SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES OF WHOLLY AROMATIC POLY(IMIDE-AMIDES) CONTAINING SI AND/OR GE IN THE MAIN CHAIN

L.H. TAGLE*, C.A. TERRAZA, P.A. ORTIZ, A. TUNDIDOR-CAMBA

Facultad de Química, Pontificia Universidad Católica de Chile, P.O. Box 306, Santiago, CHILE

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ABSTRACT

Poly(imide-amides) (PIAs) containing the heteroatoms Si and/or Ge in the main chain were obtained from diacids, which were synthesized from trimellitic anhydride and the diamines bis(4-aminophenyl)diphenylsilane or bis(4-aminophenyl)diphenylgermane. With the same diamines the polymers containing the heteroatoms Si and Ge in the main chain were obtained. Polymers were soluble in aprotic polar solvents and characterized by IR and 1H, 13C and 29Si NMR spectroscopy, and the results were in agreement with the proposed structures. Low inherent viscosity values (ninh) (0.04 – 0.12 dL/g) were obtained, indicating the presence of oligomeric species. The Tg values were obtained by differential scanning calorimetry (DSC), and the results did not show a relation with the nature of the heteroatoms, ng good thermal stability depending on the structure of the repeating unit, and the lowest TDT values with two Si atoms in the unit.

Keywords: poly(imide-amides), silicon, germanium, thermal stability, glass transition temperature.

INTRODUCTION

Poly(imides) and poly(amides) are normally condensation polymers derived from diacids or dianhydrides and diamines that have high thermal stability. The main problem of this kind of polymers is the lack of solubility in common organic solvents, being the intermolecular bonding energy developed through hydrogen bonding, and through dipole-dipole interactions, the major parameters that contribute to the insolubility (1). Also, wholly aromatic poly(imides) have been used as important materials due to their high thermal stability and other properties, including chemical stability (2,3).

Bruma et al. have reported that the presence of C-Si bonds can improve the solubility of the polymers due to the ionic character of these bonds. Other effect of the introduction of C-Si or C-Ge bonds in a polymeric chain is the possible increasing of the thermal stability due to the ionic character of these bonds. This is because silicon and germanium atoms are less electronegative than carbon, however, the energy of the C-C, C-Si and C-Ge bonds, is very similar (5).

On the other hand, poly(imide-amides) are alternative materials, which offer the thermal stability of the poly(imides) and the solubility and processability of the poly(amides) (6-8).

Silicon-containing polymers have been important to our research group, and we have described the synthesis of poly(amides) (9) and poly(imide-amides) (10), showing good thermal stability depending on the structure of the repeating unit. On the other hand, germanium-containing polymers in which the Ge atom is bonded to four organic groups, have not received much attention with the exception of our works (11-15). Also we reported the synthesis of several other kinds of condensation polymers, such as poly(carbonates), poly(thiocarbonates) and poly(esters), in which the thermal properties were strongly influenced by the nature of the heteroatom and the organic groups bonded to them. Many of these polymers showed good thermal properties and even some of them were thermally stable (16).

In this work we described the synthesis and characterization of poly(imide-amides) (PIAs) derived from trimellitic anhydride, which were reacted with the diamines bis(4-aminophenyl)diphenylsilane or germane in order to obtain two diacids. These diacids were polymerized with the respective diamines, 2-(4-((4-(5-carboxy-1,3-dioxoisoindolin-2-yl)phenyl)diphenylgermyl)phenyl)-1,3-dioxa diazooindoline-5-carboxylic acid (I-Ge) and 2-(4-((4-(5-carboxy-1,3-dioxoisoindolin-2-yl)phenyl)diphenylsilane)-1,3-dioxa diazooindoline-5-carboxylic acid (I-Si), and the mixture stirred for 12 h at room temperature, and then refluxed for 3 h. After this, the acetic acid was distilled under reduced pressure, and the residue poured into 10 % HCl. The white-color was filtered, washed with water and characterized.

I-Si: Yield: 96%. M.p.: 178-180 ºC. IR (KBr) (cm-1): 3435 (OH), 3069 (H arom.), 1781, 1721 (C=O), 1594, 1504 (C=C arom.), 854 (arom. 1,2,4-subst.), 825 (arom. p-subst.), 749, 701 (arom. mono-subst.). 1H NMR (acetone-d6) (d) (ppm): 7.44-7.79 (m, 18H, arom.), 8.07-8.12 (m,2H,arom.), 8.45 (m,2H,arom.). 13C (acetone-d6) (d) (ppm): 124.6, 124.8, 127.4, 128.1, 128.8, 129, 129.2, 129.8, 133.2, 133.4, 135.8, 136.4, 137.2, 137.7 (ppm): 7.44-7.79 (m, 18H, arom.), 8.07-8.12 (m,2H,arom.), 8.45 (m,2H,arom.).

I-Ge: Yield: 87%. M.p.: 190-192 ºC. IR (KBr) (cm-1): 3430 (OH), 3070 (H arom.), 1781, 1722 (C=O), 1596, 1503 (C=C arom.), 854 (arom. 1,2,4-subst.), 802 (arom. p-subst.), 751, 697 (arom. mono-subst.). 1H NMR (DMSO-d6) (d)
The diacids I-Si and I-Ge were obtained from trimellitic anhydride and the diamines bis(4-aminophenyl) diphenylsilane and bis(4-aminophenyl) diphenylgermane, were obtained from 4-bromo-1,2,4-trimethylsilylethyl aniline and diphenyldichlorosilane or diphenyldichlorogermane, respectively, according to a described procedure (18).

**Polymide-amides (PIAs)**

PIAs were synthesized according to the following general procedure. The diacid I-Si or I-Ge (0.152 mmol) and the respective diamine (0.152 mmol) were mixed with 0.08 mL of triphenyl phosphite, 0.3 mL of N-methyl-2-pyrrolidone, 0.08 mL of pyridine and 0.03 g of CaCl₂, and the mixture heated at 110-120 °C for three hours. After this time, the mixture was poured into methanol and the precipitated polymer filtered, washed with methanol, dried at 40 °C under vacuum until constant weight and characterized.

**RESULTS AND DISCUSSION**

The diacids I-Si and I-Ge were obtained from trimellitic anhydride and the diamines bis(4-aminophenyl)diphenylsilane and bis(4-aminophenyl)diphenylgermane, were obtained from 4-bromo-1,2,4-trimethylsilylethyl aniline and diphenyldichlorosilane or diphenyldichlorogermane, respectively, according to a described procedure (18).
Table 1 also shows the Tg values, and figure 2 the DSC thermograms, considering the change of the slope of the curve. The only structural difference between the PIAs is the nature of the heteroatoms in the main chain. If we consider that the Ge atom has higher size than Si, which implies that the C-Ge bond is longer than C-Si, PIAs with Si would have higher Tg values than those with Ge, due to the lower rotation barriers of the C-Ge bonds. Considering the Tg values of these PIAs, it can be deduced that there is not a relation in agreement with the first statement. The higher Tg value corresponds to PIA-II with one Si atom, which would be similar to that of PIA-III. PIA-IV should have the highest Tg value, but it showed the lowest. One possible explanation can be the low values of the \( \eta_{inh} \), associated to low molecular weights, which is an important parameter in the Tg values.

**Table I.** Yields, \( \eta_{inh} \), glass transition temperatures (Tg) and thermal decomposition temperatures (TDT) of the PIAs

<table>
<thead>
<tr>
<th>Yield (%)</th>
<th>X</th>
<th>Y</th>
<th>( \eta_{inh} ) (D/L.g)*</th>
<th>Tg (°C)</th>
<th>TDT** (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIA-I</td>
<td>67</td>
<td>Ge</td>
<td>Ge</td>
<td>0.04</td>
<td>144</td>
</tr>
<tr>
<td>PIA-II</td>
<td>68</td>
<td>Ge</td>
<td>Si</td>
<td>0.12</td>
<td>53</td>
</tr>
<tr>
<td>PIA-III</td>
<td>64</td>
<td>Si</td>
<td>Ge</td>
<td>0.04</td>
<td>129</td>
</tr>
<tr>
<td>PIA-IV</td>
<td>85</td>
<td>Si</td>
<td>Si</td>
<td>0.07</td>
<td>74</td>
</tr>
</tbody>
</table>

* Inherent viscosity, in DMSO at 25 °C (c = 0.3 g/dL)  
** 10% weight loss temperature

**Table 2.** Polymeric chain density and weight loss

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Condensation (% of monomer)</th>
<th>Initial weight</th>
<th>Final weight</th>
<th>Weight loss (%)</th>
<th>Remaining weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIA-I</td>
<td>97</td>
<td>500</td>
<td>400</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>PIA-II</td>
<td>98</td>
<td>500</td>
<td>450</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>PIA-III</td>
<td>98</td>
<td>500</td>
<td>475</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>PIA-IV</td>
<td>98</td>
<td>500</td>
<td>485</td>
<td>1.7</td>
<td>98.3</td>
</tr>
</tbody>
</table>

Figure 3. Thermogravimetric curves of the poly(amide-imide)

Table 1 shows the thermal decomposition temperatures (TDT), taken as the temperature at which the weight loss is 10%, and figure 3 the thermogravimetric curves. It has been reported that the bond polarity has influence on the thermal stability, in the sense that when the chain polarity increases, the thermal stability also increases (4). In this case, the only difference between the PIAs is the nature of the heteroatom. The polarity of the C-Si bond is greater than that of C-Ge, since Si has lower electronegativity than Ge, and as a consequence, polymers with Si atom would have higher TDT than those with Ge. PIA-II and PIA-III, with one Si atom, showed similar TDT values. PIA-I with only Ge atoms showed a lower value than PIA-II and PIA-III. However, PIA-IV with two Si atoms should have the higher TDT value, but has the lowest one. The only reason can be the low molecular weight, which causes a fast breaking of the polymeric chain. Nonetheless, two PIAs showed TDT values higher than 400 °C, and can be considered as thermally stable. The residue after heating at 900 °C are between 26 – 44 % corresponding probably to silicon oxide.

**CONCLUSIONS**

Four poly(amide-imide) of low molecular weight and containing two heteroatoms, Si and/or Ge, in the main chain were synthesized from the diacids obtained from trimellitic anhydride and the diamines bis(4-aminophenyl) diphenylsilane or that with germane. These diacids were reacted with the same diacids to obtain the PIAs. The yields were good but the \( \eta_{inh} \) values were low, indicating that polymers were of oligomeric nature of low molecular weight. The Tg values did not show the tendency in the sense that PIAs with Si should have higher values of this parameter than those with Ge, due to the longer length of the C-Ge bond. This is probably due to the low molecular weights of these polymers. The TDT values, influenced by the nature of the heteroatom and consequently by the polarity of the C-Si or C-Ge bonds, showed the normal tendency in the sense that PIA-II and PIA-III, with one Si atom, showed higher TDT values than PIA-I with only Ge atoms. The exception was PIA-IV with two Si atoms in its repetitive unit, which showed the lowest TDT value, probably due to the low molecular weight.

**ACKNOWLEDGEMENTS**

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