

Poly(amides) and Poly(imides) Containing Silicon and Germanium in the Main Chain: Synthesis, Characterization and Thermal Studies

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ABSTRACT: Poly(amides) and poly(imides) containing the heteroatoms Si or Ge in the main chain and bonded to four carbon atoms were synthesized and characterized by IR and ^1H , ^{13}C and ^{29}Si NMR. The acid dichlorides bis(4-chloroformylphenyl)-dimethylgermane, bis(4-chloroformylphenyl)-diphenylgermane, bis(4-chloroformylphenyl)-dimethylsilane, and bis(4-chloroformylphenyl)-diphenylsilane were synthesized from the ditolyl derivatives, which were oxidized to the respective diacids. The dianhydrides bis(3,4-dicarboxyphenyl)-dimethylgermane dianhydride, bis(3,4-dicarboxyphenyl)-diphenylgermane dianhydride, bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride, and bis(3,4-dicarboxyphenyl)-diphenylsilane dianhydride were synthesized from the dixylyl derivatives, which were oxidized to the tetraacids. Fully aromatic diamines also containing Si or Ge

were synthesized from 4-bromo-*N,N*-bis(trimethylsilyl)-aniline and diphenyl-dichlorosilane or germane. The ditolyl and dixylyl derivatives were synthesized from 4-bromo-toluene or 4-bromo-xylene and dimethyl- or diphenyl-dichlorogermane, dimethyl- or diphenyl-dichlorosilane. The glass transition temperatures and the thermal stability were determined showing in general that the polymers with Si atom in the main chain presented higher values of both parameters due to the higher ionic character of the C—Si bond compared with the C—Ge one, and due to the lower size of the Si atom that presents lower rotational barriers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2768–2776, 2006

Key words: poly(amides); poly(imides); silicon; germanium; glass transition temperature; thermal stability

INTRODUCTION

Since the first silicon-containing polymer was described by Speck,¹ many condensation polymers containing this heteroatom in the main chain have been described. Several reviews have summarized the synthesis and the properties of these polymers,^{2,3} as well as other works with respect to the synthesis of specific silicon-containing condensation polymers.^{4–7}

Bruma et al. have pointed out that the introduction of the silarylene group [—Ar—Si(R₁R₂)—Ar—] instead the Si—O linkages in aromatic polymers leads to improved solubility and the maintenance of a high thermal stability, and thus facilitates the processing of the resulting polymers. Also, the lower electronegativity of the silicon with respect to the carbon atom increases the thermal stability of the silicon-containing polymers due to the fact that the difference of electronegativity causes an ionic character of the C—Si bonds when compared with the respective C—C ones, in spite of the similar bond energy dissociation of both

linkages.² Factor et al. described this behavior for poly(carbonates) derived from analogous diphenols with Si or with C,⁵ and Ghatge et al. for poly(amides).⁴

On the other hand, polymers containing Ge in the main chain, described as poly(germanes) [(GeR₂)_n] in which the Ge atom is bonded to other Ge atoms, are of inorganic nature. These compounds, especially when R corresponds to butyl groups, have been described with photoreactive properties, which undergo a photo-scission process that makes them attractive as photo-resists.^{8,9} However, condensation polymers containing a Ge atom in the main chain and bonded to four carbon atoms have not been described. Only some very special and complex polymers with the Ge atom forming part of the side groups have been described.^{10,11}

For many years we have focused our attention on the synthesis and characterization of condensation polymers using phase transfer catalysis as the polymerization method, and we have described the synthesis of poly(carbonates), poly(thiocarbonates), and poly(esters).¹² However in the last years, we have described the synthesis of analogous condensation polymers but derived from monomers (diphenols, acid dichlorides, diamines) containing Si or Ge, with the objective of obtaining poly(carbonates), poly(thiocarbonates), poly(esters), poly(amides), and poly(urethanes) containing Si or Ge in the main chain

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and bonded to four carbon atoms.^{13–19} In these works, we have studied the synthesis and characterization of these new polymers, describing the synthetic process and evaluating the results with respect to the structure of both the monomer and the catalyst when phase transfer catalysis was used as the polymerization method, by the yields and the inherent viscosity values of the obtained polymers.

We have also studied the thermal behavior, showing in general that polymers with Si showed higher thermal stability and T_g values than that corresponding with Ge. In this behavior there are two factors. First, the higher polarity or ionic character of the C—Si bond with respect to the C—Ge one, due to the lower electronegativity of Si in front of Ge,²⁰ implies that polymers containing the Si atom would show higher thermal stability.³ Second, the C—Si bond would show lower rotational barriers due to the lower size of the Si atom with respect to the Ge one, and as a consequence polymers with Si in the main chain would show higher T_g values with respect to the analogous one with Ge. Also polymers with aliphatic side chains show higher flexibility of the polymeric chain with respect to those with more bulky and rigid groups, such as phenyl ones, and consequently would show lower T_g values.

Continuing our works on the synthesis, characterization, and thermal studies of condensation polymers containing Si or Ge in the main chain and bonded to four carbon atoms, in this work we describe the synthesis of poly(amides) and poly(imides) derived from aromatic acid dichlorides and dianhydrides containing both Si or Ge bonded to methyl or phenyl groups and fully aromatic diamines also containing Si or Ge atom. Polymers were characterized by IR and NMR, including ²⁹Si NMR when it corresponds, and determined the thermal properties: glass transition temperatures and thermal decomposition temperatures, and the results were related with the polymeric structures.

EXPERIMENTAL

Reagents and solvents (from Aldrich or Riedel de Haen) were used without purification. The IR spectra were recorded on a Perkin–Elmer 1310 spectrophotometer and the ¹H, ¹³C, and ²⁹Si NMR on a 400 MHz instrument (Bruker AC-200), using CDCl₃, acetone-*d*₆, or DMSO-*d*₆ as solvents and TMS as the internal standard. Viscosimetric measurements were made in a Desreux–Bischof²¹ type dilution viscosimeter at 25°C.

T_g values were obtained with a Mettler-Toledo DSC 821 calorimetric system. Thermogravimetric analyses were carried out in a Mettler 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 with a heating rate of 20°C min⁻¹ under N₂ flow.

All the monomers and polymers were characterized by IR and ¹H, ¹³C, and when it corresponds by ²⁹Si NMR spectroscopy, with the exception of poly(imides) for which it was only possible to do the IR.

Acid dichlorides

The acid dichlorides bis(4-chloroformylphenyl)-dimethylgermane, bis(4-chloroformylphenyl)-diphenylgermane, bis(4-chloroformylphenyl)-dimethylsilane and bis(4-chloroformylphenyl)-diphenylsilane 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.^{22–25}

Diamines

Bis(4-aminophenyl)-diphenylsilane and bis(4-aminophenyl)-diphenylgermane were obtained from 4-bromo-*N,N*-bis(trimethylsilyl)-aniline and diphenyl-dichlorosilane or diphenyl-dichlorogermane according to the procedure described previously,^{26,27} and characterized.

Dianhydrides

Bis(3,4-dimethylphenyl)-dimethylgermane, bis(3,4-dimethylphenyl)-diphenylgermane, bis(3,4-dimethylphenyl)-dimethylsilane, and bis(3,4-dimethylphenyl)-diphenylsilane were synthesized from 4-bromoxylene and dimethyl- or diphenyl-dichlorogermane, dimethyl- or diphenyl-dichlorosilane. The bis(3,4-dimethylphenyl) derivatives were oxidized to the corresponding tetraacids and then reacted with acetic anhydride according to a procedure described previously.²⁸

Bis(3,4-dimethylphenyl)-dimethylgermane. Mp: 64–65°C. IR (KBr) (cm⁻¹): 3020 (H arom.), 2926 (CH₃), 1595, 1557, 1491 (C=C), 1450, 1375 (CH₃), 888, 828 (arom 1,2,4-subst.). ¹H NMR (δ) (ppm) (CDCl₃): 0.66 (s, 6H, CH₃), 2.31 (s, 12H, CH₃), 7.16–7.31 (m, 6H, arom.). ¹³C NMR (δ) (ppm) (CDCl₃): -2.87 (Ge-CH₃), 19.77 (CH₃), 129.4, 131.3, 134.9, 136.3, 137, 137.4 (arom.).

Bis(3,4-dimethylphenyl)-diphenylgermane. Mp: 76–78°C. IR (KBr) (cm⁻¹): 3050 (H arom.), 2937 (CH₃), 1594, 1484 (C=C), 1447, 1378 (CH₃), 876, 816 (arom. 1,2,4-subst.), 736, 699 (arom. mono-subst.). ¹H NMR (δ) (ppm) (CDCl₃): 2.26 (s, 6H, CH₃), 2.31 (s, 6H, CH₃), 7.15–7.79 (m, 16H, arom.). ¹³C NMR (δ) (ppm) (CDCl₃): 19.8 (CH₃), 128.2, 128.6, 128.9, 129.6, 133.1, 133.6, 135.4, 136.5, 136.9, 137.6 (arom.).

Bis(3,4-dicarboxyphenyl)-dimethylgermane. Mp: > 350°C. IR (KBr) (cm⁻¹): 3193 (OH), 2977 (CH₃), 1700 (C=O), 1593, 1558, 1494 (C=C), 1389 (CH₃), 868, 837 (arom. 1,2,4-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 0.81 (s, 6H, CH₃), 7.73–7.81 (m, 6H, arom.), 13.1 (s, 4H, OH). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): -3.82 (CH₃), 127.8, 132.3, 132.7, 133, 135.7, 143 (arom.), 168.5, 168.7 (C=O).

Bis(3,4-dicarboxyphenyl)-diphenylgermane. Mp: > 350°C. IR (KBr) (cm⁻¹): 3433 (OH), 3022 (H arom.), 1703 (C=O), 1590, 1557, 1486 (C=C), 736, 698 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 7.45–8.16 (m, arom.). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): 128.4, 128.7, 128.8, 129.8, 133.8, 134.7, 134.9, 135.9, 137.1, 138 (arom.), 168.1, 168.3 (C=O).

Bis(3,4-dicarboxyphenyl)-dimethylgermane dianhydride. Mp: 172–174°C. IR (KBr) (cm⁻¹): 3028 (H arom.), 2982, 2915 (CH₃), 1853, 1769 (C=O), 1599 (C=C), 870, 847 (arom. 1,2,4-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 1.08 (s, 6H, CH₃), 8.12–8.36 (m, 6H, arom.). ¹³C NMR (δ) (ppm) (acetone-*d*₆): -3.06 (CH₃), 125.8, 131.5, 132.1, 133.3, 142.5, 151.6 (arom.), 164.3, 164.5 (C=O).

Bis(3,4-dicarboxyphenyl)-diphenylgermane dianhydride. Mp: 139–140°C. IR (KBr) (cm⁻¹): 3054 (H arom.), 1852, 1772, 1691 (C=O), 1595, 1486 (C=C), 731, 696 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 7.39–7.92 (M, H arom.). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): 128.8, 129.4, 130.4, 131.5, 132.8, 133.7, 134.1, 135.2, 137.8, 138.7 (arom.), 168.1, 169.1 (C=O).

Bis(3,4-dicarboxyphenyl)-dimethylsilane dianhydride. Mp: 159–162°C. IR (KBr) (cm⁻¹): 3017 (H arom.), 2962, (CH₃), 1855, 1812, 1773 (C=O), 1603 (C=C), 879, 814 (arom. 1,2,4-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 0.94 (s, 6H, CH₃), 8.14 (d, 2H, arom.), 8.35 (d, 4H, arom.). ¹³C NMR (δ) (ppm) (acetone-*d*₆): -3.26 (CH₃), 125.3, 131.4, 131.6, 133.2, 142.6, 146.6 (arom.), 163.9, 164 (C=O). ²⁹Si NMR (δ) (ppm) (DMSO-*d*₆): -6.42.

Bis(3,4-dicarboxyphenyl)-diphenylsilane dianhydride. Mp: 122–123°C. IR (KBr) (cm⁻¹): 3023 (H arom.), 1853, 1779, 1700 (C=O), 1593, 1489 (C=C), 733, 701 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 7.41–8.2 (M, H arom.). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): 125.5, 128.6, 130, 131.3, 132.1, 134.9, 135.6, 136.3, 138.8, 143.5 (arom.), 168.7, 169.1 (C=O). ²⁹Si NMR (δ) (ppm) (DMSO-*d*₆): -15.3.

Poly(amides)

The poly(amides) (PA) were synthesized according to the following general procedure. The diamine (1 mmol) was dissolved in 25 mL of *N,N*-dimethylacetamide (DMAc) and 0.8 mL of pyridine was added. The bath was cooled to -10°C and 1 mmol of the acid dichloride was added in four portions, and the mixture was stirred for 18 h and then poured into methanol. The poly(amide) was filtered, washed with methanol, dried under vacuum until constant weight, and then characterized.

PA-I. IR (KBr) (cm⁻¹): 3423 (NH), 3021 (H arom.), 1672, 1630 (C=O), 1587, 1511 (C=C), 821 (arom *p*-subst.), 737, 699 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 7.45–8 (m, 36H, arom.), 10.46 (s, 2H, NH). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): 120.8, 128.8, 129, 129.8, 130.2, 130.6, 134.2, 134.7, 135, 135.3, 135.4, 135.8, 136.3, 136.6, 139.9, 140.7 (arom.), 166.3 (C=O).

PA-II. IR (KBr) (cm⁻¹): 3422 (NH), 3021 (H arom.), 1672, 1630 (C=O), 1586, 1509 (C=C), 821 (arom *p*-subst.), 733, 700 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 7.44–7.47 (m, 24H, arom.), 7.6 (d, 4H, arom.), 7.78 (d, 4H, arom.), 7.92 (d, 4H, arom.), 10.4 (s, 2H, NH). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): 120.8, 127.7, 128.7, 128.8, 129.8, 130.6, 131.7, 133, 134.2, 134.7, 135.3, 135.8, 136.3, 136.9, 137.8, 140.6 (arom.), 166.3 (C=O). ²⁹Si NMR (δ) (ppm) (DMSO-*d*₆): -14.6. Elemental analysis for C₅₀H₃₈N₂O₂SiGe. Calcd: C, 76.13%; H, 4.76%; N, 3.51%. Found: C, 76.91%; H, 4.46%; N, 3.41%.

PA-III. IR (KBr) (cm⁻¹): 3422 (NH), 3020 (H arom.), 2947 (CH₃), 1662 (C=O), 1586, 1510 (C=C), 804 (arom *p*-subst.), 738, 699 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 0.72 (s, 6H, CH₃), 7.46–7.66 (m, 16H, arom.), 7.95–7.85 (m, 8H, arom.), 10.38 (s, 2H, NH). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): -3.11 (CH₃), 120.8, 127.6, 128.8, 129, 129.8, 130.5, 133.9, 134.2, 135.3, 135.7, 140.7, 144.6 (arom.), 166.3 (C=O).

PA-IV. IR (KBr) (cm⁻¹): 3422 (NH), 3021 (H arom.), 2957 (CH₃), 1660 (C=O), 1586, 1511 (C=C), 813 (arom *p*-subst.), 737, 699 (arom. mono-subst.). ¹H NMR (δ) (ppm) (DMSO-*d*₆): 0.63 (s, 6H, CH₃), 7.46–7.56 (m, 14H, arom.), 7.71 (d, 4H, arom.), 7.88 (d, 4H, arom.), 7.69 (d, 4H, arom.), 10.39 (s, 2H, NH). ¹³C NMR (δ) (ppm) (DMSO-*d*₆): -2.51 (CH₃), 120.8, 127.4, 128.8, 129, 129.8, 130.1, 134.2, 134.4, 135.3, 135.7, 140.1, 142 (arom.), 166.3 (C=O). ²⁹Si NMR (δ) (ppm) (DMSO-*d*₆): -7.21.

PA-V. IR (KBr) (cm^{-1}): 3407 (NH), 3020 (H arom.), 1660 (C=O), 1589, 1509 (C=C), 821 (arom *p*-subst.), 738, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 7.5–7.56 (m, 24H, arom.), 7.65 (d, 4H, arom.), 7.85 (d, 4H, arom.), 8 (d, 4H, arom.), 10.47 (s, 2H, NH) (Fig. 1). ^{13}C NMR (δ) (ppm) (DMSO- d_6): 120.3, 128.1, 128.4, 128.6, 128.8, 129.3, 130.2, 135, 135.3, 135.4, 136.3, 136.6, 138.8, 136.9, 140, 141.1 (arom.), 166.3 (C=O). ^{29}Si NMR (δ) (ppm) (DMSO- d_6): -15.3.

PA-VI. IR (KBr) (cm^{-1}): 3416 (NH), 3021 (H arom.), 1657 (C=O), 1588, 1509 (C=C), 822 (arom *p*-subst.), 735, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 7.47–7.53 (m, 24H, arom.), 7.73 (d, 4H, arom.), 7.93 (d, 4H, arom.), 8.13 (d, 4H, arom.), 10.43 (s, 2H, NH). ^{13}C NMR (δ) (ppm) (DMSO- d_6): 120.3, 128.4, 128.6, 128.8, 128.9, 130.7, 133, 134.5, 136.2, 136.3, 136.8, 136.9, 137, 137.4, 137.9, 141.1 (arom.), 166.3 (C=O). ^{29}Si NMR (δ) (ppm) (DMSO- d_6): -14.8, -15.3.

PA-VII. IR (KBr) (cm^{-1}): 3423 (NH), 3021 (H arom.), 2974 (CH_3), 1655, 1630 (C=O), 1589, 1510 (C=C), 824 (arom *p*-subst.), 744, 701 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 0.79 (s, 6H, CH_3), 7.47–7.95 (m, 26H, arom.), 10.39 (s, 2H, NH). ^{13}C NMR (δ) (ppm) (DMSO- d_6): -3.08 (CH_3), 114.2, 117.5, 120.2, 127.6, 128.4, 130.2, 134.2, 135.7, 136.2, 136.8, 141.1, 144.6 (arom.), 166.3 (C=O). ^{29}Si NMR (δ) (ppm) (DMSO- d_6): -15.3.

PA-VIII. IR (KBr) (cm^{-1}): 3410 (NH), 3047 (H arom.), 1656 (C=O), 1587, 1513 (C=C), 813 (arom *p*-subst.), 746, 701 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 0.62 (s, 6H, CH_3), 7.13–7.95 (m, 26H, arom.), 10.4 (s, 2H, NH). ^{13}C NMR (δ) (ppm)

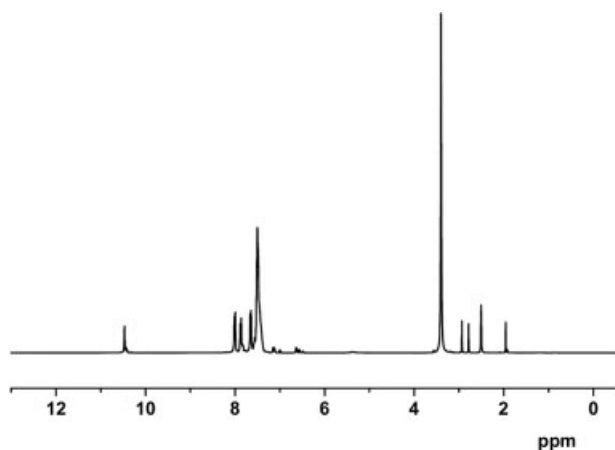


Figure 1 ^1H NMR spectrum for PA-V in DMSO- d_6 . (Peaks between 1.9 and 3.4 ppm belong to the solvent.)

(DMSO- d_6): -2.52 (CH_3), 120.3, 127.4, 128.6, 130.2, 134.4, 136.2, 136.3, 136.9, 141.1, 142.3 (arom.), 166.3 (C=O). ^{29}Si NMR (δ) (ppm) (DMSO- d_6): -7.21, -15.2. Elemental analysis for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_2\text{Si}_2$. Calcd: C, 70.59%; H, 5.88%; N, 5.49%. Found: C, 71.02%; H, 5.58%; N, 5.36%.

Poly(imides)

The poly(amic acids) (PaI) were synthesized according to the following general procedure. The diamine (1 mmol) was dissolved in 10 mL of DMAc under N_2 flow and then 1 mmol of the dianhydride was added in portions at room temperature. The mixture was stirred at 50°C for 18 h and then poured into water. The PaIs were filtered, washed with water, dried under vacuum until constant weight, and characterized. The polyamic acid was dissolved in DMAc and the solution was warmed in a vacuum stove. The film or the powder was separated from the glass and characterized by IR spectroscopy.

PaI-I. IR (KBr) (cm^{-1}): 3451 (OH), 3376 (NH), 3045 (H arom.), 1685, 1618 (C=O), 1595, 1502 (C=C), 818 (arom. *p*-subst.), 737, 699 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 6.61 (d, 4H, arom.), 7.07 (d, 4H, arom.), 7.39–7.71 (m, 26H, arom.), 10 (s, 2H, NH), 10.58 (s, 2H, OH). ^{13}C NMR (δ) (ppm) (DMSO- d_6): 113.7, 114, 119.3, 128.1, 128.2, 128.4, 128.6, 128.7, 128.8, 129.2, 129.7, 133.6, 134.7, 135.2, 135.5, 136.7, 137.6, 137.6 (arom.), 168.5, 168.8 (C=O). Elemental analysis for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_2\text{Ge}_2$. Calcd: C, 67.01%; H, 4.08%; N, 3.01%. Found: C, 66.03%; H, 4.47%; N, 2.74%.

PaI-II. IR (KBr) (cm^{-1}): 3476 (OH), 3381 (NH), 3021 (H arom.), 1722, 1625 (C=O), 1591, 1512 (C=C), 822 (arom. *p*-subst.), 741, 702 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 6.67 (d, 4H, arom.), 7.09 (d, 4H, arom.), 7.39–7.63 (m, 26H, arom.), 9.64 (s, 2H, NH), 10.28 (s, 2H, OH). ^{13}C NMR (δ) (ppm) (DMSO- d_6): 114, 128, 128.2, 128.4, 128.5, 129.1, 129.2, 129.3, 129.4, 129.6, 130.1, 134.1, 134.2, 135, 135.3, 136.2, 136.3, 137.3 (arom.), 167.7, 169 (C=O). ^{29}Si NMR (δ) (ppm) (DMSO- d_6): -15.9.

PaI-III. IR (KBr) (cm^{-1}): 3387 (OH), 3044 (H arom.), 2957 (CH_3), 1650 (C=O), 1587, 1503 (arom.), 823 (arom. *p*-subst.), 738, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) (DMSO- d_6): 0.69 (s, 6H, CH_3), 6.6–7.74 (m, 24H, arom.), 11.83 (s, 2H, OH). ^{13}C NMR (δ) (ppm) (DMSO- d_6): -3.65 (CH_3), 114.1, 119.4, 128.3, 128.7, 129.1, 133.6, 134.1, 134.7, 135.2, 135.5, 135.9, 136.8, 137.3, 140.7 (arom.), 166.9, 169.1 (C=O).

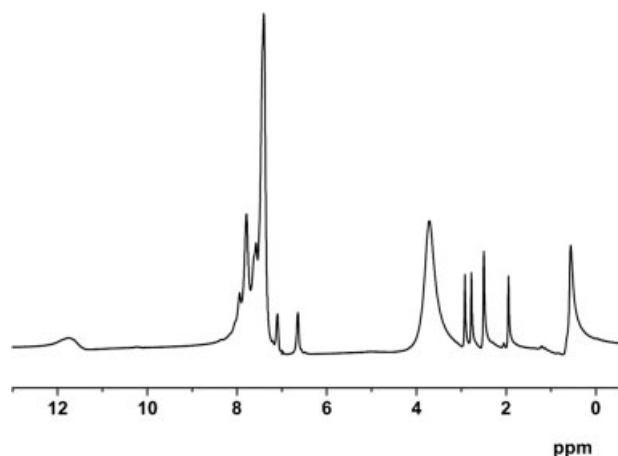


Figure 2 ^1H NMR spectrum for **PaI-IV** in $\text{DMSO-}d_6$. (Peaks between 1.9 and 3.6 ppm belong to the solvent.)

PaI-IV. IR (KBr) (cm^{-1}): 3383 (OH), 3047 (H arom.), 2957 (CH_3), 1651 ($\text{C}=\text{O}$), 1616, 1503 ($\text{C}=\text{C}$), 816 (arom. *p*-subst.), 738, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) ($\text{DMSO-}d_6$): 0.57 (CH_3), 6.6–7.89 (m, 24H, arom.), 11.58 (s, 2H, OH) (Fig. 2). ^{13}C NMR (δ) (ppm) ($\text{DMSO-}d_6$): –3.29 (CH_3), 114, 118.9, 119.4, 128.2, 128.4, 128.7, 133.6, 134.7, 135.1, 135.5, 135.6, 136.8, (arom.), 166.9, 167.1 ($\text{C}=\text{O}$). ^{29}Si NMR (δ) (ppm) ($\text{DMSO-}d_6$): –7.59.

PaI-V. IR (KBr) (cm^{-1}): 3457 (OH), 3382 (NH), 3047 (H arom.), 1720, 1685 ($\text{C}=\text{O}$), 1594, 1506 ($\text{C}=\text{C}$), 820 (arom. *p*-subst.), 739, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) ($\text{DMSO-}d_6$): 6.62 (d, 4H, arom.), 7.13 (d, 4H, arom.), 7.38–7.78 (m, 26H, arom.), 10 (s, 2H, NH), 10.5 (s, 2H, OH). ^{13}C NMR (δ) (ppm) ($\text{DMSO-}d_6$): 114, 114.2, 119.4, 128.2, 128.4, 128.5, 128.6, 129, 129.3, 129.4, 134.1, 135.2, 135.3, 136.2, 136.8, 136.9, 137.3, 137.4 (arom.), 167.7, 169 ($\text{C}=\text{O}$). ^{29}Si NMR (δ) (ppm) ($\text{DMSO-}d_6$): –15.3.

PaI-VI. IR (KBr) (cm^{-1}): 3450 (OH), 3380 (NH), 3047 (H arom.), 1700, 1618 ($\text{C}=\text{O}$), 1596, 1506 ($\text{C}=\text{C}$), 820 (arom. *p*-subst.), 739, 700 (arom. mono-subst.). ^1H NMR (δ) (ppm) ($\text{DMSO-}d_6$): 6.6 (d, 4H, arom.), 7.13 (d, 4H, arom.), 7.39–7.52 (m, 26H, arom.), 10.5 (s, 2H, OH) (Fig. 2). ^{13}C NMR (δ) (ppm) ($\text{DMSO-}d_6$): 114.1, 114.2, 119.1, 128.2, 128.4, 128.6, 128.8, 129, 129.5, 129.9, 135, 135.6, 136.2, 136.3, 136.7, 136.8, 137.3, 137.4 (arom.), 167.6, 169.4 ($\text{C}=\text{O}$). ^{29}Si NMR (δ) (ppm) ($\text{DMSO-}d_6$): –14.9, –15.3.

PaI-VII. IR (KBr) (cm^{-1}): 3475 (OH), 3378 (NH), 3020 (H arom.), 2972 (CH_3), 1718, 1673 ($\text{C}=\text{O}$), 1598, 1519 ($\text{C}=\text{C}$), 826 (arom. *p*-subst.), 744, 703 (arom. mono-subst.). ^1H NMR (δ) (ppm) ($\text{DMSO-}d_6$): 0.74 (s, 6H, CH_3), 6.61 (d, 4H, arom.), 7.12 (d, 4H, arom.),

7.43–7.92 (m, 16H, arom.), 11.1 (s, 2H, OH). ^{13}C NMR (δ) (ppm) ($\text{DMSO-}d_6$): –3.13 (CH_3), 114.1, 119.5, 128.2, 128.4, 128.6, 129.9, 130.2, 134.6, 135, 136.2, 136.3, 136.9, 137.4 (arom.), 167.8, 170.1 ($\text{C}=\text{O}$). ^{29}Si NMR (δ) (ppm) ($\text{DMSO-}d_6$): –15.3.

PaI-VIII. IR (KBr) (cm^{-1}): 3475 (OH), 3385 (NH), 3045 (H arom.), 2957 (CH_3), 1718, 1660 ($\text{C}=\text{O}$), 1592, 1506 ($\text{C}=\text{C}$), 819 (arom. *p*-subst.), 741, 702 (arom. mono-subst.). ^1H NMR (δ) (ppm) ($\text{DMSO-}d_6$): 0.62 (s, 6H, CH_3), 6.62 (d, 4H, arom.), 7.14 (d, 4H, arom.), 7.42–8.07 (m, 16H, arom.), 11.54 (s, 2H, OH). ^{13}C NMR (δ) (ppm) ($\text{DMSO-}d_6$): –2.5 (CH_3), 114.1, 119.6, 128.2, 128.4, 128.5, 128.7, 129.6, 129.8, 135.3, 136.2, 136.3, 136.8, 137.3, 137.4, (arom.), 167.6, 170.2 ($\text{C}=\text{O}$). ^{29}Si NMR (δ) (ppm) ($\text{DMSO-}d_6$): –7.37, –16.03. Elemental analysis for $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_6\text{Si}_2$. Calcd: C, 62.72%; H, 5.92%; N, 4.88%. Found: C, 61.63%; H, 5.41%; N, 5.40%.

PI-I. IR (KBr) (cm^{-1}): 3046 (H arom.), 1720 ($\text{C}=\text{O}$), 1590, 1503 ($\text{C}=\text{C}$), 818 (arom. *p*-subst.), 735, 697 (arom. mono-subst.). Elemental analysis for $\text{C}_{42}\text{H}_{30}\text{N}_2\text{O}_4\text{Ge}_2$. Calcd: C, 65.35%; H, 3.89%; N, 3.63%. Found: C, 64.91%; H, 3.99%; N, 3.83%.

PI-II. IR (KBr) (cm^{-1}): 3046 (H arom.), 1721 ($\text{C}=\text{O}$), 1596, 1504 ($\text{C}=\text{C}$), 820 (arom. *p*-subst.), 737, 699 (arom. mono-subst.).

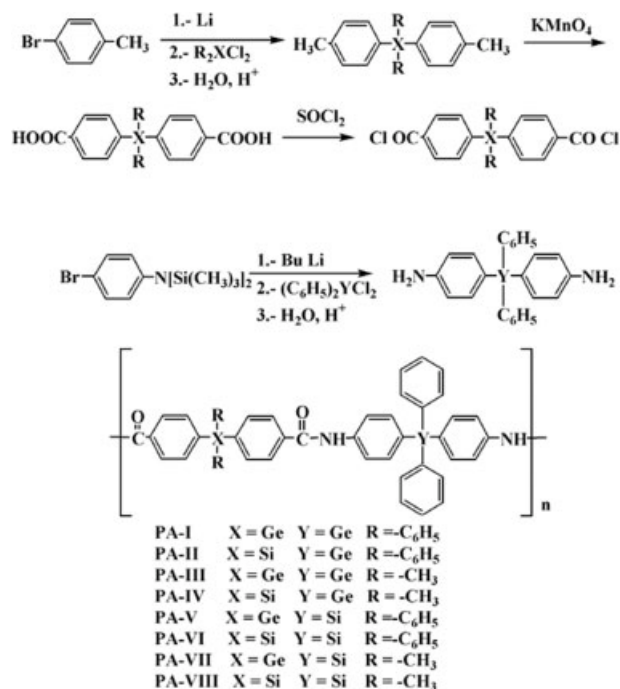
PI-III. IR (KBr) (cm^{-1}): 3045 (H arom.), 1719 ($\text{C}=\text{O}$), 1586, 1502 ($\text{C}=\text{C}$), 804 (arom. *p*-subst.), 736, 699 (arom. mono-subst.).

PI-IV. IR (KBr) (cm^{-1}): 3045 (H arom.), 2954 (CH_3), 1719 ($\text{C}=\text{O}$), 1584, 1502 ($\text{C}=\text{C}$), 814 (arom. *p*-subst.), 737, 699 (arom. mono-subst.).

PI-V. IR (KBr) (cm^{-1}): 3046 (H arom.), 1776, 1719 ($\text{C}=\text{O}$), 1592, 1504 ($\text{C}=\text{C}$), 820 (arom. *p*-subst.), 736, 699 (arom. mono-subst.).

PI-VI. IR (KBr) (cm^{-1}): 3047 (H arom.), 1776, 1721 ($\text{C}=\text{O}$), 1591, 1504 ($\text{C}=\text{C}$), 821 (arom. *p*-subst.), 739, 699 (arom. mono-subst.). Elemental analysis for $\text{C}_{52}\text{H}_{34}\text{N}_2\text{O}_4\text{Si}_2$. Calcd: C, 72.39%; H, 3.94%; N, 3.25%. Found: C, 72.95%; H, 3.73%; N, 3.43%.

PI-VII. IR (KBr) (cm^{-1}): 3044 (H arom.), 2973 (CH_3), 1719 ($\text{C}=\text{O}$), 1589, 1504 ($\text{C}=\text{C}$), 817 (arom. *p*-subst.), 738, 701 (arom. mono-subst.).



Scheme 1 Synthesis of the acid dichlorides, diamines, and PA.

PI-VIII. IR (KBr) (cm⁻¹): 3046 (H arom.), 2957 (CH₃), 1720 (C=O), 1594, 1504 (C=C), 811 (arom. *p*-subst.), 737, 701 (arom. mono-subst.).

RESULTS AND DISCUSSION

The acid dichlorides, dianhydrides, and diamines were synthesized according to procedures described previously. The spectroscopic data for the new germanium-containing monomers, as well as for all the PA, PaI, and poly(imides) (PI) are shown, and the results were in agreement with the proposed structures.

Poly(amides)

PAs were synthesized from the acid dichlorides and the diamines according to the structures proposed in the Scheme 1.

PAs were characterized by spectroscopic methods, and the results are described in the experimental part and were in accordance with the proposed structures. For all the PAs, it was possible to see the C=O signal in the ¹³C spectra at 166.3 ppm. The signal of the Si atom in the ²⁹Si spectra was observed between -14.6 and -15.3 ppm for the PAs in which the Si atom is bonded to phenyl groups. For the **PA-VI** it was possible to see two signals corresponding to the two Si atoms bonded to phenyl groups at -14.8 and -15.3 ppm. For the PAs **IV** and **VIII**, the signal corresponding to the Si atoms bonded to methyl

groups appears at -7.21 ppm. The chemical shift of the Si atom changes to a higher field when it is bonded to phenyl groups, due probably to two effects: the donor electronic inductive effect and an eventual backbonding involving the overlap of π orbitals of the aromatic ring and the d orbitals of the Si atom. When the Si atom is bonded to both phenyl and methyl groups in poly(carbonates), poly(thiocarbonates), and poly(esters), the chemical shift was between -10.5 and -12 ppm.¹⁷

PAs were soluble in aprotic polar solvents as DMAC, *N,N*-dimethylformamide, and dimethyl sulfoxide, but insoluble in common organic solvents.

Table I shows the yields and η_{inh} values obtained for the **PA-I** to **PA-VIII**. PAs were obtained in general with moderate and good yields, especially those derived from acid dichlorides in which the heteroatom is bonded to four aromatic rings. If we compare the results obtained for the PA with the same main chain, but with different side groups (**PA-I** and **III**, **II** and **IV**, **V** and **VII**, **VI** and **VIII**) it is possible to see that those with only phenyl groups as side chains showed higher yields and η_{inh} than those with methyl groups. This effect can be due to a higher solubility in the polymerization media of the PAs containing only phenyl groups bonded to the heteroatoms.

Poly(imides)

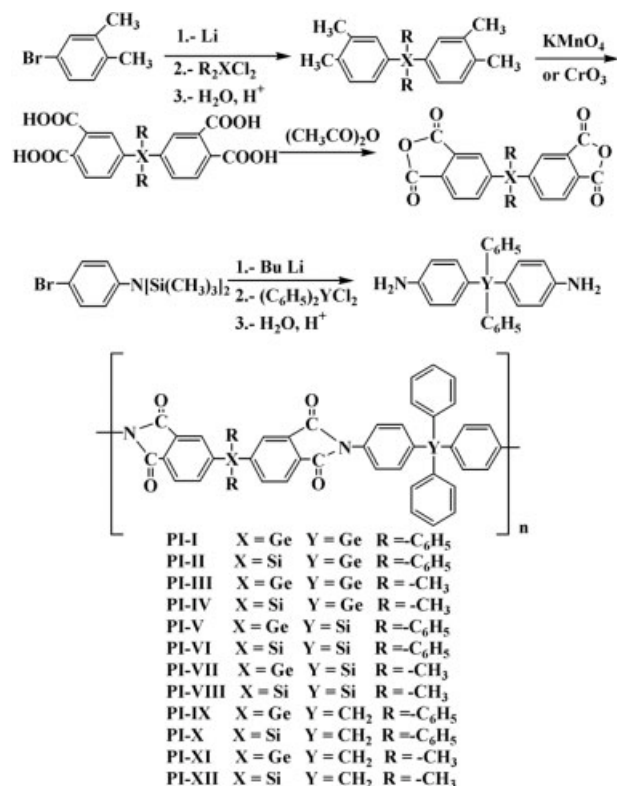
PIs were synthesized from the dianhydrides and the diamines according to the structures of the Scheme 2.

The polyamic acids (PaIs) were synthesized in DMAC solution at room temperature, and the dianhydride was added to the diamine solution in four portions. The mixture was stirred at 50°C for 18 h and then poured into distilled water. The PaIs were filtered, washed, dried until constant weight, and characterized. All the PIs were obtained by heating a DMAC solution of the PaIs at 180°C under vacuum, and the film or powder was separated and characterized by IR spectroscopy.

TABLE I
Yields, Inherent Viscosities, Glass Transition Temperatures (T_g) and Thermal Decomposition Temperatures (TDT) of the Poly(amides)

Poly(amide)	Yield (%)	η_{inh}^a (dL/g)	T_g (°C)	TDT (°C)
PA-I	60	0.21	107	403
PA-II	76	0.21	110	336
PA-III	35	0.14	83	425
PA-IV	40	0.14	100	420
PA-V	65	0.18	100	425
PA-VI	85	0.18	104	430
PA-VII	50	0.14	104	225
PA-VIII	35	0.14	95	450

^a In DMF at 25°C ($c = 0.3$ g/mL).



Scheme 2 Synthesis of the dianhydrides, diamines, and PI.

The polyamic acids were soluble in aprotic polar solvents as DMAc, *N,N*-dimethylformamide, and dimethyl sulfoxide, but insoluble in common organic solvents. PIs were insoluble in all solvents.

The PAs were characterized by IR and NMR and the results were in accordance with the proposed structures. The signal of the methyl groups bonded to Si or Ge was observed between -2.5 and -3.65 , and those that correspond to the C=O groups between 166.1 to 170.1 ppm (two signals). The signal corresponding to the Si atom in the ^{29}Si spectra showed the same tendency to that of the PAs. In fact, when the Si atom is bonded to phenyl groups, the signals were observed between -14.9 and -16 ppm, but when it is bonded to methyl groups they were observed between -7.37 and -7.59 ppm, in agreement with the chemical shift for Si-CH₃ groups described by Factor for the silicon-containing poly(carbonate).⁵

Table II shows the yields and η_{inh} values of the polyamic acids **PaI-I** to **VIII**. In general we obtained moderate and good yields, but with high η_{inh} values compared with the PAs, probably due to the higher solubility of the polyamic acids due to the free carboxylic groups in this highly polar solvent.

The PIs were characterized only by IR spectroscopy because it was impossible to have a good solvent for them.

TABLE II

Yields and Inherent Viscosities for the Poly(amic) Acids

Polymer	Yield (%)	η_{inh}^a (dL/g)
PaI-I	57	0.36
PaI-II	42	0.16
PaI-III	54	0.16
PaI-IV	58	0.36
PaI-V	74	0.21
PaI-VI	64	0.21
PaI-VII	30	0.26
PaI-VIII	46	0.36

^a In DMF at 25°C ($c = 0.3$ g/mL).

Glass transition temperatures (T_g)

Table I also shows the T_g values of the PAs, obtained from the thermograms, considering the change of the slope of the curve. In general, polymers with methyl side groups show a higher flexibility of the polymeric chain with respect to those with aromatic side rings, and consequently the motions in the main chain would be easier when the temperature is increased, and the PAs with methyl groups would have lower values of T_g (Fig. 3).

If we observe the pairs of PAs, **I** and **III**, **II** and **IV**, and **VI** and **VIII**, it is possible to see that those with methyl groups bonded to Si or Ge in the diacid show lower T_g values. The exception is the pair **V** and **VII** in which both values are very similar.

However, in the PIs (Table III) only in the pair **PI-V** and **VII**, we can observe this trend. The other pairs, **PI-I** and **III**, **PI-II** and **IV**, and **PI-VI** and **VIII**, those with methyl groups bonded to the heteroatom of the dianhydride, showed higher T_g values than those corresponding to methyl groups, due probably to the higher influence of the rigid imides groups. Also, we

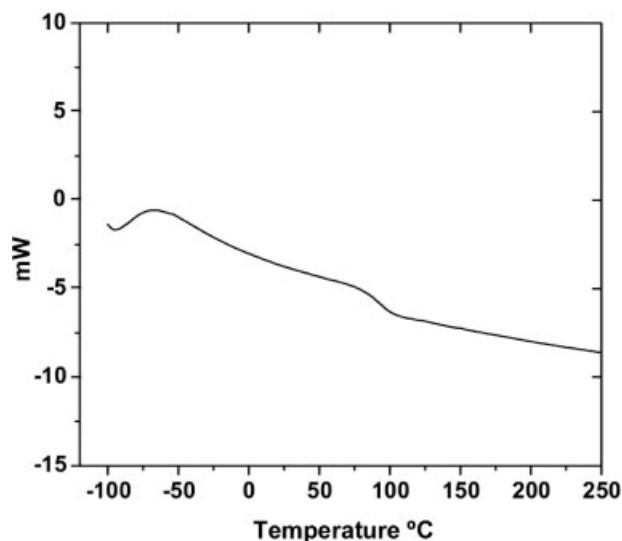


Figure 3 DSC curve for PA-I.

TABLE III
Glass Transition Temperatures and Thermal Degradation
Temperatures for the Poly(imides)

Polymer	T_g (°C)	TDT (°C)
PI-I	92	402
PI-II	149	406
PI-III	131	375
PI-IV	208	662
PI-V	180	445
PI-VI	107	440
PI-VII	127	357
PI-VIII	130	420

can see that in general the PIs showed higher T_g values than the corresponding PAs with the same heteroatoms and the groups bonded to them, due principally to the higher rigidity of the imide group.

On the other hand, when we compare the influence of the heteroatom, and considering that Ge is higher than Si, which implies that the C—Ge bond is longer than the C—Si one, PAs with Si would have higher T_g values than the similar ones with Ge, due to the lower rotation barriers of the C—Ge bonds.

In fact, if we compare PA-I with VI and PA-III with VIII, only PA-VIII with two Si atoms showed a higher T_g value than PA-III, which has two Ge atoms, and the pair PA-I and VI showed a very similar T_g value. But when only one heteroatom is changed, the mentioned trend is correct in the pairs PA-I and II, PA-III and IV, PA-V and VI, but not in the pair PA-VII and VIII, in which there is little difference.

With respect to the results for the PIs showed in Table III, those with Si atom, one or two, showed higher values than the corresponding with Ge, with the only exception of the pair PI-V and VI, in which the difference was important.

In general, the tendency of the T_g values was correct considering that we do not know the molecular weights of the polymers that have an important influence on the T_g values.

Thermal decomposition temperatures

The thermal decomposition temperatures (TDT) values were taken directly from the thermogravimetric curves % of weight loss versus temperature, when the % of weight loss was 10%.

The Ge atom is bigger than the Si one, which implies that the bond length of the Ge—C is longer than the Si—C. On the other hand, the polarity of the C—Si bond is higher than the C—Ge one, because the electronegativity of the Ge atom is higher than the Si, and both bond energies are very similar. Consequently, if the thermal stability increases with the bond polarity, polymers with Si atom would have higher TDT values than those corresponding to Ge.

Table I shows the TDT values for the PAs. If we compare the pairs of PAs I with VI and III with VIII in which the difference is the nature of the heteroatom, the results are in agreement with the above considerations, in the sense that PAs VI and VIII with two Si atoms showed higher thermal stability than those with two Ge atoms, I and III, respectively.

When the difference between the PAs is only one heteroatom, we can observe the same trend with the exception of the pairs PA-I and II, in which the PA-I with two Ge atoms showed a higher TDT value than PA-II with both heteroatoms. For the pair PA-III and IV, the difference was very low.

Table III also shows the TDT values for the PIs, and it is also possible to see the same trend in the pairs PI-I and VI and PI-III and VIII, the PIs with two Si atoms having higher values than those with two Ge atoms.

If the difference between the pairs of PIs is only one heteroatom, in the pairs PI-I and II, PI-III and IV, and PI-VII and VIII those with Si showed higher TDT values. In the other pairs, the tendency was the inverse, the difference in the pair PI-V and VI being very low.

With respect to the influence of the methyl or phenyl groups bonded to the heteroatoms, PI-I and III, PI-V and VII, PI-VI and VIII, in the PIs, it is possible to see that in all cases those with phenyl groups bonded to the heteroatoms showed higher TDT values than those with methyl ones, which was described for PA by Ghatge.²⁹ The exception was the pair PI-II and IV, in which the PI-IV showed a very high value of TDT.

In the PAs, the effect was only observed on the pair PA-V and VII. In the other pairs, those with methyl groups showed higher TDT values, but the differences were low. It is difficult to explain this behavior, but it is probably that the lower molecular weight, or η_{inh} , of the PAs with methyl groups can confer more influence to the side groups instead the polymeric chains. Ghatge also described a similar behavior for PA derived from a great number of diamines.⁴

In other work, we described that the TDT values of poly(esters) with the two heteroatoms, derived from acid dichlorides and diphenols both with Si or Ge, and bonded to methyl or phenyl groups,²⁵ showed a similar tendency.

In general, these PA and PI showed good thermal stability, both having the heteroatoms in the main chain and the groups bonded to them important influence.

CONCLUSIONS

PA and PI containing Si or Ge in the main chain with the heteroatoms bonded to methyl or phenyl groups were synthesized and characterized by spectroscopic methods. Wholly aromatic PA were obtained with

higher yields than those derived from acid dichlorides with side methyl groups bonded to the heteroatoms, due probably to the higher solubility of those PAs.

Thermal properties, T_g and TDT, were depending on the nature of the heteroatoms and the groups bonded to them. In this sense, polymers with Si showed higher T_g values than the analogous with Ge, and the same for those with phenyl groups. Respect to the TDT values, polymers with Si showed general higher values than the analogous with Ge, and the same for those with phenyl groups. However, there were several exceptions to the above statements, which are difficult to explain. One factor can be the probably low molecular weight of these condensation polymers, which affects directly the T_g values. Finally, in general both, PAs and PIs were thermostable polymers.

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