SILICON-CONTAINING AROMATIC POLY(ESTERS) DERIVED FROM BIS(4-CARBOXYPHENYL)METHYL-R-SILANE AND BIS(4-(HYDROXYMETHYL) PHENYL)METHYL-R-SILANE. SYNTHESIS, CHARACTERIZATION AND THERMAL STUDIES

LUIS H. TAGLE, CLAUDIO A. TERRAZA, LEONARDO I. PINO

Facultad de Química, Pontificia Universidad Católica de Chile, P.O. Box 306, Santiago, Chile

ABSTRACT

This work describes the synthesis, characterization and thermal studies of poly(esters) (**PE**s) containing two Si atoms in the main chain, derived from aromatic diacids and aliphatic dialcohols in which the Si atom is bonded to methyl and/or ethyl groups. **PE**s were characterized by FT-IR and ^{1}H, ^{13}C and ^{29}Si spectroscopy and the results were in agreement with the proposed structures. Poly(esters) were soluble in polar aprotic solvents, such as DMSO and DMF, and acetone, and partially soluble in ethanol. The inherent viscosity and glass transition and thermal decomposition temperatures, h_{inh}, Tg and TDT respectively, were determined. These results showed that **PE-2** and **PE-4**, derived from the dialcohol with the $-Si(CH_3)(CH_2CH_3)-$ moiety as central element, had the larger values of h_{inh}, Tg, TDT and the residual weight after heating at 900 °C, indicating that the specific structure of aliphatic dialcohols control the reaction.

Keywords: Silicon-containing aliphatic poly(esters), glass transition temperature, thermal degradation temperature

INTRODUCTION

Aromatic and aliphatic poly(esters) have been condensation polymers widely used, which have many important applications. The introduction in the polymeric chain of heteroatoms such as Si or Ge can change some of their properties such as to improve the solubility and maintain or increase the thermal stability due to the polarity of the C-Si bond, derived from the difference in electronegativity of these atoms.[1-9] Also, glass transition temperature (Tg) of the materials can be diminished due to the longer C-Si or C-Ge bond relative to that of C-C. This fact, would allow higher rotation freedom of the polymeric chain. Also, the incorporation of other functional groups or aliphatic moieties in the repetitive unit can cause similar effects.

Several types of aromatic poly(esters) containing one or two silicon atoms in the main chain have been synthesized and characterized.[2, 10-13] Likewise, it has been reported the preparation of polycondensation materials that include the ester and other functional groups.[4, 6, 14] On the other hand, Migdal *et al*.[15] reported the synthesis of a series of dimethylsilylen-containing aliphatic poly(esters). These polymers are based on the reactions of bis(*p*-carboxymethylphenyl) dimethylsilane diacid and the dialcohols bis(*p*-hydroxymethylphenyl) dimethylsilane and bis(*p*-b-hydroxyethylphenyl)dimethylsilane. Moreover, similar silicon-containing compounds have been prepared by Rotman *et al*.[16] and Kim *et al*.[17] Recently, our group has also reported the synthesis and characterization of some difunctional silicon-containing aliphatic precursors and monomers.[18]

Continuing our works on the synthesis, characterization and thermal studies of condensation polymers containing one or two Si atoms in the main chain, in this work, we describe the synthesis of four new poly(esters) derived from aromatic dicarboxylic acids and aliphatic dialcohols, all them containing two Si atoms in their structure and bonded to methyl and/or ethyl groups. In all cases, the thermal properties (Tg and thermal decomposition temperature) were related to the specific structure of the repetitive unit.

EXPERIMENTAL PART

Materials

Lithium, CH_3RSiCl_2 (R= CH_3 or CH_2CH_3), CrO_3, $LiAlH_4$, tosyl chloride (TsCl) and pyridine were obtained from Aldrich Chemical (Milwaukee, WI) and used without further purification. Solvents were purchased commercially as analytical-grade and used without further purification.

Instrumentation

The FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer (Fremont CA) 1310 spectrophotometer over the 450-4000 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, CDCl$_3$ or acetone-d_6 as solvents and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25 °C (c = 0.3 g/dL). Tg values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (20 ºC

min^{-1} under N$_2$ flow) after the second heating run. 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 30 ºC and 800 ºC with a heating rate of 20 ºC min^{-1} under N$_2$ flow. Elemental analyses (EA) were made on a Fison EA 1108-CHNS-O equipment.

### Precursors and monomers synthesis

The ditolyl derivatives, bis(4-methylphenyl)dimethylsilane (**1a**) and bis(4-methylphenyl)ethylmethylsilane (**1b**), were obtained from *p*-bromotoluene and dichlorodimethylsilane or dichloroethylmethylsilane, respectively, according to a described procedure (Scheme 1).[12, 19] The diacids, bis(4-carboxyphenyl) dimethylsilane (**2a**) and bis(4-carboxyphenyl)ethylmethylsilane (**2b**), were obtained by oxidation of the ditolyl compounds, according to a described procedure.[15] These diacids were reduced with $LiAlH_4$ in THF in order to obtain the dialcohols bis(4-hydroxymethylphenyl)dimethylsilane (**3a**) or bis(4-hydroxymethylphenyl)ethylmethylsilane (**3b**), according to the procedure described by Mingal *et al*.[15] All compounds were characterized by FT-IR and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, and the results were in agreement with the proposed structures.
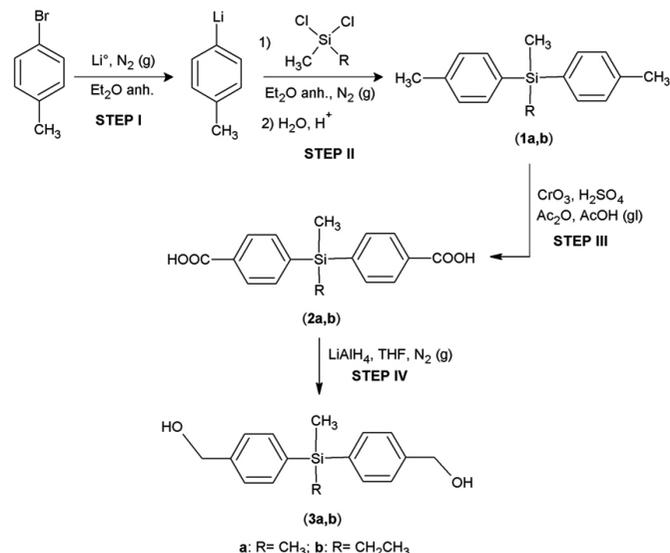
Scheme 1. Synthetic route for the preparation of the aliphatic dialcohols; bis(4-hydroxymethyl)phenyl)methyl-R-silane (**3**).

Polymer synthesis

Poly(esters) were obtained according to the following general procedure[20] (Scheme 2): 0.635 mmol of the diacid (**2**) was mixed with 2 mL of pyridine, and then 1.3 mmol of TsCl was added, and the mixture stirred by 30 min. To this solution *N,N*-dimehtylformamide (DMF) was added and the stirring continued for 20 min. After this time, a solution of 0.42 mmol of the dialcohol (**3**) in DMF was added dropwise and the mixture refluxed at 120 °C for one hour. After this time, the mixture was poured into methanol and the poly(ester) was filtered, washed with cold methanol, dried under vacuum at 40 °C and characterized.
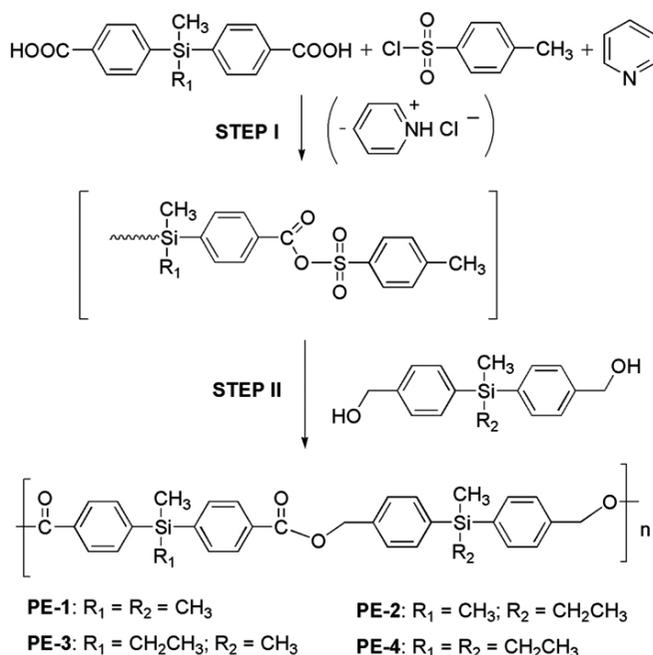
Scheme 2. Synthesis of silicon-containing aliphatic poly(esters).

PE-1. IR (KBr) (cm^{-1}) 3015 (C-H arom.), 2921 (C-H aliph.), 1715 (C=O), 1602, 1488 (C=C arom.), 1391 (Si-Ph), 1458, 1253 (Si-CH$_3$), 1107 (C-O), 821 (arom. *p*-subst.). ^{1}H NMR (DMSO-d_6) (d) (ppm): 0.56-0.89 (m, 12H, Si-CH$_3$), 5.3 (s, 4H ,CH$_2$), 7.1-8.0 (m, 16H, arom.). ^{13}C NMR (DMSO-d_6) (d) (ppm): -4.7 (Si-CH$_3$ alcohol moiety) -2.5 (Si-CH$_3$ acid moiety), 63.5 (CH$_2$), 126.4, 127.8, 128.9, 134.4, 135.5, 136.2, 137.5, 144.2 (8C arom.), 151.6 (C=O). ^{29}Si NMR (DMSO-d_6) (d) (ppm): -6.29 (acid moiety), -5.73 (alcohol moiety). Elem. Anal. Calcd. for [C$_{32}$H$_{32}$O$_4$Si$_2$]$_n$; (536.50)$_n$: C: 71.63 %; H: 5.96 %. Found: C: 71.03 %; H: 5.10 %.

PE-2. IR (KBr) (cm^{-1}) 3035 (C-H arom.), 2879 (C-H aliph.), 1719 (C=O), 1599, 1498 (C=C arom.), 1389 (Si-Ph), 1440, 1212 (Si-CH$_3$), 1090 (C-O), 809 (arom. *p*-subst.). ^{1}H NMR (DMSO-d_6) (d) (ppm): 0.46-0.53 (m, 9H, Si-CH$_3$), 1.19 (t, 3H, CH$_2$-CH$_3$), 2.0 (q, 2H, CH$_2$-CH$_3$), 5.28 (s, 4H, OCH$_2$), 7.3-7.9 (m,16H,arom.). ^{13}C NMR (DMSO-d_6) (d) (ppm): -2.7 (Si-CH$_3$ acid moiety), -2.2 (Si-CH$_3$ alcohol moiety), 5.6 (CH$_2$-CH$_3$), 7.9 (CH$_2$-CH$_3$), 66.5 (OCH$_2$), 126.6, 127.5, 128.8, 130.0, 131.0, 131.9, 134.5, 137.5 (8C arom.), 166.5 (C=O). ^{29}Si NMR (DMSO-d_6) (d) (ppm): -6.14 (acid moiety), -4.03 (alcohol moiety). Elem. Anal. Calcd. for [C$_{33}$H$_{34}$O$_4$Si$_2$]$_n$; (550.51)$_n$: C: 71.99 %; H: 6.18 %. Found: C: 71.22 %; H: 5.95 %.

PE-3. IR (KBr) (cm^{-1}) 3023 (C-H arom.), 2957 (C-H aliph.), 1718 (C=O), 1601, 1488 (C=C arom.), 1389 (Si-Ph), 1390, 1275 (Si-CH$_3$), 1107 (C-O), 809 (arom. *p*-subst.). ^{1}H NMR (DMSO-d_6) (d) (ppm): 0.45-0.55 (m, 9H, Si-CH$_3$), 0.94 (m, 3H, CH$_2$-CH$_3$), 2.2 (t, 2H, CH$_2$-CH$_3$), 5.81 (s, 4H, OCH$_2$), 7.07-8.13 (m,16H,arom.). ^{13}C NMR (DMSO-d_6) (d) (ppm): -5.31 (Si-CH$_3$ alcohol moiety), -3.4 (Si-CH$_3$ acid moiety), 5.7 (CH$_2$-CH$_3$), 7.9 (CH$_2$-CH$_3$), 63.5 (OCH$_2$), 125.9, 126.5, 127.0, 127.7, 128.0, 129.1, 134.4, 135.3 (8C arom.), 159.6 (C=O). ^{29}Si NMR (DMSO-d_6) (d) (ppm): -4.28 (acid moiety), -5.02 (alcohol moiety). Elem. Anal. Calcd. for [C$_{33}$H$_{34}$O$_4$Si$_2$]$_n$; (550.51)$_n$: C: 71.99 %; H: 6.18 %. Found: C: 71.07 %; H: 5.71 %.

PE-4. IR (KBr) (cm^{-1}): 3069 (C-H arom.), 2960 (C-H aliph.), 1719 (C=O), 1598, 1498 (C=C arom.), 1427 (Si-Ph), 1389, 1275 (Si-CH$_3$), 1089 (C-O), 821 (arom. *p*-subst.). ^{1}H NMR (DMSO-d_6) (d) (ppm): 0.49 (s, 6H, Si-CH$_3$), 0.88 (m, 6H, CH$_2$-CH$_3$), 1.04 (m, 4H, CH$_2$-CH$_3$), 5.29 (s, 4H, OCH$_2$), 7.0-7.9 (m, 16H, arom.). ^{13}C NMR (DMSO-d_6) (d) (ppm): -2.4 (Si-CH$_3$), 5.3 (CH$_2$-CH$_3$), 7.9 (CH$_2$-CH$_3$), 66.5 (OCH$_2$), 126.1, 126.6, 127.7, 128.8, 134.1, 134.5, 135.0, 138.2 (8C arom.), 165.6 (C=O). ^{29}Si NMR (DMSO-d_6) (d) (ppm): -4.84 (acid moiety), 5,01 (alcohol moiety). Elem. Anal. Calcd. for [C$_{34}$H$_{36}$O$_4$Si$_2$]$_n$; (564.52)$_n$: C: 72.33 %; H: 6.38 %. Found: C: 71.88 %; H: 5.71 %.

RESULTS AND DISCUSION

Diacid derivatives were obtained from *p*-bromotoluene as starting material following four steps (Scheme 1). In step I, an organo-lithium salt was obtained in nitrogen atmosphere, which was reacted with dichlorodimethylsilane or dichloroethylmethylsilane (step II). The heterogeneous system was stirred and heated for 16 h and then the salts remainders were filtered. The acid hydrolysis yielded the ditolyl derivatives, which were oxidized in acid medium, to the respective diacid, according to a described procedure (step III).[15, 19] The dialcohols were obtained by reduction of the corresponding diacid with LiAlH$_4$ in N$_2$ atmosphere (step IV), also according to a described procedure.[16] All the precursors and monomers were characterized by FT-IR and ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy, and the results were in agreement with the proposed structures.

Poly(esters) were obtained in two steps according to the method described by Mallakpour *et al.*[20] (Scheme 2) in which the diacid is activated by reaction with tosyl chloride in pyridine at room temperature, in order to obtain the ditosylate derivatives (step I). Then, the dialcohol reacts as a nucleophile with the carbonyl carbon of tosylate intermediate to obtain the diester (step II) and finally the poly(ester). The specific activating role of the tosylate is to convert the hydroxyl group of the diacid in a good leaving group. Poly(esters) were precipitated in cold methanol, washed and dried.

PE-2 and **PE-4** samples, both polymers derived from the dialcohol containing an ethyl group bonded to the silicon atom, presented a solid aspect, in contrast to **PE-1** and **PE-3** which showed a semi-solid consistency.

Table I shows the yields for all **PE**s. This parameter is over 95 % in all cases ratifying the activating role of TsCl in the step I of polymerization. This table also shows the inherent viscosity values obtained from DMSO solutions. Except **PE-1**, whose repetitive unit presents the lowest value, all samples showed high h$_{inh}$ indicating a moderate molecular weight. Poly(esters) showed good solubility in polar aprotic solvents such as DMF and DMSO, and also in common organic solvents such as acetone, although a partial solubility in ethanol.

TABLE I.- Yields, inherent viscosity, glass transition temperatures (Tg) and thermal decomposition temperatures (TDT) of the **PE**s.

	Yield (%)	h$_{inh}$ (dL/g)*	Tg (ºC)	TDT** (ºC)	Residue (%) (900 °C)
PE-1	95	0.15	48	227	15
PE-2	95	0.38	64	358	31
PE-3	97	0.24	7	217	14
PE-4	96	0.47	44	337	34

* Inherent viscosity, in DMSO at 25 ºC (c = 0.3 g/dL)
** 10 % weight loss temperature

PEs were also characterized by spectroscopic methods. The results are described in the Experimental Part and were in agreement with the proposed repetitive units. The FT-IR spectra showed the disappearance of the characteristic O-H band of both, the dialcohol and the diacid (Figure 1). Also the band associated to the C=O group was shifted to about 1715- 1719 cm^{-1}, corresponding to the ester group. All samples show the specific absorption bands for the Si-C bond, according with the nature of the carbon atom: aliphatic or aromatic.

^{1}H NMR analyses show, in the aliphatic zone, the protons for the methyl and ethyl groups bonded to silicon atoms, whose integration corresponds to the identity of the respective monomers used. The spectra of all polymers showed the methyl groups from the diacid and dialcohol moieties as a broad signal. The magnetic equivalence of these protons is similar; for this reason, it is not possible obtain pure singlets. Similar results are observed for the protons from the ethyl groups in **PE-4**. On the other hand, the ^{13}C NMR spectra showed clearly the effect of the silicon atom on the CH$_3$ displacement. All signals

appear at negative values due to the difference of electronegativity between Si and C atoms. ^{29}Si NMR spectra allow identifying the monomer from where the signals come. Thus, the -Si(CH$_3$)$_2$- signal from diacid moiety appears at -6.2 ppm approximately (**PE-1** and **PE-2**), while for the dialcohol, the same signal is observed between -5.02 and -5.73 ppm (**PE-1** and **PE-3**). Likewise, the –Si(CH$_3$)(CH$_2$CH$_3$)- signal can be observed at -4.6 ppm approximately for acid moiety (**PE-1** and **PE-4**) and at -4.03 and -5.01 ppm (**PE-2** and **PE-4**).
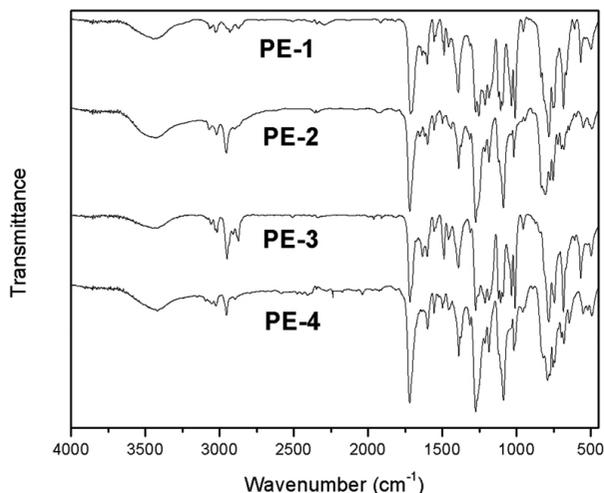

Figure 1. FT-IR spectra of the **PE**s.

Figure 2 shows the DSC curves for **PE**s and the results are summarized in Table I. From these analyses is possible to see that **PE-2** and **PE-4**, both derived from the dialcohol with an ethyl group bonded to the Si atom, show the highest Tg values. This fact is probably due to the high h$_{inh}$ values evidenced for the samples, which are associated to the molecular weights. The exception was **PE-1,** with the lowest h$_{inh}$ value, which showed a Tg value similar to that of **PE-4**. On the other hand, **PE-1** and **PE-4** are symmetric, showing similar Tg values, but different h$_{inh}$ values. In this family of poly(esters) there is no clear relation between the Tg and the h$_{inh}$ values.
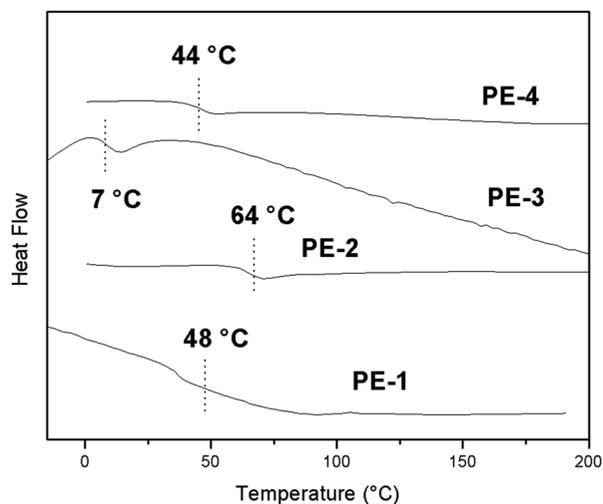

Figure 2. DSC curves of **PE**s (20 °C/min, in nitrogen).

TGA curves are shown in figure 3. From these curves, the thermal decomposition temperatures (TDT) were registered as the temperature at which the weight loss is 10% (Table 1). The tendency was the same as that observed for Tg analyses in the sense that **PE-2** and **PE-4** (solid polymers) showed the highest TDT values, and were considered as good values, especially if we take into account that **PE**s have an aliphatic moiety. On the other hand, **PE-1** and

PE-3 (semi-solid polymers) showed lower but similar TDT values.

Regarding the highest h$_{inh}$, Tg and TDT values, they correspond to **PE-2** and **PE-4**, both polymers derived from the dialcohol containing an ethyl group bonded to the Si atom. Thus, it is possible to conclude that the properties of these polymers depend on the structure of the dialcohol instead of the diacid.

The quantity of residual weight after heating at 900 °C is shown in Table I. The tendency points out that the **PE-2** and **PE-4** samples, both with a –Si(CH$_3$) (CH$_2$CH$_3$)- moiety from dialcohol, showed similar values and higher than those of **PE-1** and **PE-3**. In previous works these residues have always been high assigned to silicon oxide principally.[3-5, 21]
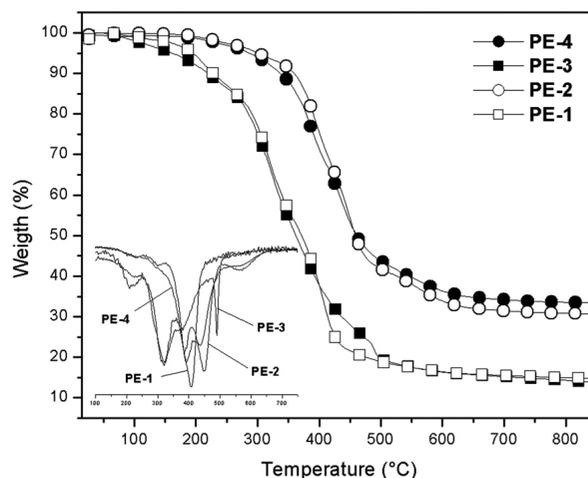

Figure 3. Thermogravimetric and differential curves for **PE**s (20 °C/min in nitrogen).

CONCLUSIONS

Four new aliphatic poly(esters) containing two silicon atoms in the main chain were synthesized and characterized, obtaining good yields and, in two cases, good inherent viscosity values. Polymers derived from the dialcohol containing ethyl and methyl groups bonded to the silicon atom, presented a solid aspect, and gave the best values of h$_{inh}$, Tg and TDT, being the most asymmetrical dialcohol moiety the most determinant part of the polymeric system, in contest to other **PE**s, which showed a semi-solid consistency only. Poly(esters) were soluble in polar aprotic solvents and in common solvents, such as acetone, and were partially soluble in ethanol. **PE-2** and **PE-4** showed a good thermal stability in spite of the aliphatic condition of the dialcohol used.

ACKNOWLEDGEMENTS

REFERENCES

1. Sava, J.; Schulz, B.; Zhu, S.; Bruma, M. High Perform. Polym., **7**, 493 (1995).
2. Bruma, M.; Schulz, B. J. Macromo.l Sci. Polym. Rev. **C41**, 1 (2001).
3. Terraza, C.A.; Tagle, L.H.; Leiva, A. Polym. Bull. **63**, 663 (2009).
4. Tagle, L.H.; Terraza, C.; Leiva, A.; Yazigi, N; Lopez, L. J. Appl. Polym. Sci. **117**, 1526 (2010).
5. Tundidor-Camba, A.; Terraza, C.A.; Tagle, L.H.; Coll, D. J. Appl. Polym. Sci. **120**, 2381 (2011).
6. Tagle, L.H.; Terraza, C.A.; Villagra, H.; Tundidor-Camba, A. Polym. Bull. **67**, 1799 (2011).
7. Tagle, L.H.; Terraza, C.A.; Leiva, A.; Devilat, F. J. Appl. Polym. Sci. **110**, 424 (2008).
8. Tagle, L.H.; Terraza, C.A.; Alvarez, P. Phosphorus Sulfur Silicon Relat. Elem. **181**, 239 (2006).
9. González-Henríquez, C. Tagle, L.H.; Terraza, C.A.; Barriga, A.; Volkmann, U.; Cabrera, A.; Ramos-Moore, E.; Pavez, M. Polym. Int. (in press).

10. Tagle, L.H.; Terraza, C.A.; Leiva, A.; Alvarez, P. J. Appl. Polym. Sci. **114**, 1080 (2009).
11. Tagle, L.H.; Terraza, C.A.; López, L.; Leiva, A. J. Chil. Chem. Soc. **51**, 1041 (2006).
12. Tagle, L.H.; Terraza, C.A.; Alhers, W.; Vera, C. J. Chil. Chem. Soc. **50**, 535 (2005).
13. Tagle, L.H.; Díaz, F.R.; Vega, J.C.; Valenzuela, P. Eur. Polym. J. **39**, 407 (2003).
14. Bruma, M.; Schulz, B.; Kopnick, T.; Robinson, J. High Perform. Polym. **12**, 429 (2000).

15. Migdal, S.; Gertner, D.; Zilkha, A. Can. J. Chem. **46**, 1125 (1968).
16. Rotman, A.; Gertner, D.; Zilkha, A. Can. J. Chem. **45**, 1957 (1967).
17. Kim, H.K.; Ryu, M.K.; Lee, M.S. Macromolecules **30**, 1236 (1997).
18. Terraza, C.A.; Tagle, L.H.; Lembach, H. J. Chil. Chem. Soc. **55**, 137 (2010).
19. Kovaks, H.N.; Delman, A.D.; Simms, B.B. J. Polym. Sci. Part A-1 Polym. Chem. **6**, 2103 (1968).
20. Mallakpour, S.; Kowsari, E. Polym. Bull. **55**, 51 (2005).
21. Tagle, L.H.; Terraza, C.A.; Leiva, A.; Alvarez, P. e-Polymers **34**, 1 (2009).