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# Synthesis and Characterization of Poly(carbonates) and Poly(thiocarbonates) Derived from Diphenols Containing Germanium as a Central Atom

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*Poly(carbonates) and poly(thiocarbonates), containing germanium in the main chain and derived from the diphenols bis(4-hydroxyphenyl)-dimethyl-germane, bis(4-hydroxyphenyl)-diethyl-germane, and bis(4-hydroxyphenyl)-dibutyl-germane reaction with phosgene and thiophosgene, respectively. The products were synthesized under phase transfer conditions, using two phase transfer catalysts. The products were characterized by spectroscopic methods. The results were evaluated by the yields and $\eta_{inh}$ values which showed different behaviors for poly(carbonates) and poly(thiocarbonates). The yields and the $\eta_{inh}$ values for the poly(carbonates) were low due to a hydrolytic process when the NaOH concentration was increased. For the poly(thiocarbonates) the phase transfer was effective and also there was an increase of both parameters when the NaOH concentration was increased, due to a salting out effect.*

**Keywords** poly(carbonates), poly(thiocarbonates), germanium, phase transfer catalysis

## Introduction

Phase transfer catalysis has been an important tool for the synthesis of condensation polymers (1). In this technique, a dianion is transferred as an ionic-pair with the catalyst from the aqueous phase to the organic one, in which the reaction takes place (2).

Several factors have influence in the transfer process, the most important being the nature of the catalyst and the concentration of the NaOH in the aqueous phase. In this last sense when this concentration is increased, it is possible to see a salting out effect of the diphenolate to the organic phase, which has as a consequence an increase of the yields and in less extension of the molecular weights, as was described in the synthesis of poly(esters) derived from diphenols containing Si or Ge as central atoms (3, 4). Also, the increase of the NaOH concentration can displace the equilibrium to the diphenolate formation.

Recently, we have focused our attention on the synthesis of several condensation polymers (5) such as poly(carbonates) (4, 6), poly(thiocarbonates) (6), poly(esters) (3, 7), derived from diphenols containing Si or Ge as the central atom and using phase transfer conditions as a polymerization method. Also, we have described poly(amides) derived from diamines containing Si or Ge in the main chain (8) and poly(urethanes) (9).

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In this work, we describe the synthesis and characterization of poly(carbonates) and poly(thiocarbonates) derived from diphenols containing Ge as a central atom bonded to aliphatic groups, and phosgene or thiophosgene respectively. We studied the qualitative behaviour of two phase transfer catalysts and three NaOH concentrations, through the yields and the $\eta_{inh}$ of the obtained polymers.

## Experimental

Reagents and solvents (from Aldrich or Riedel de Haen) were used without purification. The following catalysts (from Fluka) were used: tetrabutylammonium bromide (TBAB) and methyltrioctylammonium chloride (ALIQUAT 336). The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the $^1$H and $^{13}$C NMR on a 400 MHz instrument (Bruker), using $CDCl_3$, acetone-$d_6$ and DMSO-$d_6$ as solvents and TMS as the internal standard.

### *Monomers*

The diphenols bis(4-hydroxyphenyl)-dimethyl-germane, bis(4-hydroxyphenyl)-diethyl-germane, and bis(4-hydroxyphenyl)-dibutyl-germane were synthesized from p-bromophenol and dimethyl-, diethyl- or dibutyl-dichloro-germane, according to the procedure described by Davidson (10) in which 14.1 g (0.08 mol) of p-bromo-phenol in THF are added under $N_2$ to 75 mL of n-butyllithium (2.5 N solution in n-hexane) at $-70$°C. Then, the temperature is increased slowly until 5°C and the mixture stirred for one hour. The temperature is decreased to $-50$°C and 0.025 mol of dimethyl-, diethyl- or dibutyl-dichloro-germane are added in THF, and the temperature is increased until 10°C and stirred for 2 h. The mixture is hydrolyzed by adding 5% HCl until a yellow mixture is obtained, having pH = 1. The organic layer was dried over $MgSO_4$ and the solvent evaporated. The brown oil is poured in n-hexane, obtaining a white solid, which is recrystallized from toluene and characterized.

Bis(4-hydroxyphenyl)-dimethyl-germane (**I**): m.p. 160–161°C (Lit. (10) 162–163°C). I.R. (KBr) (cm$^{-1}$): 3321 (OH), 3024 (H arom.), 2957, 2870 ($CH_3$), 1596, 1496 (C=C arom.), 1455 ($CH_3$), 832 (arom. p-subst.). $^1$H NMR $\delta$ (ppm) (acetone-$d_6$): 0.62 (s,6H,$CH_3$), 6.92 (d,4H,arom), 7.38 (d,4H,arom), 8.44 (s,2H,OH). $^{13}$C NMR $\delta$ (ppm) (acetone-$d_6$): $-2.34$ ($CH_3$-Ge), 116.5, 130.8, 136.0, 159.2 (C arom).

Bis(4-hydroxyphenyl)-diethyl-germane (**II**): m.p.: 108–109°C. I.R. (KBr) (cm$^{-1}$): 3313 (OH), 3024 (H arom.), 2958, 2871 ($CH_3$), 2931 ($CH_2$), 1598, 1499 (C arom.), 1455 ($CH_3$), 820 (arom. p-subst.). $^1$H NMR $\delta$ (ppm) ($CDCl_3$): 1.05–1.22 (m,10H,$CH_2$-$CH_3$), 5.11 (s,2H,OH), 6.84 (d,4H,arom.), 7.32(d,4H,arom). $^{13}$C NMR $\delta$ (ppm) ($CDCl_3$): 5.25 ($CH_2$), 8.9 ($CH_3$), 115.2, 129.4, 135.9, 155.9 (C arom.).

Bis(4-hydroxyphenyl)-dibutyl-germane (**III**): m.p.: 78–80°C. I.R. (KBr) (cm$^{-1}$): 3313 (OH), 3004 (H arom.), 2957 ($CH_3$), 2924, 2854 ($CH_2$), 1957, 1499 (C=C arom.), 822 (arom. p-subst.). $^1$H NMR $\delta$ (ppm) ($CDCl_3$): 0.84–0.93 (t,6H,$CH_3$), 1.16–1.44 (m,12H,$CH_2$), 5.26 (s,2H,OH), 6.85(d,4H,arom.), 7.32 (d,4H,arom.). $^{13}$C NMR $\delta$ (ppm) ($CDCl_3$): 13.3 ($CH_2$), 13.7 ($CH_3$), 26.5, 27.2 ($CH_2$), 115.2, 130, 135.9, 155.9 (C arom.).

### *Polymers*

Poly(carbonates) and poly(thiocarbonates) were synthesized according to the following general procedure: the diphenol (1 mmol) is dissolved in 0.5 M NaOH and water (total volume 15 mL) and then 15 mL of $CH_2Cl_2$ and the catalyst (5% in mol) are added. To this mixture, 1 mmol of phosgene (**a**) (from a toluene solution) or thiophosgene (**b**) is added and the mixture stirred at 20°C for one hour. After this time the organic layer is poured into 300 mL of methanol and the polymer is filtered, washed with methanol, dried until constant weight, and characterized.

Poly(carbonate) **Ia**: IR (KBr) ($cm^{-1}$): 3025 (H arom.), 2962, 2870, ($CH_3$), 1774 (C=O), 1585, 1494 (C=C arom.), 802 (p-arom). $^1H$ NMR ($CDCl_3$) ($\delta$): 0.66 (s,6H,$CH_3$), 7.27 (d,4H,arom), 7.51 (d,4H,arom). $^{13}C$ NMR ($CDCl_3$) ($\delta$): −2.90 (Ge-$CH_3$), 120.6, 134.9, 137.9, 151.5 (arom), 151.9 (C=O).

Poly(thiocarbonate) **Ib**: IR (KBr) ($cm^{-1}$): 3030 (H arom.), 2965, 2874, ($CH_3$), 1185 (C=S), 1583, 1492 (C=C arom.), 827 (p-arom). $^1H$ NMR ($CDCl_3$) ($\delta$): 0.71 (s,6H,$CH_3$), 7.23 (d,4H,arom), 7.57 (d,4H,arom). $^{13}C$ NMR ($CDCl_3$) ($\delta$): −2.84 (Ge-$CH_3$), 121.5, 135, 138.5, 154.1 (arom), 194.4 (C=S).

Poly(carbonate) **IIa**: IR (KBr) ($cm^{-1}$): 3027 (H arom.), 2954, 2871 ($CH_3$), 2929 ($CH_2$), 1774 (C=O), 1587, 1493 (C=C arom.), 1458 ($CH_3$), 812 (arom. p-subst.). $^1H$ NMR ($CDCl_3$) ($\delta$): 1.07–1.14 (t,6H,$CH_3$), 1.22–1.30 (m,4H,$CH_2$), 7.28 (d,4H,arom.), 7.49 (d,4H,arom.). $^{13}C$ NMR ($CDCl_3$) ($\delta$): 5.16 ($CH_2$), 8.81 ($CH_3$), 120.6, 135.7, 136, 151.6 (C arom.) 151.9 (C=O).

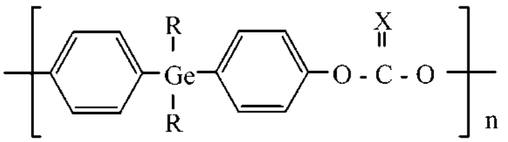
Poly(thiocarbonate) **IIb**: IR (KBr) ($cm^{-1}$): 3028 (H arom.), 2954, 2871 ($CH_3$), 2929 ($CH_2$), 1583, 1492 (C=C arom.), 1458 ($CH_3$), 1185 (C=S), 826 (arom. p-subst.). $^1H$ NMR ($CDCl_3$) ($\delta$): 1.09–1.17 (t,6H,$CH_3$), 1.25–1.36 (c,4H,$CH_2$), 7.23 (d,4H,arom.), 7.54 (d,4H,arom.). $^{13}C$ NMR ($CDCl_3$) ($\delta$): 5.23 ($CH_2$), 8.90 ($CH_3$), 121.5, 135.7, 136.6, 154.1 (C arom.) 194.2 (C=S).

Poly(carbonate) **IIIa**: IR (KBr) ($cm^{-1}$): 3027 (H arom.), 2956, ($CH_3$), 2929, 2855 ($CH_2$), 1774 (C=O), 1587, 1494 (C=C arom.), 811 (arom. p-subst.). $^1H$ NMR ($CDCl_3$) ($\delta$): 0.85–0.92 (t,6H,$CH_3$), 1.24–1.39 (m,12H,$CH_2$), 7.29 (d,4H,arom.), 7.5 (d,4H,arom.). $^{13}C$ NMR ($CDCl_3$) ($\delta$): 13.2 ($CH_2$), 13.7 ($CH_3$), 26.4, 27.1 ($CH_2$), 120.5, 135.6, 136.6, 151.6 (C arom.) 152 (C=O).

Poly(thiocarbonate) **IIIb**: IR (KBr) ($cm^{-1}$): 3028 (H arom.), 2956, ($CH_3$), 2925, 2869 ($CH_2$), 1774 (C=O), 1583, 1492 (C=C arom.), 1185 (C=S), 825 (arom. p-subst.). $^1H$ NMR ($CDCl_3$) ($\delta$): 0.85–0.92 (t,6H,$CH_3$), 1.32–1.39 (m,12H,$CH_2$), 7.22 (d,4H,arom.), 7.53 (d,4H,arom.). $^{13}C$ NMR ($CDCl_3$) ($\delta$): 13.2 ($CH_2$), 13.7 ($CH_3$), 26.4, 27.1 ($CH_2$), 121.4, 135.6, 137.2, 154 (C arom.) 194.2 (C=S).

## Results and Discussion

Poly(carbonates) and poly(thiocarbonates), with structures shown in Fig. 1, were derived from the diphenols bis(4-hydroxyphenyl)-dimethyl-germane (**I**), bis(4-hydroxyphenyl)-diethyl-germane (**II**), and bis(4-hydroxyphenyl)-dibutyl-germane (**III**), using phase



**Ia** : R = $-CH_3$, X = O
**Ib** : R = $-CH_3$, X = S
**IIa** : R = $-CH_2CH_3$, X = O
**IIb** : R = $-CH_2CH_3$, X = S
**IIIa** : R = $-CH_2CH_2CH_2CH_3$, X = O
**IIIb** : R = $-CH_2CH_2CH_2CH_3$, X = S

**Figure 1.** Poly(carbonates) and poly(thiocarbonates) prepared.

transfer conditions and two phase transfer catalysts in $CH_2Cl_2$ as solvent, at 20°C. Polymers were characterized by IR, $^1H$, and $^{13}C$ NMR, and the structures were in accord with those proposed (Fig. 1).

For all the polymers it was possible to see the disappearance of the OH IR band. In poly(carbonates) it was possible to see a new band at 1774 $cm^{-1}$ corresponding to the C=O of the carbonate group, and in the poly(thiocarbonates) there was an increase of the intensity of the band at 1185 $cm^{-1}$, corresponding to the C=S group.

In this study the catalyst concentration, solvent, reaction time and temperature remained constant. Three base concentrations were studied, the molar ratios of NaOH/phenol being 2/1, 3/1, and 4/1, respectively. The volume of the aqueous phase was the same in all cases (15 mL). The efficiency of the catalyst was studied by measuring the yields and inherent viscosity values ($\eta_{inh}$) of the obtained polymers.

The reaction takes place when the diphenolate dissolved in the aqueous phase is transferred to the organic one as an ionic pair due to the action of the catalyst. For all the polymers, comparison experiments without catalyst were made to evaluate the behavior of the interphase of the system, observing that polymers are obtained due to an interphasial polycondensation process between the diphenolate dissolved in the aqueous phase and the phosgene or thiophosgene dissolved in the organic phase. Two phase transfer catalysts were used: tetrabutylammonium bromide (TBAB) and methyltrioctylammonium chloride (ALIQUAT 336).

Table 1 shows the results obtained for poly(carbonates) **Ia** and poly(thiocarbonates) **Ib** products, derived from the diphenol bis(4-hydroxyphenyl)-dimethyl-germane (**I**). For the poly(carbonate) **Ia**, TBAB only showed an increase of the $\eta_{inh}$ when a stoichiometric NaOH/phenol ratio was used. Although this catalyst has been described as effective in the synthesis of polymers derived from bisphenol A (11, 12), due to its symmetrical structure with four butyl groups bonded to the N central atom which confers an adequate separation to the ionic pair. In this case, at higher NaOH concentrations, it was possible to see that the yields and the $\eta_{inh}$ values decreased in front of the results obtained without catalysts.

**Table 1**

Yields and inherent viscosities obtained for the poly(carbonate) **Ia** and poly(thiocarbonate) **Ib** derived from the diphenol bis(4-hydroxyphenyl)-dimethyl-germane (**I**)

| | | | | Catalyst | | | |
|---|---|---|---|---|---|---|---|
| | | | | TBAB | | ALIQUAT | |
| Polymer | NaOH/phenol[a] | %[b] | $\eta^c$ | %[b] | $\eta^c$ | %[b] | $\eta^c$ |
| **Ia** | 2/1 | 38 | 0.04 | 48 | 0.24 | 30 | 0.04 |
| **Ia** | 3/1 | 54 | 0.11 | 48 | 0.14 | 45 | 0.16 |
| **Ia** | 4/1 | 25 | 0.13 | 13 | 0.08 | — | — |
| **Ib** | 2/1 | 20 | 0.16 | 61 | 0.24 | 56 | 0.12 |
| **Ib** | 3/1 | 39 | 0.11 | 79 | 0.14 | 76 | 0.16 |
| **Ib** | 4/1 | 15 | 0.10 | 61 | 0.11 | 73 | 0.15 |

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

ALIQUAT was practically ineffective due to its more lipophilic character, and it is only possible to see an increase of the $\eta_{\text{inh}}$ when a 3/1 NaOH/phenol ratio was used. In general, when the NaOH concentration is increased, there was a decrease of the yields, due probably to a hydrolytic process, especially of the phosgene which is highly reactive in a basic media. Also the higher electronegativity of the Ge atom (13) can decrease the basicity of the diphenol, and in this sense an increase of the NaOH concentration would displace the equilibrium to the diphenolate formation and would increase the effectiveness of the total process.

For the poly(thiocarbonate) **Ib**, it is possible to see that the phase transfer process was more effective and in general, there is an increase of both parameters when the catalysts were used in front of the polymer obtained without catalyst. Apparently, thiophosgene is more resistant to a hydrolytic process, which would explain the increase of the yields when the catalysts are used at different NaOH concentrations. When TBAB was used there is a decrease of the $\eta_{\text{inh}}$ values if the NaOH concentration is increased, which can be due to hydrolysis of the polymeric chains promoted by the transfer of $OH^-$ ions with the catalyst. The latter observation was described in the synthesis of other poly(thiocarbonates) (14), where yields were shown to remain practically constant. When using ALIQUAT there is no apparent hydrolysis of the polymeric chains, since the $\eta_{\text{inh}}$ values are very similar. The latter is true even though this catalyst is lipophilic and can promote the hydrolytic process. Both catalysts are lipophilic and suitable for transporting diphenolates, having a low organic content bonded to a central atom. With this diphenol (**I**) we did not observe a "salting out" effect when the NaOH concentration was increased.

Table 2 shows the results obtained for the poly(carbonate) **IIa** and poly(thiocarbonate) **IIb**, derived from the diphenol bis(4-hydroxyphenyl)-diethyl-germane **II**. For the poly(carbonate) **IIa** the results were very poor, providing both low yields and low $\eta_{\text{inh}}$ values, which does not permit adequate conclusions. Probably in this case, the increase of the side chains bonded to the heteroatom, decreases the reactivity of the diphenol, which would increase the hydrolytic process of the phosgene and the polymeric chains.

**Table 2**

Yields and inherent viscosities obtained for the poly(carbonate) **IIa** and poly(thiocarbonate) **IIb** derived from the diphenol bis(4-hydroxyphenyl)-diethyl-germane (**II**)

| | | | | Catalyst | | | |
|---|---|---|---|---|---|---|---|
| | | | | TBAB | | ALIQUAT | |
| Polymer | NaOH/phenol[a] | %[b] | $\eta^c$ | %[b] | $\eta^c$ | %[b] | $\eta^c$ |
| **IIa** | 2/1 | — | — | — | — | 20 | 0.11 |
| **IIa** | 3/1 | 24 | 0.13 | — | — | 14 | 0.09 |
| **IIa** | 4/1 | 13 | 0.14 | 35 | 0.12 | 15 | 0.12 |
| **IIb** | 2/1 | 39 | 0.09 | 68 | 0.09 | 57 | 0.12 |
| **IIb** | 3/1 | 38 | 0.10 | 60 | 0.14 | 58 | 0.14 |
| **IIb** | 4/1 | 49 | 0.13 | 89 | 0.17 | 54 | 0.11 |

[a] Molar ratio.

[b] Yields.

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

The phase transfer process was more effective for poly(thiocarbonate) **IIb**, in the sense that it is possible to see an increase of the yields only when the catalysts were used, with no important changes in the $\eta_{\text{inh}}$ values. On the other hand, there were no important differences between the behavior of the catalysts, since an increase of the yields compared to those obtained without catalyst showed that the process was more effective. An increase of the NaOH concentration failed to show any differences.

Table 3 shows the results obtained for poly(carbonate) **IIIa** and poly(thiocarbonate) **IIIb**, derived from the diphenol bis(4-hydroxyphenyl)-dibutyl-germane **III**. Poly(carbonate) **IIIa** was not obtained in an interphasial polycondensation process without a catalyst. When TBAB was used, the polymer was obtained but with low $\eta_{\text{inh}}$ values. The longer side chains increases the organic content of the diphenolate and decreases the effectiveness of this catalyst. ALIQUAT was ineffective, probably due to its lipophilic character, which promote hydrolytic process of both phosgene and maybe the polymeric chains, especially at higher NaOH concentrations.

For poly(thiocarbonate) **IIIb**, the phase transfer process was effective in comparison with the results obtained without a catalyst. In this case, where thiophosgene is more stable to hydrolysis, it is possible that the increase of the NaOH concentration increases the $\eta_{\text{inh}}$ values, due to a salting out effect of the diphenolate from the aqueous phase to the organic one in which the reaction takes place. On the other hand, both catalysts were effective and the hydrolytic process of the thiophosgene and the polymeric chains is diminished. Although the ALIQUAT is more lipophilic and unsuitable for the transporting of diphenolates with a high organic content, in this case it was probably effective due to the effect of increasing the NaOH concentration.

Considering the three poly(carbonates) it is possible to see that when the aliphatic chains bonded to the Ge atom are increased, the effectiveness of the phase transfer is lower. The diphenols containing Ge have lower basicity than the analogous monomers with carbon, due to the lower electronegativity of this heteroatom, which implies that the effectiveness of the transfer process is low, as was described in other work (6),

**Table 3**

Yields and inherent viscosities obtained for the poly(carbonate) **IIIa** and poly(thiocarbonate) **IIIb** derived from the diphenol bis(4-hydroxyphenyl)-dibutyl-germane (**III**)

| | | | | Catalyst | | | |
|---|---|---|---|---|---|---|---|
| | | | | TBAB | | ALIQUAT | |
| Polymer | NaOH/phenol[a] | %[b] | $\eta^c$ | %[b] | $\eta^c$ | %[b] | $\eta^c$ |
| **IIIa** | 2/1 | — | — | 87 | 0.13 | 63 | 0.09 |
| **IIIa** | 3/1 | — | — | 15 | 0.10 | 7 | — |
| **IIIa** | 4/1 | — | — | 64 | 0.12 | — | — |
| **IIIb** | 2/1 | — | — | 79 | 0.08 | 86 | 0.11 |
| **IIIb** | 3/1 | 55 | 0.16 | 53 | 0.16 | 81 | 0.29 |
| **IIIb** | 4/1 | 43 | 0.16 | 94 | 0.33 | 87 | 0.26 |

[a] Molar ratio.

[b] Yields.

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

where both yields and $\eta_{inh}$ values were moderate or low. The increase of the NaOH concentration would displace the equilibrium to the phenolate formation and also would affect positively its transfer process as an ionic pair with the catalysts, by a salting out effect. But this increase of the amount of NaOH in the aqueous phase also would increase the possibility of hydrolysis of the phosgene and the polymeric chains if the $OH^-$ anions are transferred to the organic phase with lipophilic catalysts. All of these factors can be responsible for the poor results obtained in the synthesis of these poly(carbonates), most of them being oligomeric species.

However, when the three poly(thiocarbonates) are considered, the phase transfer process was effective in all cases. Thus, an increase of the yields occurs with a catalyst, compared to that without a catalyst, with catalysts being effective in the process. On the other hand, if we compare the results obtained with both catalysts, it is possible to see that there are no important differences in their behavior. The increase on the NaOH concentration in the aqueous phase does not have great influence. Only a little increase of the $\eta_{inh}$ values were observed for the poly(thiocarbonate) **IIIb**. Also, the possibility of hydrolysis of thiophosgene and the polymeric chains is diminished, considering the higher yields and that the $\eta_{inh}$ are similar or can increase as in poly(thiocarbonate) **IIIb**.

Although the results obtained for poly(thiocarbonates) were better than those obtained for poly(carbonates), it is possible to point out that also in this case the poly(thiocarbonates) are of oligomeric nature, although probably in some cases the molecular weights were a little higher.

## Conclusion

Finally, we can conclude that the phase transfer process was relatively successful in the synthesis of poly(thiocarbonates), in which there is an increase of the yields when the catalysts were used: However, the increase of the NaOH concentration had little influence. In the synthesis of the poly(carbonates) it was possible to see an important influence of the increase of the NaOH concentration due the hydrolytic process of the phosgene and the polymeric chains. However, all of the polymers, prepared under these conditions are probably of low molecular weight.

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## References

1. Tagle, L.H. (1999) Phase transfer catalysis in polymer synthesis. In *Handbook of Phase Transfer Catalysis*; Sasson, Y. and Newmann, R., Eds.; Blackie Academic and Professional, 200, and references therein.
2. Dehmlow, E.V. and Dehmlow, S.S. (1993) *Phase Transfer Catalysis 3rd ed.*; Verlag-Chemie.
3. Tagle, L.H., Diaz, F.R., Nuñez, M., and Canario, F. (2003) Polymerization by phase transfer catalysis. 27. Synthesis of polyesters containing silicon or germanium. Influence of the base concentration. Intern. *J. Polymeric Mat.*, 52: 287.
4. Tagle, L.H., Diaz, F.R., Vega, J.C., Quezada, M., and Guerrero, P. (2003) Synthesis and characterization of poly(carbonates) derived from diphenols that contain silicon or germanium. *J. Inorg. Organomet. Polym.*, 13: 21.

5. Tagle, L.H. (2003) Condensation polymers containing silicon and germanium in the main chain. *Macromol. Symp.*, 199: 499.
6. Tagle, L.H., Vega, J.C., Diaz, F.R., Radic, D., Gargallo, L., and Valenzuela, P. (2000) Polymerization by phase transfer catalysis. 25. Synthesis of polycarbonates and polythiocarbonates derived from diphenols containing germanium and silicon in the main chain. *J. Macromol. Sci., Pure & Appl. Chem.*, A37: 997.
7. Tagle, L.H., Diaz, F.R., Vega, J.C., and Valenzuela, P. (2003) Synthesis and characterization of poly(esters) derived from diacids and diphenols containing silicon and germanium. *Eur. Polym. J.*, 39: 407.
8. Tagle, L.H., Diaz, F.R., Radic, D., Opazo, A., and Espinoza, J.M. (2000) Synthesis and characterization of poly(amides) derived from diamines with germanium and silicon. *J. Inorg. Organomet. Polym.*, 10: 73.
9. Terraza, C.A., Tagle, L.H., Leiva, A., and Vega, J.C.. Synthesis and characterization of bis(4-hydroxyphenyl)-dimethyl-silane and -germane bischloroformates and their use in the synthesis of poly(urethanes)(submitted).
10. Davidson, W., Laliberte, B.R., Goddard, C.M., and Henry, M.C. (1972) Organometallic bis(p-hydroxyphenyl) derivatives of group IV elements and related compounds. *J. Organomet. Chem.*, 36: 283.
11. Tagle, L.H., Diaz, F.R., Vega, J.C., and Alquinta, P.F. (1985) Polymerization by phase transfer catalysis. 2. Polythiocarbonates by polymerization of bisphenol A with thiophosgene. *Makromol. Chem.*, 186: 915.
12. Tagle, L.H., Diaz, F.R., and Riveros, P. (1986) Polymerization by phase transfer catalysis IV. Polythiocarbonates by polymerization of diphenols with thiophosgene. *Polymer J.*, 18: 501.
13. www.webelements.com.
14. Tagle, L.H. and Diaz, F.R. (1987) Polymerization by phase transfer catalysis. 5. Polycarbonates from diphenols with aromatic side groups. *Eur. Polym. J.*, 23: 109.