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Aromatic Rigid Poly(urethanes) Containing Silicon and/or Germanium in the Main Chain

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Summary

The synthesis and characterization of aromatic rigid poly(urethanes) containing silicon and/or germanium in the main chain is described. These polymers were synthesized by condensation of aromatic diamines and the bis(chloroformates) of diphenols containing silicon or germanium as central atom and bonded to alkyl and aryl groups. The poly(urethanes) were characterized by FT-IR, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy and the results were in according with the proposed structures. In addition, thermal characterizations were developed using DSC and TG techniques and the intrinsic viscosity were determined as evaluation of the molecular size. In all cases, the thermal properties were depending of the nature of the heteroatoms present in the repetitive unit.
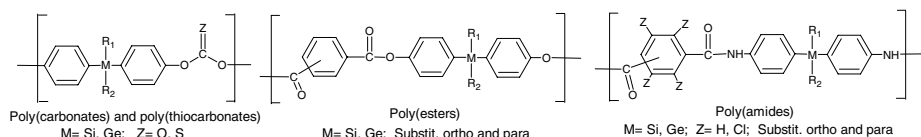
Introduction

Several kind of bifunctional compounds containing silicon bonded to four carbon atoms have been described: diphenols, diamines, diacids, dianhydrides, acid dichlorides, dihydrazides, diisocyanates, and dicyano compounds, corresponding to arilsilanes or silarylenes [1-6]. These monomers were used to obtain several condensation polymers containing phenyl-silicon bonds in the main chain.

Silicon-containing aromatic polymers present a current scientific and technological interest due to the potential application for the production of optoelectronic materials [1]. The largest part of these researches is protected by patents. In this sense, Kojima et al. have prepared electrophotographic photoreceptors materials from a silicon-containing poly(carbonates) series when the aromatic rings have been modified using several alkyl, fluoroalkyl, aryl, or fluoroaryl groups [7]. So, the photoreceptor material comprises, a charge-generating layer and a charge-transporting one, which is prepared with silicon-containing poly(carbonate). Similar materials based also on silicon containing poly(carbonates) have been prepared by Nakamori et al [8] and Yoshida et al. [9]. On the other hand, Hiroshi et al. using aromatic poly(esters) with a silicone portion, obtained photoreceptors which showed improved abrasion resistance upon direct charging and provided high quality images in repeated use [10].

Germanium-containing polymers of inorganic nature such as linear and branched poly(germanes), $(GeR_2)_n$, $(GeR_1R_2)_n$, are very known materials [11-13]. Likewise, polysilanes-polygermanes copolymers have been prepared electrochemically from the corresponding diorgano dichlorogermanes and diorgano dichlorosilanes [14,15]. In the same way, the synthesis of the structure-controlled silane-germane copolymer with a –Si-Ge-Si- sequence was achieved using similar techniques [16]. Poly(germanium acyclic enolates) have been too prepared from germanium compounds, germylenes, and cyclic α,β-unsatured ketones [17]. Similar organic polymers derived from germylenes and p-benzoquinones shown repetitive units like $(-GeN(Me_3)_2OArO-)_n$ or $(-GeN(SiMe_3)^tBuOArO-)_n$ [18]. However, polycondensation polymers with germanium as tetravalent central element and bonded to alkyl and/or aryl groups, have not been systematically described.

Our research group have used previously described techniques and developed others to incorporate tetra-substituted silicon and/or germanium in the main chain of condensation polymers such as poly(amides), poly(esters), poly(carbonates) and poly(thiocarbonates) (Scheme 1) [19-27]. The thermal stability of these polymers was studied using DSC and TG techniques. The effect of structural modifications and the presence of these heteroatoms in the polymer is not clear in some cases, and it is conflicting in others [1,25]. The replacement of carbon atom bonded to four alkyl and/or aryl groups for silicon, lead to improve the ionic character in the polymer chain. This fact is due to the difference of electronegativity between silicon and carbon atom which implies that Si is a stronger electron acceptor atom. Similar effect is expected when germanium is in the main chain as central atom. So, the thermal stability of the polymers containing Si-C and Ge-C bonds would be decreased because the higher ionic character. On the other hand, the bond energy of the bonds C-C, C-Si and C-Ge is in according with this polarity [28].

Poly(carbonates) and poly(thiocarbonates)
M= Si, Ge; Z= O, S

Poly(esters)
M= Si, Ge; Substit. ortho and para

Poly(amides)
M= Si, Ge; Z= H, Cl; Substit. ortho and para

Scheme 1. Poly(carbonates), poly(thiocarbonates), poly(esters) and poly(amides) containing silicon or germanium atoms in the main chain (R_1 and R_2 variable).

Recently, we have reported the synthesis and the spectroscopic and thermal characterization of novel poly(urethanes) containing silicon or germanium bonded to four carbon atoms in the main chain [25]. In that work, bis(chloroformates) derivatives containing Si or Ge and 4,4'-methylenedianiline were used to obtain poly(urethanes) with one heteroatom in the repetitive unit. The thermal stability of these polymers was lower than the reference poly(urethane) containing carbon as tetravalent central atom.

In the present work, we have synthesized poly(urethanes) with different combinations between silicon and germanium, according to the nature of the bis(chloroformate) and the aromatic diamine used in the synthetic process. These polymerizations were developed in benzene solution and in all cases the spectroscopic and thermal characterizations were performed.

Experimental

Tetrahydrofuran, diethyl ether and benzene were dried with sodium and then distilled. 4-Bromophenol (Merck), phosgene 20% w/w in toluene (Fluka), BuLi 1.6 molL^{-1} in n-hexane, 125 or –germane, dichlorodiphenyl-silane or germane, 4-bromo-N,N-bis(trimethylsilyl)aniline, N,N-dimethylaniline and 4-(N,N-dimethylamino)pyridine (Aldrich) were used as received. The infrared spectra were measured on a Perkin-Elmer FT-IR-1310 spectrophotometer. ^{1}H, ^{13}C, and ^{29}Si NMR analysis were recorded on a Bruker 400 MHz spectrometer in DMSO-d$_6$ using Me$_4$Si (TMS) as an internal standard. Melting points (uncorrected) were obtained on a SMP3 Stuart Scientific melting point equipment. Intrinsic viscosities values, [η], were determined in DMSO solution at 25ºC using the Solomon-Ciuta relation. DSC traces were recorded on a Mettler Toledo, DSC 821e differential scanning calorimeter and the thermal degradation temperatures in a TGA/SDTA 851e Mettler Toledo thermobalance. Both analyses were recorded at a heating rate of 20ºC min^{-1} under nitrogen atmosphere.

Synthesis of bis(4-aminophenyl)diphenylsilane (I) and bis(4-aminophenyl)diphenyl-germane (II)

Bis(4-aminophenyl)diphenylsilane (**I**) (yield: 21%, mp: 204-205ºC) and bis (4-aminophenyl) diphenylgermane (**II**) (yield: 44%, mp: 176-177ºC) were obtained according to a procedure described previously [29] as show in scheme 2. For example, n-butyllithium (5.5 mL, 1.6 molL^{-1}) in diethyl ether (10 mL) was added dropwise to a solution of 4-bromo-N,N-bis(trimethylsilyl)aniline (3.9 mL, 13.8 mmol) in anhydrous diethyl ether (10 mL) under nitrogen atmosphere at 0ºC. The mixture was stirred for two hours and then dicholorodiphenylsilane (1.42 mL, 6.8 mmol) or dicholodiphenylgermane (1.43 mL, 6.8 mmol) in anhydrous ether (10 mL) was added. The mixture was stirred overnight and then refluxed for two hours. The LiCl was removed by filtration and HCl gas was bubbled through the residual solution for 1 hour. The reaction mixture, which contained a white solid, was neutralized with 5% aqueous NaOH solution under nitrogen atmosphere. The organic layer was dried with MgSO$_4$ (anh.) and the diethyl ether evaporated.
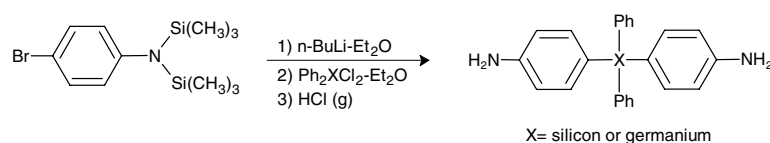

Scheme 2. Synthesis of aromatic diamine containing silicon or germanium.

Synthesis of aromatic bis(chloroformates) derivatives

Liu et al. [30] have described the synthesis of 2,2-bis-(4-chlorocarboxyphenyl)-propane using a phosgene-toluene solution in basic medium. We have modified this route for preparing bis(chloroformates) derivatives containing silicon and germanium as central atom [24]. These derivatives were obtained from the respective diphenols which were synthesized following a route previously described [31]. So, 4,4'-(dimethylsilylene)bis(phenyl chloroformate) (**III**) (white solid, yield: 42%, mp 56.0-56.4ºC) was synthesized from bis(4-hydroxyphenyl)dimethylsilane and phosgene

toluene solution in presence of N,N-dimethylaniline and 4-(N,N-dimethylamino) pyridine mixture at low temperature. On the other hand, 4,4'-(dimethyl germylene)bis(phenyl chloroformate) (**IV**) was synthesized as a yellow-oil from bis(4-hydroxyphenyl)dimethylgermane in similar conditions and purified through column, loaded with 70 mL of silica gel (Merck, 70-230 mesh), with toluene anhydrous as the eluant (yield: 77%) (Scheme 3).
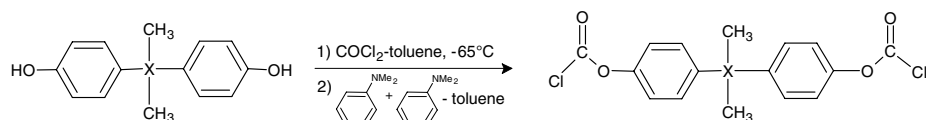
Scheme 3. Synthetic route to bis(chloroformates) derivatives: X=Si (**III**), X= Ge(**IV**).

General synthesis of poly(urethanes)

Poly(urethanes) were synthesized according to a general procedure, in which a benzene solution of the bis(chloroformate) derivative (2.8×10^{-2} molL^{-1}) was added slowly over a benzene solution of the aromatic diamine (2.8×10^{-2} molL^{-1}), containing pyridine (0.31 molL^{-1}). The polymerizations were carried out at 18ºC for 15 min. obtaining a suspension of pyridinium chloride and the corresponding poly(urethane). This mixture was turn over methanol, stirred during 10 min. at room temperature and then the polymer was filtered and washed several times with methanol or water, and characterized.

Poly(urethane) V

Yield: 53%. IR (KBr, cm^{-1}): 3388 (N-H), 3022 (C-H arom.), 2954 (C-H aliph.), 1752 (C=O), 1737 (N-H), 1597 (C=C arom.), 1514, 999, 743 (silyl-Ph), 1320, 776 (silyl-methyl), 1187 and 1107 (C-O), 820 (p-arom.), 701 (mono-substut. arom.). ^{1}H NMR (DMSO-d$_6$) (δ) (ppm): 0.49 (s, 6H, CH$_3$); 7.09-7.59 (m, 26H, aryl CH); 10.43 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$) (δ) (ppm): -1.80 (CH$_3$); 114.1-137.4 (arom.); 152.0, 159.0 (-CO$_2$-). ^{29}Si NMR (DMSO-d$_6$) (δ) (ppm): -8.72 (PhSi(CH$_3$)$_2$-Ph-); -15.30 (PhSi(Ph)$_2$-Ph-).

Poly(urethane) VI

Yield: 42%. IR (KBr, cm^{-1}): 3387 (N-H), 3022 (C-H aliph.), 1736 (overlap C=O and N-H), 1597 (C=C arom.), 1515, 1000, 743 (silyl-Ph), 1489 (germyl-Ph), 1320, 802 (germyl-methyl), 1187 and 1109 (C-O), 821 (p-arom.), 701 (mono-substut. arom.). ^{1}H NMR (DMSO-d$_6$) (δ) (ppm): 0.66 (s, 6H, CH$_3$); 7.24-7.59 (m, 26H, aryl CH); 10.49 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$) (δ) (ppm): -2.78 (CH$_3$); 118.6-140.6 (arom.); 151.6, 152.0 (-CO2-). ^{29}Si NMR (DMSO-d$_6$) (δ) (ppm): -15.28 (PhSi(Ph)$_2$-Ph-).

Poly(urethane) VII

Yield: 72%. IR (KBr, cm^{-1}): 3399 (N-H), 3024 (C-H arom.), 2961 (C-H aliph.), 1751 (C=O), 1736 (N-H), 1580 (C=C arom.), 1512 (sylil-Ph), 1490, 998, 734 (germyl-Ph),

1317, 776 (silyl-CH$_3$), 1166 and 1105 (C-O), 815 (p-arom.), 776 (mono-substut. arom.). ^{1}H NMR (DMSO-d$_6$) (δ) (ppm): 0.57 (s, 6H, CH$_3$); 7.24-7.59 (m, 26H, aryl,CH); 10.39 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$) (δ) (ppm): -2.06 (CH$_3$); 114.7-140.2 (arom.); 152.0 (-CO$_2$-). ^{29}Si NMR (DMSO-d$_6$) (δ) (ppm): -7.85 (PhSi(CH$_3$)$_2$-Ph-).

Poly(urethane) VIII

Yield: 67%. IR(KBr, cm^{-1}): 3389 (N-H), 3023 (C-H aliph.), 1734 (overlap C=O and N-H), 1595 (C=C arom.), 1491, 1002, 737 (germyl-Ph), 1319, 802 (germyl-methyl), 1199, 1089 (C-O), 819 (p-arom.), 700 (mono-substut. arom.). ^{1}H NMR (DMSO-d$_6$) (δ) (ppm): 0.51 (s, 6H, CH$_3$); 6.59-7.45 (m, 26H, aryl CH); 9.42 (s, 1H, NH). ^{13}C NMR (DMSO-d$_6$) (δ) (ppm): -2.43 (CH$_3$); 114.6-136.0 (arom.); 158.3 (-CO$_2$-).

Results and discussion

Poly(urethanes) **V-VIII** derived from the diamines **I** and **II** and the bis(chloroformates) **III** and **IV** respectively, were obtained in a benzene–pyridine solution at 18ºC and characterized by IR and NMR spectroscopy, and the results were in according with the following structures (Scheme 4).
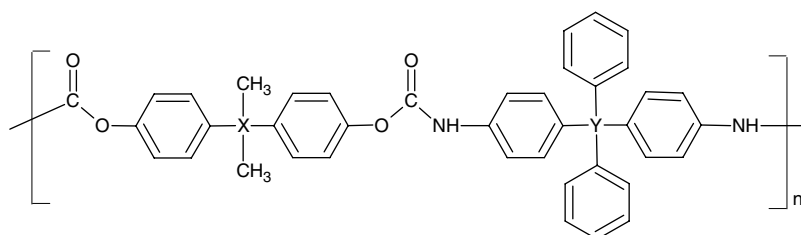
		X	Y
(a)	**Poly(urethane)**		
	V	Si	Si
	VI	Ge	Si
	VII	Si	Ge
	VIII	Ge	Ge

Scheme 4. General structure of aromatic rigid poly(urethanes) containing silicon and/or germanium.

Previously, we have reported the synthesis and characterization of a series of aromatic poly(urethanes) containing silicon or germanium in their main chain, [25] which were introduced by the bis(chloroformate) units. The thermal properties of those polymers were compared with the poly(urethane) containing only carbon atoms. In the present work, we are describing the synthesis and characterization of a series of aromatic rigid poly(urethanes) which have in the repeating unit two heteroatoms in different combinations: Si-Si (**V**), Ge-Si (**VI**), Si-Ge (**VII**) and Ge-Ge (**VIII**) (Scheme 4).

Table 1 shows the solubility data and intrinsic viscosities values of the poly(urethanes). Just as previous work, the inclusion of germanium in the repetitive unit gives a beige color to the polymeric material, while the solubility is independent of structural modifications. All polymers were highly soluble in *m*-cresol and DMSO. This last solvent was used in the determination of the intrinsic viscosities, which were used as estimation of the molecular size. It is not clear the relation between the polymer yield and the molecular size with the presence of heteroatoms. Probably, the reactivity of the monomeric units is not affected for the change in the heteroatom, due that the amine and chloroformate functional groups are sufficiently distant of the tetravalent central atom. So, the polycondensation course is independent of the silicon and germanium electronegativity values (1.90 and 2.01 respectively [28]). Similar yields and intrinsic viscosity values were obtained previously when 4,4'-methylenedianiline was used as aromatic diamine in presence of the same bis(chloroformates) derivatives [25].

Table 1. Some Physic Characteristics of Aromatic Rigid Poly(urethanes) Containing Silicon and/or Germanium in Their Main Chain.

	Polymer			
	V	VI	VII	VIII
Color	white	beige	beige	beige
Intrinsic viscosity[1] (dL g^{-1})	0.15	0.12	0.11	0.09
Acetone [2]	+	nd	+	nd
DMSO [2]	+	+	+	+
m-cresol [2]	+	+	+	+

nd = No determined, [1] In DMSO solution at 25ºC, [2] Solubility at 18ºC.

The poly(urethanes) were characterized by NMR and IR spectroscopy. In all cases, the spectroscopic patterns are in according with the structures of the repetitive units proposed in the scheme 2. The IR spectra are similar, showing clearly the N-H stretching band (3380-3400 cm^{-1}) and N-H bending vibration (1735 cm^{-1} approximately). As in the case of poly(amide)s, overlapping occurs in the observed position of N-H bending and the C=O stretching frequencies [24,32]. Also, it was possible to see the absorption bands characteristics of the *mono-* and *para*-subtituted aromatic rings and to assign the silyl- and germanyl-phenyl and silyl- and germanyl-methyl vibration frequencies [4,32,33].

In the ^{1}H NMR spectra, the silyl- and germanyl-methyl signals are shifting to high field, showing characteristic values between 0.49 and 0.66 ppm. These displacements are due to low electronegativity of tetravalent central atom of the chain (shielding effect). Likewise, the ^{13}C NMR spectra of these polymers show shifts to negative values for silyl- and germanyl-methyl groups (-1.8 to –2.8 ppm approximately). On the other hand, the resonance signals of C=O carbon are relatively insensitive to structural modifications and the changes in the polarity of the chain, maintaining values between 152 to 159 ppm approximately. ^{29}Si NMR spectra were recovered for the poly(urethanes) **V**, **VI** and **VII**. The samples **VI** and **VII** show sharp resonance signals for -PhSi(Ph)$_2$-Ph- and -PhSi(CH$_3$)$_2$-Ph- groups (-15.28 and -7.85 ppm respectively), while poly(urethane) **V** show both signals with similar values.

A summary of the thermal properties of the aromatic rigid poly(urethanes) is given in Table 2. All polymers showed similar TG curves. At 200ºC the weight loss is minimum (3% approximately) while at about 550ºC, the samples show a weight loss near to 50%. In all cases, the thermal degradation started around 250 to 275ºC. The shape of the curves is indicating that the degradation process is complex. At the final of the degradation process, up to 700ºC, the TG curves showed a variable residue of about 35 %. This fact can be due to the oxidation of silicon and germanium atoms contained in the polymer chain. On the other hand, the samples showed differences of 29ºC between their first derived maximum (TDT: 281 to 310ºC).

Table 2. Thermal Properties of Poly(urethanes) Containing Silicon and/or Germanium in Their Main Chain.

			% Weight loss at various temperatures (ºC)						Tm	TDT[1]
Nº	X	Y	200	300	400	500	600	700	ºC	ºC
V	Si	Si	2.9	11.8	35.1	47.7	58.7	67.5	225	293
VI	Ge	Si	2.5	9.3	29.2	44.0	51.4	55.8	222	303
VII	Si	Ge	3.0	17.0	35.2	50.6	63.1	66.3	212	287
VIII	Ge	Ge	3.2	11.2	32.9	52.1	63.8	67.0	201	292

[1] Taken as the temperature at 10% weight loss.

It has been described that the bond energy of the C-Ge bond is slightly higher than the C-Si bond (460 and 451 Kjoule/mol respectively) [28]. If we compare poly(urethane) **V** and **VI**, the change of a Si atom by Ge increases the thermal stability. The same occurs with poly(urethanes) **VII** and **VIII**, due to the higher bond energy of the C-Ge bond. In these two pairs the heteroatom of the diamine was the same.

On the other hand, if we remain constant the heteroatom of the bis(chloroformates) and change those of the diamines, pairs **V**-**VII** and **VI**-**VIII**, we can see the inverse: those derived from the diamine with Ge showed a slightly lower TDT values than those derived from the diamine with Si. This contradictory effect probably can be due to because the heteroatoms in the diamine are bonded to four phenyl groups, being Ge a larger atom than Si.

In the above explanation we compared poly(urethanes) derived from the same bis(chloroformate) or from the same diamine, but not changing both heteroatom at the same time, because the heteroatom have different groups bonded to them depending on the monomer.

In poly(esters) with two heteroatoms in the main chain, we described a similar situation [34]. In the same family of poly(esters), maintaining constant the groups bonded to the heteroatoms, the TDT values change with the relative position of Si or Ge in the repeating unit. These results differ from those obtained for other condensation polymers as poly(carbonates) or poly(thiocarbonates) with Si or Ge in the repeating unit [20]. In these polymers the higher thermal stability was showed by those containing Ge, which is in according with the above analysis. Analogous results were obtained in poly(esters) derived from terephthaloyl or isophthaloyl dichlorides

containing one of the heteroatoms in the main chain [35]. Also, poly(amides) synthesized from the same diamines and several aromatic acid dichlorides, showed an analogous trend in the thermal decomposition.

The DSC curves in all cases do not show glass transition temperature neither endothermic signal in the second heating. This fact was already observed in the poly(urethanes) series obtained from 4,4´-methylenedianiline and silicon- or germanium-containing bis(chloroformates) [25]. Probably, the movement of chain is limited during cooling process due to hydrogen bonds formed. This fact would hinder the formation of regular chain conformations.

In table 2 it is also possible to see that the Tm registered present a similar tendency to the TDT values. In the two pairs of poly(urethanes), **V**-**VI** and **VII**-**VIII**, there is a decrease of the Tm values when the Si atom is replaced by the Ge one, being this decrease higher when the Ge atom comes from the diamine, bonded to four phenyl groups. Probably, the larger size of germanium atom in comparison to silicon, which implies larger bond lengths to aryl carbon atom, is a factor that would explain this tendency in both polymer families. This fact could be more important that the electronegativities differences between Ge and Si ($\cong EN_{Ge-Si}= 0.11$) [25] and the lightly bond energy difference between Si-C and Ge-C bonds (451 KJmol^{-1} and 460 KJmol^{-1} respectively) [21].

Conclusions

Rigid poly(urethanes) containing the heteroatoms Si and/or Ge in the main chain were synthesized from bis(chloroformates) and diamines, containing both, one of those heteroatoms. Polymers were characterized by spectroscopic methods and the results were in according with the proposed structures. The TDT values were influenced by the presence of the heteroatoms, Si and/or Ge, in the main chain, observing an increase of the TDT values when Si in replaced by Ge in the bis(chloroformate) due to the higher energy of the C-Ge bond. The inverse was observed when the change was in the aromatic diamine, due probably to the higher siz of the Ge atom and the effect of the four phenyl groups bonded to the heteroatom.

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