

# Poly(urethanes) Containing Silarylene and/or Germarylene Units

C. A. Terraza, L. H. Tagle, A. Leiva, L. Poblete, F. J. Concha

Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, Chile

Received 19 April 2007; accepted 6 November 2007

DOI 10.1002/app.28170

Published online 28 March 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of 10 poly(urethanes) were synthesized by solution polymerization from bis(chloroformates) and aromatic diamines, containing both silicon or germanium as central atom. So, the polymers prepared contain two silicon atoms or two germanium atoms exclusively or combinations of both. Me, Et, and Ph groups were bonded to the central atoms according to the nature of the monomers employed. Poly(urethanes) were characterized by FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopy and the results agreed with the proposed structures. Additionally, intrinsic viscosity values were established in DMSO solutions and thermal analyses were developed. In all cases, thermostable oligomers were

obtained, which showed a degradation process beginning at  $\sim 240$ – $260^\circ\text{C}$ . Polymers showed a thermal dependence with the nature of the heteroatom employed. Thus, in general, when germanium was used as central atom, the thermal stability was higher than the polymers containing silicon which agrees with the lower polarity and higher energy of the C–Ge bond in comparison with the C–Si one. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 303–308, 2008

**Key words:** poly(urethanes); silicon; germanium; thermal stability; glass transition temperature; glass transition; polyurethanes

## INTRODUCTION

Polyfunctional compounds are used in the polycondensation processes. Thus, poly(esters) can be synthesized from diols by esterification reaction with diacids or ester-interchange with diesters. Poly(amides) can be synthesized by the reaction of diamines with diacids or acid dichlorides.<sup>1</sup> Because of their chemical, rheological, and mechanical properties these polymers and others such as poly(carbonates), poly(thiocarbonates), and poly(imides) have been obtained and studied for several industrial applications.

Poly(urethanes), also known as poly(carbamates), are a very important group of polymers due to the versatility and the wide range of applications that they present. They can be prepared from the reaction of diols with diisocyanates, and in this case, the polymeric structure has the same net composition of the monomers. On the other hand, if the reaction is between diamines and bis(chloroformates), one equivalent of hydrochloric acid is eliminated as a sub-product.<sup>2</sup> These procedures can be developed

in solution or by interphasial polycondensation conditions.

On the other hand, it is known that the properties of any polymer depend, principally, on the structural details, such as the nature of the organic groups bonded to the main chain, the presence of heteroatoms in the structure, etc. In this topic, some studies have been performed with the incorporation in condensation polymers of a silicon atom bonded to four carbon atoms, and their properties studied.<sup>3–6</sup> For poly(urethanes) in particular, Thames and Panjnani<sup>6</sup> synthesized a silicon-containing bis(ethyl-carbamate) from bis(4,4'-phenyl isocyanate)dimethylsilane and a diol, employing DMF as solvent. The authors pointed out the spectroscopic characteristics, but they do not give details of other properties. Other researchers have developed works in poly(urethanes) based on carbonated structures.<sup>7</sup>

Polymeric materials can be modified when other functional groups or other heteroatoms are incorporated into the polymeric chains or in the side groups. In this sense the properties of the new polymers as the glass transition and the thermal decomposition temperatures (TDT), can be changed to obtain new polymeric materials for new applications.

With the objective of obtaining new materials and to study their properties, specially thermal properties, in our laboratory we have synthesized and characterized according to the spectroscopic data, some condensation polymers series containing silicon

Correspondence to: C. A. Terraza (cterraza@uc.cl).

Contract grant sponsor: FONDECYT; contract grant number: 1030528.

and/or germanium in the main chain. So, poly(esters), poly(amides), poly(imides), poly(thiocarbonates), and poly(carbonates) containing silarylene- and/or germarylene-units in their structure have been prepared.<sup>8–15</sup> Several organic groups have been bonded to the central heteroatoms. In general, all polymers present low molecular weights and those polymers with Ge showed a small improvement in the thermal stability in comparison with the analogous with Si, which has been related to the differences in the polarity of the heteroatom–C bond and to the higher bond energy of the C–Ge bond in relation to the C–Si one.

Continuing our works related to the synthesis and characterization of condensation polymers containing Si or Ge bonded to four organic groups, in this work we present the synthesis and characterization of poly(urethanes) derived from bis(chloroformates) and wholly aromatic diamines, containing both Si or Ge, in order to obtain polymers with two heteroatoms in the main chain. TDT and the glass transition temperatures ( $T_g$ ) were analyzed as a function of the structure of bis(chloroformate) monomer employed in the synthesis and the nature of the heteroatoms present in the main chain.

## EXPERIMENTAL

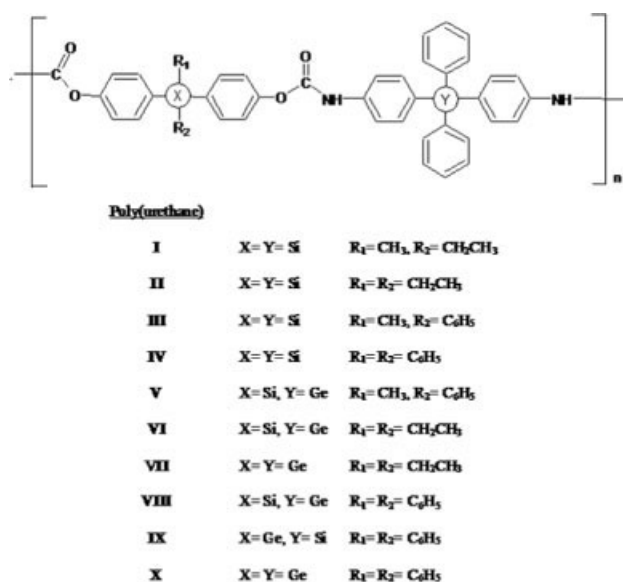
Reagents (from Aldrich) and solvents (from Riedel de Haen) were used without purification. The FTIR spectra were recorded on a Perkin–Elmer 1310 spectrophotometer, USA and the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR on a 400 MHz instrument (Bruker AC-200, Germany), using  $\text{CDCl}_3$ , acetone- $d_6$  or DMSO- $d_6$  as solvents and TMS as the internal standard.

Viscosity measurements were performed at 25°C using DMSO as solvent (0.3 g/dL) and inherent viscosity were calculated by using the Solomon–Gotesman relationship.<sup>16</sup>

$T_g$  values were obtained with a Mettler-Toledo DSC 821 calorimetric system (Mettler, Switzerland) with a heating rate of 20°C  $\text{min}^{-1}$  under  $\text{N}_2$  flow. Thermogravimetric analyses were carried out in a Mettler TA-3000 calorimetric system (Switzerland) equipped with a TC-10A processor, and a TG-50 thermobalance (Mettler, Switzerland) with a Mettler MT5 microbalance. These analyses were developed between 30 and 800°C under nitrogen flow with a rate heating of 20°C  $\text{min}^{-1}$ , using samples of 6–10 mg.

## Monomers

The diphenols bis(4-hydroxyphenyl)ethylmethylsilane, bis(4-hydroxyphenyl) diethylsilane, bis(4-hydroxy-



**Figure 1** General structure of the poly(urethanes) prepared.

phenyl)methylphenylsilane, bis(4-hydroxyphenyl) diphenylsilane, bis(4-hydroxyphenyl)diethylgermane, and bis(4-hydroxyphenyl)diphenylgermane, were obtained according to a procedure described previously and characterized by spectroscopic methods.<sup>17</sup>

The diamines bis(4-aminophenyl)diphenylsilane and bis(4-aminophenyl)diphenylgermane, were synthesized according to a procedure described previously.<sup>18</sup>

The synthesis and characterization of the bis(chloroformates) 4,4'-(ethylmethylsilylen)bis(phenylchloroformate), 4,4'-(diethylsilylen)bis(phenylchloroformate), 4,4'-(methylphenylsilylen)bis(phenylchloroformate), 4,4'-(diphenylsilylen)bis(phenylchloroformate), 4,4'-(diethylgermylen)bis(phenylchloroformate), and 4,4'-(diphenylgermylen)bis(phenylchloroformate) were described previously.<sup>19</sup>

## Poly(urethane) synthesis

Poly(urethanes) (Fig. 1) were synthesized according to a general procedure, in which a benzene or toluene solution of the bis(chloroformate) derivative ( $9.13 \times 10^{-4}$  mol) was added slowly over a benzene or toluene solution containing the aromatic diamine ( $6.8 \times 10^{-4}$  mol) and pyridine (0.31 mol). The polymerizations were carried out at 20°C for 10 min obtaining a suspension of pyridinium chloride and the corresponding poly(urethane). The mixture was turned over methanol, stirred for 10 min at room temperature and then the polymer was filtered, washed several times with methanol or water and dried under vacuum until constant weight.

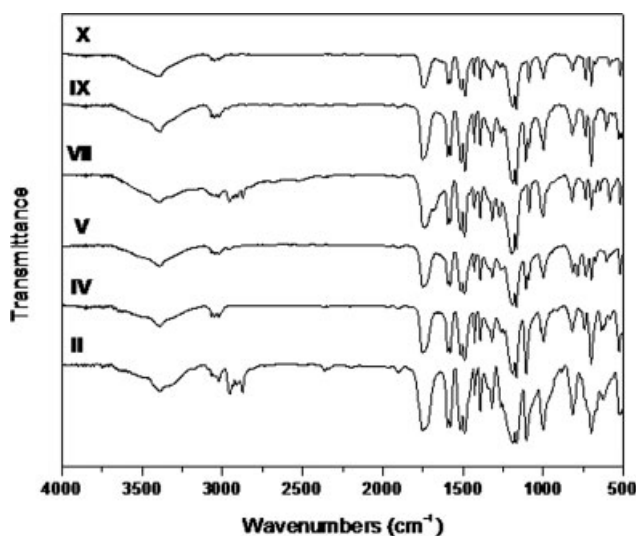


Figure 2 FTIR (film) spectra for some silarylene- and/or germarylene-containing poly(urethanes).

## RESULTS AND DISCUSSION

The diphenols, bis(chloroformates) and aromatic diamines were obtained according to the procedures described previously.<sup>17–19</sup> The poly(urethanes) were synthesized by solution polycondensation in benzene or toluene, from the diamines and the bis(chloroformates) according to the described procedure. Structurally, all polymers are derived from wholly aromatic diamines, because those with alkyl groups bonded to the heteroatom, specifically methyl group, are described as unstable.<sup>18</sup>

All poly(urethanes) were obtained as a white powder, soluble at room temperature in dimethyl-

sulfoxide and *m*-cresol at room temperature, but insoluble in methanol, ethanol, acetone, chloroform, and diethylether.

From the spectroscopic point of view, the IR data (Fig. 2) showed the characteristic patterns associated to the family: N–H stretching and bending bands (3396–3385 and 1752–1735  $\text{cm}^{-1}$ , respectively) and C=O stretching (1757–1750  $\text{cm}^{-1}$ ). In some cases, C=O and bending N–H bands appear overlapped. Also it is possible to see the heteroatom-carbon specific vibration bands (silyl-Ph: 1515, 1000, 740  $\text{cm}^{-1}$ , silyl-aliphatic: 1319, 785  $\text{cm}^{-1}$ , germyl-Ph: 1493, 1000, 730  $\text{cm}^{-1}$  and germyl-aliphatic: 1318  $\text{cm}^{-1}$ , approximately). These signals, together with the other identified absorptions agree with the main chain structure proposed in Figure 1. This proposal is strongly supported in the NMR signals obtained (Table I). Specifically, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR show signals to high field for atoms bonded to silicon or germanium. For example: a single signal for methyl group at 0.62–0.82 ppm and a multiplete signal for ethyl group at 0.6–1.45 ppm. This fact agrees with the electronegativity of the central heteroatom. When  $^{29}\text{Si}$  NMR was employed, it was possible to identify clear several types of environments for the silicon atom, according to the nature of the groups bonded to it, aromatic or aliphatic groups. We already report this phenomenon and discussed it in terms of the difference between the electron donating contribution of aliphatic groups and on the other hand, the possibility of backbonding of the  $\pi$  orbital of the aromatic ring and the d orbital of silicon atom.<sup>18</sup>

Table II shows the yields and the intrinsic viscosity values obtained for the poly(urethanes). The  $\eta_{\text{inh}}$  val-

TABLE I  
NMR Spectroscopic Data for Poly(urethanes) Containing Silarylene and/or Germarylene Units

PU	$^1\text{H}$ -NMR ( $\delta$ ; ppm)	$^{13}\text{C}$ -NMR ( $\delta$ ; ppm)	$^{29}\text{Si}$ -NMR ( $\delta$ ; ppm)
I	0.62 (s,3H,Me), 0.79–1.12 (m,5H,Et), 7.12–7.69 (m,26H,arom.), 10.40 (s,2H,NH)	–4.74 (Si-CH <sub>3</sub> ), 5.71 (CH <sub>2</sub> ), 7.84 (CH <sub>2</sub> CH <sub>3</sub> ), 115.7–140.6 (12C arom.), 152.0 (CO)	–5.62 (Me,Et), –15.27
II	0.6–1.15 (m,10H,Et), 7.22–7.80 (m,26H,arom.), 10.40 (s,2H,NH)	3.47 (CH <sub>2</sub> ), 7.75 (CH <sub>3</sub> ), 115.8–140.6 (12C arom.), 152 (CO)	–3.88 (Et <sub>2</sub> ), –15.26
III	0.82 (s,3H,Me), 7.2–7.65 (m,31H,arom.), 10.40 (s,2H,NH)	–3.18 (CH <sub>3</sub> ), 115.8–140.6 (16C arom.), 152 (CO)	–11.24 (Me,Ph), –15.28
IV	6.74–7.98 (m,36H,arom.), 10.46 (s,2H,NH)	118.7–140.5 (16 C arom.), 151.8 (CO)	–14.83 <sup>a</sup> , –15.27 <sup>b</sup>
V	0.81 (s,3H,Me), 7.2–7.65 (m,31H,arom.), 10.38 (s,2H,NH)	–3.17 (CH <sub>3</sub> ), 115.8–140.2 (16C arom.), 151.9 (CO)	–11.23
VI	0.61–1.23 (m,10H,Et), 6.55–7.70 (m,26H,arom.), 10.36 (s,2H,NH)	–4.12 (CH <sub>2</sub> ), 7.84 (CH <sub>3</sub> ), 114.6–150 (12C arom.), 158.8 (CO)	–3.85
VII	0.82–1.45 (m,10H,Et), 6.85–7.9 (m,26H,arom.), 10.39 (s,2H,NH)	–4.16 (CH <sub>2</sub> ), 8.69 (CH <sub>3</sub> ), 116.5–139.6 (12C arom.), 151 (CO)	–
VIII	7.12–7.80 (m,36H,arom.), 10.42 (s,2H,NH)	119.1–137.9 (16C arom.), 151.8 (CO)	–14.84
IX	6.99–7.87 (m,36H,arom.), 10.44 (s,2H,NH)	118.6–141.1 (16C arom.), 151.9 (CO)	–15.28
X	6.74–7.98 (m,36H,arom.), 10.46 (s,2H,NH)	118.7–140.5 (16C arom.), 151.8, 152.5 (CO)	–

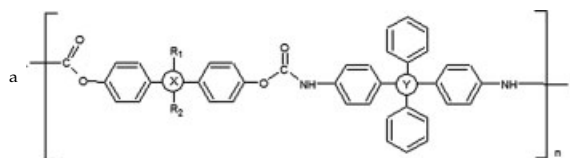
NMR spectra were measured in DMSO-*d*<sub>6</sub> solution.

<sup>a</sup> –OPh–Si(Ph)<sub>2</sub>–PhO–.

<sup>b</sup> –NPh–Si(Ph)<sub>2</sub>–PhN–.

**TABLE II**  
Yields of Reaction and Intrinsic Viscosity Data Obtained from the Poly(urethanes) Solutions

	Poly(urethane) <sup>a</sup>	Yield (%)	$\eta_{inh}^b$ (dL/g)
X = Y = Si	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = CH <sub>2</sub> CH <sub>3</sub>	<b>I</b>	64
X = Y = Si	R <sub>1</sub> = R <sub>2</sub> = CH <sub>2</sub> CH <sub>3</sub>	<b>II</b>	31
X = Y = Si	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>III</b>	48
X = Y = Si	R <sub>1</sub> = R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>IV</b>	57
X = Si, Y = Ge	R <sub>1</sub> = CH <sub>3</sub> , R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>V</b>	60
X = Si, Y = Ge	R <sub>1</sub> = R <sub>2</sub> = CH <sub>2</sub> CH <sub>3</sub>	<b>VI</b>	23
X = Y = Ge	R <sub>1</sub> = R <sub>2</sub> = CH <sub>2</sub> CH <sub>3</sub>	<b>VII</b>	30
X = Si, Y = Ge	R <sub>1</sub> = R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>VIII</b>	45
X = Ge, Y = Si	R <sub>1</sub> = R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>IX</b>	50
X = Y = Ge	R <sub>1</sub> = R <sub>2</sub> = C <sub>6</sub> H <sub>5</sub>	<b>X</b>	40



<sup>b</sup> In DMSO at 25°C (c = 0.3 g/dL).

ues and the yields were moderate and low, and they are independent of the nature and amount of the heteroatom in the main chain and the groups bonded to them. It is difficult that the reactivity of the bis(chloroformates) can be influenced by the nature of the heteroatom and its environment, due to the great distance to the active groups: amine and chloroformate, respectively. However, the low intrinsic viscosity values show that these poly(urethanes), probably are of low molecular weight; maybe oligomers.

In Table III, we have included the thermal behavior of the poly(urethanes) containing silylene and/or germerylene units. In this sense, when we have developed thermal studies in several polycondensation polymer families<sup>20–22</sup>, we have obtained results that agree with the following statement: the bond energy of the C–Ge bond is a little higher than the C–Si one, and also the bond distance of the C–Ge

one due to the bigger size of the Ge atom, and according to these statements, polymers with Ge must have a higher thermal stability than those with Si. Thus, when we analyze the beginning of the loss of weight or the TDT, taken when the sample has lost 10% of weight, it is possible to see that the poly(urethane) **II** with two Si atoms in the main chain, showed a lower thermal stability than the analogous poly(urethane) **VII** with two Ge atoms and the same substituent groups. The same can be observed for the pair **IV–X** both with aromatic rings bonded to the heteroatom. Figure 3 exemplifies this general situation showing the decomposition curve for **II** and **VII**, which are common to all poly(urethanes) analyzed.

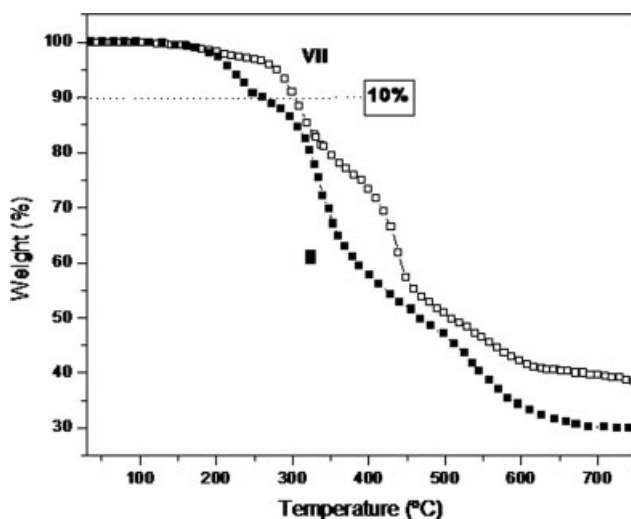
On the other hand, when we compared the TDT values of the poly(urethanes) with respect to the nature of the groups bonded to the heteroatoms, in

**TABLE III**  
Thermal Characteristics of the Poly(urethanes) Synthesized Containing Silarylene and/or Germerylene Units

Poly(urethane)	Analysis temperature (°C)								$T_g$ (°C)	TDT <sup>a</sup> (°C)
	30	100	200	300	400	500	600	700		
<b>I</b>	0	0.5	4.1	9.5	36.8	48.1	66.5	81.5	142	303
<b>II</b>	0	0	2.4	12.4	42.9	55.6	65.8	69.6	n.o.	298
<b>III</b>	0	0	1.1	9.6	10.1	37.8	56.4	63.5	n.o.	305
<b>IV</b>	0	0	0	6.9	29.6	51.9	85.2	100	73	310
<b>V</b>	0	0	0.8	5.6	26.5	42.9	57.1	60.7	n.o.	310
<b>VI</b>	0	0	6.9	9.7	41.6	52.4	65.8	69.5	n.o.	312
<b>VII</b>	0	0	1.9	9.1	26.7	49.1	58.1	60.3	120	304
<b>VIII</b>	0	0	0	3.1	21.9	40.6	53.1	62.5	117	340
<b>IX</b>	0	0	0	2.9	22.9	42.9	57.1	62.9	70	330
<b>X</b>	0	0	0	2.7	18.9	37.8	51.4	56.8	122	333

n.o.: Not observed.

<sup>a</sup> Registered when the sample has lost 10% of original weight.



**Figure 3** TGA curve of poly(urethane) II and VII at a heating rate of  $20^{\circ}\text{C min}^{-1}$  under nitrogen.

general it can be observed that those with aromatic groups (IV, VIII, IX, X) showed a higher thermal stability than those with aliphatic groups (I, II, VI, VII), due to the higher thermal stability of the aromatic rings, which has been observed previously in other polymers containing silicon and/or germanium, including poly(urethanes).<sup>14,20</sup>

When the nature of the heteroatom is analyzed, the change of Ge instead of Si shows an increase of the TDT value considering the same nature of the side chains. In fact, for those poly(urethanes) with aliphatic groups when Si is changed for Ge it is possible to see an increase of the TDT values: I with VI and VII, II with VI and VII. A similar behavior is possible to observe in those with aromatic side groups: IV–VIII, IV–IX, IV–X, IX–X. The exception was the higher value of the TDT for poly(urethane) VIII with respect to poly(urethane) X.

Finally, when the bis(chloroformate) used in the synthesis presents methyl and phenyl groups bonded to the silicon atom (III–V), also there is an increase of the TDT value if the diamine is changed from the one that contains Si (III) to one with Ge (V).

In summary, it is possible to see that the poly(urethanes) with germanium showed higher TDT values than those with silicon, although the observed differences were low.

Table II also shows the decomposition profile for the analyzed samples, through the percentage weight loss at various temperatures. All polymers showed similar curves, and at  $200^{\circ}\text{C}$ , the weight loss experimented by the samples is minimum ( $\sim 0$ –7%), whereas at  $500^{\circ}\text{C}$ , this is near to 50%. According to the TDT observed, the wholly aromatic poly(urethanes) (IV, VIII, IX, and X), showed a beginning

of decomposition higher than all samples. In general, this value is centralized at  $240$ – $260^{\circ}\text{C}$ .

Table II shows the  $T_g$  values for the some poly(urethanes). An extension of the statement written previously is that the germanium atom is bigger than a silicon one, which implies that the C–Ge bond is longer than the C–Si one. Thus, the poly(urethanes) with Si would have higher  $T_g$  values than the similar ones with Ge, due to the lower rotational barriers of the C–Ge bonds. In this case, several poly(urethanes) did not show  $T_g$ , probably due to the low molecular weights which can be deduced from the low  $\eta_{inh}$  values. The obtained  $T_g$  values are very dispersed and do not show correspondence with the above statement. Probably the wide variety of the groups bonded to the heteroatoms of the bis(chloroformate) does not permit to observe the influence of the heteroatoms, also in those in which only aromatic groups are bonded to them.

## CONCLUSIONS

New poly(urethanes) derived from bischloroformates and diamines, containing Si and/or Ge in the main chain, have been synthesized and characterized by spectroscopic methods. The molecular weights probably are low, which can be deduced from the low  $\eta_{inh}$  values.

Poly(urethanes) containing Ge in the main chain, showed higher thermal stability than the corresponding with Si, due to the higher bond energy of the C–Ge bond in front of the C–Si one, which has been observed in other systems. Also poly(urethanes) with aromatic side rings showed higher thermal stability than those with methyl groups, due to the higher rigidity of the aromatic rings.

## References

- Braun D.; Cherdron H.; Kern W. *Prácticas de Química Macromolecular*; Instituto de Plásticos y Cauchos: Madrid, España, 1968.
- Stanley, R. S. *Polymer Syntheses*; Academic Press: New York, 1974.
- Bruma, M.; Schulz, B. J. *Macromol Sci Polym Rev* 2001, C41, 1.
- Bruma, M.; Schulz, B.; Kopnick, T.; Robison, J. *High Perform Polym* 2000, 12, 429.
- Factor, A.; Engen, P. T. *J Polym Sci: Part A Polym Chem* 1993, 31, 2231.
- Thames, S. F.; Panjani, G. K. *J Inorg Organomet Polym* 1996, 6, 59.
- Bruma, M.; Schulz, B.; Kopnick, T. *High Perform Polym* 2005, 17, 483.
- Tagle, L. H. *Macromol Symp* 2003, 199, 499.
- Tagle, L. H.; Diaz, F. R.; Vega, J. C.; Quezada, M.; Guerrero, P. *J Inorg Organomet Polym* 2003, 13, 21.
- Tagle, L. H.; Terraza, C. A.; Alvarez, P.; Vega, J. C. *J Macromol Sci Pure Appl Chem* 2005, 42, 317.
- Tagle, L. H.; Terraza, C. A.; Alvarez, P. *Phosphor Sulfur Silicon Relat Elem* 2006, 181, 239.

12. Tagle, L. H.; Terraza, C. A.; Ahlers, W.; Vera, C. J *Chil Chem Soc* 2005, 50, 447.
13. Terraza, C. A.; Tagle, L. H.; Leiva, A.; Vega, J. C. *Polym Bull* 2004, 52, 101.
14. Terraza, C. A.; Tagle, L. H.; Leiva, A. *Polym Bull* 2005, 55, 277.
15. Tagle, L. H.; Terraza, C. A.; Leiva, A.; Valenzuela, P. *J Appl Polym Sci* 2006, 102, 2768.
16. Solomon O. F.; Gotesman B. S. *Makromol Chem* 1967, 104, 177.
17. Davidsohn, W.; Laliberte, B. R.; Goddard, C. M.; Henry, C. M. *J Organomet Chem* 1972, 36, 283.
18. Pratt, J. R.; Massey, W. D.; Pinkerton, F. H.; Thames, S. F. *J Org Chem* 1975, 40, 1090.
19. Terraza, C. A.; Tagle, L. H.; Concha, F.; Poblete L. *Desig Mon Polym* 2007, 10, 253.
20. Tagle, L. H.; Terraza, C. A.; Valenzuela, P.; Leiva, A.; Urzua, M. *Thermochim Acta* 2004, 425, 115.
21. Tagle, L. H.; Diaz, F. R.; Opazo, A. *Bull Soc Chil Quim* 2001, 46, 287.
22. Tagle, L. H.; Diaz, F. R.; Radic, D.; Opazo, A.; Espinoza, J. M. *J Inorg Organomet Chem* 2000, 10, 73.