to the incorporation of the fluorene moiety. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2381–2389, 2011

Key words: polyamides; fluorine; silicon-containing polymers; direct polycondensation; glass transition temperature; thermal stability

INTRODUCTION

It is known that polyamides (PAs) have high thermal stability and excellent mechanical properties, but they are very difficult to process due to their poor solubility in organic solvents and high glass transition temperature.¹

Great efforts have been made to improve solubility parameters of these polymers, while maintaining their optimal, thermal, and chemical resistance. Some strategies include introducing specific substituents on the phenyl rings from the monomer structure; using monomers containing flexible functional groups to separate the phenyl rings (e.g., esters or ethers); or using heterocyclic monomers.² It has been demonstrated that incorporation of both an ether linkage and a cyclic side cardo group such as a fluorene unit into the macromolecular backbone results

in good thermal stability, high T_g and excellent solubility in organic solvents.^{3–6}

Several groups have reported that PAs containing quaternary silicon atoms, specially dialkyl-diphenyl-silane moiety (-Ph-SiR₁R₂-Ph-), shows improved solubility in common organic solvents, facilitating their handling and work-up.^{7–18} Additionally, the introduction of C–Si bonds, maintains or increases the thermal stability of PA due to the ionic character of the C–Si bond. In fact, although the silicon atom is less electronegative than carbon atom the bond energies of C–C and C–Si are similar.¹⁰ Thus, an important number of PAs containing silicon atoms in their structure have been synthesized showing good thermal stability and adequate solubility in polar amide solvents.

In this work, we describe the synthesis and characterization of PAs from an aromatic diamine having fluorene and oxyarene units in its structure and four different dicarboxylic acids bearing a diphenyl-silane unit. We use two different synthetic methods to obtain these PA: the procedure developed by Yamazaki et al.¹⁹ that employs dicarboxylic acid directly as the monomer and the route employing an acid dichloride as monomer.

All polymers were characterized by their inherent viscosity, optical transparency, FTIR, ¹H, ¹³C, and

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^{29}Si -NMR spectra. Thermal properties of polymers (glass transition temperature and thermal stability) were determined and the results related to the proposed structures.

EXPERIMENTAL

Materials

Anhydrous *N,N*-dimethylformamide (DMF), anhydrous K_2CO_3 , 4-chloronitrobenzene, hydrazine monohydrate, Pd/C activated (10%), triphenyl phosphite (TPP), anhydrous *N*-methyl-2-pyrrolidone (NMP), and pyridine were obtained from Aldrich Chemical (Milwaukee, WI). Calcium chloride anhydrous powder was purchased from Merck (Darmstadt, Germany) and 4,4'-(9H-fluorene-9,9-diyl)bis(2-methylphenol) (**1**) was obtained from TCI (Tokyo, Japan). All other reagents and solvents were purchased commercially as analytical-grade and used without further purification.

Instrumentation

The IR spectra (KBr pellets) were recorded on a Perkin-Elmer (Fremont CA) 1310 spectrophotometer over the range of 4000–450 cm^{-1} . ^1H , ^{13}C , and ^{29}Si -NMR spectra were carried out on a 400 MHz instrument (Bruker AC-200) using DMSO-d_6 or CDCl_3 as solvent and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25°C ($c = 0.3$ g/dL). T_g values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (20°C/min under N_2 flow). Thermogravimetric analyses were carried out in a Mettler (Switzerland) TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. Samples of 6–10 mg were placed in a platinum sample holder and the thermogravimetric measurements were carried out between 25 and 900°C with a heating rate of 20°C/min under N_2 flow. Elemental analyses were made on a Fisons EA 1108-CHNS-O equipment. The UV-visible optical transmission spectra were obtained on a UV-3101PC UV-Vis-NIR scanning spectrophotometer (Shimadzu, Japan) at room temperature using solutions of NMP ($c = 5.0$ g/L).

Monomer synthesis

9,9-Bis(3-methyl-4-(4-nitrophenoxy)phenyl)-9H-fluorene (**2**) (Scheme 1)

A mixture of 3.00 g (7.92 mmol) of 4,4'-(9H-fluorene-9,9-diyl)bis(2-methylphenol) (**1**), 2.19 g (15.8 mmol) of anhydrous K_2CO_3 , toluene (20 mL) and anhydrous DMF (30 mL) was placed into a 100-mL flask

adapted with a Dean-Stark trap and reflux to remove water. After complete removal of water, toluene was distilled from the system and 2.49 g (15.8 mmol) of *p*-chloronitrobenzene dissolved in 5 mL of anhydrous DMF were added. The mixture was refluxed for 16 h. On cooling, the mixture was poured into 600 mL of an ethanol-water solution (1 : 1) and a yellow solid was collected by filtration. This solid was washed with hot ethanol, then water, and dried at 120°C. The crude product was recrystallized from a DMF-ethanol mixture (1 : 1 vol/vol) to obtain 4.32 g (88%) of a slightly yellow pure solid.

M.p.: 331–333°C. IR (KBr) (cm^{-1}): 3104, 3073 (C–H arom.), 2924, 2852 (C–Haliph.), 1610, 1589 (C=C arom.); 1510, 1339 (NO_2); 1253 (C–O–C); 851 (arom. *p*-subst.); 748 (arom. *o*-subst.). Elem. Anal. Calcd. for $\text{C}_{39}\text{H}_{28}\text{N}_2\text{O}_6$; (620.65): C: 75.47%; H: 4.54%; N: 4.51%. Found: C: 76.20%; H: 4.90%; N: 4.72%.

4-[4-[9-[4-(4-Aminophenoxy)-3-methyl-phenyl]fluorene-9-yl]-2-methyl-phenoxy]aniline (**3**) (Scheme 1)

A mixture of 4.00 g (6.44 mmol) of (**2**), 0.53 g of palladium on activated carbon at 10% and 40 mL of ethanol was placed into a 150-mL three-necked flask fitted with magnetic stirrer, condenser, and a dropping funnel. On reflux 38 mL of hydrazine monohydrate were added dropwise over a period of 1.5 h and the mixture was refluxed for 24 h. After that period the still hot mixture was filtered and the filtrate cooled to room temperature. A white solid precipitated was filtered, dried, and recrystallized in ethanol yielding 2.42 g (67%) of pure product.

M.p.: 124–126°C. IR (KBr) (cm^{-1}): 3439, 3361 (NH_2), 3037 (C–H arom.), 2922, 2853 (CH_3), 1619 (*N*–H flexion), 1508, 1491, 1446 (C=C arom.), 1243 (C–O–C), 824 (arom. *p*-subst.); 743 (arom. *o*-subst.). ^1H -NMR (CDCl_3) δ (ppm): 7.73 (d, $J = 7.5$ Hz, 2H_i), 7.40 (d, $J = 7.6$ Hz, 2H_j), 7.32 (t, $J = 7.4$ Hz, 2H_h), 7.24 (t, $J = 7.4$ Hz, 2H_g), 7.00 (d, $J = 1.5$ Hz, 2H_c), 6.91 (dd, $J = 8.6; 1.8$ Hz, 2H_e), 6.74 (d, $J = 8.6$ Hz, 4H_b), 6.57 (dd, $J = 8.6; 8.6$ Hz, $4\text{H}_a; 2\text{H}_d$), 3.45 (s, 4H_k), 2.14 (s, 6H_l) (Fig. 1). ^{13}C -NMR (CDCl_3) δ (ppm): 155.11 (C5), 151.68 (C4), 149.24 (C16), 142.03 (C11), 139.93 (C8), 139.87 (C1), 130.66 (C7), 127.89 (C6), 127.61 (C12), 127.30 (C13), 126.64 (C14), 126.17 (C15), 120.07 (C9), 120.00 (C3), 116.48 (C10), 116.17 (C2), 64.37 (C*), 16.44 (C17) (Fig. 2). Elem. Anal. Calcd. for $\text{C}_{39}\text{H}_{32}\text{N}_2\text{O}_2$; (560.68): C: 83.54%; H: 5.75%; N: 5.00%. Found: C: 82.88%; H: 6.11%; N: 5.34%.

The synthesis and characterization of the dicarboxylic acids used: bis(4-carboxyphenyl)ethylmethylsilane (**4**), bis(4-carboxyphenyl)dimethylsilane,⁵ bis(4-carboxyphenyl)methylphenylsilane,⁶ and bis(4-carboxyphenyl)diphenylsilane⁷ have been already reported.^{14,20–23} Briefly, *p*-bromotoluene was reacted with lithium metal followed by addition of the

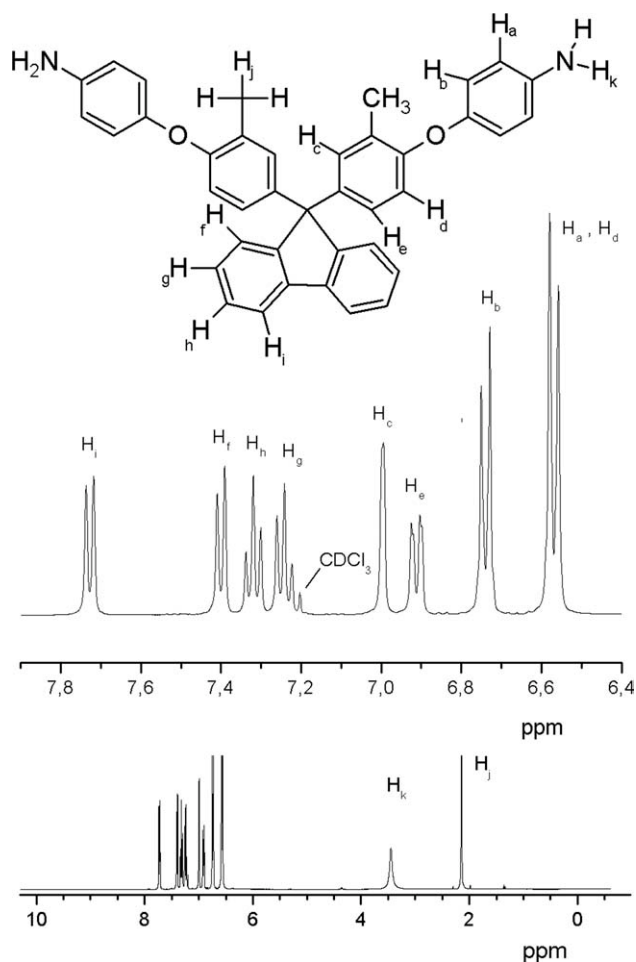


Figure 1 $^1\text{H-NMR}$ spectrum of diamine (3) in CDCl_3 .

respective R_1R_2 dichlorosilane to obtain the di(*p*-tolyl) derivatives, which were subsequently oxidized to the corresponding dicarboxylic acids (Scheme 2).

Bis(4-chlorocarbonylphenyl)diphenylsilane⁸ was synthesized by reaction of **7** with thionyl chloride, as previously described in the literature.^{22,24}

Polymer synthesis

Synthesis of polyamides by direct polycondensation (Scheme 3)

A typical polymerization procedure for the synthesis of PAs was as follows. A mixture of 0.325 g (0.58 mmol, $c = 0.38$ mol/L) of (3), 0.250 g (0.58 mmol) of (4), 0.142 g of CaCl_2 , 0.425 mL of TPP, 0.38 mL of pyridine, and 0.71 mL of NMP was heated with stirring at 110–120°C for 3 h. The solution became gradually viscous. The viscous mixture was poured in 300 mL of methanol with stirring. A fibrous white precipitate appeared and was filtered, washed thoroughly with methanol and dried. The product was dissolved in DMSO, reprecipitated in methanol, filtered, and dried. Yield: 0.5 g (86%).

PA-EM

Yield: 86%. $\eta_{\text{inh}} = 0.14$ dL/g (in DMSO at 25°C, $c = 0.3$ g/dL). IR (KBr, cm^{-1}): 3417 (NH), 3063 (C–H arom.), 2954, 2920 (C–H aliph.), 1654 (C=O), 1601, 1506 (C=C arom.), 1447 (Si–Ph), 1248 (Si–aliph.), 1216 (C–O–C), 828 (arom. *p*-subst.), 743 (arom. *mono*-subst.). $^1\text{H-NMR}$ (DMSO- d_6) (δ) (ppm): 0.56 (s,3H,Si–CH₃), 0.92 (t,3H,CH₂CH₃), 1.08 (q,2H,CH₂CH₃); 2.48 (s,6H,Ph–CH₃); 7.88–6.69 (m,30H, arom.); 10.25 (s,2H,NH). $^{13}\text{C-NMR}$ (DMSO- d_6) (δ) (ppm): –5.83 (Si–CH₃), 4.56 (CH₂CH₃), 7.11 (CH₂CH₃), 16.43 (CH₃), 64.36 (C*), 116.7–155.1 (C arom.); 165.8 (C=O). $^{29}\text{Si-NMR}$ (DMSO- d_6) (δ) (ppm): –5.06. Elem. Anal. Calcd. for $[\text{C}_{56}\text{H}_{46}\text{N}_2\text{O}_4\text{Si}]_n$; (838.67)_n: C: 80.19%; H: 5.48%; N: 3.35%. Found: C: 79.92%; H: 5.05%; N: 3.19%.

PA-MM

Yield: 95%. $\eta_{\text{inh}} = 0.21$ dL/g (in DMSO at 25°C, $c = 0.3$ g/dL). IR (KBr, cm^{-1}): 3417 (NH), 3062 (C–H arom.), 2953, 2920 (C–H aliph.), 1659 (C=O), 1602, 1506 (C=C arom.), 1447 (Si–Ph), 1248 (Si–aliph.), 1215 (C–O–C), 814 (arom. *p*-subst.), 744 (arom. *mono*-subst.). $^1\text{H-NMR}$ (DMSO- d_6) (δ) (ppm): 0.57 (s,6H,Si–CH₃), 2.49 (s,6H,Ph–CH₃); 7.93–6.64 (m,30H, arom.); 10.23 (s,2H,NH). $^{13}\text{C-NMR}$ (DMSO- d_6) (δ) (ppm): –3.46 (Si–CH₃), 15.23 (CH₃), 62.88 (C*), 116.3–155.2 (C arom.); 165.7 (C=O). $^{29}\text{Si-NMR}$ (DMSO- d_6) (δ) (ppm): –7.20. Elem. Anal. Calcd. for $[\text{C}_{55}\text{H}_{44}\text{N}_2\text{O}_4\text{Si}]_n$; (824.66)_n: C: 80.10%; H: 5.33%; N: 3.40%. Found: C: 80.05%; H: 5.17%; N: 3.23%.

PA-MP

Yield: 95%. $\eta_{\text{inh}} = 0.20$ dL/g (in DMSO at 25°C, $c = 0.3$ g/dL). IR (KBr, cm^{-1}): 3423 (NH), 3065 (C–H arom.), 2955, 2919 (C–H aliph.), 1670 (C=O), 1602, 1506 (C=C arom.), 1447, 1428 (Si–Ph), 1248 (Si–aliph.), 1215 (C–O–C), 828 (arom. *p*-subst), 742 (arom. *mono*-subst.). $^1\text{H-NMR}$ (DMSO- d_6) (δ) (ppm): 0.87 (s,3H,Si–CH₃), 2.48 (s,6H,Ph–CH₃); 7.90–6.70 (m,35H,arom.); 10.28 (s,2H,NH). $^{13}\text{C-NMR}$ (DMSO- d_6) (δ) (ppm): –3.63 (Si–CH₃), 16.89 (CH₃), 64.47 (C*), 118.9–154.0 (C arom.); 165.7 (C=O). $^{29}\text{Si-NMR}$ (DMSO- d_6) (δ) (ppm): –10.86. Elem. Anal. Calcd. for $[\text{C}_{60}\text{H}_{46}\text{N}_2\text{O}_4\text{Si}]_n$; (886.71)_n: C: 81.27%; H: 5.19%; N: 3.16%. Found: C: 80.98%; H: 4.99%; N: 3.00%.

PA-PP

Yield: 86%. $\eta_{\text{inh}} = 0.23$ dL/g (in DMSO at 25°C, $c = 0.3$ g/dL). IR (KBr, cm^{-1}): 3423 (NH), 3067 (C–H arom.), 2919 (CH₃), 1663 (C=O), 1603, 1506 (C=C arom.), 1447, 1428 (Si–Ph), 1216 (C–O–C), 828 (arom. *p*-subst), 744 (arom. *mono*-subst.). $^1\text{H-NMR}$

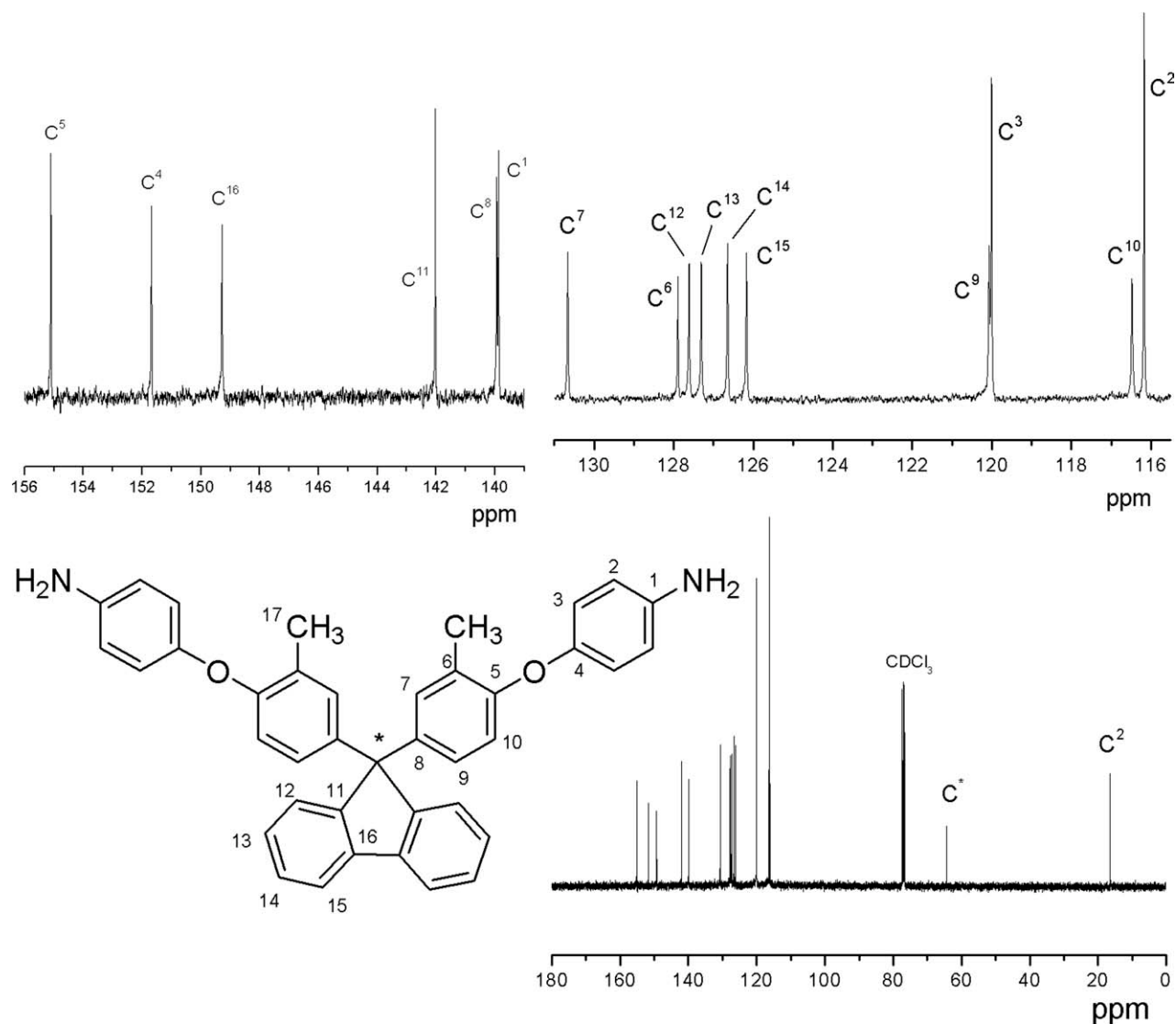


Figure 2 ^{13}C -NMR spectrum of diamine (3) in CDCl_3 .

(DMSO- d_6) (δ) (ppm): 2.49 (s,6H,Ph- CH_3); 7.96–6.70 (m,40H, arom.); 10.37 (s,2H,NH). ^{13}C -NMR (DMSO- d_6) (δ) (ppm): 16.07 (CH_3), 63.92 (C^*), 118.4–153.5 (C arom.); 165.3 ($\text{C}=\text{O}$). ^{29}Si -NMR (DMSO- d_6) (δ) (ppm): –14.81. Elem. Anal. Calcd. for $[\text{C}_{65}\text{H}_{48}\text{N}_2\text{O}_4\text{Si}]_n$; (948.76) $_n$: C: 82.28%; H: 5.06%; N: 2.95%. Found: C: 81.03%; H: 4.89%; N: 2.67%.

Synthesis of PA-PP from acid dichloride

A mixture of 0.325 g (0.58 mmol) of (3), 0.1 mL of pyridine and 14.5 mL of DMAc was cooled to -10°C followed by addition of 0.267 g (0.58 mmol) of (8) in four portions every 15 min, keeping the temperature at -10°C . When the addition was complete the mixture was left stirring for 18 h at room temperature. At this time, the mixture was poured into 300 mL of methanol with stirring. The white solid precipitated was filtered, washed thoroughly with methanol and

dried. The product was dissolved in DMSO, reprecipitated in methanol, filtered, and dried.

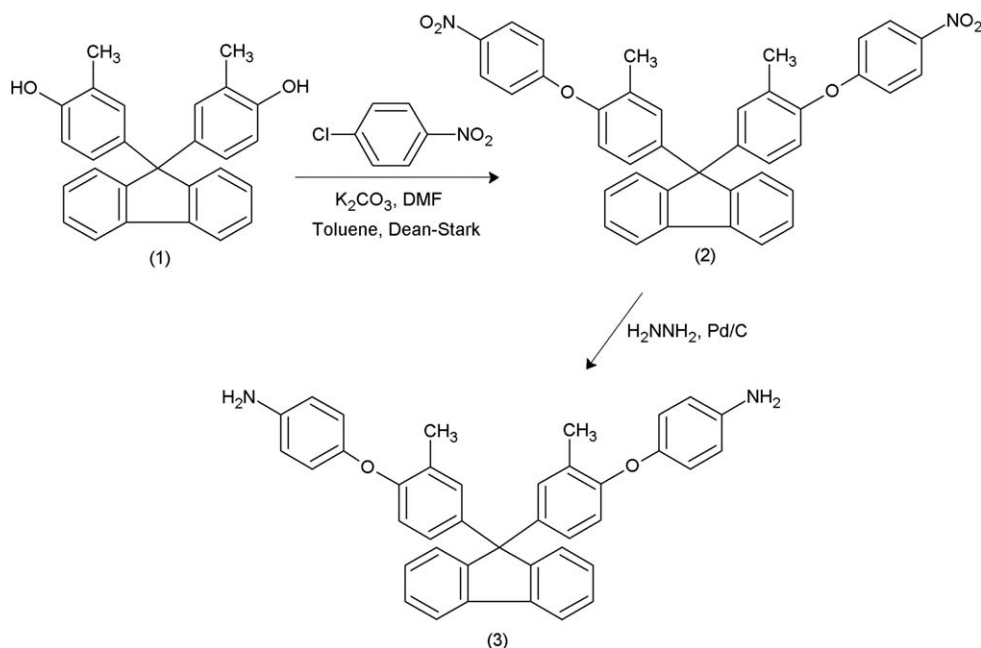
PA-PPII

Yield: 37%. $\eta_{\text{inh}} = 0.52$ dL/g (in DmsO at 25°C , $c = 0.3$ g/dL).

RESULTS AND DISCUSSION

Synthesis and characterization of the monomer

4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline (3) was prepared in two steps according to Scheme 1. First, dinitro compound (2) was synthesized by nucleophilic chlorodisplacement reaction of 4,4'-(9H-fluorene-9,9-diyl)bis(2-methylphenol) (1) and two equivalents of *p*-chloronitrobenzene in the presence of anhydrous potassium carbonate in DMF. Then, the intermediate



Scheme 1 Synthesis of the 4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline (3).

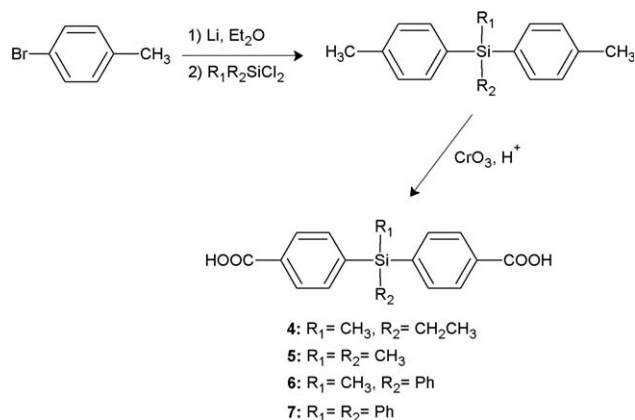
dinitro compound was reduced to (3) with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol.

The structure of the dinitro compound (2) was confirmed by FTIR spectroscopy and elemental analysis only. NMR spectroscopy was not used due to the low solubility of this compound in deuterated solvents (acetone- d_6 , CDCl_3 and $\text{DMSO-}d_6$). The structure of diamine (3) was confirmed by elemental analysis, FTIR and NMR spectroscopy.

Figure 3 shows the FTIR spectra of both compounds. Characteristic bands for $\text{N}=\text{O}$ stretch at 1510 and 1339 cm^{-1} confirmed the formation of dinitro compound (2), as well as the appearance of a signal at 1253 cm^{-1} corresponding to $\text{C}-\text{O}-\text{C}$ stretch. After the reduction, the FTIR spectrum showed the disappearance of the nitro group absorption bands

and the appearance of the characteristic bands of $\text{N}-\text{H}$ stretch (3361 , 3439 cm^{-1}) and $\text{N}-\text{H}$ flexion (1619 cm^{-1}).

Figures 1 and 2 illustrate the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the diamine (3) in CDCl_3 solution. In the $^1\text{H-NMR}$ spectrum, the protons of methyl and amino groups are clearly distinguishable as singlets at 2.14 and 3.45 ppm , respectively. The H_i and H_f protons exhibit classic doublets as they are directly coupled with the H_h and H_g protons, respectively, while H_h and H_g show a triplet due to the additional coupling between them. The H_c proton appears as a doublet due to a long-range coupling



Scheme 2 General synthetic method to obtain the silicon-containing dicarboxylic acids.

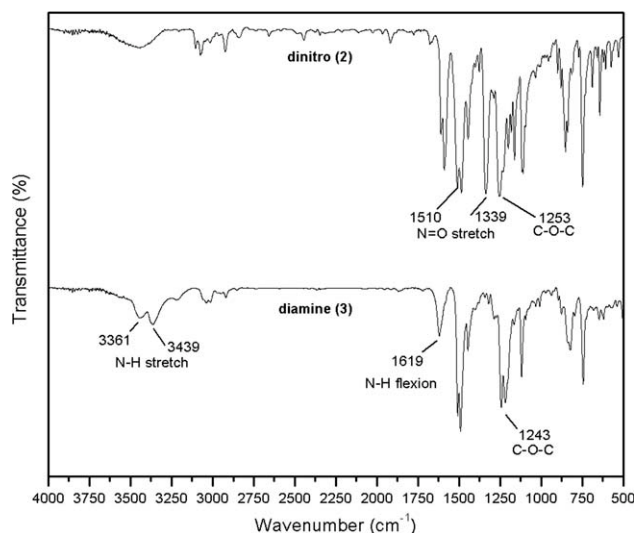
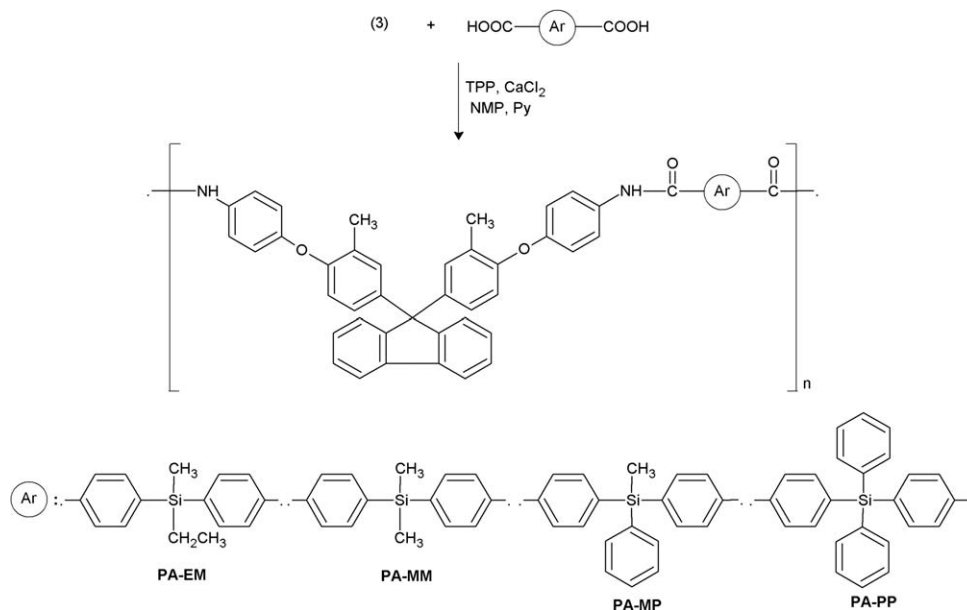


Figure 3 FTIR spectra of the dinitro (2) and diamine (3) compounds.



Scheme 3 Synthesis of polyamides PA-EM, PA-MM, PA-MP, and PA-PP.

($J = 1.5$ Hz) with the H_e proton. H_a and H_d protons are overlapped. In the ^{13}C -NMR spectrum (Fig. 2), the C(8) and C(1) atoms are partially overlapped on approximately 140 ppm, as well as carbons C(9) and C(3) at 120 ppm, whereas the rest of the carbons show good resolution.

Dicarboxylic acids (4–7) and acid dichloride (8) were prepared in high yields as previously reported.^{14,20–24} The structure of monomers was elucidated by FTIR and NMR spectroscopy.

Synthesis and characterization of polymers

Polyamides (PA-EM, PA-MM, PA-MP, and PA-PP) were prepared by phosphorylation polyamidation as developed by Yamazaki et al.¹⁹ Briefly, this method involves direct polycondensation of a dicarboxylic acid and a diamine, using TPP/pyridine as condensing agents, in calcium chloride-containing NMP as solvent.

All direct polymerizations were carried out at 120°C during 3 h. Reactions proceeded homogeneously to produce solutions of high viscosity (Scheme 3) from which the polymers were obtained in high yield (86–95%) (run 1–4, Table I).

PA-PPII was prepared from bis(4-chlorocarbonylphenyl)diphenylsilane (8) and diamine (3) by a solution polycondensation process (run 6, Table I) with DMAc as solvent (Scheme 4).

Results of elemental analysis for PAs are in good agreement with the proposed structures.

All PAs FTIR spectra are illustrated in Figure 4. The amidic linkage relates to a wide stretching band of the $N-H$ group between 3417 and 3423 cm^{-1} and the absorption at 1654 and 1670 cm^{-1} corresponding to $C=O$ stretching. The $\text{Si}-\text{C}$ aliph. and $\text{Si}-\text{C}$ arom. bonds appear at 1248 cm^{-1} and 1428–1447 cm^{-1} , respectively.

All PAs ^1H -NMR spectra (Fig. 5) show the expected $N-H$ singlet between 10.23 and 10.37 ppm.

TABLE I
Yields, Inherent Viscosity, Solubility and Optical Behavior of PAs

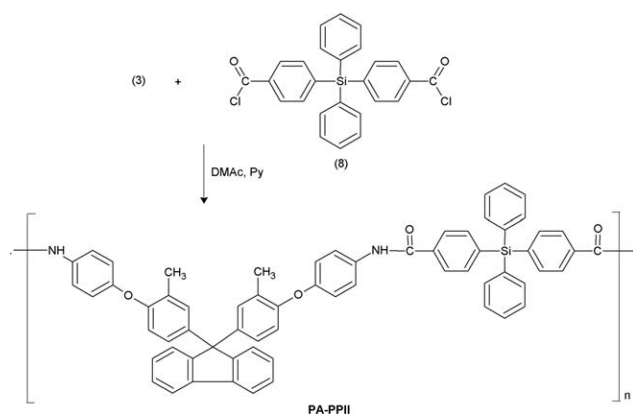
Run	Polyamide	Yield (%)	η_{inh}^a (dL/g)	$\lambda_{\text{cutoff}}^b$ (nm)	Solvent ^c					
					DMF	DMSO	DMAc	NMP	<i>m</i> -Cresol	THF
1	PA-EM	86	0.14	331	+	+	+	+	+	±
2	PA-MM	95	0.21	333	+	+	+	+	+	±
3	PA-MP	95	0.20	331	+	+	+	+	+	±
4	PA-PP	86	0.23	334	+	+	+	+	+	±
5	PA-PP ^d	96	0.43	n.d.	+	+	+	+	+	±
6	PA-PPII	37	0.52	n.d.	+	+	+	+	+	±

^a Values were taken from DMSO solutions ($c = 0.3$ g/dL) at 25°C.

^b Obtained from NMP solution (5 g/L) at room temperature. n.d.= Non determined.

^c Solubility: +, soluble at room temperature; ±, partially soluble.

^d Polymerization developed using a diamine concentration of 0.13 mol/L.



Scheme 4 Synthesis of polyamide PA-PPII.

The peak at approximately 2.48 ppm is assigned to the methyl protons of the fluorene unit. Polyamides PA-EM, PA-MM, and PA-MP show peaks at higher field corresponding to protons of the methyl and methylene groups directly attached to the silicon atom. In the ^{13}C -NMR spectra, the peaks corresponding to the C=O amidic group appear between 165.3 and 165.8 ppm (Polymer Synthesis section). It is also possible to see the effect of silicon, which modifies the chemical shift of the carbon atoms directly bonded to it, moving them to high field.

Figure 6 shows the ^{29}Si -NMR spectra for all PAs. It can be observed that replacement of an aliphatic group by an aromatic ring shifts the silicon signal to a higher field. This is due to the high electronic density of the silicon atom aromatically substituted.²⁵

Properties of polyamides

Table I shows the yields, inherent viscosity (η_{inh}), cutoff wavelength, and solubility data obtained for all PAs. Because of the differences in the experimen-

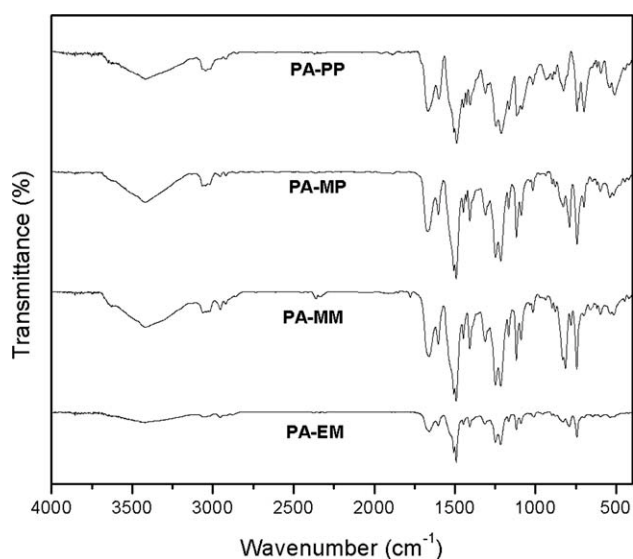


Figure 4 FTIR spectra of PAs.

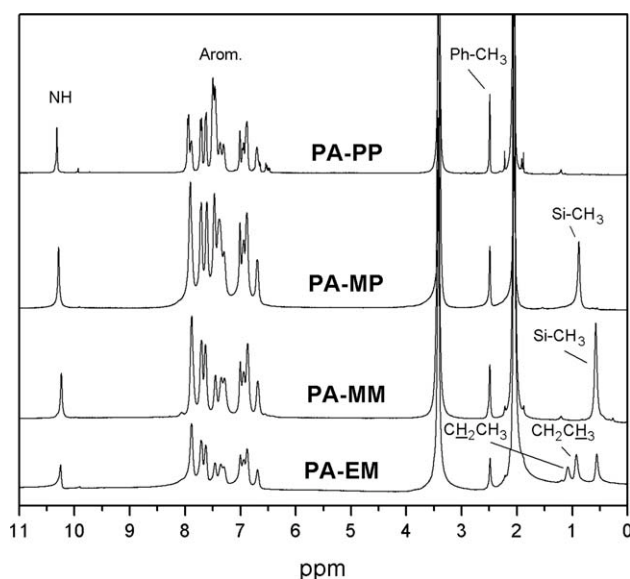


Figure 5 ^1H -NMR spectra of PAs in DMSO-d_6 .

tal conditions of each method, it is not possible to directly compare the yields obtained by direct polymerization with those obtained through the use of the acid dichloride. The Yamazaki's procedure needs 3 h of reaction to 120°C, while the "acid dichloride method" takes 1 h at -10°C plus 18 h at room temperature.

According to Table I, the η_{inh} values are low and similar, except for the case of PA-EM, suggesting the presence of low-molecular weight oligomeric chains. A possible explanation for this could be the limited growth of the chain due to the high viscosity of the polymeric system observed after a few minutes of reaction. To lower the viscosity of the reaction medium, a polymerization was carried out using a

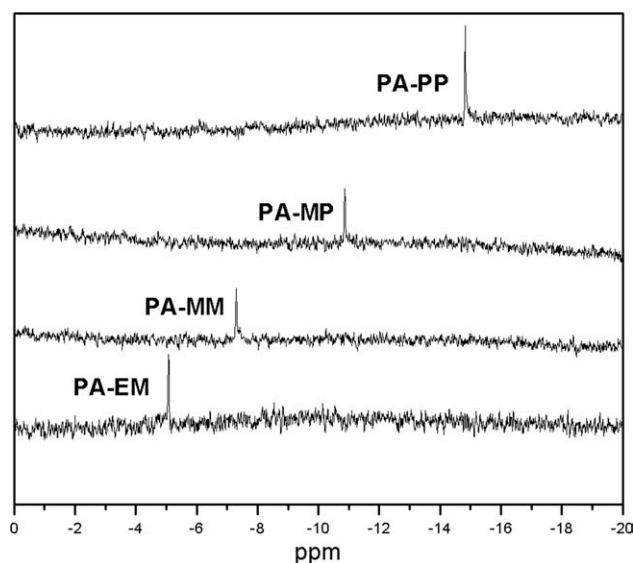


Figure 6 ^{29}Si -NMR spectra of PAs (DMSO-d_6).

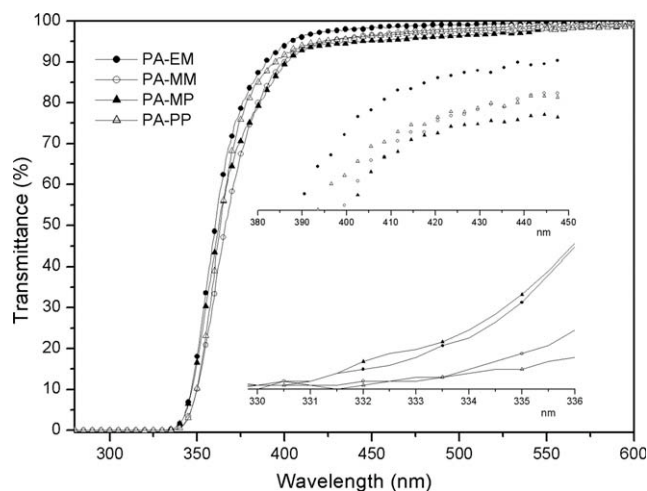


Figure 7 UV-vis optical transmission spectra of PAs.

more diluted system ($C_{\text{diamine}} = 0.13$ mol/L). Also, the concentration of pyridine in the pyridine and NMP mixture was modified from 38 to 42% to obtain higher viscosity values. (run 5, Table I). The results showed that both the yield and inherent viscosity increased significantly, demonstrating that the modification of the viscosity of the polymeric system strongly affects these parameters.

The high η_{inh} value obtained for PA-PPII, relative to PA-PP, reflects the impact of the polymerization method used over this property. In the Yamazaki's method, a great number of activated species are formed from dicarboxylic acid units. These react rapidly with the diamine leading to obtain high yields but low molecular weight chain after short reaction time. On the other hand, when the acid dichloride was used as monomer, the better solubility of the growing polymer allows longer polymeric chains to form. This fact results in higher intrinsic viscosity value.

The solubility of PAs was qualitatively studied. It was found that at room temperature, PAs are soluble in all solvents used except THF, in which the polymers are only partially soluble. The higher solubility of these polymers compared with conventional aromatic polyamides could be attributed to the introduction of oxyether flexible linkages, the fluorene unit and to the presence of silicon in their structure.

UV-vis optical transmission spectra (Fig. 7) showed that the incorporation of the fluorene moiety endows PAs with high transparency. The spectra shapes are similar and the transmittances are higher than 85% at 400 nm and over 90% above 410 nm. This could be associated with the low molecular packing of the chains due the presence of the bulky fluorene structure which increases the free volume of the polymer. Cutoff wavelength values for PAs are very similar (331–334 nm) and show no influence of the different structural details of the repetitive unit in the polymeric chain.

TABLE II
Thermal Properties of PAs

Polyamide	TDT _{10%} ^a (°C)	Char Yield ^b (%)	T _g ^c (°C)
PA-EM	428	39	205
PA-MM	465	45	198
PA-MP	465	40	188
PA-PP	428	36	211
PA-PP ^d	431	38	210
PA-PPII	426	41	211

^a Thermal decomposition temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min in nitrogen.

^b Residual weight (%) when heated to 900°C at scan rate of 20°C/min in nitrogen.

^c Glass transition temperature taken from the second heating scan (20°C/min in nitrogen).

^d Polymerization developed using a diamine concentration of 0.13 mol/L.

Thermal analysis

Thermal properties of PAs derivatives were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. The results are summarized in Table II. TGA curves (Fig. 8) indicate that PAs begin to decompose over 350°C exhibiting good thermal stability as judged by the thermal decomposition temperature at 10% weight loss (TDT_{10%}) between 428 and 465°C. PA-EM presents the lower thermal stability showing 8% weight loss at 350°C approximately. 34–51% weight was retained even at 900°C, corresponding probably to silicon oxide. Apparently, the higher content of aromatic rings in PA-MP and PA-PP did not make a strong difference in the thermal decomposition values obtained. Thus, PA-EM and PA-PP show a TDT_{10%} of 428°C, while PA-MM and PA-MP a TDT_{10%} of 465°C. PA-PP obtained in dilute

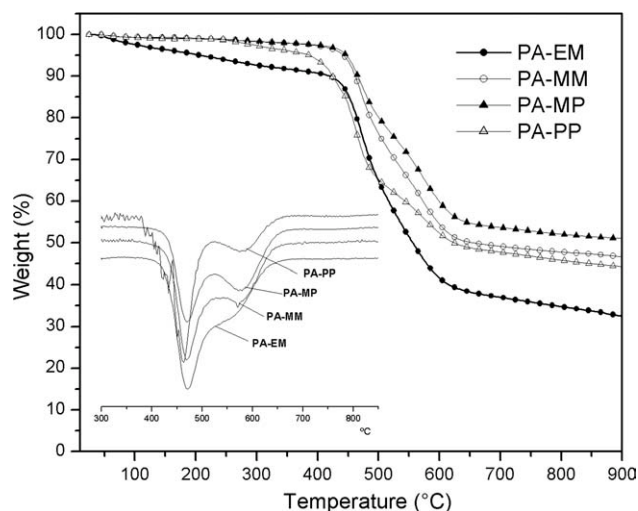


Figure 8 TGA and differential curves for PAs in nitrogen atmosphere.

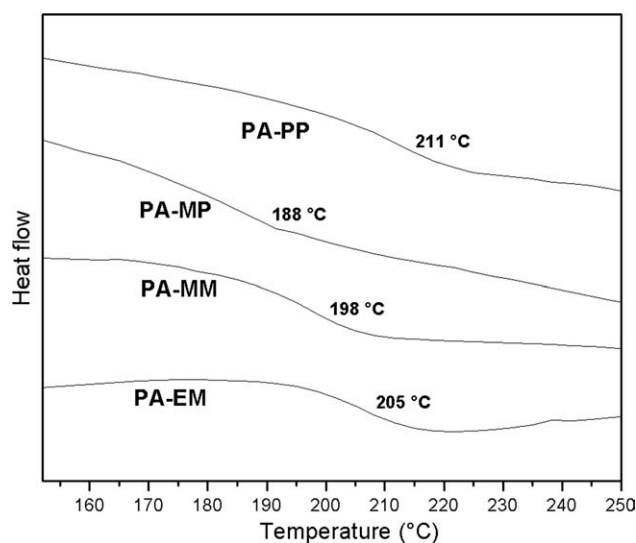


Figure 9 DSC traces of PAs (second run heating between -100 and 400°C at $20^{\circ}\text{C}/\text{min}$, in nitrogen).

condition (run 5, Table I) and PA-PPII showed similar thermal properties to PA-PP (Table II). This fact indicates that the experimental polymerization conditions do not significantly affected the T_g and TDT parameters.

PAs showed two principal decomposition peaks in the TGA differential curves. According with the bond enthalpies,²⁶ the first peak should correspond to the C–N amidic bond cleavage, while the second peak, at higher temperature, could be associated to the C–O bond cleavage.

T_g values were obtained at $20^{\circ}\text{C}/\text{min}$ under N_2 flow from a two-scan experiment. The first scan was up to 400°C and then rapidly cooled down to -100°C to eliminate solvent traces and to have the same thermal history in all polymers. The second scan allows identification of the T_g values as judged by the inflection point in the curve (Fig. 9).

It is known that T_g values depend on the polymer structure and decrease with increasing flexibility and asymmetry of the polymer backbone. The values obtained for the PAs are in agreement with the aforesaid. PA-PP shows the highest T_g value in the series which agrees with the rigidity conferred by the high aromatic content. In the case of PA-MP, the T_g value is low due to the structural asymmetry of dicarboxylic acid moiety ($\text{R}_1 = \text{methyl}$ and $\text{R}_2 = \text{phenyl}$).

CONCLUSIONS

PAs containing fluorene, oxyether and diphenyl-silane moieties in the main chain were synthesized by two different ways and characterized by thermal and spectroscopic methods. PAs were obtained by direct polycondensation in yields higher than 85% with η_{inh} values associated to low molecular weight material, probably of oligomeric nature. Dilution of the poly-

meric systems decreased the gelation allowing obtaining higher yields and viscosity values. The ^{29}Si -NMR spectra of the PAs showed a high field shift of the phenyl-substituted silicon atom due to its high electronic density. In agreement with the structural details incorporated, all PAs were soluble in various polar aprotic solvents, being partially soluble in THF. PA-PP with $\text{R}_1 = \text{R}_2 = \text{phenyl}$ rings in their structure showed the highest T_g values due to higher structural rigidity. In general, PAs derivatives can be classified as thermally stable due to the low weight loss below 420°C . The bulky fluorene moiety in the repetitive unit decreases the molecular packing of polymeric chains as seen by the high transparency of all PAs (over 85% at 400 nm).

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