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POLYMERIZATION BY PHASE TRANSFER CATALYSIS. 27. SYNTHESIS OF POLYESTERS CONTAINING SILICON OR GERMANIUM. INFLUENCE OF THE BASE CONCENTRATION

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Polyesters derived from diphenols containing Si or Ge and isophthalic and terephthalic acids dichlorides have been synthesized using phase transfer conditions, and characterized by spectroscopic methods. Two phase transfer catalysts and three molar ratios NaOH/diphenol were used, and the results evaluated by the yields and the inherent viscosity values; these are compared with those obtained without catalyst. When the catalysts were used there was an increase of the yields and the η_{inh} values, due to the effectivity of the phase transfer process. Also, when the base concentration was increased, there was an increase of the yields due to a salting out effect which permits a higher transference of the diphenolate to the organic phase in which the reaction takes place, and an increase in the amount of the polyesters and, to a lesser extent, the molecular weight. There was no influence of the higher NaOH concentration on the stability of either the acid dichloride or the polyesters.

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

INTRODUCTION

Condensation polymers with different functional groups and containing Si in the main chain bonded to aliphatic or aromatic groups have been synthesized and their properties studied. In this respect polyamides, polyesters, polyimides, poly(amide-imides), polyhydrazides

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and polyoxydiazols and the respective monomers have been described [1].

However, polymers containing Ge in the main chain and bonded to four carbon atoms have not been described. Only polygermanes, inorganic polymers with a general formula $(\text{GeR}_2)_n$ in which R can be aliphatic or aromatic, have been synthesized by means of chemical and electrochemical methods [2,3].

On the other hand, phase transfer catalysis has been used successfully in the synthesis of several kinds of condensation polymers because it offers important advantages respect to other polymerization methods [4]. By this technique, the dianion is transferred in the form of a ionic pair from the aqueous phase to the organic one, in which the reaction takes place, the concentration of the ionic species in the aqueous phase being an important factor.

Continuing our investigations on the synthesis of condensation polymers containing Si or Ge in the main chain [5,6], in this work we have focused our attention on the synthesis of polyesters derived from diphenols containing Si or Ge and isophthalic or terephthalic acids dichlorides, and also on the study of the influence of the NaOH concentration in the aqueous phase, through the yields and the inherent viscosity values obtained for the polyesters.

EXPERIMENTAL PART

Reagents and solvents (from Aldrich or Riedel de Haen) were used without purification. Isophthaloyl (**m**) and terephthaloyl (**p**) dichloride were recrystallized from petroleum ether. The following catalysts (from Fluka) were used: tetrabutylammonium bromide (TBAB) and benzyltriethylammonium chloride (TEBAC).

The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^1H and ^{13}C NMR on a 200 MHz instrument (Bruker AC-200), using CDCl_3 or acetone- d_6 as solvents and TMS as the internal standard. Viscosimetric measurements were made in a Desreux – Bischoff [7] type dilution viscosimeter at 25°C.

Diphenols

Bis(4-hydroxyphenyl)-dimethyl-silane (**Ia**), bis(4-hydroxyphenyl)-dimethyl-germane (**Ib**), bis(4-hydroxyphenyl)-diphenyl-silane (**IIa**) and bis(4-hydroxyphenyl)-diphenyl-germane (**IIb**) were synthesized according to the procedure described by Davidson [8], 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 up to 5°C and the mixture stirred for one hour. The temperature is decreased to -50°C and 0.025 mol of dimethyl- (**Ia**) or diphenyl-dichloro-silane (**IIa**), dimethyl- (**Ib**) or diphenyl-dichloro-germane (**IIb**) are added in THF, and the temperature is increased up to 10°C and stirred for 2 hours. The mixture is hydrolyzed by adding 5% HCl until a yellow solution (pH = 1) is obtained. The organic layer is dried under MgSO₄ and the solvent evaporated. The brown oil is poured in n-hexane obtaining a white solid which is recrystallized from toluene and characterized.

Bis(p-hydroxyphenyl)-dimethyl-silane (**Ia**): m.p. 170–171°C (Lit. [8] 173–174°C). ¹H NMR δ (ppm) (acetone-d₆): 0.45 (s, 6H, CH₃), 6.84 (d, 4H, arom), 7.35 (d, 4H, arom), 8.41 (s, 2H, OH). ¹³C NMR δ (ppm) (acetone-d₆): -1.36 (CH₃-Si), 116.2, 129.2, 136.8, 159.6 (arom).

Bis(p-hydroxyphenyl)-dimethyl-germane (**Ib**): m.p. 160–161°C (Lit. [8] 161–163°C). ¹H NMR δ (ppm) (acetone-d₆): 0.62 (s, 6H, CH₃), 6.92 (d, 4H, arom), 7.38 (d, 4H, arom), 8.44 (s, 2H, OH). ¹³C NMR δ (ppm) (acetone-d₆): -2.34 (CH₃-Ge), 116.5, 130.8, 136.0, 159.2 (arom).

Bis(p-hydroxyphenyl)-diphenyl-silane (**IIa**): m.p. 219–220°C (Lit. [8] 221–222°C). ¹H NMR δ (ppm) (acetone-d₆): 6.99 (d, 4H, arom), 7.44–7.65 (m, 14H, arom), 8.74 (s, 2H, OH). ¹³C NMR δ (ppm) (acetone-d₆): 116.5, 124.9, 129.1, 130.6, 136.7, 137.3, 139, 160.2 (arom).

Bis(p-hydroxyphenyl)-diphenyl-germane (**IIb**): m.p. 218–219°C (Lit. [8] 218–219°C). ¹H NMR δ (ppm) (acetone-d₆): 7.02 (d, 4H, arom), 7.40–7.62 (m, 14H, arom), 8.70 (s, 2H, OH). ¹³C NMR δ (ppm) (acetone-d₆): 116.9, 126.5, 129.5, 130.2, 136.4, 137.8, 138.4, 159.8 (arom).

Polyesters

Polyesters were synthesized according to the following general procedure: 1 mmol of the diphenol and the catalyst (5% mol) were dissolved in 15 mL of aqueous NaOH, and then a solution of 1 mmol of isophthaloyl (**m**) or terephthaloyl (**p**) dichloride in 15 ml of CHCl₂-CHCl₂ was added at 20°C and the mixture stirred for one hour. After this time, the mixture was poured into methanol and the polymer filtered, washed with methanol, dried until constant weight and characterized.

Polyester **I-a-m**: IR (KBr) (cm⁻¹): 1743 (C=O), 835 (p-arom.), 904, 775, 721 (m-arom.). ¹H NMR (CDCl₃) (δ): 0.6 (s, 6H, CH₃), 7.26 (d, 4H, arom), 7.62 (d, 4H, arom), 7.7 (t, 1H, arom), 8.46 (d, 2H, arom), 9.03 (s, 1H, arom). ¹³C NMR (CDCl₃) (δ): -2.17 (Si-CH₃), 121.1, 129.1, 130.3, 131.8, 135, 135.6, 135.8, 151.8 (arom), 164.2 (C=O).

Polyester **I-a-p**: IR (KBr) (cm^{-1}): 1739 (C=O), 836 (p-arom.). ^1H NMR (CDCl_3) (δ): 0.61 (s, 6H, CH_3), 7.26 (d, 4H, arom), 7.61 (d, 4H, arom), 8.35 (s, 4H, arom). ^{13}C NMR (CDCl_3) (δ): -2.17 (Si- CH_3), 121.1, 129.8, 130.3, 133.9, 135.7, 151.8 (arom), 164.3 (C=O).

Polyester **I-b-m**: IR (KBr) (cm^{-1}): 1742 (C=O), 827 (p-arom.), 904, 800, 722 (m-arom.). ^1H NMR (CDCl_3) (δ): 0.71 (s, 6H, CH_3), 7.27 (d, 4H, arom), 7.58 (d, 4H, arom), 7.7 (t, 1H, arom), 8.48 (d, 2H, arom), 9.03 (s, 1H, arom). ^{13}C NMR (CDCl_3) (δ): -2.82 (Ge- CH_3), 121.4, 129.1, 130.3, 131.8, 134.4, 135, 137.7, 151.4 (arom), 164.3 (C=O).

Polyester **I-b-p**: IR (KBr) (cm^{-1}): 1739 (C=O); 825 (p-arom.). ^1H NMR (CDCl_3) (δ): 0.72 (s, 6H, CH_3), 7.27 (d, 4H, arom), 7.59 (d, 4H, arom), 8.36 (s, 4H, arom). ^{13}C NMR (CDCl_3) (δ): -2.85 (Ge- CH_3), 121.3, 130, 130.3, 134.5, 135.1, 151.4 (arom), 164.3 (C=O).

Polyester **II-a-m**: IR (KBr) (cm^{-1}): 1744 (C=O), 847 (p-arom.), 904, 772, 701 (m-arom.). ^1H NMR (CDCl_3) (δ): 7.27–7.75 (m, 19H, arom), 8.49 (d, 2H, arom), 9.05 (s, 1H, arom). ^{13}C NMR (CDCl_3) (δ): 121.3, 128.1, 129.2, 129.9, 130.2, 131.5, 132, 133.6, 135.1, 136.4, 137.8, 151.2 (arom), 164.2 (C=O).

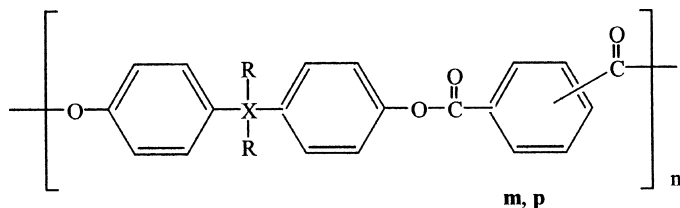
Polyester **II-a-p**: IR (KBr) (cm^{-1}): 1742 (C=O), 827 (p-arom.). ^1H NMR (CDCl_3) (δ): 7.27–7.73 (m, 18H, arom), 8.4 (s, 4H, arom). ^{13}C NMR (CDCl_3) (δ): 121.2, 128.1, 130, 130.4, 132.1, 133.6, 133.9, 136.4, 137.9, 152.2 (arom), 164.1 (C=O).

Polyester **II-b-m**: IR (KBr) (cm^{-1}): 1743 (C=O), 844 (p-arom.), 903, 799, 721 (m-arom.). ^1H NMR (CDCl_3) (δ): 7.27–7.73 (m, 19H, arom), 8.47 (d, 2H, arom), 9.03 (s, 1H, arom). ^{13}C NMR (CDCl_3) (δ): 121.6, 126.5, 129.1, 129.4, 130.3, 131.9, 133.7, 135.1, 135.3, 135.4, 136.7, 151.8 (arom), 164.1 (C=O).

Polyester **II-b-p**: IR (KBr) (cm^{-1}): 1741 (C=O), 825 (p-arom.). ^1H NMR (CDCl_3) (δ): 7.27–7.69 (m, 18H, arom), 8.37 (s, 4H, arom). ^{13}C NMR (CDCl_3) (δ): 121.6, 128.5, 129.5, 130.4, 133.8, 133.9, 135.3, 135.5, 136.7, 151.8 (arom), 164.2 (C=O).

RESULTS AND DISCUSSION

Polyesters derived from the diphenols bis(4-hydroxyphenyl)-dimethylsilane (**Ia**), bis(4-hydroxyphenyl)-dimethyl-germane (**Ib**), bis(4-hydroxyphenyl)-diphenyl-silane (**IIa**), and bis(4-hydroxyphenyl)-diphenyl-germane (**IIb**) with isophthaloyl (**m**) and terephthaloyl (**p**) dichloride, were synthesized under phase transfer conditions in $\text{CHCl}_2\text{-CHCl}_2$ as solvent at 20°C using tetrabutylammonium bromide (TBAB) and benzyltriethylammonium chloride (BTEAC) as catalysts, and characterized by IR and ^1H and ^{13}C NMR spectroscopy. The spectral data were in accordance to the proposed structures.



- Ia** : R = -CH₃; X = Si
Ib : R = -CH₃; X = Ge
IIa : R = -C₆H₅; X = Si
IIb : R = -C₆H₅; X = Ge

In the reaction of all polyesters it was possible to see the disappearance of the OH band, and to observe a new band between 1739–1744 cm⁻¹ corresponding to the C=O of the ester group.

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

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 polyesters experiments without

TABLE 1 Yields and Inherent Viscosities Obtained for the Polyesters Derived from Bis(4-hydroxyphenyl)-dimethyl-silane (**I-a**)

Polyester	NaOH/phenol*	Catalyst					
		-		TBAB		TEBAC	
		%	η^{**}	%	η^{**}	%	η^{**}
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

*Molar ratio.

**Inherent viscosity, in N-methyl-pyrrolidone at 25°C (c = 0.3 g/dL).

TABLE 2 Yields and Inherent Viscosities Obtained for the Polyesters Derived from Bis(4-hydroxyphenyl)-dimethyl-germane (**I-b**)

Polyester	NaOH/phenol*	Catalyst					
		–		TBAB		TEBAC	
		%	η^{**}	%	η^{**}	%	η^{**}
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

*Molar ratio.

**Inherent viscosity, in N-methyl-pyrrolidone at 25°C ($c = 0.3$ g/dL).

catalyst were made for evaluating the interphase of the system. In all cases the polyesters were obtained due to an interphasial polycondensation process between the diphenolate dissolved in the aqueous phase and the isophthaloyl or terephthaloyl dichloride dissolved in the organic phase.

Tables 1–4 show the yields and η_{inh} values obtained for the four diphenols with terephthalic (**p**) or isophthalic (**m**) acid dichlorides at the three NaOH/phenol molar ratios with two catalysts (TBAB and TEBAC), and without catalyst.

TABLE 3 Yields and Inherent Viscosities Obtained for the Polyesters Derived from Bis(4-hydroxyphenyl)-diphenyl-silane (**II-a**)

Polyester	NaOH/phenol*	Catalyst					
		–		TBAB		TEBAC	
		%	η^{**}	%	η^{**}	%	η^{**}
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

*Molar ratio.

**Inherent viscosity, in CHCl₃, at 25°C ($c = 0.3$ g/dL).

TABLE 4 Yields and Inherent Viscosities Obtained for the Polyesters Derived from Bis(4-hydroxyphenyl)-diphenyl-germane (**II-b**)

Polyester	NaOH/phenol*	Catalyst					
		–		TBAB		TEBAC	
		%	η^{**}	%	η^{**}	%	η^{**}
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

*Molar ratio.

**Inherent viscosity, in CHCl_3 , at 25°C ($c=0.3\text{ g/dL}$).

It is possible to see in all cases, with and without catalyst, that there is an increase of the yields when the NaOH concentration is increased, due to a salting out effect which increases the transfer of the ionic pair from the aqueous phase to the organic one. This effect has been described for the dichlorocarbene generation in a concentrated NaOH solution [9].

The same tendency was observed with the η_{inh} values. In fact, for polyesters derived from diphenol **I-a** (Table 1) this increase was observed in all cases and both catalysts were effective as phase transfer agents. Due to the structure of this diphenol and according to the behaviour of bisphenol A poly(thiocarbonate) synthesis [10], TBAB would have been more effective as a consequence of its greater lipophilic structure. In this system TBAB was not as effective as described [10], probably due to the high extraction constant of this catalyst in 1,1,2,2-tetrachloroethane, which implies that is partitioned preferably in the organic phase [11]. On the other hand, TEBAC was more effective probably due to its more hydrophilic character, which induces it to be distributed in both phases.

For polyesters derived from diphenol **I-b** (Table 2), the increase of the η_{inh} values was lower, being TEBAC only effective in increasing of the yields respect to the essays without catalyst. With TBAB it was possible to see an increase of the η_{inh} values, instead of the high extraction constant of this catalyst in this organic solvent. There is no explanation for the low yields obtained with TBAB for the polyester **I-b-m**.

Table 3 shows the results obtained for polyesters derived from diphenol **II-a**. It can be observed that the yields increase when both,

the NaOH concentration is increased and the catalysts is present. However, there is no increase of the η_{inh} values, being the catalysts ineffective to improve the molecular weight of the polyesters, due probably to the high organic content of this diphenol.

Table 4 shows the results obtained for the polyesters derived from the diphenol **II-b**, and the results were analogous to those obtained with the diphenol **II-a**, with the exception that when TBAB was used as catalyst, there was a low increase of the η_{inh} values, being this catalyst more effective than TEBAC.

On the other hand, there were no differences between the diphenols with Si or Ge, probably due to the similar characteristics of these heteroatoms that belong to the same family of the periodic system.

Finally it is possible to conclude that there is an important effect of salting out of the diphenolate from the aqueous phase to the organic one when the NaOH concentration is increased, and this effect would have more influence than the nature of the diphenol and the catalyst. By increasing the ionic concentration in the aqueous phase it would increase the transfer of the ionic pair or the diphenolate to the organic phase. In this sense it is necessary to point out that the limiting step of the phase transfer polymerizations is the transfer process of the dianion to the organic phase rather than the reaction in that phase due to the high reactivity of the acid dichlorides.

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