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Condensation Polymers Containing Silicon and Germanium in the Main Chain

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Summary: Poly(carbonates), poly(thiocarbonates) and poly(esteres) containing silicon and/or germanium in the main chain were obtained under phase transfer conditions. Polymers were synthesized in a biphasic system NaOH/CH_2Cl_2 at 20°C using several phase transfer catalysts, and characterized by IR and ^{1}H and ^{13}C NMR. The results were evaluated by the yields and the inherent viscosity values. The process was effective observing an increase of both parameters in comparison with the essays without catalyst. The increases depended of the nature of the polymer and the catalyst. In poly(ester) synthesis there was an increase of these parameters when the NaOH concentration was increased due to a salting out effect of the diphenolate from the aqueous phase to the organic one. Also poly(amides) containing silicon or germanium were synthesized by solution polymerization.

Keywords: condensation polymers, germanium, phase transfer catalysis, silicon

Introduction

Organosilicon condensation polymers such as poly(amides), poly(esters), poly(imides) and others, in which the silicon atom is in the main chain, and bonded to aromatic or aliphatic groups, have been described and their properties studied.[1]

However, condensation polymers containing a germanium atom in the main chain and bonded to four carbon atoms have not been described. Only some very special polymers with the germanium atom forming part of the side groups have been described.[2-3] Also inorganic poly(germanes) with this structure $(GeR_2)_n$, have been described and their properties studied.[4]

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For many years we have focussed our attention on the synthesis of condensation polymers, using phase transfer catalysis as the polymerization method. In this sense we have described and studied the synthesis of several kinds of polymers, such as poly(carbonates), poly(thiocarbonates) and poly(esters). This technique offers advantages compared to solution or interphase polymerization.[5]

In the classical scheme, the catalyst, normally a quaternary onium salt has the function of transferring the diphenolate in the form of an ionic pair from the aqueous phase, to the organic one, in which the polymerization takes place.[6-7] We have studied the influence of the nature of the catalysts in the yields and in the inherent viscosity values of the obtained polymers. The principal limitation of this technique can be the insolubility of the polymeric chain in the reaction media, because this factor has an important effect on the molecular weight.

In this paper we summarise our works with respect to the synthesis of poly(carbonates) and poly(thiocarbonates) derived from diphenols or acid dichlorides, containing silicon or germanium bonded to four organic groups. The objective is to obtain polymers containing one or both heteroatoms in the main chain using the phase transfer catalysis as the polymerization method. Also poly(amides) from diamines containing these heteroatoms but by solution polymerization were obtained.

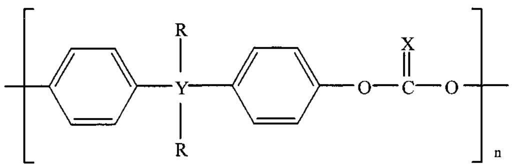
Experimental

Monomers were obtained according to described procedures from dichloro-dimethyl or dichloro-diphenyl-silane or -germane, and 4-bromo-phenol for the diphenols,[7] 4-bromo-toluene for the acid dichlorides,[8-10] and 4-bromo-N,N-bis(trimethylsilyl)-aniline for the diamines.[11]

In general the polymerizations were carried out in a biphasic system. Normally CH_2Cl_2 was used as organic solvent in which the acid dichloride, phosgene or thiophosgene were dissolved. The diphenol and the catalyst were dissolved in a sodium hidroxide aqueous solution. In all the polymerizations essays without catalysts were made, in order to evaluate the behaviour of the interphase of the system. Monomers and polymers were characterized by IR, ^1H and ^{13}C NMR spectroscopy.

Results and Discussion

Poly(carbonates) and poly(thiocarbonates) with the following structures derived from four diphenols with silicon or germanium and phosgene or thiophosgene respectively, were obtained and characterized.[12] Table 1 shows the results obtained for poly(carbonates) **Ia** and **IIa** and poly(thiocarbonates) **Ib** and **IIb**.



Ia: Y = Ge; R = $-CH_3$; X = O **Ib**: Y = Ge; R = $-CH_3$; X = S
IIa: Y = Ge; R = $-C_6H_5$; X = O **IIb**: Y = Ge; R = $-C_6H_5$; X = S
IIIa: Y = Si; R = $-CH_3$; X = O **IIIb**: Y = Si; R = $-CH_3$; X = S
IVa: Y = Si; R = $-C_6H_5$; X = O **IVb**: Y = Si; R = $-C_6H_5$; X = S

Table 1. Yields and inherent viscosities obtained for poly(carbonates) **Ia** and **IIa** and poly(thiocarbonates) **Ib** and **IIb** (Ref. 12).

Polymer	**Ia**		**Ib**		**IIa**		**IIb**	
Catalyst	%	$\eta^{a)}$	%	$\eta^{a)}$	%	$\eta^{a)}$	%	$\eta^{a)}$
none	38	0.04	20	0.16	45	0.08	29	0.04
TBAB	48	0.24	61	0.24	27	0.17	39	0.21
ALIQUAT	30	0.04	56	0.12	37	0.13	18	0.13
BTEAC	57	0.20	52	0.12	36	0.25	37	0.17
HDTMAB	35	0.04	42	0.16	46	0.13	19	0.08
HDTBPB	7	0.20	55	0.16	41	0.13	20	0.04

a) Inherent viscosity in $CHCl_3$ at 25°C (conc. = 0.3 g/dl).

In general, there is an increase of the yields when the catalysts were used, showing the effectiveness of the transfer process, and in less proportion of the inherent viscosity values. For polymers in which the heteroatom is bonded to mehtyl groups, good results were obtained with tetrabutylammonium bromide (TBAB), which due to its symmetrical structure, has been described as effective for the transfer process of the diphenolate derived from bisphenol A. Benzyltriethylammonium chloride (BTEAC) due to its more hydrophilic character, showed a relatively good behaviour for polymers in which the heretoatom is bonded to phenyl groups.

Table 2 shows the results obtained for poly(carbonates) **IIIa** and **IVa** and poly(thiocarbonates) **IIIb** and **IVb**.

Table 2. Yields and inherent viscosities obtained for poly(carbonates) **IIIa** and **IVa** and poly(thiocarbonates) **IIIb** and **IVb** (Ref. 12).

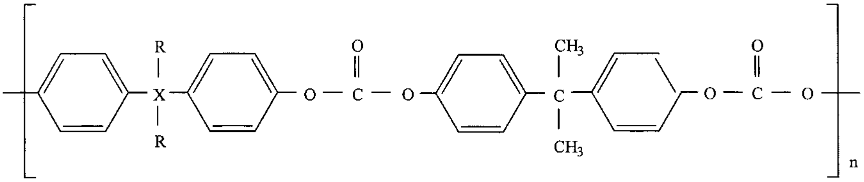
Polymer	**IIIa**		**IIIb**		**IVa**		**IVb**	
Catalyst	%	$\eta^{a)}$	%	$\eta^{a)}$	%	$\eta^{a)}$	%	$\eta^{a)}$
none	---	-----	---	-----	32	0.04	13	0.04
TBAB	38	0.16	14	0.08	48	0.08	33	0.08
ALIQUAT	17	0.13	16	0.08	41	0.08	31	0.08
BTEAC	35	0.16	7	0.04	42	0.08	34	0.08
HDTMAB	23	0.13	21	0.08	54	0.13	46	0.13
HDTBPB	7	0.10	4	0.04	40	0.08	19	0.04

a) Inherent viscosity in $CHCl_3$ at 25°C (conc. = 0.3 g/dl).

It is possible to see an increase of the yields with respect to the value obtained without catalyst. However the increase of the inherent viscosity values was low, the behaviour of the catalysts being very similar. In general the yields and the inherent viscosity values obtained for these polymers were low, due probably to a hydrolytic process of both, the phosgene or thiophosgene, and the polymeric chain, promoted by lypophilic catalysts, which has been described for other poly(carbonates) and poly(thiocarbonates).[5] Due to the low values of inherent viscosity we have principally oligomeric species.

On the other hand, in this work we used a stoichiometric amount of sodium hydroxide in order to avoid the decomposition of the monomer. In another work of poly(carbonates) and poly(thiocarbonates) synthesis, in which we used a higher concentration of sodium hydroxide, we obtained high yields, probably due to a salting out effect.

Poly(carbonates) derived from the bischloroformate of bisphenol A and the same diphenols with silicon or germanium were obtained. The resulting polymers contain two carbonate groups and silicon or germanium in the main chain.[13] In this synthesis we used two catalysts: tetrabutylammonium (TBAB) bromide and benzyltriethylammonium chloride (BTEAC), and three sodium hydroxide concentrations: stoichiometric, twice the stoichiometric and three times the stoichiometric. The results are summarised in Table 3.



V: X = Si R = CH_3

VI: X = Ge R = CH_3

VII: X = Si R = C_6H_5

VIII: X = Ge R = C_6H_5

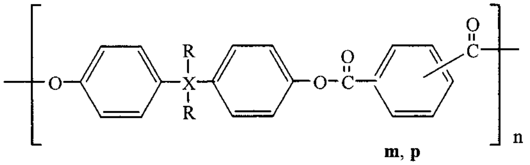
In the results it is possible to see that in several cases there is an increase of the yields when the sodium hydroxide concentration is increased and also when the catalysts are used. In general, there are no important differences between the use of twice or three times the sodium hydroxide concentration with respect to the stoichiometric. With all the diphenols the effect was similar. In general both parameters have the tendency to increase when the sodium hydroxide concentration is increased and when the catalysts are used. These effects were attributed to a salting out effect of the diphenolate from the aqueous phase to the organic one when the sodium hydroxide concentration is increased.

Table 3. Yields and inherent viscosities obtained for the poly(carbonates) **V** and **VI** derived from the diphenols bis(4-hydroxyphenyl)-dimethyl-silane and bis(4-hydroxyphenyl)-dimethyl-germane, poly(carbonates) **VII** and **VIII** derived from the diphenols bis(4-hydroxyphenyl)-diphenyl-silane and bis(4-hydroxyphenyl)-diphenyl-germane (Ref. 13).

		Catalyst					
		---		TBAB		BTEAC	
Poly(carbonate)	NaOH/phenol[a]	%	η[b]	%	η[b]	%	η[b]
V	2 / 1	32	0.04	56	0.08	58	0.08
V	4 / 1	49	0.11	63	0.11	58	0.11
V	6 / 1	44	0.11	55	0.11	54	0.11
VI	2 / 1	13	0.08	56	0.12	55	0.08
VI	4 / 1	72	0.07	95	0.18	88	0.14
VI	6 / 1	73	0.11	91	0.18	83	0.14
VII	2 / 1	31	0.0459	0.04	55	0.08	
VII	4 / 1	42	0.0850	0.12	86	0.20	
VII	6 / 1	48	0.1272	0.16	71	0.16	
VIII	2 / 1	37	0.0869	0.08	60	0.12	
VIII	4 / 1	45	0.0862	0.12	67	0.12	
VIII	6 / 1	39	0.0867	0.12	62	0.12	

[a] Molar ratio.
[b] Inherent viscosity, in $CHCl_3$ at 25°C (c = 0.3 g/dL).

Poly(esters) of two different type were also synthesized. The first group is derived from the same diphenols with silicon or germanium and methyl of phenyl groups bonded to the heteroatoms, and terephthaloyl or isophthaloyl dichlorides.[14] The results are summarised in



Ia : R = $-CH_3$; X = Si **Ib** : R = $-CH_3$; X = Ge
IIa: R = $-C_6H_5$; X = Si **IIb**: R = $-C_6H_5$; X = Ge

Table 4.

Table 4. Yields and inherent viscosities obtained for poly(esters) derived from the diphenols **I-a**, **I-b**, **II-a** and **II-b** (Ref. 14).

		Catalyst					
		---		TBAB		TEBAC	
Poly(ester)	NaOH/phenol [a]	%	$\eta^{b)}$	%	$\eta^{b)}$	%	$\eta^{b)}$
I-a-m	2 / 1	43	0.25	47	0.12	15	0.12
I-a-m	3 / 1	52	0.25	77	0.24	58	0.12
I-a-m	4 / 1	83	0.30	90	0.23	64	0.24
I-a-p	2 / 1	22	0.20	17	0.10	16	0.10
I-a-p	3 / 1	40	0.20	46	0.20	40	0.30
I-a-p	4 / 1	49	0.30	54	0.20	61	0.44
I-b-m	2 / 1	25	0.10	14	0.24	37	0.05
I-b-m	3 / 1	45	0.10	17	0.24	75	0.10
I-b-m	4 / 1	73	0.15	26	0.24	81	0.10
I-b-p	2 / 1	43	0.10	24	0.15	60	0.05
I-b-p	3 / 1	76	0.10	80	0.15	83	0.05
I-b-p	4 / 1	87	0.15	80	0.25	77	0.15
Poly(ester)	NaOH/phenol	%	$\eta^{c)}$	%	$\eta^{c)}$	%	$\eta^{c)}$
II-a-m	2 / 1	27	0.06	40	0.08	30	0.09
II-a-m	3 / 1	49	0.10	84	0.10	72	0.08
II-a-m	4 / 1	65	0.13	94	0.12	80	0.09
II-a-p	2 / 1	33	0.15	50	0.07	26	0.12
II-a-p	3 / 1	48	0.12	62	0.10	84	0.12
II-a-p	4 / 1	65	0.16	88	0.16	92	0.18
II-b-m	2 / 1	8	0.08	28	0.20	23	0.10
II-b-m	3 / 1	37	0.08	77	0.23	82	0.08
II-b-m	4 / 1	73	0.24	98	0.28	97	0.09
II-b-p	2 / 1	31	0.08	20	0.10	25	0.10
II-b-p	3 / 1	42	0.11	83	0.20	59	0.08
II-b-p	4 / 1	55	0.23	95	0.23	83	0.15

[a] Molar ratio

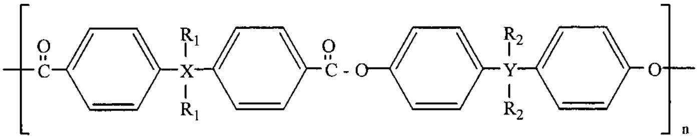
[b] Inherent viscosity, in N-methyl-pirrolidone, at 25°C (c = 0.3 g/dL)

[c] Inherent viscosity, in $CHCl_3$, at 25°C (c = 0.3 g/dL)

Two catalysts (TBAB and BTEAC) and three sodium hydroxide concentrations were used and in all cases there was an increase of the yields when this concentration was increased, with and without catalysts. This tendency was also attributed to a salting out effect, which increases the transfer process of the ionic pair from the aqueous phase to the organic one.

Also in some cases there was an increase of the inherent viscosity values. It is difficult to explain the decrease of the inherent viscosity values when the catalysts were used. Probably there is a hydrolytic process of the polymeric chains. Neither were there any differences between the diphenols containing silicon or germanium atoms.

The second group of poly(esters), are the following sixteen polymers derived from four acid dichlorides with germanium or silicon and methyl or phenyl groups and the same diphenols shown previously. The resulting poly(esters) contain two heteroatoms and in the synthesis we used twice the stoichiometric amount of sodium hydroxide.[15] The results are shown in Table 5.



I : X = Si , Y = Si, R_1 = $-C_6H_5$, R_2 = $-CH_3$
II : X = Si , Y = Ge , R_1 = $-C_6H_5$, R_2 = $-CH_3$
III: X = Ge , Y = Si , R_1 = $-C_6H_5$, R_2 = $-CH_3$
IV: X = Ge , Y = Ge , R_1 = $-C_6H_5$, R_2 = $-CH_3$

V : X = Si , Y = Si, $R_1 = R_2$ = $-C_6H_5$
VI : X = Si , Y = Ge, $R_1 = R_2$ = $-C_6H_5$
VII : X = Ge , Y = Si , $R_1 = R_2$ = $-C_6H_5$
VIII : X = Ge , Y = Ge, $R_1 = R_2$ = $-C_6H_5$

IX : X = Si , Y = Si, $R_1 = R_2$ = $-CH_3$
X : X = Si , Y = Ge, $R_1 = R_2$ = $-CH_3$
XI : X = Ge , Y = Si , $R_1 = R_2$ = $-CH_3$
XII : X = Ge , Y = Ge, $R_1 = R_2$ = $-CH_3$

XIII : X = Si , Y = Si , R_1 = $-CH_3$, R_2 = $-C_6H_5$
XIV : X = Si , Y = Ge, R_1 = $-CH_3$, R_2 = $-C_6H_5$
XV : X = Ge , Y = Si , R_1 = $-CH_3$, R_2 = $-C_6H_5$
XVI : X = Ge , Y = Ge, R_1 = $-CH_3$, R_2 = $-C_6H_5$

The results for poly(esters) **I** - **XVI** showed that when the catalysts were used, it is possible to see very low increases of the yields and in some cases, of the inherent viscosity values. Neither are there important differences in the behaviour of the catalysts. A very negative effect was the insolubility of these poly(esters) in the reaction media, which hindered the growth of the polymeric chain and implies in the future the use of other organic solvents. In spite of these results, the phase transfer process had certain effectiveness in this polyester synthesis. With respect to these polymers, at this moment we are working on the effect of lower polymerization temperatures in the inherent viscosity values.

Table 5. Yields and inherent viscosities obtained for poly(esters) **I** – **XVI** (Ref. 15).

	Catalyst					
	---		TBAB		BTEAC	
Poly(ester)	%	η[a]	%	η[a]	%	η[a]
I	75	0.12	85	0.16	80	0.20
II	55	0.08	62	0.12	67	0.12
III	72	0.16	74	0.20	76	0.28
IV	57	0.08	66	0.12	67	0.12
V	70	0.16	78	0.24	89	0.28
VI	80	0.08	87	0.20	89	0.24
VII	57	0.12	72	0.24	89	0.24
VIII	71	0.16	78	0.20	87	0.24
IX	35	0.08	50	0.12	89	0.16
X	47	0.12	69	0.20	60	0.16
XI	40	0.12	51	0.16	74	0.12
XII	35	0.08	50	0.12	48	0.12
XIII	36	0.12	50	0.12	89	0.16
XIV	67	0.12	75	0.16	70	0.12
XV	71	0.12	89	0.20	68	0.16
XVI	78	0.16	79	0.20	64	0.12

[a] Inherent viscosity, in $CHCl_3$ at 25°C (c = 0.3 g/dL).

Poly(amides) derived from two aromatic diamines with silicon or germanium and isophthaloyl or terephthaloyl dichlorides were synthesized, according to the following structures, and the results are summarised in Table 6.[16]

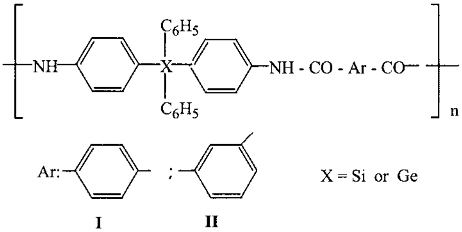


Table 6. Yields, inherent viscosity, thermogravimetric data and glass transition temperatures obtained for the poly(amides) (Ref. 16).

Poly(amide)	Yield (%)	η_{inh} a)	$TDT^{10\%}$ (°C)	Tg (°C)
I-Si	91	0.45	400	178
I-Ge	95	0.50	410	133
II-Si	99	0.42	200	138
II-Ge	84	0.49	225	127

a) inherent in o-chloro-phenol at 25°C (c = 0.3 g/dL)

In general the yields and the inherent viscosity values were good and similar between the poly(amides).

In this case the thermal properties were studied, showing that the poly(amides) derived from terephthalic acid had higher thermal stability attributed to the more symmetrical structures. On the other hand those with germanium showed a little more stability than those with silicon. The bond carbon-silicon has a little higher polarity than the bond carbon-germanium, and this has higher bond enthalpy. This difference would explain the higher stability of the germanium containing poly(amides).

The higher Tg values were obtained for the more symmetrical structures. Poly(amides) with silicon showed higher Tg values, which can be due to the larger size of the germanium atom, which increases the flexibility of the polymeric chain and consequently lower values of Tg are obtained.

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