Polym. Bull. (2009) 63:663–672
DOI 10.1007/s00289-009-0106-3

ORIGINAL PAPER

Synthesis and characterization of poly(urethanes) containing sulfone and silarylene or germarylene moieties

C. A. Terraza · L. H. Tagle · A. Leiva

Received: 15 December 2008 / Revised: 5 March 2009 / Accepted: 7 May 2009 /

Abstract 4,4′-Sulfonyldianiline (SDA) is reacted with 4,4′-(R_1R_2-silylene) bis(phenyl chloroformates) or 4,4′-(R_1R_2-germylene)bis(phenyl chloroformates) (where R_1 and R_2 are Me, Et, Ph combinations) in solution yielding poly(urethanes) (PUs) of moderate molecular weight containing silarylene, germarylene and sulfone moieties. DSC and TGA analyses were carried out. The highest glass temperatures (Tg) were obtained when one or two Ph groups were bonded to a heteroatom. However, these values were always low due to the flexibility gained by the chain due to the incorporation of the sulfone function. No-significant differences in Tg were observed when silicon was replaced by germanium in the main chain. All polymers were stable up to 200–220 °C and underwent a complex decomposition process with a higher rate for PUs with side aliphatic groups. The thermal decomposition temperature (TDT) (10 wt%) for PUs based on Ph–Si–Ph moiety were higher than those obtained from germarylene-containing polymers.

Keywords Poly(urethanes) · Silicon · Germanium · Sulfone group · Thermal stability

Introduction

Poly(urethanes) or poly(carbamates) are engineering materials that show several applications due to their excellent properties. Normally they are prepared by the reaction between diols and diisocyanates, and in this case poly(urethanes) have the same net composition of the monomers. They can also be prepared by the reaction between diamines and bis(chloroformates) but in this case HCl is eliminated [1]. On the other hand, Thames and Panjnani [2] described the synthesis of poly(urethanes)

C. A. Terraza (✉) · L. H. Tagle · A. Leiva
Facultad de Química, Pontificia Universidad Católica de Chile, P.O. Box 306, Santiago, Chile
e-mail: cterraza@uc.cl

containing Si in the main chain and those derived from diisocyanates and diols in DMF solution, showing only the spectroscopic characteristics without mentioning other properties.

In the last years our research group has been working in the synthesis of condensation polymers containing Si and/or Ge in the main chain, with the objective to study the behavior of the monomer in the synthesis of this kind of polymer [3–14]. Another objective has been to study the influence of both, the nature of the heteroatom and the groups bonded to them, aliphatic or aromatic, on the thermal properties of these condensation polymers. In this sense, the presence of the heteroatoms in the main chain implies a polarity due to the difference of electronegativity between Si or Ge versus C, which as a consequence has an increase of the thermal stability of the polymers, according to Bruma et al. [15, 16].

Continuing our works on the synthesis of condensation polymers and poly(urethanes) containing Si or Ge in the main chain [5, 8, 12, 17], in this work we present the synthesis of poly(urethanes) derived from several bis(chloroformates) containing Si or Ge bonded to several aliphatic or aromatic groups and 4,4′-sulfonyldianiline in CH_2Cl_2 solution. The results were evaluated by the yields and the inherent viscosity values. The thermal properties, glass transition temperature (Tg) and thermal decomposition temperature (TDT) were studied and discussed according to the nature of the heteroatoms, Si or Ge, and the aliphatic or aromatic groups bonded to them.

Experimental part

Monomers

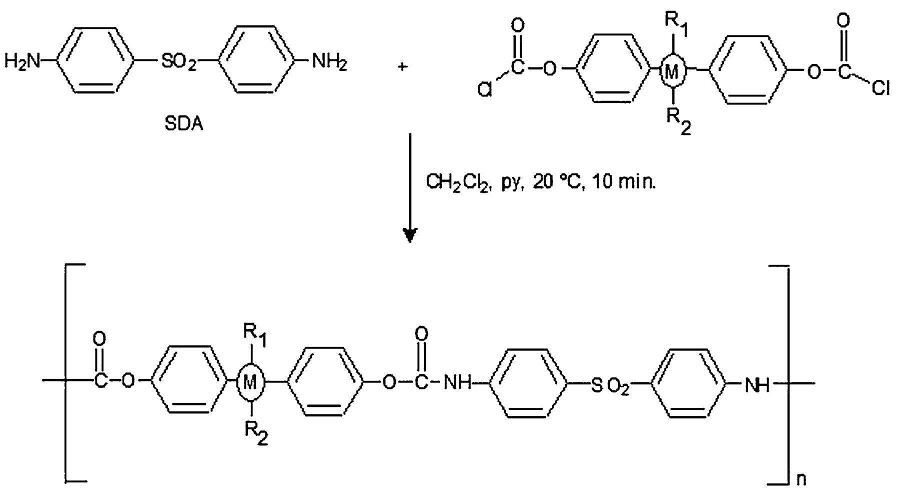
4,4′-Sulfonyldianiline (SDA) (Aldrich) was recrystalized from ethanol. 4,4′-(R_1R_2-silylene)bis(phenyl chloroformates) and 4,4′-(R_1R_2-germylene)bis(phenyl chloroformates) (Scheme 1) were synthesized according to described procedures [5, 17].

Poly(urethanes)

Polymers were synthesized according to a general procedure, in which a CH_2Cl_2 solution of the bis(chloroformate) derivative (9.13×10^{-4} mol) was added slowly over a CH_2Cl_2 solution containing the aromatic diamine (6.8×10^{-4} mol) and pyridine (0.31 mol). The solution was stirred at 20 °C for 10 min, finally obtaining a suspension of pyridinium chloride and the corresponding poly(urethane). The mixture was poured into methanol, stirred for 10 min at room temperature and the polymer filtered, washed several times with methanol and dried under vacuum until constant weight.

Characterization

The IR spectra (KBr disks) were recorded on a Perkin-Elmer 1310 spectrophotometer over the range of 4,000–450 cm^{-1}. ^{1}H, ^{13}C and ^{29}Si NMR spectra were carried



M	Poly(urethane)	R_1, R_2
Si	PU-1	$R_1 = R_2 = C_2H_5$
	PU-2	$R_1 = CH_3$, $R_2 = CH_2CH_3$
	PU-3	$R_1 = R_2 = CH_3$
	PU-4	$R_1 = CH_3$, $R_2 = C_6H_5$
	PU-5	$R_1 = R_2 = C_6H_5$
Ge	PU-6	$R_1 = R_2 = CH_2CH_3$
	PU-7	$R_1 = R_2 = C_6H_5$

Scheme 1 Synthesis and structural detail of the poly(urethanes)

out on a 400 MHz instrument (Bruker AC-200) using DMSO-d_6 as solvent and TMS as the internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25 °C ($c = 0.3$ g/dL). Tg values were obtained with a Mettler-Toledo DSC 821 calorimetric system (20 °C min^{-1} under N_2 flow). 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 10 °C min^{-1} under N_2 flow.

Results and discussion

The bis(chloroformates) derivatives were prepared with similar yields to whose already described [5, 17] and were used, together with SDA, in the synthesis of the poly(urethanes). Usually, we have used toluene or benzene as solvent in the reactions to obtain poly(urethanes) containing silarylene and/or germarylene units in their structure [5, 8, 12]. In this work, we replaced these solvents by CH_2Cl_2 due to

Table 1 Yield of reaction, viscosimetric and thermal characterizations of the PUs

Poly(urethane)	Yield (%)	η_{inh}[a] (dL/g)	Tg (°C)	TDT[b] (°C)	R_{w750}[c] (%)
Series I					
PU-1	81	0.18	n.o.	279	7
PU-2	77	0.14	n.o.	271	20
PU-3	73	0.19	n.o.	280	22
PU-4	84	0.22	−16.4	316	34
PU-5	83	0.21	19.6	326	37
Series II					
PU-6	63	0.21	−28.0	271	11
PU-7	66	0.19	20.3	299	21

n.o. not observed

[a] In DMSO solution at 25 °C ($c = 0.3$ g/dL)

[b] Values taken when the polymers has lost 10 wt%

[c] Residual weight percentage at 750 °C

the good solubility shown in this solvent by SDA and the bis(chloroformates) compounds.

Scheme 1 shows the general procedure for obtaining the PUs and the structure of their repetitive units. A combination of Me, Et and Ph are used as lateral groups bonded to the silicon (series I) or germanium (series II) atom. All polymers were obtained as a slightly yellow powder after a drying process, with yields between 63 and 84% (Table 1). The samples are highly soluble in aprotic polar solvents such as DMSO, NMP, DMAc, DMF and insoluble in $CHCl_3$, toluene and C_3, C_4 alcohols. On the other hand, the measurements of the η_{inh} in DMSO solutions showed low values, indicative of low molecular weights. Because the purity of the monomers was controlled by spectroscopic methods, the low molecular weight obtained could be attributed to the low solubility of the growing polymeric chains in the reaction media.

Table 2 summarizes the spectroscopic characterization of poly(urethanes). The IR spectra show common pattern in which it is possible to see the urethanic N–H and C=O stretching between 3,312–3,382 and 1,737–1,751 cm^{-1}, respectively. Aromatic C–H and C=C stretching appear at 3,064 and 1,595 cm^{-1}, respectively, while S=O stretching is observed with two bands: 1,492–1,200 and 1,106–1,150 cm^{-1}. The sylil-C and germyl-C stretching are assigned depending on the aliphatic or aromatic nature of the carbon atom. A visual representation of the IR common patterns in PUs spectra is given in Fig. 1.

The NMR spectra show the effect of the Si and Ge atom on the neighboring groups. Signals for protons of methyl or methylene groups bonded directly to the heteroatom appear displaced to high field; 0.87–0.48 and 0.85 ppm, respectively (Table 2). In all spectra it is possible to see the urethanic N–$\underline{H}$ signal between 10.71 and 10.84 ppm. On the other hand, the ^{13}C NMR spectra also show the signal associated to the urethanic carbonyl group at 151.5 ppm approximately. The signal of ^{29}Si NMR follows the pattern already described for the bis(chloroformate)

Table 2 IR and NMR spectroscopic data of PUs

PU	IR (υ, cm^{-1})	^{1}H-NMR (δ, ppm)	^{13}C-NMR (δ, ppm)	^{29}Si-NMR (δ, ppm)
1	3,317 (NH), 3,062 (CH arom.); 2,954 (CH aliph.); 1,751 (overlap C=O, NH); 1,595 (C=C arom.); 1,494, 1,004, 716 (silyl-Ph); 1,321, 888 (silyl-Et); 1,265, 1,148 (SO_2); 1,199, 1,105 (C–O); 835 (*p*-arom.)	0.85–1.21 (m,10H,Et); 7.42 (dd,8H,CH arom.); 7.83 (dd,8H,CH sulfonated arom); 10.80 (s,2H,NH)	3.1 ($\underline{C}H_2CH_3$); 7.2 (CH_3); 118.5–143.2 (8$\underline{C}$ arom.); 151.3, 151.4 (–$\underline{C}O_2$–)	−3,8
2	3,316 (NH); 3,060 (CH arom.); 2,955 (CH aliph.); 1,751 (overlap C=O, N–H); 1,595 (C=C arom.); 1,495, 1,005, 659 (silyl-Ph); 1,321, 1,149 (SO_2); 1,200, 1,106 (C–O); 888 (silyl-alkyl); 817 (*p*-arom.)	0.48 (s,3H,CH_3); 0.85–1.15 (m,5H,Et); 7.37 (dd,8H,CH arom.); 7.76 (dd,CH sulfonated arom); 10.73 (s,2H,NH)	−5.3 (CH_3); 5.1 ($\underline{C}H_2CH_3$); 7.3 ($CH_2\underline{C}$H3); 118.5–143.2 (8$\underline{C}$ arom.); 152.2, 152.4 (–$\underline{C}O_2$–)	−5,6
3	3,315 (NH); 3,062 (CH arom.); 2,955 (CH alif.); 1,751 (overlap C=O, N–H), 1,594 (C=C arom.); 1,495, 644 (silyl-Ph); 887 (silyl-alkyl); 1,322, 1,150 (SO_2); 1,200, 1,106 (C–O); 822 (*p*-arom.)	0.56 (s,6H,CH_3); 7.39 (dd,8H,CH arom.); 7.73 (dd,8H,CH sulfonated arom); 10.73 (s,2H,NH)	−2.63 ($\underline{C}$H3); 115.1–135.3 (8$\underline{C}$ arom.); 151.0, 151.6 (–$\underline{C}O_2$–)	−7,8
4	3,314 (NH); 3,066 (CH arom.); 2,957 (CH aliph.), 1,751 (overlap C=O, N–H); 1,594 (C=C arom.); 1,495, 648 (silyl-Ph); 1,321, 1150 (SO_2); 1,200, 1106 (C–O); 887 (silyl-alkyl); 817 (*p*-arom.); 787, 683 (mono-arom.)	0.87 (s,3H,CH_3); 7.21–8.23 (m,21H, CH arom.); 10,80 (s, 2H, NH)	−3.18 ($\underline{C}$H3); 113.0–143.2 (14$\underline{C}$ arom.); 151.3, 151.5 (–$\underline{C}O_2$–)	−11,20
5	3,382 (NH); 3,067 (CH arom.), 1,752 (overlap C=O, N–H); 1,595 (C=C arom.); 1,494, 1,003, 738 (silyl-Ph); 1,321, 1,149 (SO_2), 1,199, 1,106 (C–O); 738, 652 (mono-arom.); 700 (*p*-arom.)	7.06–8.15 (m,26H,CH arom.); 10.84 (s,2H,NH)	113.0–143.2 (14$\underline{C}$ arom.); 151.3, 151.8 (–$\underline{C}O_2$–)	−14,80

Table 2 continued

PU	IR (υ, cm^{-1})	^{1}H-NMR (δ, ppm)	^{13}C-NMR (δ, ppm)	^{29}Si-NMR (δ, ppm)
6	3,312 (NH); 2,059 (CH arom.), 2,954 (CH aliph.), 1,737 (overlap C=O, N–H); 1,595 (C=C arom.); 1,321, 1,008 (germyl-Et); 1,270, 1,150 (SO_2); 1,198, 1,107 (C–O); 836 (*p*-arom.)	0.71–1.27 (m,10H,Et); 7.36 (dd,8H,CH arom.); 7.79 (dd,8H,CH sulfonated arom); 10.67 (s,2H,NH)	4.4 ($\underline{C}H_2CH_3$); 8.6 (CH_3); 118.6–143.2 (8$\underline{C}$ arom.); 151.3; 151.4 (–$\underline{C}O_2$–)	–
7	3,314 (NH), 3,050 (CH aliph.); 1,749 (overlap C=O, N–H); 1,594 (C=C arom.); 1,492, 1,003 (germyl-Ph); 1,270, 1,151 (SO_2); 1,198, 1,106 (C–O); 834 (*p*-arom.)	7.19–8.08 (m,26H,CH arom.); 10.71 (s,2H,NH)	118.4–143.1 (14$\underline{C}$ arom.); 151.3 (–$\underline{C}O_2$–)	–

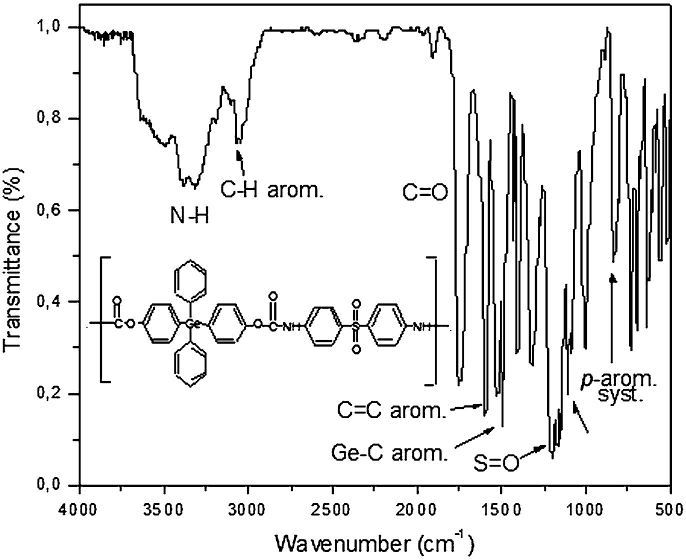


Fig. 1 FT-IR spectrum of PU-7 showing the common pattern

monomers where the presence of phenyl groups bonded directly to silicon atom displace the resonance to high field [17].

The thermal properties were established by DSC and TGA analyses under N_2 atmosphere and are shown in Table 1. In series I, Tgs were not observed for PUs with aliphatic group bonded to Si, in accordance to the high chain flexibility. However, when phenyl groups were incorporated, higher values were obtained in both series. Therefore, the Tg values agree with the nature and amount of the R group bonded to the heteroatom. PU-5 and PU-7, both with two Ph groups as side groups, showed a Tg near 20 °C, in agreement with a higher molecular rigidity. If these Tg values are compared with those obtained from PUs derived from the same bis(choloroformates) but with wholly aromatic diamines [12], or 4,4′-methylenedianiline [5] it is possible to see the effect of the sulfone function. In these latter polymers, Tg values were between 70 and 142 °C. It is clear that a higher chain mobility is obtained when the SO_2 group replaces the R_1–M–R_2 (where M = Si, Ge; R_1, R_2 = aliphatic and/or aromatic group) or –CH_2– moieties, allowing to obtain very low Tg values. For PU-5 and PU-7, both with two phenyl groups bonded to the central heteroatom (Si or Ge, respectively), no-significant difference was observed in their Tg values.

As is shown in Fig. 2 (TGA curves) for the PUs it is possible to see good thermal stability up to 200–220 °C. The TDTs, considering a 10% weight loss, were between 271 and 326 °C, with a variable content of solid at 750 °C (R_{w750}: 7–37%). The curves also show that the decomposition process occurs in two stages: the first stage near 260–320 °C and a second at 410–460 °C for all polymers, with a higher decomposition rate for PUs based only on aliphatic lateral groups. The TDT (10 wt%) and the content of solid for each sample are summarized in Table 1. In series I, it is not possible to observe great differences between the TDT of the samples with Me, Et combinations as side groups (PU-1, PU-2 and PU-3). However,

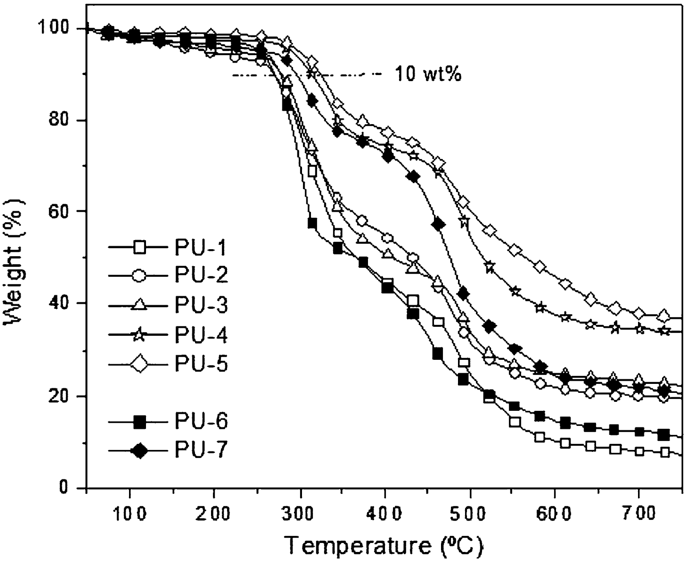


Fig. 2 TGA curves of poly(urethanes) (heating rate: 10 °C min^{-1} in nitrogen). PUs 1–5 contain silarylene units, PUs 6 and 7 contain germarylene moieties

when one or two Ph groups were incorporated (PU-4 and PU-5, respectively), the TDT values were increased in agreement with the number of aliphatic groups replaced. This behavior is also observed in series II, when the TDT of PU-7 is almost 30 °C higher than that for PU-6.

If we compare PUs of similar structure, in which the heteroatom used is the only difference (PU-1/PU-6 and PU-5/PU-7 pairs), higher TDT values for those with silicon atom are observed. Bruma et al. [16] have compared the behavior of systems based on C–C and C–Si of similar energy bond. These authors propose that because the ionic character of the bond is increased according to the difference in the electronegativity between C and Si atoms, the thermal stability would also be increased. Therefore, the polymer with C–Si bond would be more stable thermally in comparison with those based on a C–C one. Although our current results agree with this idea, we have already reported that PUs based on germanium atom show higher TDT values than those based on a silicon one [5]. We think that this latter behavior is in agreement with the C-heteroatom bond energy [18] and with the micro polarity inside the chain. Because the electronegativity of the silicon atom is slightly smaller than that shown by germanium [18], the C–Si bond is more polar than C–Ge, and therefore the polymers containing C–Si bond should be more stable than those containing C–Ge bond.

Conclusions

Poly(urethanes) based on silarylene and germarylene units containing sulfone function were prepared by polycondensation from bis(chloroformates) derivatives and SDA in solution. The yields are between 63 and 84% and the η_{inh} recovered in DMSO solutions indicate a low to moderate molecular weight. This fact is due probably to the low solubility of the growing chain in the reaction medium. The solubility of the samples is the characteristic for the poly(urethane) family: They are soluble in DMSO, DMF and *m*-kresol and insoluble in alcohols. All polymers were characterized by IR and NMR spectroscopy, including ^{29}Si-NMR when was appropriate. These analyses are in agreement with the repetitive units structure proposed. The thermal characterizations were carried out by DSC and TGA. The incorporation of SO_2 group conveys a higher flexibility to the chain, associated to very low Tg values. The PUs with Ph side groups showed higher Tg values without significant differences when silicon was replaced by germanium as the central atom. The TGA curves showed a decomposition process of two stages with a higher rate for PUs with Me and Et combinations as side groups. Finally, the PUs based on silarylene units were thermally more stable compared to germarylene-containing polymers.

Acknowledgments The authors acknowledge the financial support of Fondo Nacional de Ciencia y Tecnología (FONDECYT) through grant 1030528.

References

1. Stanley RS (1974) Polymer syntheses. Academic Press, New York
2. Thames SF, Panjnani GK (1996) Organosilane polymer chemistry: a review. J Inorg Organomet Polym 6:59
3. Tagle LH, Terraza CA, Lopez L, Leiva A (2006) Synthesis and characterization of comb-like poly(esters) containing silicon and/or germanium in the main chain. J Chil Chem Soc 51(4):1041
4. Tagle LH (2003) Condensation polymers containing silicon and germanium in the main chain. Macromol Symp 199:499 and the references therein
5. Terraza CA, Tagle LH, Leiva A, Vega JC (2004) Synthesis and characterization of 4,4′-(dimethylsilylene)bis(phenylchloroformate) and 4,4′-(dimethylylengermylene)bis(phenylchloroformate) and their use in the synthesis of poly(urethanes). Polym Bull 52:101
6. Tagle LH, Terraza CA, Valenzuela P, Leiva A, Urzúa M (2005) Thermal studies of poly(esters) containing silicon or germanium in the main chain. Thermochim Acta 425:115
7. Tagle LH, Terraza CA, Alvarez P, Vega JC (2005) Synthesis and characterization of poly(carbonates) and poly(thiocarbonates) derived from diphenols containing germanium as central atom. J Macromol Sci Part A Pure Appl Chem 42:317
8. Terraza CA, Tagle LH, Leiva A (2005) Matic rigid poly(urethanes) containing silicon and/or germanium in their main chain. Polym Bull 55:277
9. Tagle LH, Terraza CA, Ahlers W, Vera C (2005) Synthesis of condensation polymers derived from silylated monomers under phase transfer catalysis. J Chil Chem Soc 50:535
10. Tagle LH, Terraza CA, Alvarez P (2006) Synthesis and characterization of poly(carbonates) and poly(thiocarbonates) derived from diphenols containing silicon as central atom. Phosphor Sulfur Silicon Rel Elem 181:239
11. Tagle LH, Terraza CA, Leiva A, Valenzuela P (2006) Poly(amides) and poly(imides) containing silicon and/or germanium in the main chain. Synthesis, characterization and thermal studies. J Appl Polym Sci 102:2768
12. Terraza CA, Tagle LH, Leiva A, Poblete L, Concha F (2008) Poly(urethanes) containing silarylene and/or germarylene units. J Appl Polym Sci 109:303
13. Tagle LH, Terraza CA, Leiva A, Devilat F (2008) Synthesis, characterization and thermal studies of poly(amides) and poly(imides) that contain two silarylene units in the main chain. J Appl Polym Sci 110:2424

14. Tagle LH, Terraza CA, Leiva A, Alvarez P (2009) Poly(amide) oligomers with silarylene and/or germarylene units—synthesis, characterization and thermal studies. e-Polymers 034
15. Bruma M, Schulz B, Köpnick T, Robinson J (2000) Silicon-containing polyesterimides. High Perfom Polym 12:429
16. Bruma M (2007) High performance polymers containing phenylquinoxaline and silicon in the main chain. Rev Roumaine Chim 52:309
17. Terraza CA, Tagle LH, Concha F, Poblete L (2007) Synthesis and characterization of new bifunctional monomers based on germarylene and silarylene units. 4,4′-(R_1,R_2-silylene)bis(phenyl chloroformates) and 4,4′-(R_1,R_2-germarylene)bis(phenyl chloroformates). Des Monom Polym 10(3):253
18. WebElements: the periodic table on the web. http://www.webelements.com