Thermal studies of poly(esters) containing silicon or germanium in the main chain

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Abstract

The thermal properties of poly(esters) containing Si and/or Ge in the main chain derived from the acid dichlorides bis(4-chloroformyl-phenyl)-dimethyl-silane, bis(4-chloroformyl-phenyl)-dimethyl-germane, bis(4-chloroformyl-phenyl)-diphenyl-silane and bis(4-chloroformyl-phenyl)-diphenyl-silane, and the diphenols bis(4-hydroxyphenyl)-dimethyl-silane, bis(4-hydroxyphenyl)-dimethyl-germane, bis(4-hydroxyphenyl)-diphenyl-silane and bis(4-hydroxyphenyl)-diphenyl-germane were studied by differential scanning calorimetry and dynamic thermogravimetry. Poly(esters) with two Si atoms in the main chain showed higher values of T_g than those with two Ge atoms, and the same was observed for poly(esters) with phenyl groups bonded to the heteroatoms, instead of those with methyl groups. Thermal decomposition temperatures were also higher for those poly(esters) with two Si atoms in the main chain and those in which the heteroatom is bonded to phenyl groups, due to the higher polarity of the Si─C bond in front of the Ge─C.

Keywords: Germanium; Silicon; Poly(esters); Glass transition temperatures; Thermal decomposition temperatures

1. Introduction

Polymers may undergo several transformations when they are exposed to different environmental conditions, especially temperature and moisture, and the changes can be of a chemical or physical character. In this sense, thermal degradation under normal conditions of use is one of the principal factors limiting the applications of these materials, and therefore, important properties are affected adversely as the degradation proceeds [1,2].

Silicon-containing polymers, in which the heteroatom is bonded to four organic groups, have been described and their properties studied [3,4]. However, germanium-containing polymers have had less attention, with the exception of inorganic polymers in which the Ge atom is bonded to itself in the main chain. In other papers we have described the synthesis of several kinds of condensation polymers containing silicon or germanium in the main chain and bonded to four aromatic or aliphatic groups [5], as poly(esters) [6,7], poly(carbonates) [8,9], poly(thiocarbonates) [8] and poly(amides) [10].

This work describes the thermal characterization of poly(esters) containing two heteroatoms, silicon and/or germanium, in the main chain. Glass transition temperatures and thermogravimetric behaviour were determined by DSC and dynamic thermogravimetry, respectively. The results are discussed in light of the nature of the heteroatoms present in the polymeric chain, and the nature of the side groups, phenyl or methyl, bonded to them.

2. Experimental part

Poly(esters) were synthesized from the diphenols bis(4-hydroxyphenyl)-dimethyl-silane, bis(4-hydroxyphenyl)-dimethyl-germane, bis(4-hydroxyphenyl)-diphenyl-silane and

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bis(4-hydroxyphenyl)-diphenyl-germane and the acid dichlorides bis(4-chloroformyl-phenyl)-dimethyl-silane, bis(4-chloroformyl-phenyl)-dimethyl-germane, bis(4-chloroformyl-phenyl)-diphenyl-silane and bis(4-chloroformyl-phenyl)-diphenyl-silane under phase transfer conditions according to a procedure described earlier [7].

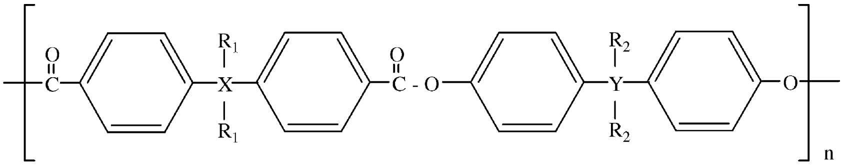
T_g values were obtained with a Mettler–Toledo DSC 821 calorimetric system. Thermogravimetric analyses were carried out in a Mettler TA-3000 calorimetric system equiped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. Samples of 6–10 mg were placed in a platinum sample holder and the thermogravimetric measurements were carried out between 30 and 800 °C with a heating rate of 20 °C min^{-1} under N_2 flow.

Table 1
Glass transition and thermal decomposition temperatures of the poly(esters)

Poly(ester)	X	Y	R_1	R_2	T_g (°C)	TDT (°C)
I	Si	Si	C_6H_5	CH_3	149	427
II	Si	Ge	C_6H_5	CH_3	182	429
III	Ge	Si	C_6H_5	CH_3	177	408
IV	Ge	Ge	C_6H_5	CH_3	184	421
V	Si	Si	C_6H_5	C_6H_5	192	446
VI	Si	Ge	C_6H_5	C_6H_5	171	448
VII	Ge	Si	C_6H_5	C_6H_5	152	435
VIII	Ge	Ge	C_6H_5	C_6H_5	162	440
IX	Si	Si	CH_3	CH_3	144	426
X	Si	Ge	CH_3	CH_3	117	401
XI	Ge	Si	CH_3	CH_3	165	437
XII	Ge	Ge	CH_3	CH_3	104	412
XIII	Si	Si	CH_3	C_6H_5	172	445
XIV	Si	Ge	CH_3	C_6H_5	174	437
XV	Ge	Si	CH_3	C_6H_5	185	439
XVI	Ge	Ge	CH_3	C_6H_5	151	452

3. Results and discussion

Poly(esters) with the following structures:



I : X = Si , Y = Si , R_1 = -C_6H_5 , R_2 = -CH_3
II : X = S i , Y = Ge , R_1 = -C_6H_5 , R_2 = -CH_3
III: X = Ge , Y = Si , R_1 = -C_6H_5 , R_2 = -CH_3
IV: X = Ge , Y = Ge , R_1 = -C_6H_5 , R_2 = -CH_3

V : X = Si , Y = Si , R_1 = R_2 = -C_6H_5
VI : X = Si , Y = Ge, R_1 = R_2 = -C_6H_5
VII : X = Ge , Y = Si , R_1 = R_2 = -C_6H_5
VIII : X = Ge , Y = Ge, R_1 = R_2 = -C_6H_5

IX : X = Si , Y = Si , R_1 = R_2 = -CH_3
X : X = Si , Y = Ge, R_1 = R_2 = -CH_3
XI : X = Ge , Y = Si , R_1 = R_2 = -CH_3
XII : X = Ge , Y = Ge, R_1 = R_2 = -CH_3

XIII : X = Si , Y = Si , R_1 = -CH_3 , R_2 = -C_6H_5
XIV : X = Si , Y = Ge, R_1 = -CH_3 , R_2 = -C_6H_5
XV X = Ge , Y = Si , R_1 = -CH_3 , R_2 = -C_6H_5
XVI : X = Ge , Y = Ge, R_1 = -CH_3 , R_2 = -C_6H_5

were synthesized under phase transfer conditions using several phase transfer catalysts in CH_2Cl_2 as solvent at 20 °C, according to a procedure described previously [7]. Polymers were characterized by IR, ^1H and ^{13}C NMR, and the structures were in accord with those proposed.

Table 1 shows the T_g values obtained for poly(esters). Well-defined and reproducible glass transitions were observed for all the poly(esters) samples.

When the T_g values are compared as a function of the nature of the heteroatom, Si or Ge, it is possible to see that poly(esters) with two Si atom showed in general, higher values of T_g than the analogous polymers with Ge, with the exception of poly(ester) **IV**. Si is larger than C, which implies longer bond lengths, lower rotational energy barriers and lower T_g values [3]. On the other hand, Ge is larger and has a higher volume than Si, and therefore the bond lengths will be longer and the rotational energy barriers will be lower, and therefore poly(esters) with two Ge atoms in the main chain would show lower T_g values. A similar behaviour was observed in other poly(esters) containing Si and Ge in the main chain [11]. The exception was poly(ester) **IV** which showed a surprisingly high T_g value.

On the other hand, poly(ester) **V** with two Si atoms and with only phenyl groups as side chains, showed higher T_g values than poly(ester) **IX** the analogous polymer with methyl groups. A similar situation can be observed with poly(esters) **VIII** and **XII** with two Ge atoms in the main chain, which can be due to higher volume and steric hindrance of the phenyl groups, which hinders the motion of the polymeric chains.

When both heteroatoms are in the main chain, there is no relation with the size and nature of them. However, we can observe some influence of the nature of the side groups. In fact, if we compare analogous poly(esters) but with different side groups, it is possible to see an increase of the T_g values when the methyl groups are changed to the phenyl ones in the case of the pairs of poly(esters) **II–VI**, **III–VII**, **X–XIV**, **XI–XV**, and **VI–X**. The exception is the pair **VII–IX**, in which the difference is low.

Finally, when the difference in the poly(esters) is only the position of the heteroatom with respect to the repeat unit, there is not a relation with the T_g values. In the poly(esters) **II–III** the difference is very low, but between poly(esters) **X–XI** is very high.

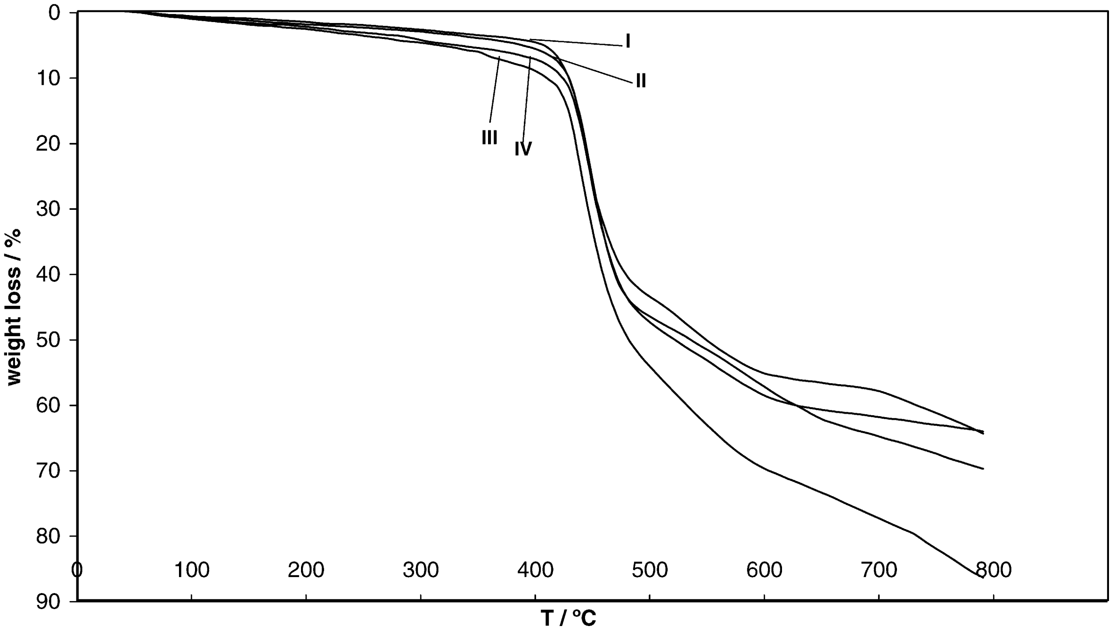


Fig. 1. Thermogravimetric curves for poly(esters) **I**–**IV**.

In general it is possible to see that both elements, the nature and size of the heteroatoms and the groups bonded to it, influence the T_g values.

The thermal stability of the polymers was analyzed by dynamic thermogravimetry. Figs. 1–4 show the thermogravimetric curves and Table II summarizes the thermal decomposition temperatures (TDT) for all the polymers. The data of TDT are reported as the temperature at 10% weight loss.

From the TDT values it can be seen that the poly(esters) degrade at very similar temperatures, the range in each group being low. However, if we compare the poly(esters) with two Si or Ge atoms in the main chain, it is possible to see that those with Si have slightly higher TDT values than those with Ge, with the exception of poly(esters) **XIII**–**XVI**, in which the TDT values are very close. One explanation can be due to the larger size of Ge in comparison to Si, which implies larger bond lengths. The relationship between electronegativity, bond polarity and thermal stability has been described [12]. The polarity of the C–Si bond is higher than that of the C–Ge bond [13], and although C–Si and C–Ge bonds have similar energies, the thermal stability would be increased due to the ionic character of these bonds, Si being less electronegative than Ge [4,14].

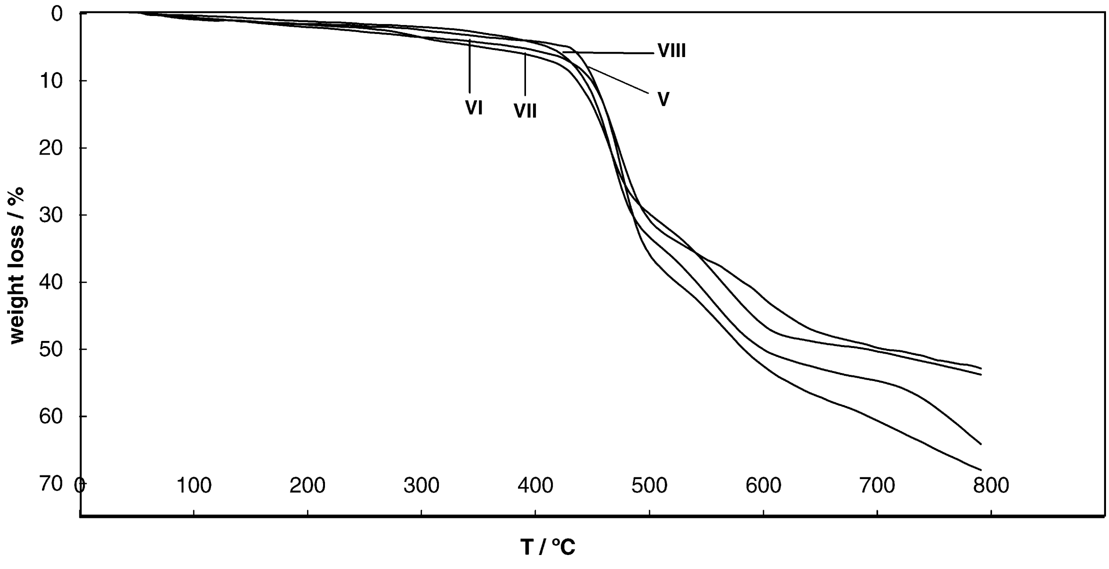


Fig. 2. Thermogravimetric curves for poly(esters) **V**–**VIII**.

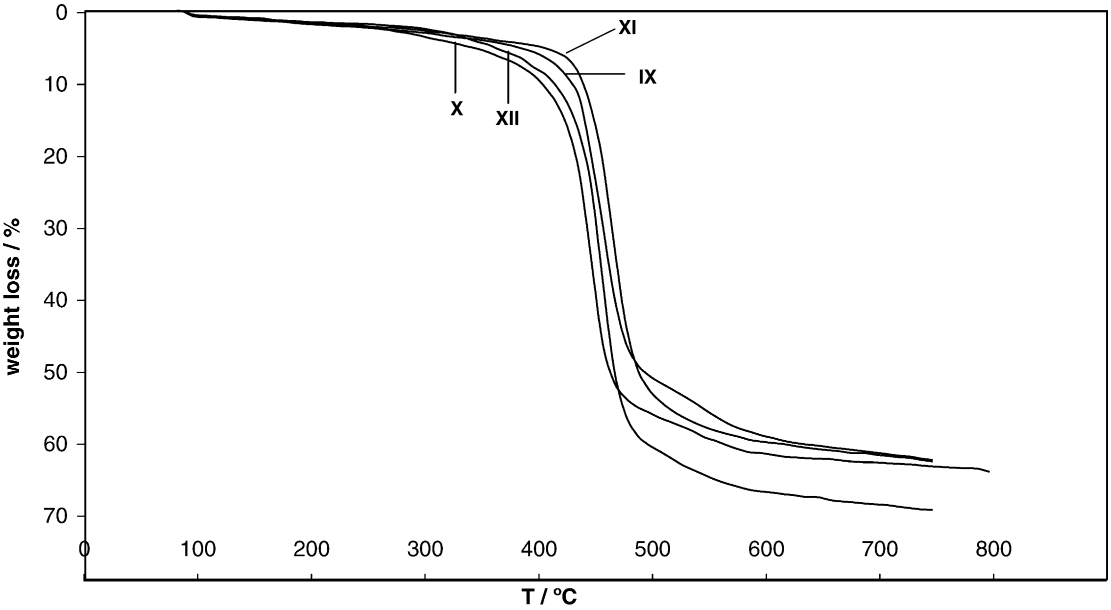


Fig. 3. Thermogravimetric curves for poly(esters) **IX**–**XII**.

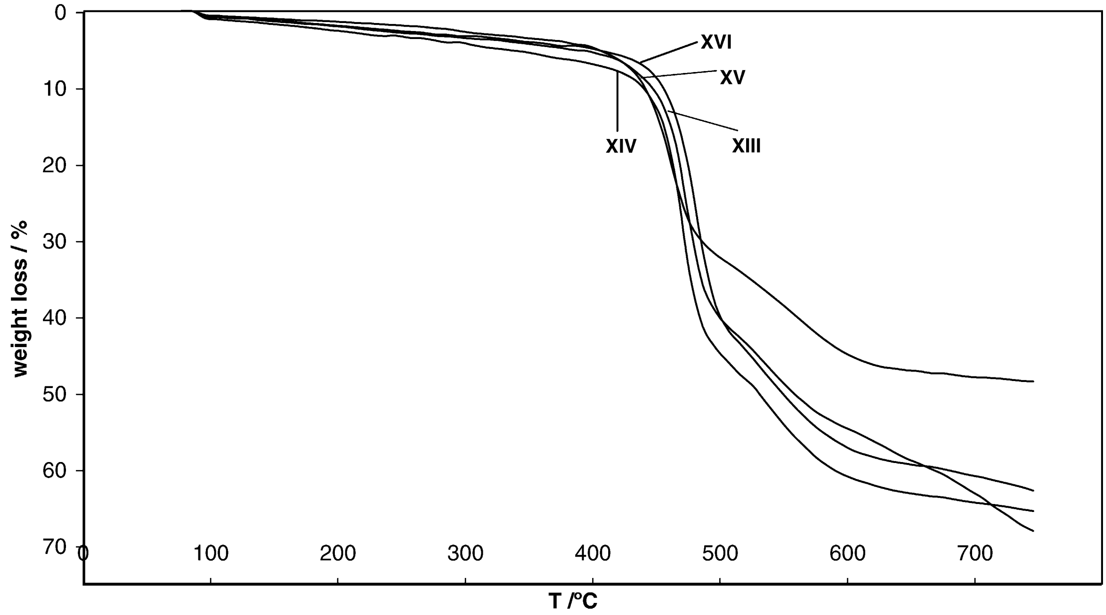


Fig. 4. Thermogravimetric curves for poly(esters) **XIII**–**XVI**.

However, of more influence it is possible to see the effects of methyl or phenyl groups bonded to the heteroatoms. In this sense if we compare poly(esters) **V**–**VIII** with only phenyl groups, with the corresponding poly(esters) **IX**–**XII** with only methyl groups, the former show higher TDT values in all cases. The same behaviour can be seen when we compare poly(esters) **V**–**VIII** with four phenyl groups, with the analogous **I**–**IV** with two phenyl groups, and also for poly(esters) **XIII**–**XVI** with two phenyl groups with the analogous **IX**–**XII** without phenyl groups.

On the other hand, when both heteroatoms are present in the main chain, there are important differences between the TDT values in poly(esters) with similar structure, with the exception of the pair **XIV**–**XV** which have very close values.

In general, in these poly(esters) it was possible to observe that they have a good thermal stability, with the groups bonded to the heteroatoms having more influence than the nature of the heteroatoms.

Acknowledgements

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References

[1] W.L. Hawkins, Polymer degradation and stabilization, Springer-Verlag, Berlin, 1984.
[2] Z. Dobkowsky, E. Rudnik, J. Therm. Anal. 48 (1997) 1393.
[3] S.F. Thames, K.G. Panjnani, J. Inorg. Organomet. Chem. 6 (1996) 59.
[4] M. Bruma, B. Schulz, J. Macromol. Sci. Polym. Rev. C41 (2001) 1.
[5] L.H. Tagle, Macromol. Symp. 199 (2003) 499.
[6] L.H. Tagle, F.R. Diaz, M. Nuñez, F. Canario, Intern. J. Polym. Mater. 52 (2003) 287.
[7] L.H. Tagle, F.R. Diaz, J.C. Vega, P. Valenzuela, Eur. Polym. J. 39 (2003) 407.
[8] L.H. Tagle, J.C. Vega, F. Diaz, D. Radic, L. Gargallo, P. Valenzuela, J. Macromol. Sci. Pure Appl. Chem. A37 (2000) 997.
[9] L.H. Tagle, F.R. Diaz, J.C. Vega, M. Quezada, P. Guerrero, J. Inorg. Organomet. Polym. 13 (2003) 21.
[10] L.H. Tagle, F.R. Diaz, D. Radic, A. Opazo, J.M. Espinoza, J. Inorg. Organomet. Polym. 10 (2000) 73.
[11] L.H. Tagle, F.R. Diaz, A. Opazo, Bol. Soc. Chil. Quim. 46 (2001) 287.
[12] D. Wöhrle, in: H.R. Kricheldorf (Ed.), Handbook of Polymers Synthesis, Polymers with Metal in the Backbone, Part B, Dekker, 1992, p. 1133.
[13] http://weblements.com/.
[14] D.A. Armitage, in: A.R. Katritzky (Ed.), Comprehensive Heterocyclic Chemistry, vol. 1, Pergamon Press, Oxford, 1984, p. 573.