

Poly(imide-amide)s and Poly(imide-ester)s Obtained from *N,N'*-(4,4'-Me,R-diphthaloyl)-bis-Glycine Acid Dichloride (R = Me, Et): Synthesis, Characterization, and Thermal Studies

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ABSTRACT: Poly(imide-amide)s (PIAs) and poly(imide-ester)s (PIEs) containing two Si-atoms in the repeating unit were synthesized from acid dichlorides and diamines and diphenols, respectively. The acid dichlorides were obtained from the dianhydrides, which reacted first with glycine and then with thionyl chloride. The dianhydrides were obtained from the tetramethyl derivatives, which were oxidized to the tetra acids and then the dianhydrides were obtained with acetic anhydride. PIAs were obtained in *N,N*-dimethylacetamide solution at low temperature and the PIEs in a CHCl₃ solution. Monomers and polymers were characterized by IR and ¹H-, ¹³C-, and ²⁹Si-NMR spectroscopy and the results were in agreement with

the proposed structures. The η_{inh} values were indicative of low molecular weight species and of oligomeric nature. The glass transition (T_g) and thermal decomposition temperatures (TDT) values of PIAs were higher than those of PIEs due to the presence of the aromatic rings of the diamine. The aliphatic groups bonded to the Si atom of the acid dichloride moiety promoted the decrease of the thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1526–1534, 2010

Key words: silicon-containing polymers; poly(imide-amide)s; poly(imide-ester)s; aminoacids; glass transition temperature; thermal stability

INTRODUCTION

Polyimides are important high-performance materials due to their excellent properties such as thermal stability, electric insulation, and chemical resistance. However, their applications are limited due to their high softening or melting temperatures and their very low solubility in most common organic solvents.¹

To overcome these drawbacks, some modifications of the polymeric structure are used, such as the introduction of flexible linkages, nonsymmetrical structures, or bulky substituents in the polymeric chain.² Also, the introduction of other functional groups such as imide or ester groups can improve their solubility. In this sense, poly(imide-amide)s (PIAs) and poly(imide-ester)s (PIEs) offer the advantages of both polyimides and polyamides, high thermal stability, this is good mechanical properties and convenient processability.^{3–5}

Additionally, Bruma et al. have described that the introduction of silarylene groups [-Ar-Si(R₁R₂)-Ar-]

in aromatic polymers can improve their solubility maintaining a high stability. Also, the lower electronegativity of the Si-atom compared to carbon, increases the thermal stability of the silicon-containing polymers due to a higher ionic character of the C–Si bond compared to the respective C–C bond due to the difference of electronegativity, in spite of the similar bond energy dissociation of both linkages.⁶ In this sense, the behavior of polycarbonates and polyimides has been described.^{7,8}

In this work, we describe the synthesis and characterization of PIEs and PIAs derived from a dianhydride containing Si as central atom and glycine as aminoacid in order to obtain a diacid containing two imide groups. The diacids were polymerized with a diamine, also containing a Si atom (PIAs), or with diphenols (PIEs), all both carrying two Si atoms in the repeating unit. Polymers were characterized by their inherent viscosity, IR ¹H-, ¹³C-, and ²⁹Si-NMR spectra. Thermal properties of polymers glass transition temperature and thermal stability, were determined and the results related to the proposed structures.

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EXPERIMENTAL

Materials

Glycine, CH₃Si(R)Cl₂ (R = Me, Et), *p*-bromophenol and 4-bromo-*N,N*-bis(trimethylsilyl)aniline were

obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Tetrahydrofuran (THF) and diethylether (Aldrich Chemical, Milwaukee, WI) were dried over sodium previous to use. 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 ($c = 0.3 \text{ g/dL}$). T_g values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (20°C min^{-1} 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 30°C and 800°C with a heating rate of 10°C min^{-1} under N_2

flow. Elemental analyses were developed in a Fisons EA 1108-CHNS-O equipment.

Precursors synthesis

The precursors bis(3,4-dimethylphenyl)-dimethylsilane, bis(3,4-dimethylphenyl)-ethylmethylsilane, bis(3,4-dicarboxyphenyl)-dimethylsilane, bis(3,4-dicarboxyphenyl)-ethylmethylsilane, bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, and bis(3,4-dicarboxyphenyl)-ethylmethylsilane dianhydride (Fig. 1) were synthesized following a previously described procedure.^{9–12} All compounds were characterized by IR, ^1H -, ^{13}C -, and ^{29}Si -NMR spectroscopy, and the results were in agreements with the proposed structures. The characterization of compounds based on the $-\text{Si}(\text{Et})_2-$ moiety is determined below. Spectral data of $-\text{Si}(\text{ME})_2-$ compounds can be found elsewhere.

Bis(3,4-dimethylphenyl)ethylmethylsilane (1b)

Yield: 89%. M.p.: 140–141°C. IR (KBr, cm^{-1}): 3001 (C–H arom.), 2957 (C–H aliph.), 1599 (C=C arom.), 1557, 1010 (Si-Ph), 1250 (Si-aliph.), 891, 813 (arom. 1,2,4-subst.). ^1H -NMR (CDCl_3) (δ) (ppm): 1.03 (s, 3H, Si- CH_3); 1.55 (m, 5H, CH_2CH_3); 7.58–7.82 (m, 6H, CH arom.). ^{13}C -NMR (CDCl_3) (δ) (ppm): -4.21 (Si- CH_3); 6.72 (CH_2); 8.10 (CH_2CH_3); 20.14 (Ar-

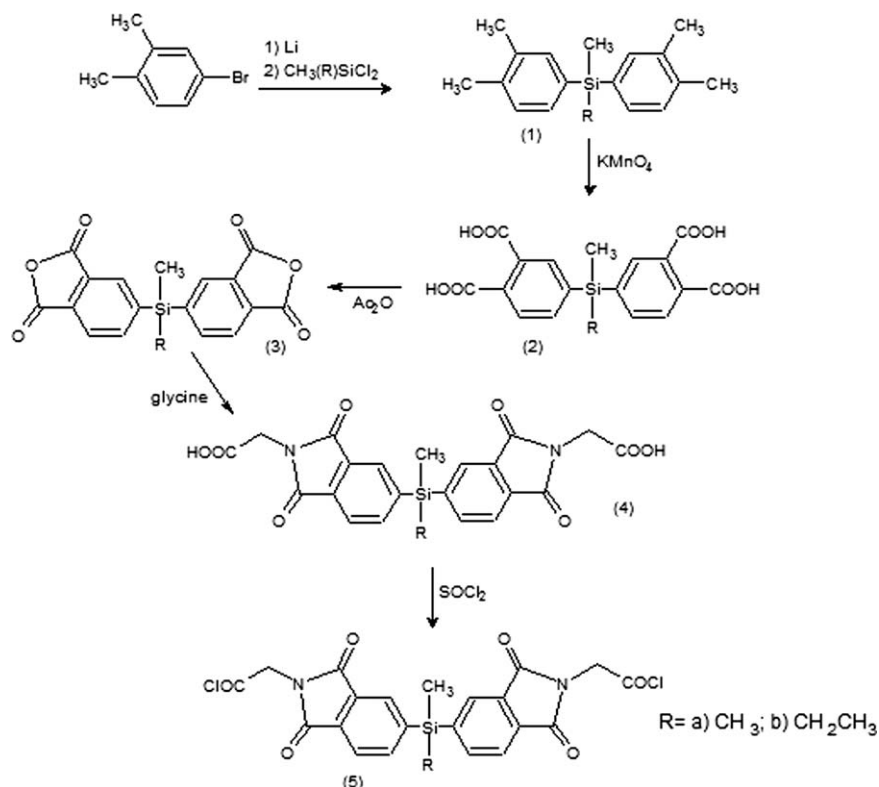


Figure 1 Synthesis of the acid dichloride derivatives from 4-bromo-*o*-xylene.

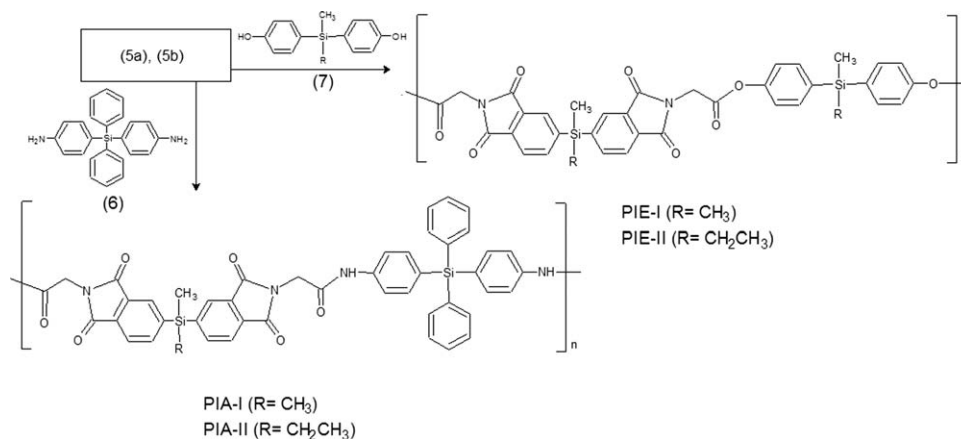


Figure 2 Synthesis of PIA and PIE based on silarylene units containing glycine moieties.

CH₃); 129.7; 132.7; 134.9; 136.1; 136.2; 137.9. ²⁹Si-NMR (CDCl₃) (δ) (ppm): -5.84.

Bis(3,4-dicarboxyphenyl)ethylmethylsilane (2b)

Yield: 52%. M.p.: > 350°C. IR (KBr, cm⁻¹): 3023 (O—H overlap with C—H arom.), 2958 (C—H aliph.), 1711 (C=O), 1593 (C=C arom.), 1556, 1491 (Si-Ph), 1257 (Si-aliph.), 875, 846 (arom. 1,2,4-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.59 (s, 3H, Si—CH₃); 0.94 (t, 3H, *J* = 6.3 Hz, CH₂CH₃); 1.08 (q, 2H, *J* = 6.3 Hz, CH₂CH₃); 7.30–7.80 (m, 6H, CH arom.). ¹³C-NMR (CDMSO-d₆) (δ) (ppm): -5.36 (Si—CH₃); 5.02 (CH₂); 7.58 (CH₂CH₃); 128.2; 132.5; 134.1; 134.3; 137.1; 140.2; 169.1; 169.2 (COOH). ²⁹Si-NMR (DMSO-d₆) (δ) (ppm): -4.38.

Bis(3,4-dicarboxyphenyl)ethylmethylsilane dianhydride (3b)

Yield: 71%. M.p.: 179–181°C. IR (KBr, cm⁻¹): 3040 (C—H arom.), 2960 (C—H aliph.), 1854, 1776, 1706 (C=O), 1595 (C=C arom.), 1488, 1408 (Si-Ph), 1275 (Si-aliph.), 876, 852 (arom. 1,2,4-subst.). ¹H-NMR (CDCl₃) (δ) (ppm): 0.77 (s, 3H, Si—CH₃); 1.08 (t, 3H, *J* = 6.4 Hz, CH₂CH₃); 1.26 (q, 2H, *J* = 6.4 Hz, CH₂CH₃); 8.02–8.13 (m, 6H, CH arom.). ¹³C-NMR (CDCl₃) (δ) (ppm): -5.43 (Si—CH₃); 5.11 (CH₂CH₃); 7.03 (CH₂CH₃); 125.1; 130.1; 131.1; 132.4; 141.6; 146.7; 162.8; 162.9. ²⁹Si-NMR (CDCl₃) (δ) (ppm): -1.83.

The diacids *N,N'*-(4,4'-dimethylsilylenedipthaloyl)-bis-glycine (4a) and *N,N'*-(4,4'-ethylmethylsilylenedipthaloyl)-bis-glycine (4b) were synthesized according to reported procedures.¹³ Briefly, the dianhydride derivative (3) (2.8 × 10⁻³ mol) and the glycine (5.6 × 10⁻³ mol) were refluxed for 3 h in 30 mL of acetic anhydride. The solvent was removed by distillation and the liquid residue was treated under reduced pressure with occasional cycles of heating. The light brown solid obtained was treated with *n*-

hexane, filtered and washed with petroleum ether. The pale yellow-solid obtained was dried and then treated with water to remove unreacted α-amino acid. Finally, the diacid was filtered, dried at 40°C under vacuum, and characterized.

N,N'-(4,4'-dimethylsilylenedipthaloyl)-bis-glycine diacid (4a)

Yield: 70%. M.p.: 248–252°C. IR (KBr, cm⁻¹): 3050 (O—H overlap with C—H arom.), 2934 (C—H aliph.), 1777 (C=O imide), 1714 (C=O acid), 1608 (C=C arom.), 1421 (Si-Ph), 1273, 813 (Si—CH₃), 879, 813 (arom. 1,2,4-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.69 (s, 6H, Si—CH₃); 4.26 (s, 2H, CH₂); 7.86–8.22 (m, 6H, CH arom.). ¹³C-NMR (DMSO-d₆) (δ) (ppm): -2.91 (Si—CH₃); 39.41; 123.1; 128.7; 131.3; 132.8; 140.9; 146.2; 167.7; 167.9; 169.3. ²⁹Si-NMR (DMSO-d₆) (δ) (ppm): -4.97.

N,N'-(4,4'-ethylmethylsilylenedipthaloyl)-bis-glycine diacid (4b)

Yield: 57%. M.p.: 203–206°C. IR (KBr, cm⁻¹): 3209 (O—H overlap with C—H arom.), 2957 (C—H aliph.), 1778 (C=O imide), 1717 (C=O acid), 1612 (C=C arom.), 1424 (Si-Ph), 1322 (Si-aliph.), 880, 788 (arom. 1,2,4-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.73 (s, 3H, Si—CH₃); 0.97 (t, 3H, *J* = 6.4 Hz, CH₂CH₃); 1.26 (q, 2H, *J* = 6.4 Hz, CH₂CH₃); 4.31 (s, 2H, N—CH₂); 7.91–8.13 (m, 6H, CH arom.). ¹³C-NMR (DMSO-d₆) (δ) (ppm): -5.44 (Si—CH₃); 4.74 (CH₂CH₃); 7.52 (CH₂CH₃); 39.4; 123.1; 128.9; 131.2; 132.9; 141.2; 145.2; 167.6; 167.9; 169.3. ²⁹Si-NMR (DMSO-d₆) (δ) (ppm): -2.56.

Monomer synthesis

Bis(4-aminophenyl)diphenylsilane (6) and diphenol derivatives (7) (Fig. 2) were prepared according to

described procedures.^{14–17} The synthesis of acid dichlorides derivatives was also based on previously works^{12,18–20} in which the acid dichloride derivative (2×10^{-3} mol), 40–50 mL of thionyl chloride and 3 drops of DMAc were refluxed for 4 h at 80°C. Unreacted thionyl chloride was removed under reduced pressure and the viscous residue was treated with petroleum ether until a white solid appeared. The product was filtered, washed several times with *n*-hexane or petroleum ether and, dried under reduced pressure.

N,N'-(4,4'-dimethylsilylenedipthaloyl)-bis-glycine acid dichloride (5a)

Yield: 74%. M.p.: 116.4–121.7°C. IR (KBr, cm^{-1}): 3200 (C–H arom.), 2972 (C–H aliph.), 1808, 1779 (C=O imide), 1718 (C=O acid chloride), 1610 (C=C arom.), 1420 (Si-Ph), 1383 (Si–CH₃), 840, 787 (arom. 1,2,4-subst.), 812 (arom. *p*-subst), 703 (arom. *mono*-subst.). ¹H-NMR (CDCl₃) (δ) (ppm): 0.72 (s, 6H, Si–CH₃); 4.83 (s, 4H, CH₂); 7.88–8.04 (m, 6H, CH arom.). ¹³C-NMR (CDCl₃) (δ) (ppm): –2.8 (Si–CH₃); 47.7; 123.4; 129.1; 131.0; 132.6; 140.4; 146.0; 166.5; 169.1; 172.0. ²⁹Si-NMR (CDCl₃) (δ) (ppm): –4.52. Elem. Anal. Calcd. for C₂₂H₁₆N₂O₆SiCl₂; (503.23): C: 52.50%, N: 5.57% H: 3.18%. Found: C: 52.41%, N: 5.38%, H: 3.20%.

N,N'-(4,4'-ethylmethylsilylenedipthaloyl)-bis-glycine acid dichloride (5b)

Yield: 56%. M.p.: 137.7–141.2°C. IR (KBr, cm^{-1}): 3200 (C–H arom.), 2958 (C–H aliph.), 1803, 1779 (C=O imide), 1723 (C=O acid chloride), 1611 (C=C arom.), 1419 (Si-Ph), 1397 (Si-aliph.), 850, 790 (arom. 1,2,4-subst.). ¹H-NMR (CDCl₃-d₆) (δ) (ppm): 0.71 (s, 3H, Si–CH₃); 0.91 (q, 2H, *J* = 6.3 Hz, CH₂CH₃); 1.08 (t, 3H, *J* = 6.3 Hz, CH₂CH₃); 4.50 (s, 4H, N–CH₂); 7.85–8.10 (m, 6H, CH arom.). ¹³C-NMR (CDCl₃-d₆) (δ) (ppm): –5.3 (Si–CH₃); 5.3 (CH₂CH₃); 7.2 (CH₂CH₃); 38.7; 123.1; 129.2; 131.2; 132.9; 140.4; 144.9; 167.3; 167.6; 172.2 (C10). ²⁹Si-NMR (CDCl₃) (δ) (ppm): –2.58. Elem. Anal. Calcd. for C₂₃H₁₈N₂O₆SiCl₂; (517.24): C: 53.40%, N: 5.42% H: 3.48%. Found: C: 53.3%, N: 5.31%, H: 3.40%.

Synthesis of poly(imide-amide)s and poly(imide-ester)s

Poly(imide-amide)s

PIAs were synthesized according with a standard procedure. Briefly, bis(4-aminophenyl)diphenylsilane (1 mmol) was dissolved in 25 mL of DMAc in presence of 0.2 mL of pyridine and cooled to –10°C. Next, 1 mmol of the acid dichloride was added in four portions every 15 min with stirring. The mixture was stirred 18 h at room temperature and the

solution obtained was poured in methanol. The polymer was filtered, washed several times with methanol-water and dried under vacuum (Fig. 2).

PIA-I. Yield: 62%. $\eta_{\text{inh}} = 0.27$ dL/g (in DMSO at 25°C, *c* = 0.3 g/dL). IR (KBr, cm^{-1}): 3372 (NH), 3050 (C–H arom.), 2937 (C–H aliph.), 1876, 1776 (C=O imide), 1717 (C=O amide), 1623,1592 (C=C arom.), 1425 (Si-Ph), 1392 (Si-aliph.), 883, 784 (arom. 1,2,4-subst.), 812 (arom. *p*-subst), 703 (arom. *mono*-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.72 (s, 6H, Si–CH₃); 4.44 (s, 4H, CH₂); 7.30–8.32 (m, 24H, arom.); 10.46 (s, 2H, NH). ¹³C-NMR (DMSO-d₆) (δ) (ppm): –3.31 (Si–CH₃); 40.8 (CH₂); 118.9–145.7 (14C arom.); 165.0 (C=O amide); 167.5; 167.7 (C=O imide). ²⁹Si-NMR (DMSO-d₆) (δ) (ppm): –4.62 (Ph-Si(CH₃)₂-Ph); –15.33 (Ph-Si(Ph)₂-Ph). Elem. Anal. Calcd. for C₄₆H₃₆N₄O₆Si₂; (796.68): C: 69.35%, N: 7.03%, H: 4.52%. Found: C: 69.01%, N: 6.95%, H: 4.18%.

PIA-II. Yield: 58%. $\eta_{\text{inh}} = 0.35$ dL/g (in DMSO at 25°C, *c* = 0.3 g/dL). IR (KBr, cm^{-1}): 3369 (NH), 3067 (C–H arom.), 2876 (C–H aliph.), 1870, 1769 (C=O imide), 1716 (C=O amide), 1592,1518 (C=C arom.), 1420 (Si-Ph), 1391 (Si-aliph.), 880, 786 (arom. 1,2,4-subst.), 822 (arom. *p*-subst.), 701 (arom. *mono*-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.73 (s, 3H, Si–CH₃); 0.97 (t, 3H, *J* = 6.2 Hz, CH₂CH₃); 1.28 (q, 2H, *J* = 6.2 Hz, CH₂CH₃); 4.46 (s, 4H, CH₂); 6.62–8.07 (m, 24H, arom.); 10.51 (s, 2H, NH). ¹³C-NMR (DMSO-d₆) (δ) (ppm): –5.46 (Si–CH₃); 4.76 (CH₂CH₃); 7.54 (CH₂CH₃); 41.3 (N–CH₂); 114.2–140.4 (14C arom.); 165.5 (C=O amide); 167.9, 170.0 (C=O imide). ²⁹Si-NMR (DMSO-d₆) (δ) (ppm): –2.57 (Ph-Si(CH₃)(CH₂CH₃)Ph); –15.35 (Ph-Si(Ph)₂-Ph). Elem. Anal. Calcd. for C₄₇H₃₈N₄O₆Si₂; (810.69): C: 69.63%, N: 6.91%, H: 4.69%. Found: C: 69.48%, N: 6.82%, H: 4.51%.

Poly(imide-ester)s

PIEs were synthesized following the general procedure²¹ in which a solution of acid dichlorides (1 mmol) in 2 mL of dried chloroform was added dropwise over an ice-cold solution containing the diphenol (0.61 mmol), triethylamine (2 mmol) and dried chloroform (2 mL). The mixture was stirred for 2 h at 0°C and then 3 h at room temperature. The solution was poured over methanol and the polymer was filtered, washed with methanol and dried at 80°C under vacuum (Fig. 2).

PIE-I. Yield: 17%. $\eta_{\text{inh}} = 0.19$ dL/g (in DMSO at 25°C, *c* = 0.3 g/dL). IR (KBr, cm^{-1}): 3045 (C–H arom.), 2934 (C–H aliph.), 1776 (C=O ester), 1716 (C=O imide), 1592 (C=C arom.), 1426 (Si-Ph), 1391 (Si-aliph.), 880, 786 (arom. 1,2,4-subst.), 822 (arom. *p*-subst.), 701 (arom. *mono*-subst.). ¹H-NMR (DMSO-d₆) (δ) (ppm): 0.45–0.53 (d, 6H, Si–CH₃); 0.73 (s, 6H, Si–CH₃); 4.74 (s, 4H, CH₂); 6.73–8.09 (m, 14H,

arom.). ^{13}C -NMR (DMSO- d_6) (δ) (ppm): $-3, 4, -2, 7, -2, 4$ (Si- CH_3); 39.6 (CH_2); 115.2 – 151.0 (10C arom.); 166.5 (C=O ester); $166.9, 167.2$ (C=O imide). ^{29}Si -NMR (DMSO- d_6) (δ) (ppm): -4.69 (Ph-Si(CH_3) $_2$ -Ph); $-8.62, -7.61$ (-O-Ph-Si(CH_3) $_2$ -Ph-O-). Elem. Anal. Calcd. for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_8\text{Si}_2$; (674.56): C: 64.09%, N: 4.15%, H: 4.45%. Found: C: 64.20%, N: 4.08%, H: 4.25%.

PIE-II. Yield: 23%. $\eta_{\text{inh}} = 0.23$ dL/g (in DMSO at 25°C , $c = 0.3$ g/dL). IR (KBr, cm^{-1}): 3059 (C-H arom.), 2956 (C-H aliph.), 1774 (C=O ester), 1720 (C=O imide), $1624, 1589$ (C=C arom.), 1420 (Si-Ph), 1392 (Si-aliph.), $787, 749$ (arom. 1,2,4-tri-subst.), 830 (arom. *p*-subst.), 680 (arom. *mono*-subst.). ^1H -NMR (DMSO- d_6) (δ) (ppm): 0.21 – 1.30 (m, 16H, Si(CH_3) CH_2CH_3); 4.74 (s, 4H, CH_2); 6.78 – 8.07 (m, 14H, arom.). ^{13}C -NMR (DMSO- d_6) (δ) (ppm): $-6.1, -5.5, -5.2$ (Si- CH_3); $4.1, 5.0, 5.4$ (CH_2CH_3); $7.1, 7.2, 8.4$ (CH_2CH_3); 39.6 (CH_2); 115.1 – 150.9 (10C arom.); $166.8; 166.8, 167.1$ (C=O). ^{29}Si -NMR (DMSO- d_6) (δ) (ppm): -2.55 (Ph-Si(CH_3)(CH_2CH_3)Ph); $-6.30, -5.44$ (-O-Ph-Si(CH_3)(CH_2CH_3)Ph-O-). Elem. Anal. Calcd. for $\text{C}_{38}\text{H}_{34}\text{N}_2\text{O}_8\text{Si}_2$; (702.58): C: 64.96%, N: 3.99%, H: 4.84%. Found: C: 64.79%, N: 3.86%, H: 4.6%.

RESULTS AND DISCUSSION

The tetramethyl derivatives (1a-b), tetra acids (2a-b) and dianhydrides (3a-b) were synthesized according to procedures previously described. The spectroscopic data for the new compounds derived from ethylmethylchlorosilane are shown in the experimental part.

The dianhydrides were reacted with glycine in acetic anhydride at reflux in order to obtain the aliphatic diacids bonded to the imide groups. The diacids were purified by washing with distilled water in order to eliminate the residues of glycine, followed by IR spectroscopic analysis (Fig. 3). The reaction of the pure diacids with thionyl chloride gave the acid dichlorides according to the normal procedure. Based on their purity, some samples were recrystallized from a benzene solution. The spectroscopic data are summarized in the experimental part and showed in Figures 4 and 5. Spectroscopic and elemental analysis were in agreement with the proposed structures.

Poly(imide-amide)s

PIAs were obtained in *N,N*-dimethylacetamide (DMAc) solution with pyridine as acid acceptor. The acid dichloride was added to the solution of the diamine in DMAc in four portions at -10°C and then the mixture was stirred at room temperature for 18 h. PIAs were obtained by precipitation in a methanol/water mixture, filtered, washed, and dried.

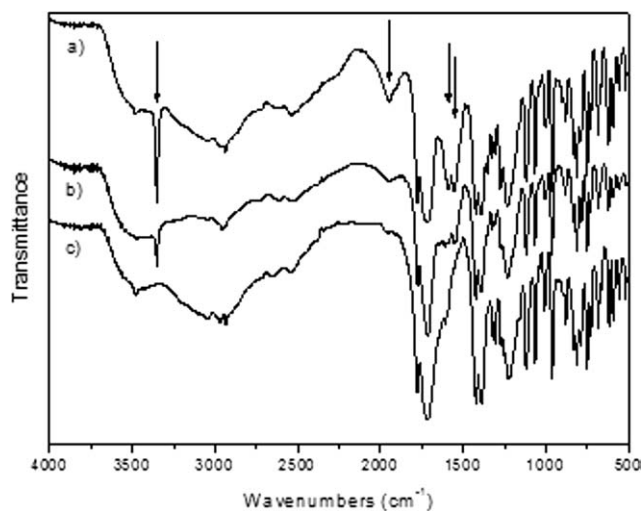


Figure 3 Spectroscopic results of *N,N'*-(4,4'-dimethylsilylene-nedipthaloyl)-bis-glycine diacid (4a) purification, according with the days of treatment: (a) without treatment, (b) 1 day, and (c) 3 days.

The repetitive unit structures of PIAs were established by spectroscopic methods. In the IR spectra, it was possible to observe a band at 3370 cm^{-1} approximately corresponding to the N-H stretching and the characteristic band of the carbonyl group of the amides at 1717 cm^{-1} . The frequency of the imide, Si-Ph and Si-C aliphatic bands are not significantly modified in comparison with values observed in dichloride acids. Additionally, the ^1H -NMR (Fig. 6) spectra showed a signal at 10.5 ppm corresponding to the amidic hydrogen ($-\text{CONH}-$), while the ^{13}C -NMR analysis showed the signal at 165 ppm corresponding to the C=O of the amide group. The signals corresponding to the groups directly bonded to the silicon atom of the acid dichloride moiety appear at high field in a similar way to the chemical shift observed in the respective monomers: -3.31 ppm for the methyl group of PIA-I and at -5.46 ppm for the methyl group of PIA-II. The ^{29}Si -NMR spectra showed a common signal at -15.3 ppm, which is characteristic for the Si atoms bonded to four aromatic rings. Likewise, the spectra allowed to observe the characteristic chemical shifts for aliphatic carbon atoms bonded to silicon: -4.62 ppm for the PIA-I with two methyl groups, and -2.57 ppm for PIA-II with methyl and ethyl. These shifts are very similar to those observed for the spectroscopic analysis of the PIEs.

Table I shows the yields and η_{inh} values obtained for the two PIAs. The low η_{inh} values suggested oligomeric chains of low molecular weight. The higher yields of PIAs compared to those of PIEs is consistent with the higher solubility of the growing polymeric chain in the polymerization medium (DMAc).

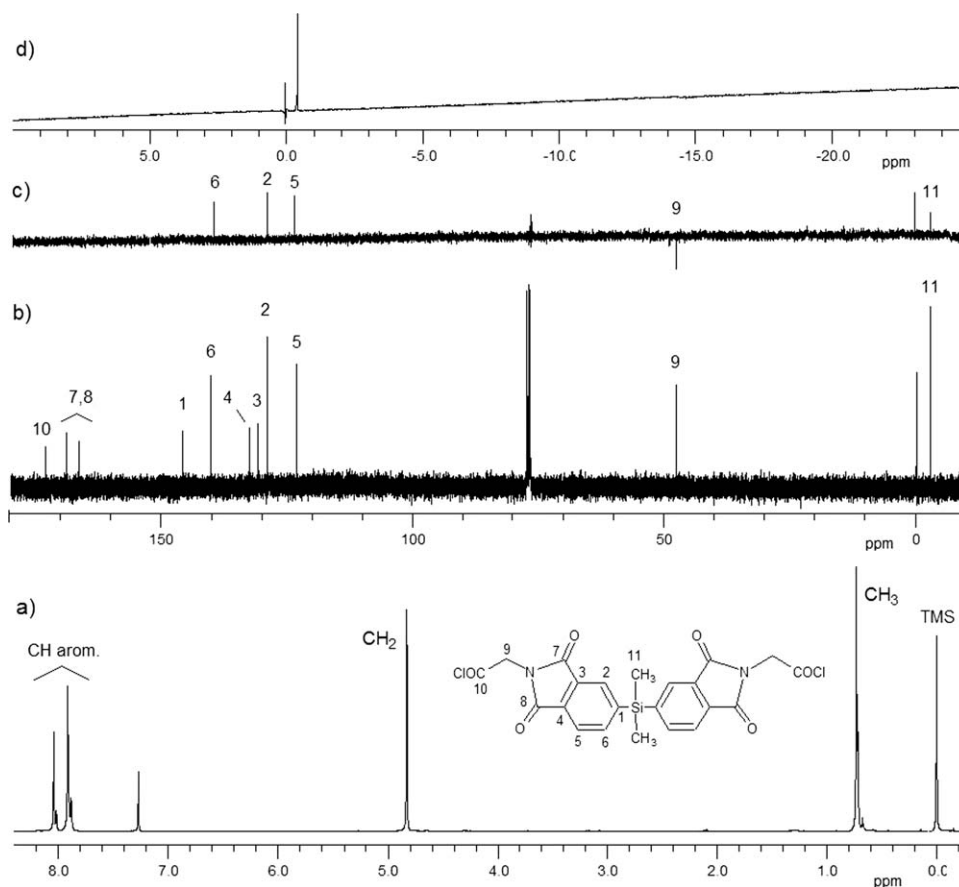


Figure 4 RMN-spectrum *N,N'*-(4,4'-dimethylsilylenedipthaloyl)-bis-glycine acid dichloride (5a). (a) ^1H -NMR, (b) ^{13}C -NMR, (c) DEPT- 135° , and (d) ^{29}Si -RMN.

Poly(imide-ester)s

The (PIEs) were obtained in solution, in which the diphenol was dissolved in anhydrous CHCl_3 and drops of pyridine as acid acceptor, and the acid dichloride in CHCl_3 were added at 0°C .²¹ No polymer was obtained when we used *N*-methylpyrrolidine (NMP) and pyridine at high temperature⁸ or under common phase transfer conditions such as several organic solvents, aq. NaOH. and tetrabutylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC) or methyltrioctylammonium chloride (ALQUAT 336).^{17,22} Likewise, the use of microwaves as polymerization medium did not produce positive results.¹⁹

PIEs were characterized by spectroscopic methods and the results are shown in the experimental part and were in accordance with the proposed structures. The IR spectra of the two PIEs show the absence of the broad band associated to the O–H vibration and a new signal corresponding to the C=O stretching band of the ester group at 1775 cm^{-1} approximately. The presence of the carbonyl group is also verified by ^{13}C -NMR spectroscopy in which a signal at 167 ppm appears. The stretching of C=O imide group ($1716\text{--}1720\text{ cm}^{-1}$), Si–C aro-

matic ($1420\text{--}1426\text{ cm}^{-1}$) and Si–C aliphatic (1392 cm^{-1}) were also present.

The ^1H -NMR spectra of PIE-I, shows two singlets for the methyl groups bonded to the Si atom of the diphenolic moiety at 0.46 and 0.52 ppm, respectively. The methyl groups bonded to the Si atom coming from the acid dichloride portion appeared as a single signal at 0.73 ppm integrating for 6H. For PIE-II (Fig. 7) a very complex group of signals in the aliphatic zone was observed. The aforementioned results would be indicative of a magnetic nonequivalence of the protons bonded to the Si atom of the phenolic moiety, because of the rigid structure of the chains due to the aromatic rings. That rigidity would give a low conformational mobility in which it would be possible to find two kinds of Si atoms in the phenolic moiety.

The ^{13}C -NMR results for PIE-I show two signals for the methyl groups bonded to the Si atom of the phenolic moiety at -2.35 and -2.66 ppm and only one signal at -3.4 ppm for the methyl groups bonded to the Si atom of the acid dichloride portion. In the PIE-II analysis, the methyl groups bonded to the Si atom showed three signals: -6.14 , -5.47 , and -5.18 ppm corresponding to the methyl group of

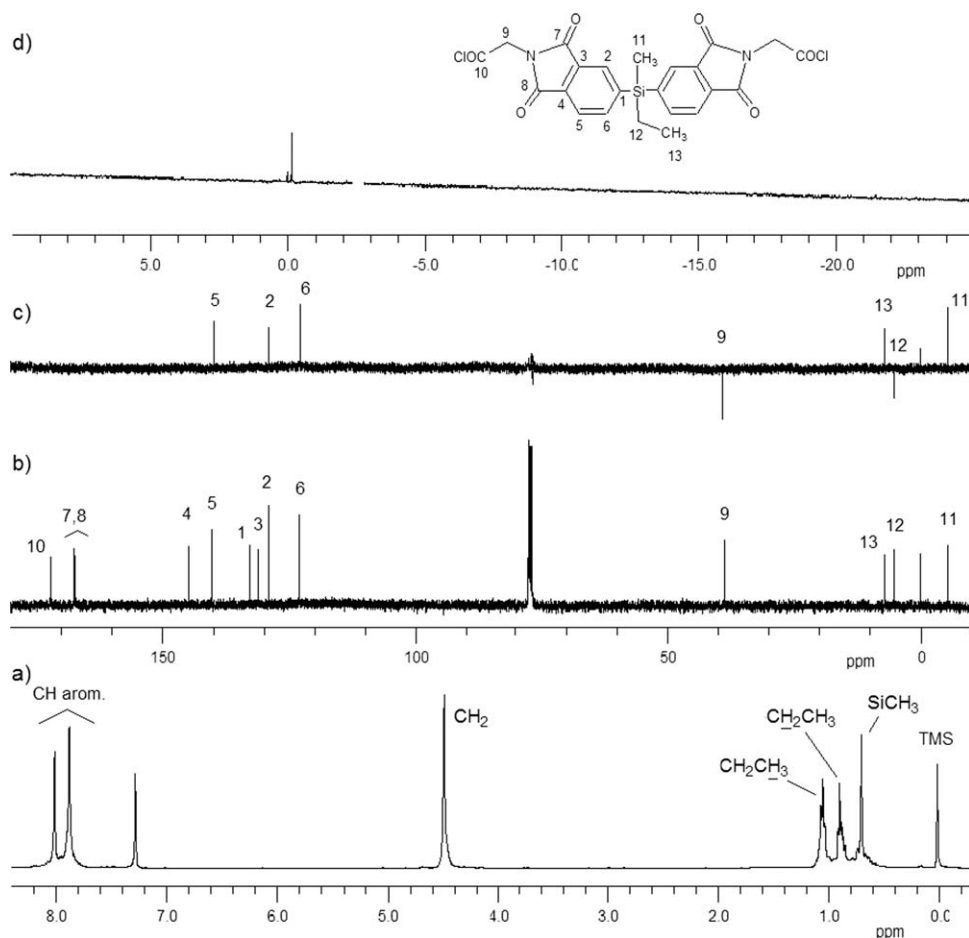


Figure 5 RMN-spectrum *N,N'*-(4,4'-ethylmethylsilylenedipthaloyl)-bis-glycine acid dichloride (5b). (a) ^1H -NMR, (b) ^{13}C -NMR, (c) DEPT-135°, and (d) ^{29}Si -RMN.

the acid dichloride moiety, and the two methyl groups on the phenolic Si atom, respectively.

The ^{29}Si -NMR spectra of compounds are in agreement with the ^{13}C data. In fact, the signals for the Si atom of the acid dichloride portion appear at -4.69 ppm for PIE-I and at -2.55 ppm for PIE-II, respectively. For the phenolic moieties two signals at -8.62 and -7.71 ppm for PIE-I and at -6.30 and -5.55 ppm for PIE-II were observed, supporting the idea about the low conformational mobility and the magnetic nonequivalence of the methyl groups bonded to the Si atoms of these moieties.

The ^{29}Si -NMR spectra also showed a shift to lower fields with increasing the number of carbon atoms on the groups bonded to the silicon center. This is consistent with an unshielding of the Si atom together with the lower electron donating effect when the aliphatic chains are increased. A similar behavior has been observed in other systems such as polyesters and bis(chloroformates) as precursors of polyurethanes.^{16,22}

Table I shows the yields and η_{inh} values for the PIEs. The very low yields of these products are most likely due to their poor solubility in CHCl_3 rather

than potential impurity presence as confirmed by NMR analysis. Yields did not improve by using better solvents such as *N*-methylpyrrolidinone or similar at high temperatures. The low η_{inh} values of these products suggested that PIEs could be of oligomeric nature.

Thermal analysis

The T_g values were obtained at $20^\circ\text{C}/\text{min}$ under N_2 flow in a second scan. The first scan was up to 250°C and then fast cooled down to -100°C in order to eliminate solvent traces and to have the same thermal history. The second scan gave the T_g values considering the change of the slope of the curve, and are summarized in Table I.

PIAs gave practically the same T_g values suggesting that the influence of the two aromatic rings bonded to the Si atom of the diamine moiety is higher than those of the aliphatic groups bonded to the other Si atom. The influence of methyl versus ethyl groups of the acid dichloride moiety was not important. On the other hand, in a previous work we exposed that polyamides with aromatic rings

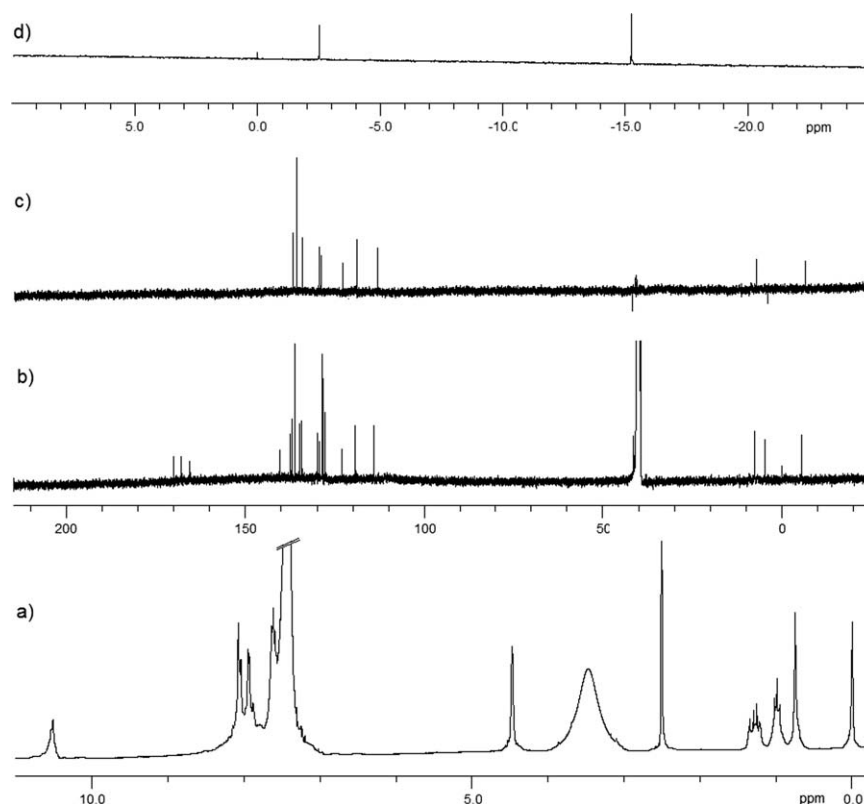


Figure 6 RMN-spectrum for PIA-II (19°C, DMSO-d₆-TMS). (a) ¹H-NMR, (b) ¹³C-NMR, (c) DEPT-135° and (d) ²⁹Si-RMN.

bonded to the Si atoms showed higher T_g values than those in which one Si atom is bonded to aliphatic groups.¹¹ In the present case the difference is only a methyl or ethyl group and is not significant compared with the rest of the polymeric chain.

PIEs showed lower T_g values than those of PIAs, since no aromatic rings are bonded to the Si atoms, generating a more flexible polymeric chains (Fig. 2). Additionally, the PIAs can show H-bonds due to the amide groups. Also PIE-II showed a $T_g \sim 40^\circ\text{C}$ lower than that for PIE-I. This is due to ethyl groups on the Si atoms, increasing the flexibility of the chain, probably by favoring a higher free volume of ethyl groups, when compared to the methyl groups on PIE-I.

Table I also shows the thermal decomposition temperatures (TDT) recorded when polymers lost a

10% weight. These polymers can not be considered as thermally stable because the 10% weight loss occurred at $T < 400^\circ\text{C}$, which is commonly considered the limit temperature for thermally stable polymers. Nevertheless, PIE-I was more stable than PIE-II, and PIA more stable than PIA-II. At 50% weight loss similar trend is observed, being the PIAs more stable than PIEs, and polymers carrying only methyl groups being more stable than those bearing methyl and ethyl groups. An analogous situation was described by Ghatge et al.¹⁰ and by our group for the TDT of polyesters,²³ polyamides, and polyimides.¹¹

The residue obtained after heating at 900°C was similar in all samples and varied between 30 and 39%, corresponding probably to silicon oxide.

TABLE I
Yields, Inherent Viscosities, Glass Transition Temperatures and TDT of the PIEs and PIAs

	Yield (%)	η_{inh} (dL/g) ^a	T_g (°C)	TDT ^b (°C)	TDT ^c (°C)
PIA-I	62	0.27	178	294	572
PIA-II	58	0.35	179	275	558
PIE-I	17	0.19	174	296	444
PIE-II	23	0.23	126	220	428

^a Inherent viscosity, in DMSO at 25°C ($c = 0.3$ g/dL).

^b 10% weight loss temperature.

^c 50% weight loss temperature.

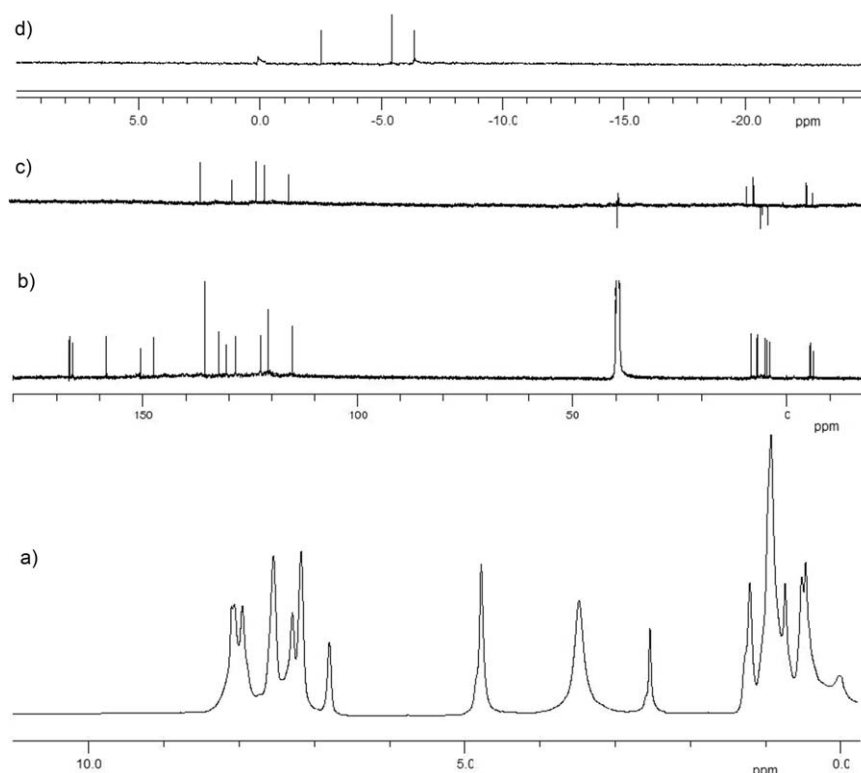


Figure 7 RMN-spectrum for PIE-II (19°C, DMSO-d₆-TMS). (a) ¹H-NMR, (b) ¹³C-NMR, (c) DEPT-135°, and (d) ²⁹Si-RMN.

CONCLUSIONS

PIEs and PIAs containing two Si atoms in the main chain and bonded to aliphatic groups, methyl, or ethyl, and aliphatic and aromatic groups respectively, were synthesized and characterized by spectroscopic methods. ²⁹Si-NMR analysis, showed chemical shifts in agreement with the nature of the groups bonded to silicon. Thus, the silicon atom bonded to phenyl groups showed a lower field shift compared to that from aliphatically substituted Si.

The yields for PIAs were higher than for the PIEs due to the low solubility of the latter in the reaction media. The values of η_{inh} were indicative of low molecular weight material, probably of oligomeric nature.

PIAs carrying aromatic rings showed high T_g values, while aliphatically substituted PIEs had lower T_g values, consistent with the latter having higher molecular flexibility. PIEs and PIAs obtained can not be classified as thermally stable because of the high weight loss at $T < 400^\circ\text{C}$. In general, the PIAs showed higher TDT due to the aromatic rings coming from the diamine moiety. In all cases, the presence of ethyl groups bonded to the Si atoms promotes a decrease in thermal stability.

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