

Polyesters Based on Two Silarylene or Germarylene Moieties: Synthesis Under Phase-Transfer Conditions

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ABSTRACT: Polyesters (PEs) containing two heteroatoms (Si and/or Ge) in the main chain, derived from the acid dichlorides bis(4-chloroformylphenyl) ethylmethylsilane, bis(4-chloroformylphenyl) diethylsilane, bis(4-chloroformylphenyl) diethylgermane, and bis(4-chloroformylphenyl) di-ⁿbutylgermane and from the diphenols bis(4-hydroxyphenyl) ethylmethylsilane, bis(4-hydroxyphenyl) diethylsilane, bis(4-hydroxyphenyl) diethylgermane, and bis(4-hydroxyphenyl) di-ⁿbutylgermane, were synthesized under phase-transfer conditions with three quaternary ammonium salts as phase-transfer catalysts and three NaOH concentrations in the aqueous phase. PEs were characterized

with IR and NMR spectroscopy, including ²⁹Si-NMR. In general, the yields and intrinsic viscosities were low, and in some cases, an increase in these parameters was shown as a result of the catalyst effect. An increase in the NaOH concentration caused a decrease in the yields because of a hydrolytic process. PEs with Si were thermally more stable than those with Ge. The glass-transition temperatures decreased when the side chains bonded to the heteroatoms were longer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1080–1085, 2009

Key words: glass transition; phase transfer catalysis; polyesters; thermogravimetric analysis (TGA)

INTRODUCTION

Silicon-containing polymers in which the Si atom is bonded to four organic groups have been described by several authors. In this sense, the properties of polyamides, polyimides, polyesters (PEs), polycarbonates, polythiocarbonates, and others have been described and related to the molecular structure of the polymer chain.^{1–13} These works have reported a higher electronegativity of the Si atom in front of the C atom; as a result, the C–Si bond has an ionic character with an increase in the solubility of polymers with silyl aromatic groups, but high thermal stability is maintained.^{3,7} In this sense, the replacement of a carbon atom bonded to four organic groups by silicon or germanium leads to an improvement in the ionic character of the polymer chain because of the difference in the electronegativity between these atoms and C atoms, Si and Ge being stronger acceptor atoms. Therefore, the thermal stability of polymers containing Si–C or Ge–C bonds would be increased because of this higher ionic character.⁴ Also, the bond energy of the bonds C–C, C–Si, and C–Ge is in agreement with this polarity.¹⁴

Our research group has developed the synthesis of condensation polymers containing Ge in the main chain analogous to those with Si. In this sense, we have described the synthesis of polycarbonates, polythiocarbonates, polyurethanes, and PEs containing Ge bonded to four organic groups; moreover, some of them contain Si atoms.^{15–25} In those works, we have described the synthetic processes, the characterization, and the thermal properties [glass-transition temperature (T_g) and thermal decomposition temperature (TDT)], which are influenced by the nature of the heteroatoms and the organic groups bonded to them, which are normally thermally stable.

Two heteroatoms (Si and/or Ge) were incorporated into the main chains of PEs and bonded to four organic aliphatic groups to study the behavior of these kinds of monomers in the synthetic process. There was also the objective of determining how the thermal properties are influenced by the nature of the heteroatoms and the length of the side groups bonded to them in view of the results obtained for those polymers with methyl groups bonded to the heteroatoms.

On the other hand, phase-transfer catalysis has been a very useful technique for the synthesis of condensation polymers such as polycarbonates, polythiocarbonates, and PEs.²⁶ In this process, a diphenolate dissolved in a basic aqueous phase is transferred as an ionic pair with the catalyst,

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normally an onium salt, from the aqueous phase to the organic one, in which the reaction takes place. In this work, we studied the effect of the nature of the catalyst and the influence of the NaOH concentration in the aqueous phase, which can be affected in two ways. First, an increase in the NaOH concentration can increase the yields and the intrinsic viscosity (η_{inh}) because of a salting-out effect, and second, the same increase can hydrolyze either the acid dichloride or the polymeric chains, a decrease in the yields or the η_{inh} value, respectively, being observed. Both effects have been described in the synthesis of polycarbonates and polythiocarbonates with one silarylene or germarylene moiety in the main chain.^{16,19,22}

Continuing our work on the synthesis of condensation polymers containing Si and/or Ge in the main chain, in this work we describe the synthesis of PEs derived from acid dichlorides and diphenols containing the heteroatoms, obtained under phase-transfer conditions, with several ammonium salts used as phase-transfer catalysts, and we evaluate the results on the basis of the yields and the inherent viscosity values. Also, the thermal properties, T_g and TDT, were studied and discussed according to the nature of the heteroatoms (Si or Ge) and the aliphatic groups bonded to them.

EXPERIMENTAL

Materials and measurements

Reagents and solvents (from Aldrich, USA or Riedel de Häen, Seelze, Germany) were used without purification. The following catalysts (from Fluka, Buchs, Switzerland) were used: tetra-*n*-butylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC), and methyltriocetylammmonium chloride (ALIQAT). The IR spectra (KBr pellets or film liquid) were recorded on a PerkinElmer (Waltham, MA) 1310 spectrophotometer, and the ^1H -, ^{13}C -, and ^{29}Si -NMR were recorded on a Bruker (Rheinstetten, Germany) AC-200 400-MHz instrument with CDCl_3 , acetone- d_6 , and dimethyl sulfoxide- d_6 as solvents and tetramethylsilane (TMS) as the internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25°C.

The T_g values were obtained with a Mettler-Toledo (Barcelona, Spain) DSC 821 calorimetric system under an atmosphere of N_2 at 10°C/min. Thermogravimetric analyses were carried out with a Mettler 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 and 800°C at a heating rate of 20°C/min under an N_2 flow.

All the monomers and polymers were characterized with IR and ^1H - and ^{13}C -NMR spectroscopy and, when it was appropriate, with ^{29}Si -NMR spectroscopy.

Monomer synthesis

Diphenols

Bis(4-hydroxyphenyl) ethylmethylsilane, bis(4-hydroxyphenyl) diethylsilane, bis(4-hydroxyphenyl) diethylgermane, and bis(4-hydroxyphenyl) di-*n*-butylgermane were synthesized according to the reported procedures.^{19,22,27}

Acid dichlorides

The acid dichlorides bis(4-chloroformylphenyl) ethylmethylsilane, bis(4-chloroformylphenyl) diethylsilane, bis(4-chloroformylphenyl) diethylgermane, and bis(4-chloroformylphenyl) di-*n*-butylgermane were obtained according to the procedures described previously, in which the ditolyl derivatives bis(*p*-tolyl) ethylmethylsilane, bis(*p*-tolyl) diethylsilane, bis(*p*-tolyl) diethylgermane, and bis(*p*-tolyl) di-*n*-butylgermane were oxidized to the diacids bis(4-carboxyphenyl) ethylmethylsilane, bis(4-carboxyphenyl) diethylsilane, bis(4-carboxyphenyl) diethylgermane, and bis(4-carboxyphenyl) di-*n*-butylgermane, respectively, and then treated with SOCl_2 . All the compounds were characterized with IR and NMR spectroscopy.^{28–31}

PE synthesis

PEs were synthesized according to the following general procedure: 1 mmol of the diphenol was dissolved in 0.5M NaOH and water (total volume = 15 mL), and the catalyst (5% in mol) was added. To this solution, 1 mmol of the acid dichloride in 15 mL of CH_2Cl_2 was added, and the mixture was stirred for 1 h at 20°C. Then, the mixture was poured into 350 mL of methanol. PEs were filtered, washed with methanol, and dried *in vacuo* at 40°C until a constant weight was obtained, and they were characterized.

PE-I

IR (KBr, cm^{-1}): 3024 (H aromatic), 2955, 2875 (CH_3), 2910 (CH_2), 1739 (C=O), 1589, 1495 (C=C aromatic), 1459 (CH_3), 830 (aromatic *p* substitution). ^1H -NMR (CDCl_3 , δ , ppm): 0.52 (s, 3H, CH_3), 0.59 (s, 3H, CH_3), 1.00–1.06 (m, 10H, CH_2CH_3), 7.17 (d, 4H, aromatic), 7.54 (d, 4H, aromatic), 7.62 (d, 4H, aromatic), 8.13 (d, 4H, aromatic). ^{13}C -NMR (CDCl_3 , δ , ppm): -5.32 (Si- CH_3), -4.76 (Si- CH_3), 5.50 (CH_2), 6.01 (CH_2), 7.21 (CH_3CH_2), 7.34 (CH_3CH_2), 121.1, 129.2, 130.3, 134.5, 135.8, 143.6, 151.9 (C aromatic), 165.0 (C=O). ^{29}Si -NMR (CDCl_3 , δ , ppm): -5.25, -4.45.

PE-II

IR (KBr, cm^{-1}): 3025 (H aromatic), 2956, 2875 (CH_3), 2910 (CH_2), 1739 ($\text{C}=\text{O}$), 1589, 1495 (C aromatic), 1459 (CH_3), 829 (aromatic p substitution). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.04–1.21 (m, 20H, CH_2CH_3), 7.23 (d, 4H, aromatic), 7.59 (d, 4H, aromatic), 7.67 (d, 4H, aromatic), 8.20 (d, 4H, aromatic). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 3.57 (CH_2), 4.05 (CH_2), 7.27 (CH_3), 7.37 (CH_3), 121.1, 129.2, 130.3, 133.6, 135.4, 135.2, 142.8, 151.9 (C aromatic), 165.2 ($\text{C}=\text{O}$). $^{29}\text{Si-NMR}$ (CDCl_3 , δ , ppm): -2.56, -3.33.

PE-III

IR (KBr, cm^{-1}): 3024 (H aromatic), 2953, 2871 (CH_3), 2930 (CH_2), 1738 ($\text{C}=\text{O}$), 1587, 1493 (C aromatic), 1458 (CH_3), 824 (aromatic p substitution). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 1.12–1.75 (m, 20H, CH_2CH_3), 7.21–8.25 (m, 16H, aromatic). $^{13}\text{C-NMR}$ (CDCl_3 , δ , ppm): 5.02, 5.28 (CH_2), 8.83, 8.88 (CH_3), 121.4, 128.9, 129.4, 130, 134, 134.7, 135.7, 151.6 (C aromatic), 165.3 ($\text{C}=\text{O}$).

PE-IV

IR (KBr, cm^{-1}): 3024 (H aromatic), 2956 (CH_3), 2925, 2855 (CH_2), 1740 ($\text{C}=\text{O}$), 1597, 1493 ($\text{C}=\text{C}$ aromatic), 1462 (CH_2), 824 (aromatic p substitution).

RESULTS AND DISCUSSION

PEs derived from the diphenols bis(4-hydroxyphenyl) ethylmethylsilane, bis(4-hydroxyphenyl) diethylsilane, bis(4-hydroxyphenyl) diethylgermane, and bis(4-hydroxyphenyl) di- n -butylgermane and the acid dichlorides bis(4-chloroformylphenyl) ethylmethylsilane, bis(4-chloroformylphenyl) diethylsilane, bis(4-chloroformylphenyl) diethylgermane, and bis(4-chloroformylphenyl) di- n -butylgermane were synthesized under phase-transfer conditions in CH_2Cl_2 as the solvent at 20°C with TBAB, BTEAC, and ALIQUAT as catalysts. PEs were characterized with IR and ^1H -, ^{13}C -, and ^{29}Si -NMR spectroscopy, and the spectral data were in agreement with the proposed structures (Fig. 1). PE-IV was insoluble in deuterated solvents, and it was not possible to obtain the NMR spectra.

In all IR spectra of the PEs, it was possible to see the disappearance of the O–H stretching band and to observe a new band between 1738 and 1741 cm^{-1} corresponding to the $\text{C}=\text{O}$ of the ester group. Likewise, no $\text{C}=\text{O}$ band associated with acid chloride was observed in the spectra.

In this study, the catalyst concentration, solvent, reaction time, and temperature remained constant. The nature of the catalyst and the base concentration effects were studied by the measurement of the

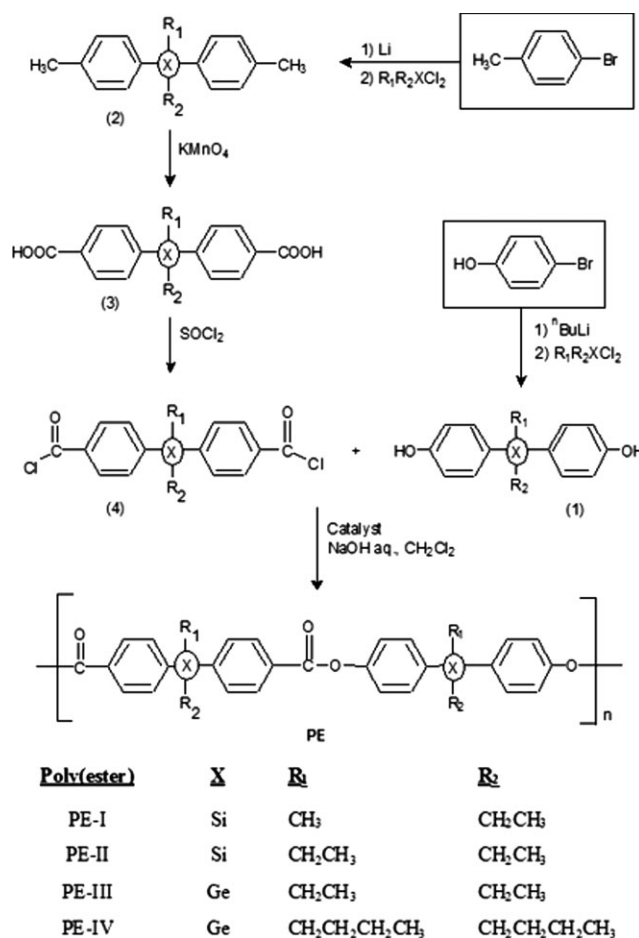


Figure 1 Synthesis and repetitive units of the PEs containing two silarylene or germarylene units.

yields and η_{inh} values. Three base concentrations were studied, the NaOH/diphenol molar ratios being 2/1, 3/1, and 4/1. The volume of the aqueous phase was the same in all cases (15 mL).

The reaction took place when the diphenolate dissolved in the aqueous phase was transferred to the organic one as an ionic pair because of the action of the catalyst. For all PEs, assays without the catalyst were made to evaluate the behavior of the interphase of the system. In all cases, PEs were obtained because of an interphase polycondensation process between the diphenolate dissolved in the aqueous phase and the acid dichlorides dissolved in the organic one. In general, the obtained yields were lower in comparison with those of the systems containing a catalyst.

Table I shows the yields and η_{inh} values obtained for the four PEs at the three NaOH/diphenol molar ratios with the catalysts and for the free-catalyst systems.

PE-I derived from bis(4-chloroformylphenyl) ethylmethylsilane and bis(4-hydroxyphenyl) ethylmethylsilane was obtained with relatively good results but with a low influence of the catalysts, which

TABLE I
Yields and Inherent Viscosities Obtained for the PEs

PE	NaOH/diphenol ^b	Catalyst							
		—		TBAB		ALIQUAT ^a		BTEAC	
		% ^c	η^d	% ^c	η^d	% ^c	η^d	% ^c	η^d
PE-I	2/1	71	0.08	82	0.13	75	0.17	82	0.14
PE-I	3/1	24	0.12	63	0.15	37	0.12	62	0.14
PE-I	4/1	56	0.15	32	0.13	71	0.18	86	0.17 ^e
PE-II	2/1	38	0.12	38	0.13	43	0.14	37	0.15 ^e
PE-II	3/1	7	0.12	14	0.12	30	0.14	17	0.11
PE-II	4/1	2	—	8	0.10	13	0.10	5	0.09
PE-III	2/1	22	0.09	56	0.09	31	0.25	63	0.09
PE-III	3/1	58	0.28	67	0.08	75	0.14 ^e	54	0.09
PE-III	4/1	55	0.26	56	0.14	57	0.12	68	0.08
PE-IV	2/1	55	0.27	23	0.25 ^e			84	0.31
PE-IV	3/1	68	i	91	0.38			70	1.13
PE-IV	4/1	3	—	65	1.09			94	1.12

^a Not used for PE-IV.

^b Molar ratio.

^c Yield.

^d Inherent viscosity in dimethylacetamide at 25°C (concentration = 0.3 g/dL). i = insoluble.

^e Samples used to obtain the T_g values.

showed similar behavior, and the transfer process was in general effective because it was possible to see some increases in the yields and η_{inh} values when the catalysts were used in comparison with the values obtained without them.

Without a catalyst, there was a small increase in the η_{inh} values when the NaOH concentration was increased, but there was a decrease in the yields with a NaOH/diphenol ratio of 3/1, which was probably due to a hydrolytic process. When the NaOH concentration was increased, it was possible to observe an increase in the yield because of a possible salting-out effect.

When TBAB was used as the catalyst, there was a decrease in the yields as the NaOH concentration was increased because of a hydrolytic process of the acid dichloride: the η_{inh} values were practically constant, and normally the hydrolysis of acid chlorides is easier than the hydrolysis of esters. With ALIQUAT and BTEAC, it was possible to see a decrease in the yields at a NaOH/diphenol ratio of 3/1 due to a hydrolytic process, especially with ALIQUAT, which is a lyophobic compound because of its three *n*-octyl chains bonded to the N atom. At higher NaOH concentrations, an increase in the yields was observed, which was probably due to a salting-out effect of the diphenolate from the aqueous phase to the organic one.

For PE-II derived from bis(4-chloroformylphenyl) diethylsilane and bis(4-hydroxyphenyl) diethylsilane, it was possible to see a decrease in the yields when the NaOH concentration was increased as a result of a hydrolytic process of the acid dichloride or the polymeric chains. The influence of the catalysts was

low; in general, similar values of η_{inh} were shown, except at the higher NaOH concentration, at which a decrease in this parameter could be observed. This effect was observed in the polycarbonate derived from the same diphenol²² and was attributed to the length of the chains bonded to the Si atom, in the sense that the phase-transfer process was less effective because of the decrease in the basicity of the diphenol due to the electron-donor effect of the alkyl groups.

PE-III, derived from bis(4-chloroformylphenyl) diethylgermane and bis(4-hydroxyphenyl) diethylgermane, was obtained with good yields in all cases. Without a catalyst, there was an increase in the yields and η_{inh} values when the NaOH concentration was increased because of a salting-out effect of the diphenolate from the aqueous phase to the organic one, which has been described for other systems not showing hydrolytic effects.¹⁹ BTEAC and TBAB were not effective as catalysts for this system and showed practically the same behavior without important differences at the several NaOH concentrations. With ALIQUAT, it was possible to see a decrease in the η_{inh} values when the NaOH concentration was increased. This fact could be due to hydrolysis of the polymeric chains promoted by this lyophobic catalyst, which could transfer the OH⁻ anions necessary for the hydrolysis of the polymeric chains. This behavior has already been observed in other systems.²⁶ The increase in the yields when the NaOH concentration was increased was probably due to a salting-out effect.

For PE-IV derived from bis(4-chloroformylphenyl) di-*n*-butylgermane and bis(4-hydroxyphenyl) di-ⁿ

TABLE II
 T_g and TDT Values for the PEs

PE	T_g (°C)	TDT (°C) ^a	R_{W750} (%) ^b
PE-I	100	465	41
PE-II	64	453	40
PE-III	123	433	40
PE-IV	103	421	39

^a Values taken when the polymers had lost 10 wt %.

^b Residual weight percentage at 750°C.

butylgermane, the process was effective with TBAB and BTEAC in comparison with the results obtained without a catalyst. In fact, there was an increase in the yields and especially the η_{inh} values when BTEAC and TBAB were used as catalysts. BTEAC has been described as a hydrophilic compound and therefore would be adequate for transporting diphenols with high organic contents such as this, in which the Ge central atom is bonded to two ⁿbutyl groups.³² At higher NaOH concentrations, there was an important increase in the η_{inh} values probably due to a salting-out effect of the diphenolate from the aqueous phase to the organic one and also due to a lack of hydrolysis, which was not promoted by this hydrophilic catalyst. With TBAB, the increase in the η_{inh} values was lower than with BTEAC because TBAB is less effective for the transfer of diphenols with high organic contents. The decrease in the yields at higher NaOH concentrations could be due to a hydrolysis of the acid dichloride promoted by this catalyst. This PE was not obtained with ALIQUAT because this catalyst is very lyophobic and is not adequate for the transfer of this diphenol with high organic contents.

On the other hand, the yield of 68% obtained without a catalyst probably corresponded to a very low-molecular-weight species, and it was not possible to obtain the η_{inh} value.

Table II shows the T_g and TDT values obtained for the PEs, with the samples showing very similar η_{inh} values (the samples are shown in Table I). When the side chain was increased, the T_g values decreased in the following order: PE-I and PE-II and then PE-III and PE-IV. Nevertheless, the T_g values would be higher when the side chains have a greater volume (e.g., phenyl vs methyl), but in this case, the increase in the aliphatic side chains also increased the flexibility and consequently led to lower T_g values. However, the T_g value obtained for PE-II was abnormally low.

The TDT values were taken when the PEs showed a 10% weight loss in dynamic thermogravimetry. In other works, it has been pointed out that polymers with Si in the main chain would have a higher thermal stability than those with Ge. It has been reported that the bond polarity has an influence on the thermal stability, in the sense that when the chain polarity is increased, the thermal stability is

also increased. In this case, the C—Si bond has a higher polarity than the C—Ge one because the Ge atom has a higher electronegativity than the Si atom, and consequently, the difference in electronegativity is higher in the C—Si bond.⁴

In this case, PEs with Si in the main chain (PE-I and PE-II) showed a higher TDT than those with Ge (PE-III and PE-IV), without the side groups bonded to the heteroatoms being taken into account. If we compare the increase in the size of the side groups bonded to the heteroatoms, it is also possible to see a decrease in the TDT values for the PE-I and PE-II and PE-III and PE-IV pairs because of the increase in the flexibility of these groups bonded to Si or Ge. On the other hand, the four PEs showed thermal stability above 400°C and can be considered thermally stable, with practically the same residual weight percentage at 750°C (Table II).

CONCLUSIONS

PEs containing two silarylene or germarylene units were synthesized from diphenols and acid dichlorides under phase-transfer conditions. The phase-transfer process was not very effective; in some cases, an increase in the yields was shown when the catalysts were used, but when the NaOH concentration was increased over the stoichiometric condition, there was a decrease in the yields due to the hydrolytic process of the acid dichlorides. PE-IV with two ⁿbutyl groups was obtained with high yields and η_{inh} values with BTEAC, this catalyst being a hydrophilic compound and therefore adequate for transporting a diphenolate derivative with high organic contents.

The thermal properties were in agreement with the statement that PEs with Si atoms are more thermally stable than those with Ge because of the higher ionic character of the C—Si bond compared to the C—Ge bond. On the other hand, the T_g values decreased when the side chains were longer because of the higher flexibility of those chains.

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