

Synthesis, Characterization, and Thermal Studies of Polyamides and Polyimides Containing Two Silarylene Units in the Main Chain

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ABSTRACT: Polyamides (PAs) and polyimides (PIs) containing two silarylene units were synthesized and characterized by their spectroscopic properties. Bis(4-aminophenyl)methylphenylsilane was employed as a unique diamine, whereas acid dichloride and dianhydride monomers contained combinations of methyl and phenyl groups bonded to the silicon atom. The PAs were obtained in dimethylformamide solutions, and the PIs were prepared by thermal cyclization of the respective poly(amic acid)s (PAAs). The yields were low (32–51%), and the inherent viscosities for PAAs were slightly higher than the PA values. The low inherent viscosities were indicative of oligomeric species. The thermal stability was also eval-

uated by thermogravimetric analysis and differential scanning calorimetry analysis. In both series, the glass-transition temperatures increased with the replacement of methyl groups by aromatic rings according to the lower mobility of the polymeric chain. On the other hand, an increase in the aromatic content also increased the thermal stability of the PAs and PIs, and this was registered through their thermal decomposition temperatures. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2424–2431, 2008

Key words: glass transition; polyamides; polyimides; thermogravimetric analysis

INTRODUCTION

Silicon-containing polymers such as polycarbonates, polythiocarbonates, polyesters, polyurethanes, polyamides (PAs), and polyimides (PIs) in which the silicon atom is bonded to four organic groups have been described by several authors^{1–5} and also by our research group.^{6–10}

In this sense, in the last years we have focused our attention on the synthesis and characterization of condensation polymers derived from monomers containing a silicon atom in the main chain, describing the synthetic process, studying the thermal properties, glass-transition temperatures (T_g 's), and thermal decomposition temperatures (TDTs), and relating the results to the presence of the silicon atom and the aliphatic or aromatic units bonded to it.

PAs and PIs are condensation polymers derived from acid dichlorides or dianhydrides and diamines, which normally have high thermal stability. However, aromatic PAs and PIs are normally insoluble in organic solvents, with the major parameter that contributes to insolubility being the intermolecular

bonding energy developed through hydrogen bonding and through dipole–dipole interactions.¹¹ Bruma et al.¹² reported that the introduction of Si–C bonds can lead to improved solubility and consequently facilitate the processing of the polymers from their solutions.

Also, the introduction of Si–C bonds as diarylsilylene units maintains or increases the thermal stability because of the ionic character of the Si–C bond, the silicon atom being less electronegative than the carbon atom, although the bond energies of the C–C and Si–C bonds are similar.¹³ These observations are some of the factors that promote more scientific interest in this class of polymers because of the potential applications for the production of optoelectronic materials.

Continuing our work on the synthesis, characterization, and thermal studies of silicon-containing polymers, in this work we describe the synthesis of PAs and PIs containing two silicon atoms in the main chain derived from three acid dichlorides or dianhydrides with methyl, phenyl, or methyl and phenyl groups bonded to the silicon atom and one diamine, bis(4-aminophenyl)methylphenylsilane. Polymers were characterized with IR and NMR spectroscopy, including ²⁹Si-NMR. The thermal properties, T_g 's and TDTs specifically, were determined and related to the polymeric structures with special attention paid to the groups bonded to the silicon atoms.

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EXPERIMENTAL

Reagents (Aldrich, Milwaukee, WI) and solvents (Riedel de Haen) were used without purification. The FTIR spectra were recorded on a PerkinElmer (Fremont, CA) 1310 spectrophotometer, and the ^1H -, ^{13}C -, and ^{29}Si -NMR spectra were taken on a Bruker AC-200 400-MHz instrument with CDCl_3 , acetone- d_6 , or dimethyl sulfoxide- d_6 (DMSO- d_6) as a solvent and tetramethylsilane as the internal standard. Elemental analysis was performed on a Fison EA (San Carlos, CA) 1108-CHNS-O apparatus. Melting points (uncorrected) were obtained on an Stuart Scientific SMP3 (Grants Pas, OR) melting point apparatus. Viscosimetric measurements were made in a Desreux-Bischof-type dilution viscosimeter at 25°C (0.3 g/dL). The T_g values were obtained from a second scan with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system at a heating rate of 20°C/min under an N_2 flow. Thermogravimetric analysis (TGA) was carried out on 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 30 and 800°C at a heating rate of 20°C/min under an N_2 flow.

Diamine

Bis(4-aminophenyl)methylphenylsilane was obtained from 4-bromo-*N,N*-bis(trimethylsilyl)aniline and methylphenyldichlorosilane with a 28% yield (mp = 94–95°C) according to a procedure described previously [Scheme 1(i)].^{14,15}

Acid dichlorides

The acid dichlorides bis(4-chloroformylphenyl)dimethylsilane (**Ic**; 68%, mp = 78–80°C), bis(4-chloroformylphenyl)methylphenylsilane (**Iic**; 61%, mp = 87–88°C), and bis(4-chloroformylphenyl)diphenylsilane (**IIic**; 65%, mp = 180–182°C) were synthesized according to described procedures in which the di(*p*-tolyl) derivatives were oxidized to the corresponding diacids and then reacted with thionyl chloride [Scheme 1(ii)].^{8,16–18}

Dianhydrides

Bis(3,4-dicarboxyphenyl)dimethylsilane (**IVb**; 57%, mp = 175–177°C) and bis(3,4-dicarboxyphenyl)diphenyl silane (**VIb**; 60%, mp > 350°C) were obtained according to a described procedure in which the bis(3,4-dimethylphenyl) derivatives were oxidized to tetraacids and then reacted with acetic anhydride [**IVc** (41%, mp = 159–162°C) and **VIc** (43%, mp = 122–123°C); Scheme 1(iii)].¹⁷

Bis(3,4-dicarboxyphenyl)methylphenylsilane dianhydride (**Vc**) was synthesized from 1-bromo-3,4-dimethylbenzene and methylphenyldichlorosilane according to the same procedure, then was oxidized to the tetraacid and reacted with acetic anhydride, and was characterized [Scheme 1(iii)].

Bis(3,4-dimethylphenyl)methylphenylsilane (**Va**)

Yield: 55%. mp: 66–68°C. IR (KBr, cm^{-1}): 3048 (H aromatic), 2950, 2917 (CH_3), 1597, 1490 (C=C aromatic), 1427 (silyl-Ph), 1267 (silyl-aliphatic), 891, 819 (aromatic 1,2,4-substituted), 739, 700 (aromatic monosubstituted). ^1H -NMR (δ , ppm, CDCl_3): 0.84 (s, 3H, CH_3), 2.29 (s, 12H, CH_3), 7.17–7.59 (m, 11, H, aromatic). ^{13}C -NMR (δ , ppm, CDCl_3): –3.01 (Si- CH_3), 19.79, 19.86 (CH_3), 127.8, 129.2, 129.3, 133.1, 133.4, 135.3, 135.9, 136.5, 136.9, 137.9 (aromatic). ^{29}Si -NMR (δ , ppm, CDCl_3): –11.4.

Bis(3,4-dicarboxyphenyl)methylphenylsilane (**Vb**)

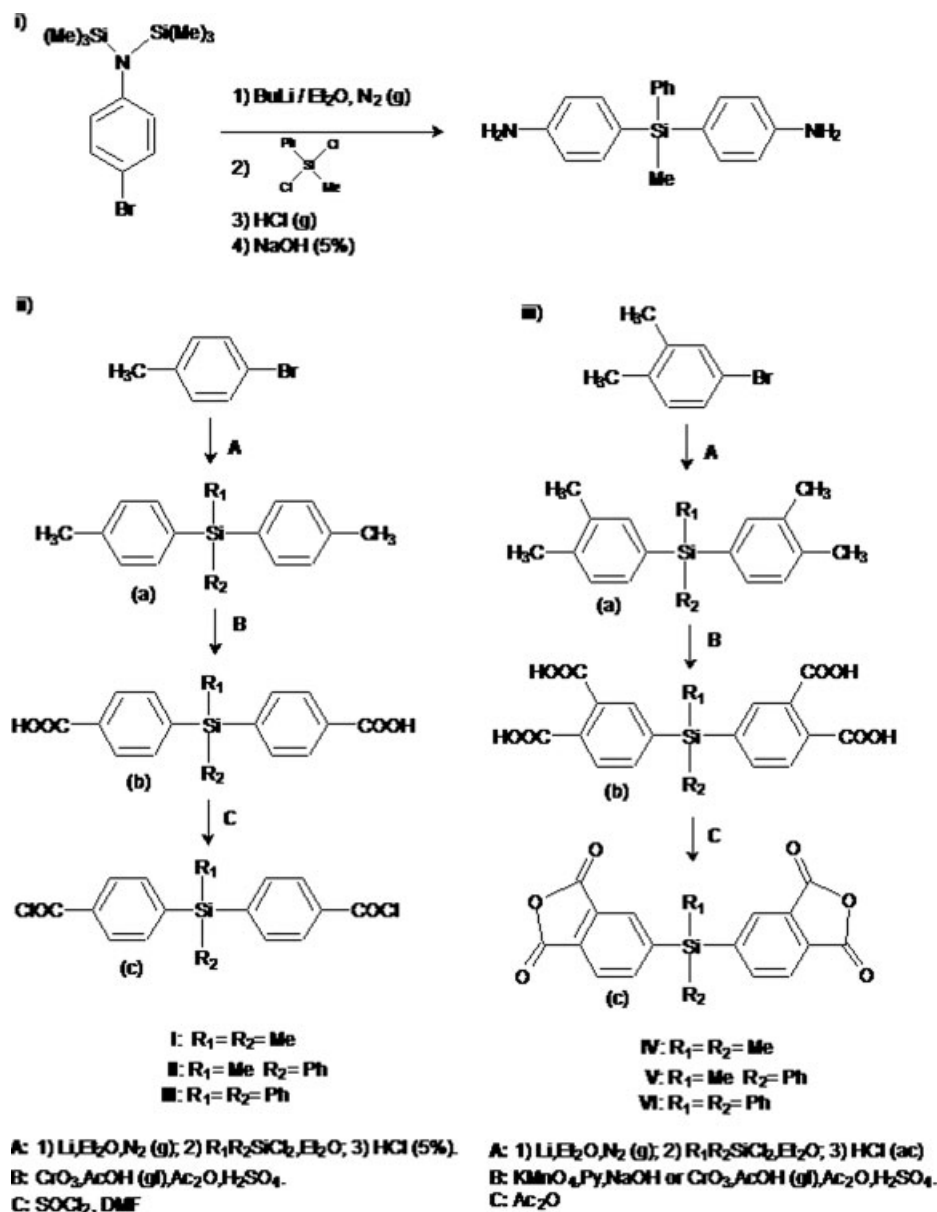
Yield: 45%. mp: >350°C. IR (KBr, cm^{-1}): 3434 (OH), 3022 (H aromatic), 2959 (CH_3), 1699 (C=O), 1593, 1492 (C=C aromatic), 1492 (silyl-Ph), 1280 (silyl-aliphatic), 845 (aromatic 1,2,4-substituted), 731, 699 (aromatic monosubstituted). ^1H -NMR (δ , ppm, acetone- d_6): 0.95 (s, 3H, CH_3), 7.45–7.94 (m, 11, H, aromatic), 13.12 (s, 4H, OH). ^{13}C -NMR (δ , ppm, acetone- d_6): –4.7 (Si- CH_3), 128.1, 128.3, 130.1, 132, 133.9, 134.1, 135.1, 135.7, 138.2, 139.3 (aromatic). ^{29}Si -NMR (δ , ppm, DMSO- d_6): –10.8.

Vc

Yield: 42%. mp: 137–138°C. IR (KBr, cm^{-1}): 3021 (H aromatic), 1853, 1780, 1701 (C=O), 1593, 1490 (C=C aromatic), 1405 (silyl-Ph), 1247 (silyl-aliphatic), 880, 814 (aromatic 1,2,4-substituted), 738, 701 (aromatic monosubstituted). ^1H -NMR (δ , ppm, CDCl_3): 0.89 (s, 3H, CH_3), 7.47–7.61 (m, 11H, aromatic). ^{13}C -NMR (δ , ppm, CDCl_3): –3.92 (CH_3), 128.3, 128.7, 128.8, 132.4, 135.3, 135.4, 137.8, 138.1, 138.9, 142.7 (aromatic), 167.4, 167.9 (C=O). ^{29}Si -NMR (δ , ppm, CDCl_3): –8.6.

PAs

PAs were synthesized according to the following general procedure. The diamine (1 mmol) was dissolved in 25 mL of *N,N*-dimethylacetamide (DMAc), and 0.2 mL of pyridine was added. The bath was cooled to –10°C, and 1 mmol of acid dichloride was added in four portions; the mixture was stirred for 18 h and then poured into methanol. The PA was filtered, washed with methanol, dried *in vacuo* until a constant weight was obtained, and then characterized [Scheme 2(i)].



Scheme 1 Synthesis of (i) bis(4-aminophenyl)methylphenylsilane, (ii) acid dichlorides, and (iii) dianhydride derivatives.

PA-I

¹H-NMR (CDCl₃, δ, ppm): 0.63 (s, 6H, CH₃), 0.82 (s, 3H, CH₃), 7.4–7.87 (m, 21H, aromatic), 10.33 (s, 2H, NH). ¹³C-NMR (CDCl₃, δ, ppm): –3.12 (CH₃), –2.49 (CH₃), 127.3, 127.4, 128.4, 129, 130.4, 134.4, 135.3, 135.8, 136.2, 136.7, 140.8, 142.2 (C aromatic), 166.2 (C=O). ²⁹Si-NMR (CDCl₃, δ, ppm): –7.2 (acid dichloride moiety), –12.0 (diamine moiety).

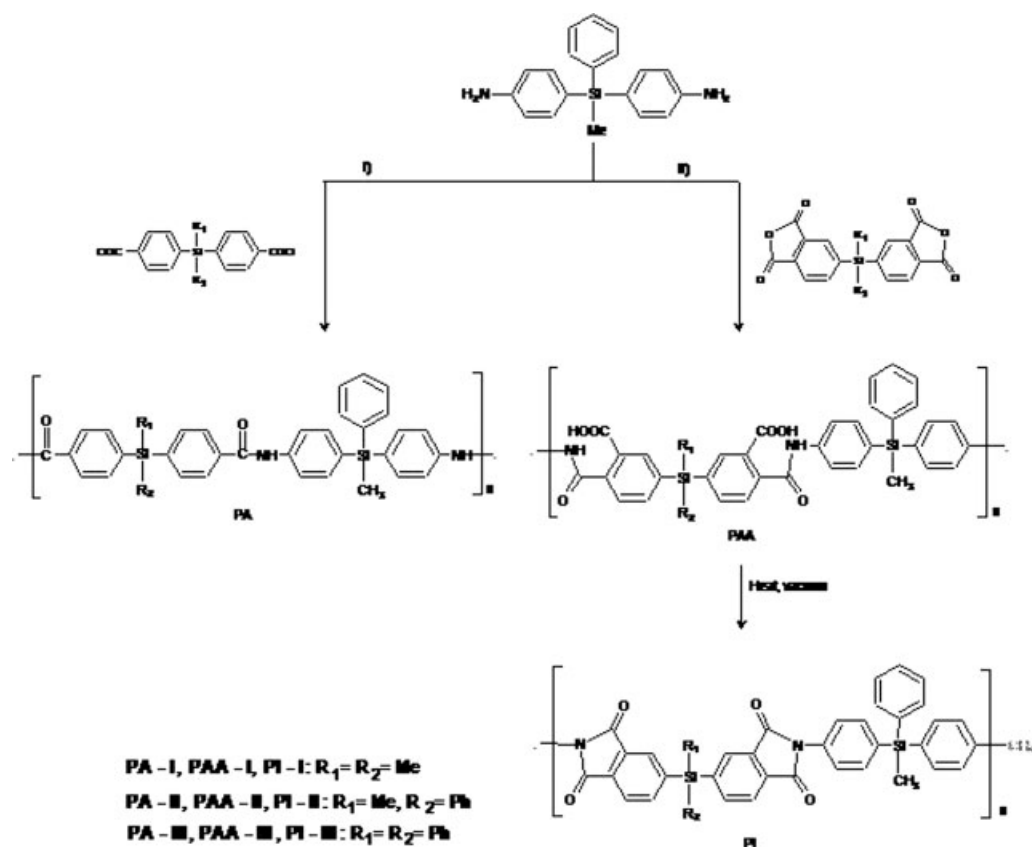
PA-II

¹H-NMR (CDCl₃, δ, ppm): 0.8 (s, 3H, CH₃), 0.92 (s, 3H, CH₃), 7.41–7.47 (m, 14H, aromatic), 7.64 (d, 4H, aromatic), 7.8 (d, 4H, aromatic), 7.94 (d, 4H, aromatic), 10.36 (s, 2H, NH). ¹³C-NMR (CDCl₃, δ, ppm):

–4.1 (CH₃), –4.08 (CH₃), 119.7, 127.1, 127.9, 128.2, 130.4, 134.7, 134.8, 135.3, 136.1, 136.2, 139.5, 140.3 (C aromatic), 165.7 (C=O). ²⁹Si (CDCl₃, δ, ppm): –10.8 (acid dichloride moiety), –12.0 (diamine moiety).

PA-III

¹H-NMR (CDCl₃, δ, ppm): 0.81 (s, 3H, CH₃), 7.36–7.55 (m, 19H, aromatic), 7.66 (d, 4H, aromatic), 7.8 (d, 4H, aromatic), 7.99 (d, 4H, aromatic), 10.41 (s, 2H, NH). ¹³C-NMR (CDCl₃, δ, ppm): –3.14 (CH₃), 120.2, 127.7, 128.1, 128.4, 128.8, 130.1, 131, 133, 134, 135.3, 135.9, 136.3, 136.7, 137, 137.8, 140.8 (C=C aromatic), 166.2 (C=O). ²⁹Si-NMR (CDCl₃, δ, ppm): –14.8 (acid dichloride moiety), –12.0 (diamine moiety).



Scheme 2 Synthesis of (i) PAs and (ii) PAAs and PIs.

PIs

The poly(amic acid)s (PAAs) were synthesized according to the following general procedure [Scheme 2(ii)]. The diamine (1 mmol) was dissolved in 10 mL of DMAc under an N_2 flow, and then 1 mmol of dianhydride was added in portions at room temperature. The mixture was stirred at 50°C for 18 h and then poured into water. The PAAs were filtered, washed with water, dried *in vacuo* until a constant weight was obtained, and characterized.

PAA-I

IR (KBr, cm^{-1}): 3601 (OH), 3380 (NH), 3047 (H aromatic), 2955 (CH_3), 1716, 1653 ($\text{C}=\text{O}$), 1597, 1507 ($\text{C}=\text{C}$ aromatic), 1429 (silyl-Ph), 1320 (silyl-aliphatic), 834 (aromatic p-substituted), 730, 701 (aromatic monosubstituted). $^1\text{H-NMR}$ (δ , ppm, CDCl_3): 0.52 (s, 6H, CH_3), 0.58 (s, 3H, CH_3), 6.62 (d, 4H, aromatic), 7.15 (d, 4H, aromatic), 7.38–8.04 (m, 16H, aromatic), 10.5 (s, 2H, NH). $^{13}\text{C-NMR}$ (δ , ppm, CDCl_3): -3.13, -3.23 (Si- CH_3), 119.6, 128.2, 128.4, 128.5, 128.7, 129.6, 129.8, 135.3, 136.2, 136.3, 136.8, 137.3 (aromatic), 167.8, 172.1 ($\text{C}=\text{O}$).

PAA-II

IR (KBr, cm^{-1}): 3630 (OH), 3378 (NH), 3046 (H aromatic), 2958 (CH_3), 1714, 1655 ($\text{C}=\text{O}$), 1589, 1518 ($\text{C}=\text{C}$ aromatic), 1427 (silyl-Ph), 1391 (silyl-aliphatic), 844 (aromatic p-substituted), 732, 700 (aromatic monosubstituted). $^1\text{H-NMR}$ (δ , ppm, CDCl_3): 0.52 (s, 3H, CH_3), 0.6 (s, 3H, CH_3), 6.46 (d, 4H, aromatic), 7 (d, 4H, aromatic), 7.21–7.92 (m, 16H, aromatic), 10.36 (s, 2H, NH). $^{13}\text{C-NMR}$ (δ , ppm, CDCl_3): -3.14, -3.17 (Si- CH_3), 120.5, 127.6, 127.7, 128.8, 130.7, 130.9, 133.4, 135.5, 135.7, 136.7, 137, 140.8 (aromatic), 166.2, 175.3 ($\text{C}=\text{O}$).

PAA-III

IR (KBr, cm^{-1}): 3630 (OH), 3422 (NH), 3047 (H aromatic), 2958 (CH_3), 1717, 1655 ($\text{C}=\text{O}$), 1591, 1499 ($\text{C}=\text{C}$ aromatic), 1428 (silyl-Ph), 1363 (silyl-aliphatic), 845 (aromatic p-substituted), 742, 700 (aromatic monosubstituted). $^1\text{H-NMR}$ (δ , ppm, CDCl_3): 0.51 (s, 3H, CH_3), 6.82 (d, 4H, aromatic), 7.18–7.46 (m, 25H, aromatic). $^{13}\text{C-NMR}$ (δ , ppm, CDCl_3): -3.31 (CH_3), 128.2, 128.4, 128.6, 128.8, 129, 129.5, 129.9, 135, 135.6, 136.2, 136.3, 136.7 (aromatic), 167.3, 177.9 ($\text{C}=\text{O}$).

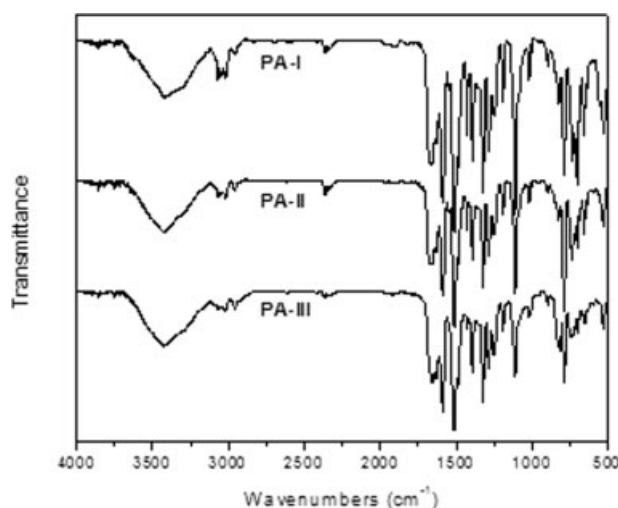


Figure 1 FTIR spectra of PAs.

To obtain the PIs, the PAAs were dissolved in DMAc, and then the solutions were heated in a vacuum stove at 50°C for 2 h until all the solvent was removed. Later, the samples were heated at 150°C for 3 h. The obtained film or powder was separated from the glass and characterized with FTIR spectroscopy (Fig. 1).

RESULTS AND DISCUSSION

Synthesis of the diamine

Certain *p*-aminophenylsilanes are unstable versus a vacuum-distilled procedure or alcoholic recrystallization.^{19,20} In particular, when methyl groups are substituted over the silicon central atom, the obtained diamine is highly unstable. On the other hand, when phenyl is used, the product is a white solid with high stability.^{14,15} Bis(4-aminophenyl)methylphenylsilane has been already described, and its stability is also low.¹⁴ The synthetic procedure described for these diamines is the same [Scheme

1(i)]; however, the isolation of bis(4-aminophenyl)methylphenylsilane requires a strict control of the pH in the neutralization process and a very long time of freezing before and after recrystallization from ethanol. Similarly to the described dimethyl diamine, the recrystallization process showed partial solvolysis, and aniline was identified as one of the products of decomposition. The recrystallized bis(4-aminophenyl)methylphenylsilane was employed in the synthesis of these PAs and PIs.

PAs

PAs were obtained from the silyl aromatic acid dichlorides described in the Experimental section and bis(4-aminophenyl)methylphenylsilane by a solution polycondensation process with DMAc as a solvent [Scheme 2(i)]. All the PAs were soluble in aprotic solvents such as DMAc, dimethylformamide (DMF), and DMSO but insoluble in other common organic solvents. The structure of the main chain, which contained two silicon atoms, was characterized by elemental analysis (Table I), FTIR, and ¹H, ¹³C, and ²⁹Si-NMR, and the results were in agreement with the proposed structures.

In the IR spectra, it is possible to see the stretching band of the NH group between 3419 and 3441 cm⁻¹ and the bands at 1627–1650 and 1630 cm⁻¹ corresponding to C=O stretching (amide I) and N–H bending (amide II), respectively (Fig. 1). Also, it is possible to see the silyl–Ph and silyl–aliphatic vibrations at 1427–1429 and 1320–1391 cm⁻¹, respectively. In the ¹H-NMR spectrum, a single signal was obtained for the NH group at approximately 10.4 ppm for all the PAs, and in the ¹³C-NMR spectrum, the signal corresponding to the C=O group appeared between 165.7 and 166.4 ppm.

The ²⁹Si results showed that the chemical shifts followed the pattern described in another work.²¹ A single signal was observed for the silicon atom of

TABLE I
Elemental Analysis Results for PAs and PIs

| | | C (%) | H (%) | N (%) |
|--------|----------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|
| PA-I | Calcd for (C ₃₅ H ₃₂ N ₂ O ₂ Si ₂) _n [(568.55) _n] | 73.93 | 5.63 | 4.93 |
| | Found | 73.11 | 5.12 | 4.89 |
| PA-II | Calcd for (C ₄₀ H ₃₄ N ₂ O ₂ Si ₂) _n [(630.60) _n] | 76.18 | 5.39 | 4.44 |
| | Found | 76.02 | 5.29 | 4.09 |
| PA-III | Calcd for (C ₄₅ H ₃₆ N ₂ O ₂ Si ₂) _n [(692.65) _n] | 78.03 | 5.20 | 4.05 |
| | Found | 77.84 | 5.09 | 3.97 |
| PI-I | Calcd for (C ₃₇ H ₂₈ N ₂ O ₄ Si ₂) _n [(620.57) _n] | 71.61 | 4.51 | 4.51 |
| | Found | 71.19 | 4.42 | 4.48 |
| PI-II | Calcd for (C ₄₂ H ₃₀ N ₂ O ₄ Si ₂) _n [(682.62) _n] | 73.89 | 4.39 | 4.10 |
| | Found | 73.50 | 4.40 | 4.02 |
| PI-III | Calcd for (C ₄₇ H ₃₂ N ₂ O ₄ Si ₂) _n [(744.67) _n] | 75.80 | 4.30 | 3.76 |
| | Found | 75.69 | 4.22 | 3.65 |

TABLE II
Yield, η_{inh} , T_g and TDT Values for the PAs and PIs

| Polymer | Yield (%) | η_{inh} (dL/g) ^a | T_g (°C) | TDT (°C) ^b |
|---------|-----------|----------------------------------|------------|-----------------------|
| PA-I | 44 | 0.13 | 46 | 422 |
| PA-II | 40 | 0.14 | 152 | 434 |
| PA-III | 32 | 0.18 | 169 | 437 |
| PI-I | 47 | 0.25 | 37 | 382 |
| PI-II | 51 | 0.29 | 122 | 463 |
| PI-III | 43 | 0.35 | 130 | 473 |

^a These values were taken from PAA-DMF solutions at 25°C (concentration = 0.3 g/mL).

^b These values were determined when the polymers had lost 15 wt %.

the diamine moiety at -12.0 ppm, but the silicon signal corresponding to the acid dichloride moiety was displaced from -7.2 ppm when it was bonded to two methyl groups to -10.8 when one methyl was replaced by one aromatic ring and to -14.8 ppm when it was bonded to two phenyl groups. The phenyl group presented two effects: the donor electronic inductive effect and eventual backbonding involving the overlap of the π orbital of the aromatic ring. These effects induced a higher electronic density of the silicon atom, shifting its signals to a higher field. This trend has been observed in other silicon-containing polymers.^{7,21}

Table II shows the yields and inherent viscosity (η_{inh}) values obtained for all the PAs, which were low, probably because of the low solubility of the polymeric chains in the reaction media, which limited their growth. This phenomenon has been already described for other PAs with silicon, and it has been related to oligomeric chains being obtained.⁷ A low increase in η_{inh} could be observed when the silicon atom of the acid dichloride moiety was bonded to aromatic rings. This fact is related to the higher solubility in the reaction media of the chains with higher aromatic contents, and this has also been observed in other systems.⁷

PAA and PIs

The PAAs were synthesized from the dianhydrides and diamine according to the proposed structures with DMAc as the solvent at room temperature [Scheme 2(ii)]. The dianhydride was added to the diamine solution in four portions with heating at 50°C for 18 h. The PAAs were characterized with IR spectroscopy and ¹H- and ¹³C-NMR. In the IR spectra, it was possible to see the NH and OH broad stretching bands at 3630–3600 and 3420–3380 cm⁻¹, respectively, and the C=O bands at approximately 1717 and 1653 cm⁻¹. In the ¹H-NMR spectrum, it was possible to observe the CH₃ signal between 0.57

and 0.62 ppm, whose normal chemical shift was affected by the silicon directly bonded. Also, it was possible to observe a complex signal for the aromatic protons between 6.60 and 8.08 ppm and a single signal for OH at approximately 10 ppm. For the PAAs, it was impossible to obtain good ²⁹Si spectra because of their low solubility in DMSO-*d*₆.

Table II shows the yields and η_{inh} values obtained for the PAAs. Even though that the yields were moderate and the η_{inh} values obtained from DMAc solutions were higher than those obtained for the PAs, the products were probably oligomeric in nature because of the higher solubility of the polymeric chains with free carboxylic groups in this highly polar solvent, which has been described for other similar systems.⁷ Also, it was possible to see an increase in the η_{inh} values when the number of aromatic rings increased because of their higher solubility.

The PI films were prepared by the thermal imidization of PAA-DMAc solutions [Scheme 2(ii)]. The thermal curing of the samples was developed by slow evaporation of the solvent and a later heating process at 150°C. Therefore, the obtained films did not show strong coloration but showed only a soft yellow color. The PIs were insoluble in all common organic solvents, and it was possible to obtain only the Fourier transform infrared (FTIR) spectra (Fig. 2). In these, it is possible to see that the curing process was complete because of the absence of the NH and OH stretching bands, which are characteristic for PAAs. A common pattern appeared between all PIs (cm⁻¹): 3059 (C–H aromatic), 2959 (C–H aliphatic), 1778 and 1721 (C=O imide), 1592 and 1501 (C=C), 1370 (C–N–C), 818 (aromatic *p*-substituted), and 735 and 699 (aromatic monosubstituted). The spectra were completed with the absorption bands associated with silyl-Ph and silyl-aliphatic bonds, which appeared at 1429 and 1318 cm⁻¹, respectively.

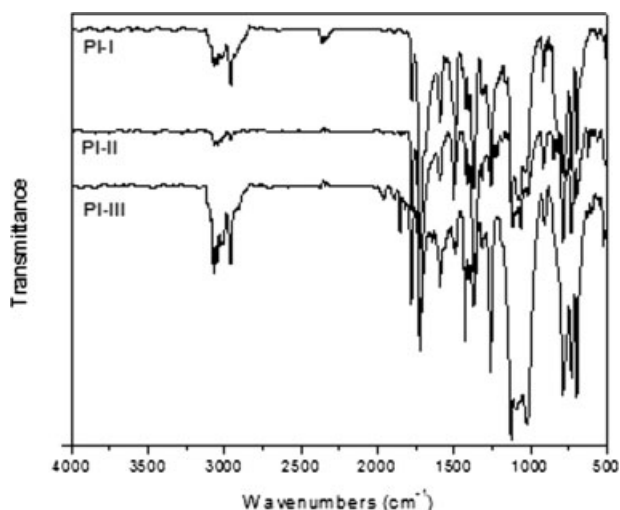


Figure 2 FTIR spectra of PIs.

Elemental analysis (Table I) also supported the formation of PIs.

Thermal properties

The thermal properties of all the polymers were evaluated under a nitrogen atmosphere by TGA and differential scanning calorimetry (DSC) analysis. These results are summarized in Table II. The T_g values were considered as changes in the slope in the DSC thermogram. These values are low and agree with the idea of oligomeric products, which is derived from the viscosity values obtained.

Figure 3 shows the second run of the DSC traces for PAs and PIs. In general, the polymers with methyl groups showed higher flexibility than those with aromatic rings; consequently, the motions in the main chain were easier when the temperature was increased, and PAs with phenyl side groups had higher T_g values. In these PAs, there was an increase in the T_g values when the content of the aromatic rings was increased, the value for PA-I, which contained three methyl groups in its main chain, being very low. For the PIs, the trend was the same, and the T_g value of PI-I was also low.

Figure 4 shows the TGA (50–750°C) traces for PAs and PIs. In the PA series, the decomposition started at approximately 150°C, whereas in the PI series, this value was over 200–250°C. This fact agreed with the following general observation: the PIs showed higher thermal stability than the PAs when the same substituted groups were used. The exceptions to this rule were PA-I and PI-I, with two methyl groups as substitutes for the silicon atom in the dichloride acid and dianhydride units, respectively. It is clear that in both series, the thermal stability of the polymers

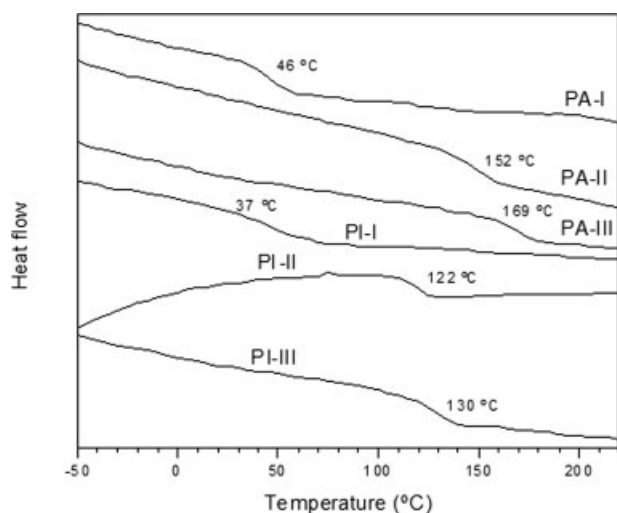


Figure 3 DSC traces of PAs and PIs (second run, heating rate = 10°C/min, in nitrogen).

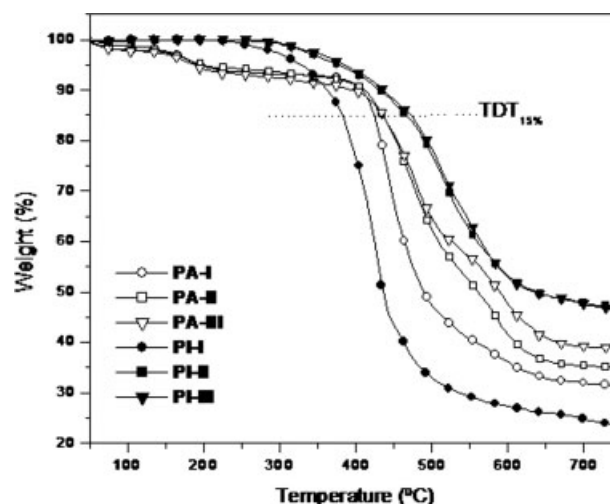


Figure 4 TGA curves of PAs and PIs.

increased with the replacement of the methyl groups by phenyl groups. This fact agreed with the higher thermal stability of the phenyl group versus the methyl group, as already described by Ghatge and Jadhav.²² In Table II, we report the TDT values taken when the polymers had lost 15% of their weight. According to what has already been described, this parameter increased when the number of side aromatic rings increased, although for PA-II and PA-III, the observed values were very similar. On the other hand, the higher aromatic content of the polymers resulted in a remainder mass after the heating process (Fig. 2).

CONCLUSIONS

PAs and PIs containing two silicon atoms in the main chain were obtained in low yields from acid dichlorides for the PA series and from dianhydrides for the PAAs, both with the diamine bis(4-aminophenyl)methylphenylsilane. The PAAs were used as precursors of PIs in a thermal treatment. Methyl-methyl, methyl-phenyl, and phenyl-phenyl combinations bonded to the silicon atom of the acid dichloride or dianhydride were used in the main chains of the polymers. The thermal stability of the materials was evaluated by DSC and TGA under a nitrogen atmosphere. The T_g values increased with the replacement of methyl groups for phenyl groups because of the lower mobility of the chain. Also, the TDT of the PAs and PIs increased with the aromatic content.

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