# Synthesis of Poly(urethane)s Based on Diphenyl-Silane/Germane and Oxyphenyl Units: Structure–Properties Relationship

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**ABSTRACT:** A series of poly(urethane)s (PUs) based on diphenyl-silane or -germane and oxyphenyl units were synthesized by polycondesation of 4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline (3) and four bis(chloroformate)s (**I–IV**). These monomers were prepared and characterized in previous works. The best conditions for the polymerization reactions were investigated by a kinetic study. Also, a selection of the best solvent for the reaction was developed. Polymers were characterized by IR and $^1H$, $^{13}C$, and $^{29}Si$-NMR spectroscopy and the results were in agreement with the proposed structures. Poly(urethane)s showed inherent viscosity values between 0.12 and 0.31 dL/g, indicative of low molecular weight species, probably of oligomeric nature. The glass transition temperature ($T_g$) values were observed in the 127–168°C range by DSC analysis. Thermal decomposition temperature ($TDT_{10\%}$) values were above 300°C. All PUs showed good transparency in the visible region (>80% at 350 nm) due to the incorporation of the bulky monomer (fluorene) and oxyether linkages. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1036–1041, 2012

**Key words:** silicon-containing polymers; poly(urethane)s; bis(chloroformate); glass transition temperature; thermogravimetric analysis

## INTRODUCTION

Condensation polymers are materials with wide applications in several industrial fields.[1,2] Specifically, poly(urethane)s (PUs) are employed for producing articles with different electrical, optical, mechanical, and chemical properties. However, depending on the nature of the backbone, PUs generally exhibit poor resistance to heat (thermal degradation begins around 200°C) and low solubility in common organic solvents.[3,4]

However, changing the structure of the polymer backbone is possible to control some characteristics of the final material. It is known that the incorporation of both, ether linkage and a cyclic side cardo group, such as a fluorene unit, into the macromolecular backbone results in good thermal stability and excellent solubility in organic solvents.[5–8] On the other hand, various combinations of atoms and groups linked with *p*-phenylene units, such as silicon, sulfur, oxygen, and methylene groups, have been used in several high-temperature polymers.[9]

In this work, we report the synthesis of four PUs containing silarylene or germarylene and oxyphenyl units in the main chain. The incorporation of the heteroatoms in the polymer structure implies a gain in the polarity of the chain due to the difference of electronegativity between the heteroatom (Si or Ge) and the C atom, which increases the thermal stability. Both heteroatoms and ether linkages increase flexibility, causing a decrease of the $T_g$ values and an increase of the solubility in common organic solvents. Also, we synthesized a poly(urethane) without these heteroatoms in the main chain to compare the properties.

## EXPERIMENTAL

### Materials

*N*-methyl-2-pyrrolidone (NMP), 4-fluornitrobenzene, dimethylsulfoxide, pyridine, toluene, chloroform, hydrazine monohydrate, Pd/C activated, *N,N*-dimethylaniline, 4-(*N,N*-dimethylamino)pyridine, and bisphenol A bis(chloroformate) were obtained from Aldrich Chemical (Milwaukee, WI). Phosgene (20% w/w in toluene) was purchased from Fluka (Switzerland). Reagents and solvent were used

without further purification except bisphenol A bis(chloroformate), which was recrystallized from *n*-hexane.

## Instrumentation

The IR spectra (KBr pellets) were recorded on a Perkin–Elmer (Fremont CA) 1310 spectrophotometer over the 4000–450 cm$^{-1}$ range. $^1$H, $^{13}$C, and $^{29}$Si-NMR spectra were carried out on a 400-MHz instrument (Bruker AC-200), using DMSO-$d_6$ as solvent and TMS as internal standard. The unmodified carbons in$^{135}$dept analysis are shown with an asterisk over their chemical shift. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25°C using DMSO as solvent ($c = 0.5$ g/dL). $T_g$ values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (20°C min$^{-1}$ under N$_2$ flow). Thermogravimetric analyses were carried out in a Mettler (Switzerland) 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 25°C and 900°C with a heating rate of 20°C min$^{-1}$ under N$_2$ flow. Elemental analyses were carried out on a Fisons EA 1108-CHNS-O equipment. The UV-visible optical transmission spectra were obtained on a UV-3101PC UV-Vis-NIR scanning spectrophotometer (Shimadzu, Japan) at room temperature using solutions of NMP ($c = 5.0$ g/L).

## Monomers synthesis

Diamine 4-[4-[9-[4-(4-aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline was synthesized according to procedures previously described.[10] Briefly, 4,4′-(9H-fluorene-9,9-diyl)bis(2-methylphenol) (1) was reacted first with potassium carbonate and then with *p*-chloronitrobenzene to obtain the dinitro derivative, (2) which was reduced to the corresponding diamine (3) (Scheme 1).

On the other hand, the bis(chloroformate)s, 4,4′-(dimethylsililene)bis(phenyl chloroformate) (**II**), 4,4′-(diphenylsililene)bis(phenyl chloroformate) (**III**) and 4,4′-(diphenylgermarylene)bis(phenyl chloroformate) (**IV**), were synthesized following a previously described procedure,[11–14] whereby bis(4-hydroxyphenyl)derivative (4) was reacted with phosgene/toluene solution and then with a N,N-dimethylaniline and 4-(N,N-dimethylamine)pyridine mixture at low temperature (Scheme 2).

## Polymer synthesis

A typical polymerization procedure for the synthesis of PUs was as follows (Scheme 3): A mixture of 0.200 g (0.35 mmol) of (**3**) 0.5 mL of pyridine and 2 mL of toluene was heated with stirring until the diamine was completely dissolved. The mixture was cooled to room temperature and then a solution of 0.126 mg (0.35 mmol) of bis(chloroformate) derivative dissolved in 2 mL of toluene was added. The suspension formed was stirred for 10 min and then the mixture was poured into 300 mL of methanol. The fibrous white precipitate was filtered, washed thoroughly with methanol and dried until constant mass.

## PU—C—MM

Yield: 30%. $\eta_{inh} = 0.21$ dL/g (in DMSO at 25°C, $c = 0.5$ g/dL). IR (KBr, cm$^{-1}$): 3397 (NH), 3039 (C—H arom.), 2967 (C—H aliph.), 1745 (C=O), 1603, 1506, 1492 (C=C arom.), 1246 (C—O—C), 1196 (C(O)—O), 830 (arom. *p*-subst). $^1$H-NMR (DMSO-$d_6$) (δ) (ppm): 1.65 (s,6H,CH$_3$—C aliph.), 2.07 (s,6H,Ph—CH$_3$); 6.49–7.90 (m, 30H, arom.); 10.17 (s, 2H, NH). $^{13}$C-NMR (DMSO-$d_6$) (δ) (ppm): 16.6* (Ph—CH$_3$), 31.0* (CH$_3$—C aliph.), 42.3 (Ph$_2$C(CH$_3$)$_2$), 64.4 (cardo-carbon), 119.0*, 120.6*, 120.7, 121.0*, 121.2*, 121.8*, 126.6*, 127.2*, 127.9*, 128,1, 128.2*, 128.4*, 130.8*, 134.4, 139.9, 141.0, 147.6, 151.2, 152.3, 152.9 (20C arom.); 155.2 (C=O). Elem. Anal. Calcd. for [C$_{56}$H$_{44}$N$_2$O$_6$]$_n$; (840.58)$_n$: C, 80,01%; H, 5.23%; N, 3.33%. Found: C, 78.92%; H, 5.01%; N, 3.11%.

## PU—Si—MM

Yield: 60%. $\eta_{inh} = 0.31$ dL/g (in DMSO at 25°C, $c = 0.5$ g/dL). IR (KBr, cm$^{-1}$): 3396 (NH), 3026 (C—H arom.), 2954 (C—H aliph.), 1750 (C=O), 1590, 1508, 1492 (C=C arom.), 1390, (Si—C aliph.), 1414, 997 (Si—C arom.), 1249 (C—O—C), 1194 (C(O)—O), 813 (arom. *p*-subst). $^1$H-NMR (DMSO-$d_6$) (δ) (ppm): 0.49 (s, 6H, CH$_3$—Si), 2.01 (s, 6H, Ph—CH$_3$); 6.61–7.84 (m, 30H, arom.); 10.17 (s, 2H, NH). $^{13}$C-NMR (DMSO-$d_6$) (δ) (ppm): –2.1* (Si—CH$_3$), 16.5* (Ph—CH$_3$), 64.4 (cardo-carbon), 118.2*, 119,1*, 120.7, 121.0*, 121.3, 122.0*, 126.6*, 127.2*, 128.1*, 128.4*, 130.8*, 134.4, 135.1, 135.6*, 135.9*, 140.0, 141.0, 151.3, 152.1, 152.7 (20C arom.); 154.2 (C=O). $^{29}$Si-NMR (DMSO-$d_6$) (δ) (ppm): –7.90. Elem. Anal. Calcd. for [C$_{55}$H$_{44}$N$_2$O$_6$Si]$_n$; (856.66)$_n$: C, 77.11%; H, 5.13%; N, 3.27%. Found: C, 76.57%; H, 5.05%; N, 3.11%.

## PU—Si—PP

Yield: 40%. $\eta_{inh} = 0.12$ dL/g (in DMSO at 25°C, $c = 0.5$ g/dL). IR (KBr, cm$^{-1}$): 3397 (NH), 3068, 3048, 3024 (C—H arom.), 2922 (C—H aliph.), 1752 (C=O), 1590, 1509, 1492 (C=C arom.), 1428 (Si—C arom.), 1246 (C—O—C), 1193 (C(O)—O), 827 (arom. *p*-subst), 743 (arom. *mono*-subst.). $^1$H-NMR (DMSO-$d_6$) (δ)
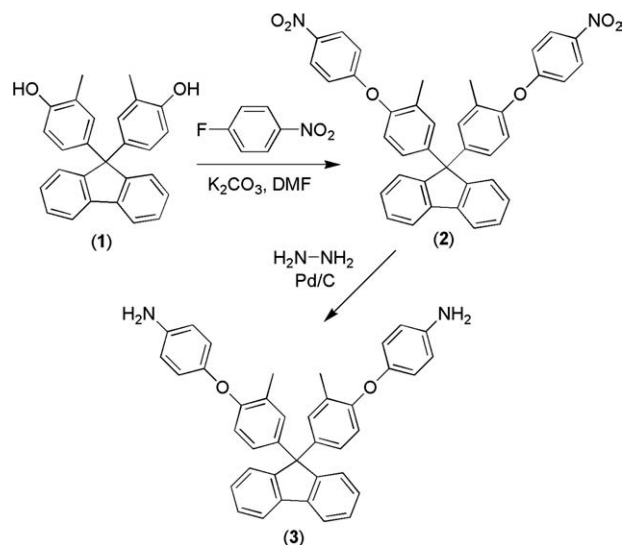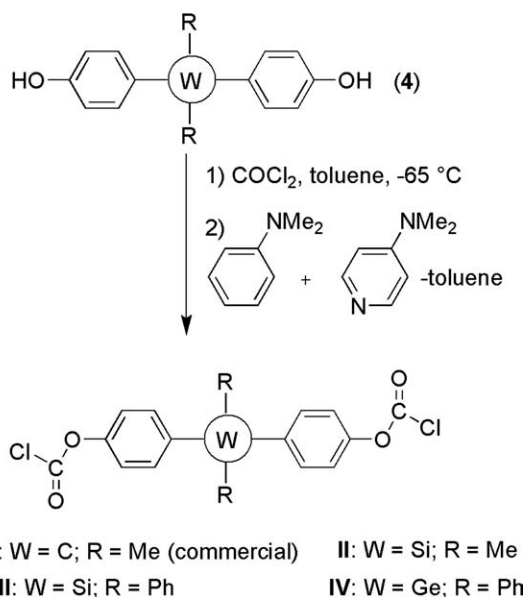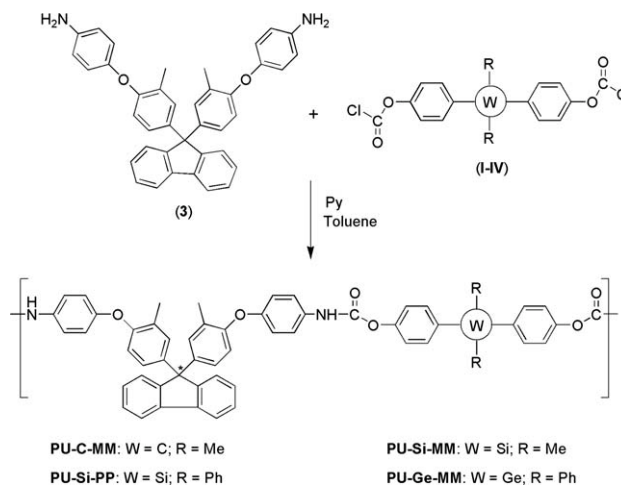
**Scheme 1** General synthesis of diamine.

(ppm): 2.05 (s, 6H, CH$_3$); 6.48–7.88 (m, 40H, arom.); 10.25 (s, 2H, NH). $^{13}$C-NMR (DMSO-$d_6$) ($\delta$) (ppm): 16.6* (CH$_3$), 64.4 (cardo-carbon), 115.4*, 115.9*, 116.0*, 119.1*, 120.8, 121.0, 121.7*, 122.1, 126.6*, 128.1*, 128.4*, 128.6*, 128.8, 130.2*, 130.8, 134.3, 136.3*, 137.6*, 137.9*, 138.0*, 139.9, 151.3, 152.6, 152.7 (24C arom.); 154.2 (C=O). $^{29}$Si-NMR (DMSO-$d_6$) ($\delta$) (ppm): –14.92 Elem. Anal. Calcd. for [C$_{65}$H$_{48}$N$_2$O$_6$Si]$_n$; (980.76)$_n$: C, 79.60%; H, 4.89%; N, 2.86%. Found: C, 79.32%; H, 4.56%; N, 2.66%.

### PU—Ge—PP

Yield: 60%. $\eta_{inh}$ = 0.18 dL/g (in DMSO at 25°C, $c$ = 0.5 g/dL). IR (KBr, cm$^{-1}$): 3405 (NH), 3049 (C—H



**Scheme 2** Synthetic route to silicon- or germanium-containing bis(chloroformate)s.

**Scheme 3** General synthesis of poly(urethane)s.

arom.), 2922 (C—H aliph.), 1750 (C=O), 1602, 1587, 1509, 1491 (C=C arom.), 1431 (Ge—C arom.), 1248 (C—O—C), 1193 (C(O)—O), 826 (arom. *p*-subst), 741 (arom. *mono*-subst.). $^1$H-NMR (DMSO-$d_6$) ($\delta$) (ppm): 2.07 (s, 6H, CH$_3$); 6.68–7.90 (m, 40H, arom.); 10.26 (s, 2H, NH). $^{13}$C-NMR (DMSO-$d_6$) ($\delta$) (ppm): 16.6* (CH$_3$), 64.4 (cardo-carbon), 118.2*, 119.0*, 120.7*, 121.0, 122.0, 122.7*, 126.6*, 127.2*, 128.1*, 128.4*, 128.8*, 129.1*, 130.8*, 134.2*, 134.3, 135.3*, 135.6, 136.4*, 136.7, 139.9, 141.1, 151.3, 152.0, 152.2 (24C arom.); 154.2 (C=O). Elem. Anal. Calcd. for [C$_{65}$H$_{48}$N$_2$O$_6$Ge]$_n$; (1025.26)$_n$: C, 76.14%; H, 4.68%; N, 2.73%. Found: C, 75.87%; H, 4.56%; N, 2.35%.

## RESULTS AND DISCUSSION

### Determination of the polymerization conditions

Two experimental conditions of polymerization were studied: solvent and reaction time. For this purpose, the reaction between the diamine (3) and the bis (chloroformate) derivatives (**II**) was chosen (Scheme 3). Table I shows the results of inherent viscosity and yields obtained using different solvents and polymerization times. The reaction time was not an important parameter to consider. The obtained yields at 10, 30 and 60 min were similar for a particular solvent. In agreement with these values, toluene was the best solvent for the polymerization reaction, with yield of 60%, although the polymer precipitated immediately when the bis(chloroformate) solution was dripped on the diamine/pyridine/solvent mixture. In the case of NMP and CHCl$_3$ the precipitate was not observed, but as can be seen in Table I, the yields were lower than those obtained in toluene. Inherent viscosities were determined for all the polymerizations developed in toluene and at 10 min for reactions in NMP and CHCl$_3$. It is clear that toluene allows obtaining the highest value, which is not

**TABLE I**
**Yield and Inherent Viscosity Obtained for PU—Si—MM in Different Solvents**

| Solvent | $\eta_{inh}{}^a$ (dL/g) | Yield at 10 min (%) | Yield at 30 min (%) | Yield at 60 min (%) |
|---------|------------------------|---------------------|---------------------|---------------------|
| Toluene | 0.31 | 60 | 60 | 59 |
| NMP | 0.16 | 15 | 16 | 15 |
| CHCl₃ | 0.20 | 36 | 35 | 35 |

[a] Recovered from DMSO solution ($c = 0.5$ g/dL) at 25°C for polymerization at 10 min.

affected by the polymerization time (0.30 dL/g at 30 min and 0.33 dL/g at 60 min). This fact could be attributed to the early precipitation of the polymer (phenomenon commented previously). The biggest polarity of NMP and chloroform relative to toluene, probably allows maintaining the polymer in solution, without increasing the molecular size of the chains. For this reason, the polymerization reactions developed using the bis(chloroformate)s **I**, **III**, and **IV** were all made in toluene solution for 10 min.

### Synthesis and characterization of PUs

Poly(urethane)s were synthesized by condensation of the aromatic diamine and several bis(chloroformate)s containing silicon, germanium, or carbon as central atom. All the reactions were carried out in a toluene-pyridine solution at room temperature (19°C approximately) and all of them proceeded heterogeneously. The obtained yield's range was between 30 and 60% (Table II). Results of elemental analysis for PUs show a good accordance with the structures proposed.

Polymers were characterized by NMR and IR spectroscopy. In all cases, the spectroscopic patterns were in agreement with the structures of the repetitive units proposed in Scheme 3. Figure 1 illustrates the FT-IR spectra of all PUs. The classic wide stretching band of the N—H group due to amidic bond appears between 3396 and 3405 cm⁻¹. It is also possible to see the absorption between 1745 and 1752 cm⁻¹ corresponding to the C=O stretching band and the absorption between 1193 and 1196 cm⁻¹ associated to the C—O stretching of the urethanic group.

According to the nature of the carbon atom bonded to silicon, it is possible to observe values of 1428–1414 cm⁻¹ and 1390 cm⁻¹ for the aromatic C—Si and aliphatic C—Si stretching, respectively. Also, in **PU—Ge—PP**, the aromatic C—Ge stretching is observed at 1431 cm⁻¹.

All PUs ¹H-NMR spectra are shown in Figure 2. When **PU—C—MM** and **Pu—Si—MM** are compared, it is observed that the chemical shift of the methyl group decreases when the carbon atom is replaced by the silicon atom (1.65–0.49 ppm). This is expected due to the lower electronegativity of the silicon atom. Results obtained from ¹³C-NMR analysis also evidence the electronegativity effect over carbon atoms directly bonded to silicon. Thus, it is possible to see the CH₃ group at –2.1 ppm. On the other hand, the peaks between 10.16 and 10.25 ppm (N—H signal, ¹H-NMR spectra) and 151.2–151.8 (C=O signal, ¹³C-NMR spectra) confirm the formation of amide linkages.

### Inherent viscosity and solubility of polymers

Yields and inherent viscosities of the PUs are reported in Table II. The inherent viscosities of poly(urethane)s were determined in DMSO with a concentration of 0.5 g/dL at 25°C. These values were in the range of 0.12–0.31 g/dL, which could indicate a low to moderate molecular weight. One explanation for this could be the early precipitation of the polymers in the reaction medium. To avoid this, the already mentioned polymerization study in different solvents was performed, but the yields and inherent viscosity values were lower when toluene was replaced by NMP or CHCl₃ (Table I).

**TABLE II**
**Yield and Properties of PUs Derivied from Bis(chloroformate)s I–IV**

| PU | Yield (%) | $\eta_{inh}{}^a$ (dL/g) | TDT$_{10\%}{}^b$ (°C) | Char yield$^c$ (%) | $T_g{}^d$ (°C) |
|----|-----------|------------------------|----------------------|--------------------|----------------|
| **PU—C—MM** | 30 | 0.21 | 320 | 27 | 168 |
| **PU—Si—MM** | 60 | 0.31 | 314 | 37 | 135 |
| **PU—Si—PP** | 40 | 0.12 | 358 | 52 | 127 |
| **PU—Ge—PP** | 60 | 0.18 | 334 | 48 | 150 |

[a] Values were taken from DMSO solutions ($c = 0.5$ g/dL) at 25°C.
[b] 10% Weight loss temperature (in nitrogen, 20°C/min).
[c] Residual weight (%) at 900°C (in nitrogen, 20°C/min).
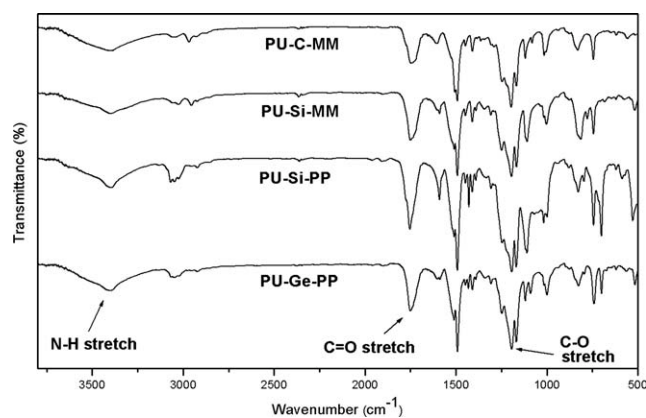[d] Glass transition temperature (second heating scan in nitrogen at 20°C/min).

Figure 1  FT-IR spectra of poly(urethane)s.



Figure 3  TGA and differential curves of PUs (20°C/min in nitrogen atmosphere).

The solubility of the poly(urethane)s was determined at room temperature in various common organic solvents. PUs were soluble in DMSO, DMF, DMAc, NMP, and *m*-cresol, even in low boiling point solvents, such as THF and CHCl₃. This fact could be justified by two reasons: The presence of small polymeric chains, which is strongly suggested by the inherent viscosities values obtained and the inclusion of ether linkages into repetitive units. This latter fact would provide an increased flexibility of the chain, increasing in this way its solubility. Additionally, a great free volume is generated by the use of a bulky diamine. The central cardo-carbon also helps to increase the interchains distance reducing in this way the interactions between them.

## Thermal properties

Thermal properties of poly(urethane)s were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere at 20°C min$^{-1}$. The glass transition temperatures ($T_g$), thermal decomposition temperatures at 10% of mass loss (TDT$_{10\%}$), and final char yield are summarized in Table II.
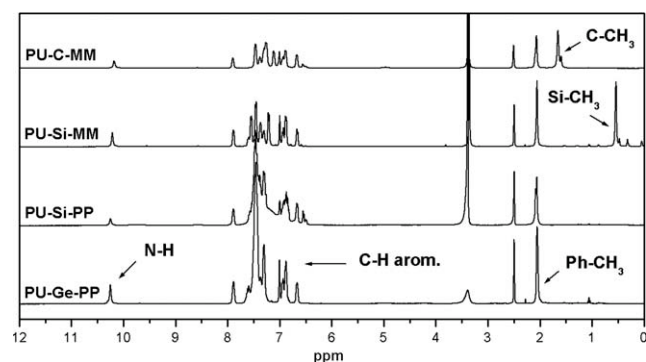
As can be seen in Figure 3, all poly(urethane)s lost 10% of initial weight above 300°C indicating good thermal stability. **PU—Si—PP** and **PU—Ge—PP** show higher TDT$_{10\%}$ and char yield than **PU—C—MM** and **PU—Si—MM**. This result agrees with the higher aromatic content of the former two samples. The percentage of residue at 900°C is variable and corresponds probably to silicon oxide. TGA differential curves show two decomposition stages. The first stage (about 300°C) could correspond to the C—N amidic bond cleavage, while the second stage, at higher temperature (about 390–400°C), could be associated to the C—O bond cleavage.[15]

The $T_g$ values were obtained from the second heating scan at 20°C/min. The DSC curves of PUs are shown in Figure 4. As can be seen, the order of the glass transition temperature of samples is **PU—C—MM** > **PU—Ge—PP** > **PU—Si—MM** > **PU—Si—PP**. Therefore, the replacement of the



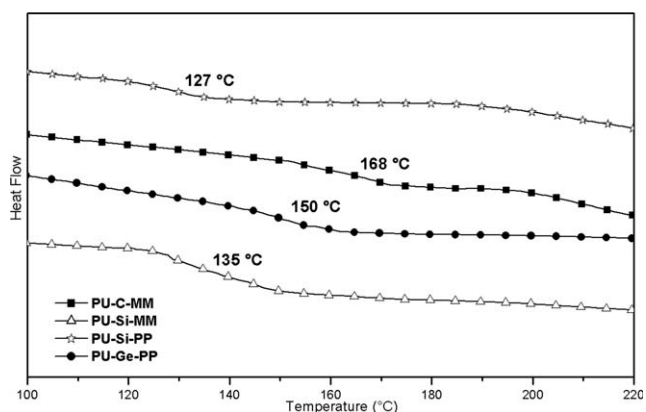Figure 2  $^1$H-NMR spectra (400 MHz, DMSO-*d6*) of poly(urethane)s.



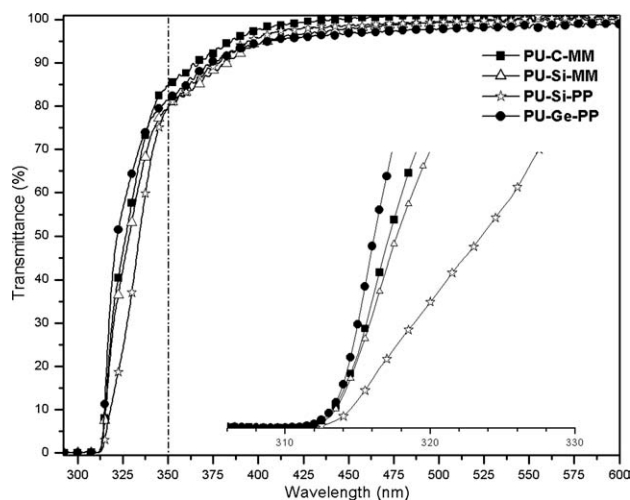Figure 4  DSC traces of PUs (20°C/min in nitrogen atmosphere).

**Figure 5** UV-vis optical transmission spectra of PUs.

carbon atom by silicon or germanium decreases the glass transition temperature, maintaining still high TDT values. Probably, the larger size of silicon and germanium atoms implies an important increase in the bond distances, resulting in greater mobility of the chains.

It is known that the incorporation of aromatic rings in the polymeric chain provides a greater rigidity, so higher $T_g$ values should be expected for **PU—Si—PP** and **PU—Ge—PP** than PUs with methyl groups bonded to central atom (C or Si). On the other hand, the molecular weight is a factor to consider. The lowest $T_g$ of **PU—Si—PP** (127°C) is probably due to the low molecular weight of this polymer, which is evidenced by its inherent viscosity ($\eta_{inh}$ = 0.12 dL/g). However, the aromatic rings had more influence on **PU—Ge—PP** despite the fact that germanium atom is larger than the silicon atom and therefore it would constitute by more flexible chain. Probably, the effect of the rings is more important than the atomic size of the central element.

## Optical properties

The optical transparency of all poly(urethane)s was obtained at room temperature from NMP solution ($c$ = 5.0 g/L). UV-vis optical transmission spectra (Fig. 5) shows that the transmittances of all PUs is higher than 90% at 400 nm and it stays above 80% to 350 nm. This could be associated with the loose packing resulting from bulky diamine employed, which increases the free volume of the polymer chain. The $\lambda_{cutoff}$ for all the PUs is close to 312 nm (Fig. 5). Seemingly, the replacement of the carbon atom by silicon and the substitution of the latter by germanium in similar structures do not affect significantly the studied optical properties.

## CONCLUSIONS

4-[4-[9-[4-(4-Aminophenoxy)-3-methyl-phenyl]fluoren-9-yl]-2-methyl-phenoxy]aniline and four bis(chloroformate)s containing carbon, silicon, or germanium as central element were employed for preparing poly (urethane)s. The optimal experimental conditions were determined from polymerizations developed in solution of several solvents and at different polymerization times. Toluene was the best solvent, originating the highest yields and inherent viscosity values. Because the polymer precipitates to the contact with the diamina-solvent mixture, the polymerization time does not affect the above-mentioned parameters, and similar yields and inherent viscosity at 10, 30, and 60 min are obtained. All PUs were soluble at room temperature in various organic solvents, even in THF and CHCl3. The inherent viscosity values were in the range of 0.12–0.31 indicating low to moderate molecular weight. All the poly(urethane)s exhibited good thermal stability losing 10% of weight above 300°C. **PU—Si—PP** and **PU—Ge—PP** showed the highest decomposition temperatures due to the high aromatic contribution. The replacement of the carbon atom by silicon or germanium decreased the glass transition temperature. All the PUs exhibited high optical transparency in the visible light region, with transmittance values above 90% at 400 nm and $\lambda_{cutoff}$ close to 312 nm.

## References

1. Mittal, K. L. Polyimides: Synthesis, Characterization and Applications; Plenum: New York, 1984.
2. Abade, M. J. M., Ed. Polyimides and Other High-Temperature Polymers; Elsevier: New York, 1984.
3. Radhakrishnan-Nair, P.; Reghunadhan-Nair, C. P.; Francis, D. J. J Appl Polym Sci 1998, 70, 1483.
4. Pielichowski, K.; Njuguna, J. Thermal Degradation of Polymeric Materials; Rapra Technology Ltd., Crewe, UK, 2005.
5. Yang, C. P.; Lin, J. H. J Polym Sci Part A Polym Chem 1993, 31, 2153.
6. Yang, C. P.; Lin, J. H. J Polym Sci Part A Polym Chem 1994, 32, 369.
7. Yang, C. P.; Lin, J. H. J Polym Sci Part A Polym Chem 1994, 32, 423.
8. Yang, C. P.; Lin, J. H. Polymer 1995, 36, 2607.
9. Conley, R. T. Thermal Stability of Polymers; Marcel Dekker: NewYork, 1970; Vol. 1.
10. Tundidor-Camba, A.; Terraza, C. A.; Tagle, L. H.; Coll, D. J Appl Polym Sci 2011, 120, 2381.
11. Terraza, C. A.; Tagle, L. H.; Leiva A. Polym Bull 2005, 55, 277.
12. Terraza, C. A.; Tagle, L. H.; Leiva, A.; Vega, J. C. Polym Bull 2004, 52, 101.
13. Terraza, C. A.; Tagle, L. H.; Concha, F.; Poblete, L. Desig Monom Polym 2007, 10, 253.
14. Terraza, C. A.; Tagle, L. H.; Leiva, A. Polym Bull 2009, 63, 663.
15. The periodic table. University of Sheffield, Webelements Ltd., UK. Available at: http://www.webelements.com (accesed May 2011).