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Synthesis and characterization of 4,4'-(dimethylsilylene)bis(phenyl chloroformate) and 4,4'-(dimethylgermylene)bis(phenyl chloroformate) and their use in the synthesis of poly(urethanes)

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Summary

The synthesis of 4,4'-(dimethylsilylene)bis(phenyl chloroformate) and 4,4'-(dimethylgermylene)bis(phenyl chloroformate) is described according to the same route for the synthesis of bisphenol-A bischloroformate. These compounds were characterized using elemental analysis, FT-IR and NMR spectroscopy. Poly(urethanes) derived from these bischlororformates containing silicon or germane in the main chain, were obtained in benzene solution by reaction with 4,4'-methylenedianiline in the presence of pyridine. Poly(urethanes) were characterised by spectroscopic methods and the thermal properties (Tg and thermal stability) were compared with the homologue poly(urethane) obtained from bisphenol-A chloroformate.

Introduction

Silicon-containing polymers with the heteroatom in the main chain and bonded to four organic groups, have been described and their properties studied [1-2]. However, germanium-containing condensation polymers in which the Ge atom is in the main chain and bonded to four organic groups have been not described. Only inorganic polymers in which the Ge atom is bonded to itself in the main chain have been studied [3-4]. For this reason, we have reported the synthesis and characterization of different kinds of condensation polymers containing Si and/or Ge and studied some of their thermal properties [5].

Poly(esters) have been synthesized from isophthaloyl or terephthaloyl acid dichlorides and diphenols containing silicon or germanium using the phase transfer catalysis technique as the polymerization method and also derived from the same diphenols and acid dichlorides containing silicon or germanium [6-7]. Likewise, poly(carbonates) and poly(thiocarbonates) derived diphenols containing silicon or germanium in their structure were obtained by reaction with phosgene or thiophosgene respectively, or by reaction with bisphenol A bischloroformate using the same technique [8-9]. On the other hand, we have also reported the synthesis of poly(amides) derived from diamines with silicon or germanium and acid dichlorides [10]. These polymerizations were developed in solution conditions and the poly(amides) were characterized by spectroscopy and thermal properties.

The thermal properties of these polymers have been studied, showing in general that polymers containing germanium have a higher thermal stability with respect to polymers with silicon in the main chain [11-12]. This fact was associated to the higher polarity of the C-Si bond in front of the C-Ge one [13].

Continuing our works in the synthesis of condensation polymers containing Si or Ge in the main chain, in this paper we report on the synthesis of 4,4'-(dimethylsilylene)bis(phenyl chloroformate) and 4,4'-(dimethylgermylene)bis(phenyl chloroformate) following the route described for the preparation of the bisphenol-A derivative [14]. The characterization was carried out using elemental analysis, FT-IR and multinuclear resonance magnetic spectroscopy. These compounds reacted with 4,4-methylenedianiline obtaining the poly(urethanes) containing silicon or germane in the main chain, which were characterized using the same techniques. Spectroscopic and thermal properties were compared with the poly(urethane) obtained from the bisphenol-A bischloroformate, and the influence of the Si and Ge atoms on the thermal properties, was studied.

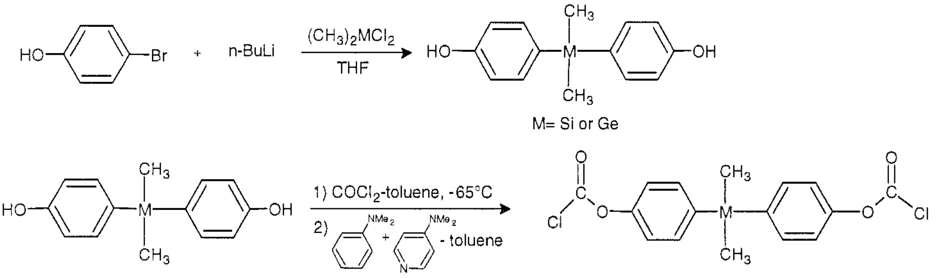
Experimental

The infrared spectra (KBr-pellet) were recorded on a Perkin-Elmer FT-IR-1310 spectrophotometer. ^1H and ^{13}C NMR spectra were measured on Bruker 200 MHz and Bruker 400 MHz spectrometers in DMSO-d_6 with TMS as the internal standard. Elemental analyses were developed on a Fisons EA 1108-CHNS-O equipment. Melting points (uncorrected) were obtained on a SMP3 Stuart Scientific melting point apparatus. Intrinsic viscosities values, $[\eta]$, were obtained in DMSO solution at 25°C using the Solomon-Ciuta relation. [15]. DSC traces were recovered in a Mettler Toledo, DSC 821e differential scanning calorimeter and the degradation temperatures were registered in a TGA/SDTA 851e Mettler Toledo thermobalance. Both analyses were recorded at a heating rate of $20°C min^{-1}$ under N_2 ($60\ mL min^{-1}$). Tetrahydrofuran (THF) and diethylether were dried with sodium and then distilled. Bis(4-hidroxyphenyl)-dimethyl-propane bischloroformate (Bisphenol-A, Aldrich) and 4,4'-methylenedianiline (Aldrich) were recrystallized in n-hexane and benzene respectively. Phosgene (Fluka), dichloro-dimethyl-silane (Aldrich), dichloro-dimethyl-germane (Aldrich) and the other reagents (from Aldrich, Riedel de Häen or Merck) were used as received.

Synthesis of bischloroformates derivatives. Common part

The synthesis of bis(4-hydroxyphenyl)dimethylsilane or -germane has been previously reported from the reaction of dichlorodimethyl-silane or –germane respectively and p-bromophenol with n-BuLi in THF solution [16]. 4,4'-(dimethylsilylene)bis(phenyl chloroformate) and 4,4'-(dimethylgermylene)bis(phenyl chloroformate) were obtained according to the following procedure: 12.8 mL of a phosgene solution (20 wt % in toluene, $2.6x10^{-2}$ mol) were added to bis(4-hydroxyphenyl)dimethylsilane (2.07 g, $8.5x10^{-3}$ mol) under nitrogen atmosphere. The white suspension was stirred and cooled at –65°C, and then 5.5 mL of a toluene solution of N,N'-dimethylaniline (2.15

mL, 1.7x10^{-2} mol) and 4-(N,N'-dimethylamino)pyridine (0.05 g, 4.2x10^{-4} mol) were slowly added through a dropping funnel. The colored suspension obtained was stirred and allowed to gradually warm and kept for 19 h at room temperature. The N,N'-dimethylaniline hydrochloride salt was filtered and the phosgene gas removed under reduced pressure during 3 hours.



Scheme 1.- Synthesis of bischloroformate from *p*-bromophenol.

4,4'-(dimethylsilylene)bis(phenyl chloroformate)

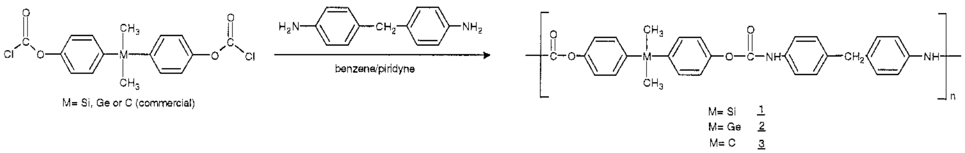
The solution containing bischloroformate was concentrated and the green-blue residue was poured on anhydrous n-hexane and kept for 24 hours. Then a blue-oil containing oligomers was removed. The concentration of the solution allowed to obtain a yellow-oil that solidifies. Through filtration and wash with n-hexane, 3.13 g (42.2%) of product were obtained (m.p.: 56.0-56.4°C). Calculated for $C_{16}Cl_2H_{14}O_4Si$: C: 52.00; H: 3.79. Found: C: 52.04; H: 3.72. FT-IR (KBr, cm^{-1}): 3036 (C-H aromatic), 2960 (C-H aliphatic), 1792 (C=O), 1584 (C=C aromatic), 1496 (Si-C aromatic), 1353 (Si-C aliphatic), 1163 and 1127 (C-O), 839 (*p*-aromatic system). ^{1}H NMR (acetone-d_6): 0.96 (s, 6H); 7.46 (d, 2H, *J*= 8.6 Hz): 7.76 (d, 2H, *J*= 8.6 Hz) ppm. ^{13}C NMR (acetone-d_6): -2.54 (s,-$\underline{C}H_3$); 121.0, 136.6, 138.2, 153.6 (s, aromatic); 149.8 (s, C=O) ppm.

4,4'-(dimethylgermylene)bis(phenyl chloroformate)

The solution containing bischloroformate was concentrated and the green-blue residue was passed through a column, loaded with 25 mL of Merck silica gel (70-230 mesh ASTM), with toluene as an eluant. The toluene was evaporated and a residue was obtained. This residue was treated with n-hexane and then concentrated obtaining 2.56 g (76.9 %) of a yellow-oil which has the following spectroscopic patterns: FT-IR (film, cm^{-1}): 3032, 2975 (C-H aromatic), 2910 (C-H aliphatic), 1788 (C=O), 1583 (C=C aromatic), 1493 (Si-C aromatic), 1352 (Si-C aliphatic), 1165 and 1121 (C-O), 877 (*p*-aromatic system). ^{1}H NMR (acetone-d_6): 0.79 (s, 6H); 7.47 (d, 2H, *J*= 8.6 Hz): 7.69 (d, 2H, *J*= 8.6 Hz) ppm. ^{13}C NMR (acetone-d_6): -2.66 (s,-CH_3); 121.6, 136.4, 140.6, 153.7 (s, aromatic.); 150.3 (s, C=O) ppm.

Poly(urethane) synthesis

Poly(urethanes) were obtained according to the following general procedure: 20 mL of the bischloroformate derivative ($5.7x10^{-4}$ mol) benzene solution were added slowly over 20 mL of a benzene solution of 4,4'-methylenedianiline (0.11 g, $5.7x10^{-4}$ mol) and pyridine (0.5 mL, $6.2x10^{-3}$ mol). The polymerizations were carried out at 18°C for 15 min. to obtain pyridinium chloride and the corresponding poly(urethane) as precipitate. The suspension was poured over methanol, stirred during 10 min. at room temperature, and then filtered and washed several times with methanol, dried under vacuum until constant weight, and characterized.



Scheme 2.- Preparation of poly(urethanes) and the repetitive unit respective.

Results and discussion

Two routes are known to prepare poly(urethanes): a) Condensation of diisocyanates with dihydric alcohols and b) reaction between bischloroformates and diamines, in interfacial polycondensation or solution polymerization conditions [17]. Using the second route, in solution polymerization conditions we have prepared poly(urethanes) containing silicon or germanium atoms in the main chain. For this, 4,4'-(dimethylsilylene)bis(phenyl chloroformate) and 4,4'-(dimethylgermylene)bis(phenyl chloroformate) were synthesized from the corresponding diphenols. Elemental analyses and spectroscopic techniques were employed to verify the structures.

Bischloroformate sililated was obtained as a white solid through a concentration process. This solid was successively crystallized from a n-hexane warm solution in order to remove oligomers. In the case of 4,4'-(dimethylgermylene)bis(phenyl chloroformate), the isolation route allowed to obtain a yellow-oil which was purified using chromatographic techniques. Their spectroscopic patterns are in accordance with the proposed structure and was used as an oil.

Table 1. Yield and some physical characteristic of poly(urethanes) prepared.

	Poly(urethane)		
	1	2	3[a]
Yield (%)	70	48	63
Intrinsic viscosity* (dL g^{-1})	0.172	0.258	0.195
Glass transition temperature (°C)	125	103	--
Melting point (°C)	132	174	149
Degradation temperature** (°C)	307	292	340

[a] Used like comparison

* Recovered in DMSO at 25°C.

** First derived maximum covered at 20°C/min under nitrogen atmosphere.

All polymers were white-beige solid and soluble at room temperature in DMSO and m-cresol. Methanol, acetone and diethyl-ether were non-solvent. Table I shows other physical characteristic of the poly(urethanes) containing silicon (**1**) or germanium (**2**) tetravalent in the repetitive unit, including the carbon polymer as reference (**3**). The intrinsic viscosity values, as an indirect measure of the molecular size, are similar in all cases, while the polymer yields are slightly lower for poly(urethane) containing germanium. These results are indicative that the reactivity of bischloroformates in front of the diamine is not notably modified due to the replacement of the tetravalent carbon atom for silicon or germanium respectively.

Table I shows the thermal stability of the poly(urethanes), this parameter depending on the nature of the central atom present in the portion proceeding of bischloroformate. In all cases, the TG traces indicate a weight loss started at around 290°C. Nevertheless, the poly(urethanes) containing silicon or germanium have lower degradation temperatures in front of the analogous with carbon. This loss of thermal stability would be related with two factors: the electronegativity of the central atom and the bond energy of these atoms with carbon. So, the replacement of the carbon atom for silicon or germanium in the repetitive unit gives a higher polarity in the bonds and therefore in the chain, being the stability of poly(urethanes) **1** and **2** similar, but lower than the analogous with carbon, in which this factor does not exist. This fact is in accordance with their respective electronegative values. On the other hand, the bond energy of the C-Si and C-Ge bonds are very similar between them (451 vs. 460 KJ/mol) but lower than the energy of the C-C bond (607 KJ/mol) [13], which also would explain the lower thermal stability of the poly(uretanes) containing the heteroatoms respect to the analogous with carbon, and the very close values of the TDT of poly(uretanes) containing Si or Ge. We have already reported similar results for other kinds of polymers. [10-12, 18]

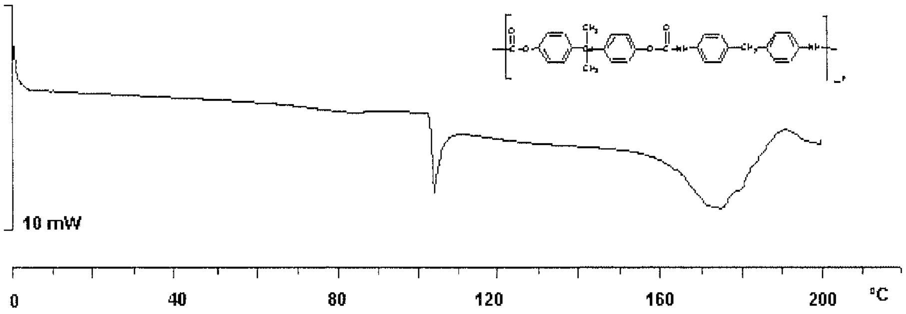


Figure 1. DSC curve of first-heating process for poly(urethane) **2** (20°C min^{-1}, under N_2).

DSC measurement on powder samples was performed and the results are summarized in Table I. The DSC traces of first-heating process for poly(urethanes) **1** and **2** are similar in shape, as figure 1, showing a change of base line due the glass transition temperature (Tg). These two polymers and the reference poly(urethane) showed an endothermic peak on the 130-170°C range approximately, which are related with melting point (Tm). In all cases, no endothermic peak was observed in the second-heating DSC traces. Similar DSC results were reported for Hikita et al. studying the thermal properties of a poly(urethane-urea)s series [19]. In his work, these authors propose that the hydrogen bonds formed during the cooling process from the melting state would restrict the chain movement, hindering the formation of regular chain conformations.

The spectroscopic analysis of the poly(urethanes) was performed using FT-IR and NMR and the results are summarised in Table II. All IR spectra showed the C=O, N-H and C-O signals associated to the stretching of the urethanic groups. It is clear that structural modification from bischloroformate section does not significantly affect the IR patterns of the poly(urethanes). On the other hand, the chemical shift, multiplicity and integration values from ^{1}H and ^{13}C NMR spectra are in accordance with the structures proposed in scheme 2.

In both NMR spectra, the chemical shift of the methyl groups is effected by the carbon atom replacement for other tetravalent atoms of lower electronegativity. So, in comparison with poly(urethane) derived from bisphenol-A, ^{1}H NMR spectra for polymers **1** and **2** show low values for methyl protons (0.56 ppm and 0.65 ppm respectively) while ^{13}C NMR present values for methyl group carbon below 0 pm (-2.61 ppm and –3.33 ppm respectively). These results are expected due to the shielding effect derived from the change in the electronegativity of the tetravalent central atom. The urethanic carbon atom chemical shift (C=O) is the same in all cases (151.5 ppm approximately) indicating that the polarity does not affect them.

Table 2. IR-FT and RMN spectroscopic characteristics of poly(urethanes).

		Poly(urethane)		
Analysis	Assignation	1	2	3[a]
FT-IR (v/cm^{-1})	N-H	3385	3388	3385
	C-H arom.	3027	3028	3017
	C-H aliph.	2593	2973	2965
	C=O	1734	1731	1733
	C-C arom.	1588	1600	1596
	C-O	1198	1198	1200
	p-arom. system	813	804	815
^{1}H NMR (ppm)	-CH$_3$	0.56 (s)	0.65 (s)	1.66 (s)
	-CH$_2$-	3.82 (s)	3.82 (s)	3.82 (s)
	-CH arom.	7.05 - 7.70 (m)	7.12-7.53 (s)	6.90 - 7.60 (m)
	-NH	10.18 (s)	10.15 (s)	10.12 (s)
^{13}C NMR (ppm)	-CH$_3$	-2.61	-3.33	30.4
	-CH$_2$-	39.7	40.3	39.7
	-$\underline{C}(CH_3)_2$-	---	---	41.8
	C arom.	118.6-136.4	118.6-136.4	118.6-148.3
	-CO$_2$-	151.5	151.5	151.7

[a] Used like comparison

Conclusions

Following the route described for bisphenol-A derivative, it is possible to prepare bischloroformates containing silicon or germanium as the tetravalent central atom. These molecules show a similar reactivity to that presented for bisphenol-A derivative. So, poly(urethanes) can be prepared for reaction in solution with a diamine as 4,4'-methylenedianiline. The IR spectra are similar in pattern, while the RMN signals are in accordance with the structural change studied. It is possible to observe a strong shielding in the methyl protons and carbon bonded to silicon or germanium. The thermal stability of poly(urethanes) containing Si or Ge are lower in comparison to the reference polymer which contains carbon as the tetravalent central atom.

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