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L. H. Tagle^a; F. R. Diaz^a; A. Donoso^a

^a Organic Chemistry Department, Faculty of Chemistry Catholic University of Chile, Santiago, Chile

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POLYMERIZATION BY PHASE-TRANSFER CATALYSIS. PART 20. SYNTHESIS OF POLYCARBONATES AND POLYTHIOCARBONATES WITH AN ESTER GROUP IN THE SIDE CHAIN†

L. H. TAGLE,* F. R. DIAZ, and A. DONOSO

Organic Chemistry Department
Faculty of Chemistry
Catholic University of Chile
P.O. Box 306, Santiago 22, Chile

ABSTRACT

Poly(ester-carbonate)s and poly(ester-thiocarbonate)s were synthesized from diphenols containing an ester group in the side chain and phosgene or thiophosgene under phase-transfer conditions. The polymers were characterized by elemental analysis and IR spectroscopy, and the molecular weights were estimated by inherent viscosity measurements. The influence of the nature of the catalysts and the structure of the diphenols on the yields and inherent viscosities was studied. We found that the catalysts were effective for all monomers, although the inherent viscosity values were low due to the insolubility of the polymers in the reaction media. Without catalyst, the polymers were not obtained.

†For Part 19, see Reference 18.

INTRODUCTION

Polymers containing two functional groups have been synthesized, with both functional groups in the main chain or one of them in the side chain. The position of the second group is an important factor in the polymeric properties. Mikroyanidis has synthesized poly(amide-carbonate)s that contain two functional groups in the repeating unit, the amide group being in the main chain and/or the side chain, resulting in different properties that depend on the position of the amide group [1].

The monomeric sequence in copolymers is also an important factor in the control of their properties. Jin and Chang showed that an ordered sequence in the synthesis of copolyesters allows copolymers with thermal and crystalline properties to be obtained that are better than those of copolymers with disordered sequences but with the same total composition [2].

Phase-transfer catalysis [3] is a technique widely used in organic synthesis, due principally to the technical advantages it offers such as mild conditions compared to conventional methods. The catalyst transfers the salt, in the form of an ionic pair, from the aqueous medium to the organic medium where the reaction occurs. The nature of the catalyst and the solvent are important factors in this technique.

Phase-transfer catalysis has been widely used in a great number of condensation polymer syntheses with several functional groups. Imai published works describing the synthesis of polysulfonates, polyphosphonates, polyethers, and polythioethers, and showing the influence of the nature of the catalyst on the inherent viscosities of the polymers [4]. The synthesis of polyesters derived principally from iso or terephthalic acid and bisphenol A have been described [5]. Polycarbonates derived from diphenols with phosgene [6] or 1,4-bis(halomethyl)-benzene with potassium carbonate [7] have been synthesized. In the first case, good yields and high molecular weights were obtained; in the second, good yields, but with low molecular weights, were obtained. In the last case, it is important to point out that potassium carbonate was incorporated into the organic molecule using crown ethers as catalysts. Phase-transfer catalysis has also been used by us in the syntheses of several kinds of condensation polymers, especially polycarbonates [8–12] and polythiocarbonates [8, 10, 12–16].

We are continuing our work on the application of phase-transfer catalysis to polymer synthesis, and in particular to the synthesis of polymers that contain two functional groups in the repeat unit [17, 18], describing the synthesis of poly(ester-carbonate)s and poly(ester-thiocarbonate)s derived from diphenols containing the ester group in the side chain. We also analyzed the effect of several phase-transfer catalysts on the yields and inherent viscosities of the obtained polymers.

EXPERIMENTAL

Materials

Reagents and solvents (from Aldrich or Riedel de Haen) were used without further purification. The following catalysts (from Fluka) were used: benzyltriethylammonium chloride (BTEAC), tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), and methyltrioctylammonium chloride (ALIQAT 336).

Measurements

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 acetone- d_6 as solvent and TMS as internal standard. Viscometric measurements were made in a Desreux-Bischoff [19] type dilution viscometer at 25°C.

Monomers

2,2-Bis(4-hydroxyphenyl)-propanoic acid [20]: 1 mol of phenol and 0.2 mol of pyruvic acid were dissolved in 100 mL of acetic acid and then saturated with dry HCl for 5 hours. After 7 days the mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution until pH 7 was reached. The acid was extracted with NaHCO_3 solution and then poured into a HCl solution, forming a yellow oil which was dissolved in ethyl acetate, washed with NaCl solution, and dried. When ethyl acetate was evaporated, a white solid crystallized, which was filtered, washed with petroleum ether, and recrystallized in a mixture of toluene/ethyl acetate (3/1 v/v). 2,2-Bis(4-hydroxyphenyl)-propanoic acid with a melting point of 177–178°C (lit. 177.5–179°C [24]) was characterized by IR, ^1H -NMR, and ^{13}C -NMR spectroscopy.

3,3-Bis(4-hydroxyphenyl)-butanoic acid [21]: 1 mol of phenol and 0.2 mol of ethylacetoacetate were dissolved in 100 mL of acetic acid and then saturated with dry HCl for 6 hours. After 7 days the mixture was poured into water and the excess of phenol was steam-distilled. Then NaOH was added and the mixture refluxed for 3 hours, after which it was poured into HCl solution. The crude acid separated as a dark oil. The oil was dissolved in ethyl acetate, washed with NaCl solution, and extracted with NaHCO_3 . The aqueous layer was neutralized with HCl, and the oil was dissolved in ethyl acetate. The organic layer was washed with NaCl and dried. When the ethyl acetate was evaporated, the oil was dissolved in toluene at 100°C and the acid crystallized as a white solid, which was filtered, washed with petroleum ether, dried, and characterized by melting point (174–176°C) and IR, ^1H -NMR, and ^{13}C -NMR spectroscopy.

4,4-Bis(4-hydroxyphenyl)-valeric acid was a commercial product.

The methyl and the ethyl esters of the acids 2,2-bis(4-hydroxyphenyl)-propanoic, 3,3-bis(4-hydroxyphenyl)-butanoic, and 4,4-bis(4-hydroxyphenyl)-valeric were obtained according to the following general procedure [21]: 0.15 mol of the acid was dissolved in 2.55 mol of the respective alcohol (methanol or ethanol), and 1.5 mL of H_2SO_4 acid was added. The mixture was refluxed for 16 hours, and then the excess alcohol was evaporated. The oil formed was extracted with diethyl ether and washed with water, NaHCO_3 solution, and dried. When the diethyl ether was evaporated, the crude product was precipitated in a methanol/water mixture (5/1 v/v) and recrystallized in toluene. The methyl and ethyl esters were characterized by melting point and IR, ^1H NMR, and ^{13}C NMR.

Methyl 2,2-bis(4-hydroxyphenyl)-propanoate: mp 129–130°C (lit. 129–130°C [20]). IR (cm^{-1}) (KBr): 3280 (OH); 2980, 2940, 2860 (C–H); 1720 (C=O); 1600, 1500 (C=C); 1260, 1220, 1190 (C–O); 860 (*p*-subst.). ^1H NMR (δ) (ppm) (acetone- d_6): 8.4 (s, 2H, OH); 7.1 (d, 2H, *p*-arom.); 6.8 (d, 2H, *p*-arom.); 3.7 (s, 3H, CH_3); 1.9 (s, 3H, CH_3). ^{13}C NMR (δ) (ppm) (acetone- d_6): 176.8 (C=O); 157.2

(C—OH); 137.2 (C arom.); 130.2 (C arom.); 115.8 (C arom.); 56.1 (C quat.); 52.7 (O—CH₃); 28.2 (C—CH₃).

Ethyl 2,2-bis(4-hydroxyphenyl)-propanoate: mp 125–127°C. IR (cm⁻¹) (KBr): 3240 (OH); 2980, 2940, 2860 (C—H); 1690 (C=O); 1600, 1500 (C=C); 1260, 1210, 1190 (C—O); 860 (*p*-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 8.4 (s, 2H, OH); 7.1 (d, 2H, *p*-arom.); 6.8 (d, 2H, *p*-arom.); 4.2 (q, 2H, O—CH₂); 1.9 (s, 3H, CH₃); 1.2 (t, 3H, CH₂—CH₃). ¹³C NMR (δ) (ppm) (acetone-*d*₆): 176.2 (C=O); 157.2 (C—OH); 137.2 (C arom.); 130.2 (C arom.); 115.8 (C arom.); 61.7 (O—CH₂); 56.1 (C quat.); 28.2 (C—CH₃); 14.7 (CH₂—CH₃).

Methyl 3,3-bis(4-hydroxyphenyl)-butanoate: mp 132–133°C. IR (cm⁻¹) (KBr): 3280 (OH); 2980, 2960, 2880 (C—H); 1710 (C=O); 1600, 1500 (C=C); 1260, 1220, 1190 (C—O); 860 (*p*-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 8.2 (s, 2H, OH); 7.1 (d, 2H, *p*-arom.); 6.8 (d, 2H, *p*-arom.); 3.6 (s, 3H, CH₃); 3.1 (s, 2H, CH₂); 1.9 (s, 3H, CH₃). ¹³C NMR (δ) (ppm) (acetone-*d*₆): 173.2 (C=O); 156.5 (C—OH); 141.2 (C arom.); 129.2 (C arom.); 115.8 (C arom.); 52.7 (O—CH₃); 47.1 (CH₂); 44.9 (C quat.); 28.2 (C—CH₃).

Ethyl 3,3-bis(4-hydroxyphenyl)-butanoate: mp 125–127°C (lit. 127°C [21]). IR (cm⁻¹) (KBr): 3240 (OH); 2940, 2880, 2860 (C—H); 1700 (C=O); 1600, 1500 (C=C); 1260, 1220, 1190 (C—O); 840 (*p*-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 8.2 (s, 2H, OH); 7.1 (d, 2H, *p*-arom.); 6.8 (d, 2H, *p*-arom.); 4.2 (q, 2H, O—CH₂); 3.1 (s, 2H, CH₂); 1.9 (s, 3H, CH₃); 1.2 (t, 3H, CH₂—CH₃). ¹³C NMR (δ) (ppm) (acetone-*d*₆): 173.0 (C=O); 157.2 (C—OH); 141.5 (C arom.); 129.5 (C arom.); 115.6 (C arom.); 61.7 (O—CH₂); 47.1 (CH₂); 44.9 (C quat.); 29.1 (C—CH₃); 14.7 (CH₂—CH₃).

Methyl 4,4-bis(4-hydroxyphenyl)-valerate: mp 137–138°C. IR (cm⁻¹) (KBr): 3280 (OH); 2980 (C—H); 1690 (C=O); 1600, 1500 (C=C); 1260, 1220, 1180 (C—O); 830 (*p*-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 8.3 (s, 2H, OH); 7.0 (d, 2H, *p*-arom.); 6.7 (d, 2H, *p*-arom.); 3.5 (s, 3H, CH₃); 2.3 (t, 2H, CH₂—CH₂); 2.1 (t, 2H, CH₂—CH₂); 1.5 (s, 3H, CH₃). ¹³C NMR (δ) (ppm) (acetone-*d*₆): 174.8 (C=O); 156.5 (C—OH); 141.2 (C arom.); 129.2 (C arom.); 116.0 (C arom.); 52.0 (O—CH₃); 45.4 (C quat.); 37.9 (CH₂—CO); 31.0 (CH₂—CH₂); 28.4 (C—CH₃).

Ethyl 4,4-bis(4-hydroxyphenyl)-valerate: mp 133–135°C (lit. 134–135°C [22]). IR (cm⁻¹) (KBr): 3240 (OH); 2980 (C—H); 1660 (C=O); 1600, 1500 (C=C); 1260, 1220, 1170 (C—O); 830 (*p*-subst.). ¹H NMR (δ) (ppm) (acetone-*d*₆): 8.2 (s, 2H, OH); 7.0 (d, 2H, *p*-arom.); 6.7 (d, 2H, *p*-arom.); 4.0 (q, 2H, CH₂); 2.3 (t, 2H, CH₂—CH₂); 2.1 (t, 2H, CH₂—CH₂); 1.5 (s, 3H, CH₃); 1.1 (t, 3H, CH₂—CH₃). ¹³C NMR (δ) (ppm) (acetone-*d*₆): 177.0 (C=O); 159.1 (C—OH); 143.9 (C arom.); 132.0 (C arom.); 118.6 (C arom.); 63.5 (O—CH₂); 48.0 (C quat.); 40.5 (CH₂—CO); 33.9 (CH₂—CH₂); 31.1 (C—CH₃); 17.5 (CH₂—CH₃).

Polymers

Poly(ester-carbonates) and poly(ester-thiocarbonates) were synthesized according to the following general procedure: 5 mmol of the monomer was dissolved in 25 mL of NaOH 0.5 N and then 0.25 mmol (5%) of the catalyst dissolved in 20 mL of dichloromethane was added. Then, 5 mmol of phosgene (from a toluene solution) or thiophosgene, dissolved in 25 mL of dichloromethane, was added and the mixture was stirred for 60 minutes at 20°C. After this time the mixture was

poured into 400 mL of methanol and the precipitated polymer was filtered, washed with methanol, dried under vacuum to constant weight, and characterized.

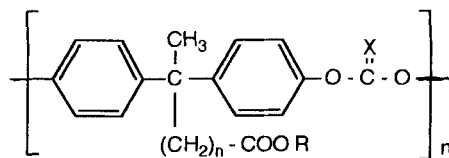
RESULTS AND DISCUSSION

Poly(ester-carbonate)s and poly(ester-thiocarbonate)s with the structures shown in Fig. 1 were synthesized in CH_2Cl_2 as solvent at 20°C under phase-transfer conditions. Their characterizations by IR spectroscopy and elemental analysis were in accord with the proposed structures. In all polymers it was possible to see the absence of the band at $3400\text{--}3250\text{ cm}^{-1}$ corresponding to the OH group. All the poly(ester-carbonate)s showed an absorption band at 1780 cm^{-1} corresponding to the $\text{C}=\text{O}$ of the carbonate group and at 1710 or 1720 cm^{-1} corresponding to the $\text{C}=\text{O}$ of the ester group. Poly(ester-thiocarbonates) showed absorption bands at 1710 or 1720 cm^{-1} corresponding to the $\text{C}=\text{O}$ of the ester group, and at 1200 cm^{-1} corresponding to the stretching of the $\text{C}=\text{S}$ group.

The reaction time was determined by evaluating the hydrolysis of the monomers in the reaction media, for which the monomer was dissolved in 0.5 N NaOH and mixed with CH_2Cl_2 and the catalyst. After 60 minutes the monomer was recovered quantitatively.

In this study only the nature of the catalyst was considered; reaction time, catalyst and base concentrations, and temperature remained constant. In respect to the reaction time, some experiments were carried out for 30 minutes, but the results were very similar to those obtained at 60 minutes.

For all monomers, experiments without catalyst were made in which the polymers were not obtained or where the traces obtained did not allow for any measure-



- | | |
|---|---|
| I a $n=0, X=O, R=-\text{CH}_3$ | III a $n=1, X=O, R=-\text{CH}_3$ |
| I b $n=0, X=S, R=-\text{CH}_3$ | III b $n=1, X=S, R=-\text{CH}_3$ |
| II a $n=0, X=O, R=-\text{CH}_2\text{CH}_3$ | IV a $n=1, X=O, R=-\text{CH}_2\text{CH}_3$ |
| II b $n=0, X=S, R=-\text{CH}_2\text{CH}_3$ | IV b $n=1, X=S, R=-\text{CH}_2\text{CH}_3$ |
| V a $n=2, X=O, R=-\text{CH}_3$ | |
| V b $n=2, X=S, R=-\text{CH}_3$ | |
| VI a $n=2, X=O, R=-\text{CH}_2\text{CH}_3$ | |
| VI b $n=2, X=S, R=-\text{CH}_2\text{CH}_3$ | |

FIG. 1. Structures of poly(ester-carbonate)s and poly(ester-thiocarbonate)s.

ments. These results showed that there is no interfacial polycondensation between the diphenolate dissolved in the aqueous phase and phosgene or thiophosgene dissolved in the organic one.

Table 1 shows the yields and η_{inh} obtained for polymers **Ia** and **Ib**. For poly(ester-carbonate) **Ia** the higher value of η_{inh} was obtained with BTEAC, but with very low yield. For poly(ester-thiocarbonate) **Ib**, the higher values of η_{inh} were obtained with HDTMAB and ALIQUAT, but with BTEAC no polymer was obtained. It is important to point out that the low values of η_{inh} can be due to the insolubility of the polymers in the reaction media, which does not permit the growth of the polymeric chain.

BTEAC is a catalyst with a hydrophilic character [3, 23], even more in dilute aqueous media, and consequently we would expect a low efficiency in the transport of this diphenolate anion, which moreover has an ester group with polar characteristics. However, the behavior of this catalyst with both polymers was very different; it was effective for **Ia** but ineffective for **Ib**, the only difference being the nature of the reagent, phosgene or thiophosgene, which have very similar reactivities with diphenolates. The anomalous result should arise from the synthesis of the poly(ester-carbonate). On the other hand, HDTMAB and ALIQUAT have more lipophilic characteristics and showed better behavior. Moreover, ALIQUAT and BTEAC have Cl^- as a counterion, which is interchanged more easily than Br^- , which is the counterion of the other catalysts [3].

Table 1 also shows the results for polymers **IIa** and **IIb**. All the catalysts showed a similar behavior for the poly(ester-carbonate) **IIa** due to the insolubility of the polymer in the reaction media. For the poly(ester-thiocarbonate) **IIb** the results were very similar to that of poly(ester-thiocarbonate) **Ib**. There is no apparent effect caused by the change of the methyl group by ethyl except for an increase of the yield obtained with BTEAC, which showed a similar behavior. It was effective for **IIa** but ineffective for **IIb**.

Table 2 shows the yields and η_{inh} for polymers **IIIa** and **IIIb**. All the catalysts were effective for the poly(ester-carbonate); the values of η_{inh} were very similar. Also, these polymers were insoluble in the reaction media, which hindered the growth of the polymeric chain. For poly(ester-thiocarbonate), BTEAC was ineffec-

TABLE 1. Yields and Inherent Viscosities Obtained for Poly(Ester-Carbonate)s **Ia** and **IIa** and Poly(Ester-Thiocarbonate)s **Ib** and **IIb**^a

Catalyst	Ia		Ib		IIa		IIb	
	%	η	%	η	%	η	%	η
None	4	—	—	—	2	—	3	—
BTEAC	20	0.12	Traces	—	85	0.13	4	—
TBAB	60	0.10	5	0.07	64	0.12	55	0.07
HDTMAB	22	0.09	65	0.12	85	0.13	45	0.13
ALIQUAT	91	0.08	94	0.13	90	0.12	60	0.12

^a η : inherent at 25°C in *N,N*-dimethylformamide ($c = 0.3$ g/dL).

TABLE 2. Yields and Inherent Viscosities Obtained for Poly(Ester-Carbonate)s **IIIa** and **IVa** and Poly(Ester-Thiocarbonate)s **IIIb** and **IVb**^a

Catalyst	IIIa		IIIb		IVa		IVb	
	%	η	%	η	%	η	%	η
None	1	—	Traces	—	1	—	—	—
BTEAC	50	0.09	Traces	—	42	0.10	Traces	—
TBAB	50	0.12	15	0.09	63	0.11	10	0.06
HDTMAB	35	0.08	60	0.14	31	0.10	76	0.13
ALIQUAT	75	0.09	90	0.13	94	0.08	91	0.13

^a η : inherent at 25°C in *N,N*-dimethylformamide ($c = 0.3$ g/dL).

tive but the other catalysts showed similar results. Table 2 shows the results obtained for polymers **IVa** and **IVb**; the results are very similar to those obtained for analogous polymers with the methyl group. It is possible to see that the change of the methyl group by ethyl in the ester group, which implies an increase of the lipophilicity, does not produce important changes in the η_{inh} values. Also, the behavior of BTEAC was anomalous in the sense that it was effective in the synthesis of **IIIa** and **IVa** but ineffective for **IIIb** and **IVb**.

Table 3 shows the results obtained for polymers **Va** and **Vb**. The η_{inh} values were similar for all catalysts and lower than those obtained for the other polymers. The solubility of these polymer was poor, and it was only possible to measure η_{inh} in a mixture of phenol/1,1,2,2-tetrachloroethane [24]. It is possible that because of this fact, a decrease of both values, yields and η_{inh} , takes place. The exception was the poly(ester-thiocarbonate) **Vb**, obtained with HDTMAB. This catalyst has the characteristics of a micellar agent, and it has an exceptional behavior as was described in previous papers [3, 13, 14, 16].

TABLE 3. Yields and Inherent Viscosities Obtained for Poly(Ester-Carbonate)s **Va** and **VIa** and Poly(Ester-Thiocarbonate)s **Vb** and **VIIb**^a

Catalyst	Va		Vb		VIa, %	VIIb, %
	%	η	%	η		
None	4	—	—	—	2	—
BTEAC	8	0.05	Traces	—	19	2
TBAB	32	0.06	Traces	—	50	6
HDTMAB	17	0.07	81	0.13	62	56
ALIQUAT	59	0.07	48	0.07	73	44

^a η : inherent at 25°C in phenol/tetrachloroethane (6.5/4 v/v) ($c = 0.3$ g/dL).

Table 3 also shows the results obtained for polymers **VIa** and **VIb**. These polymers are insoluble in the reaction media and in all organic solvents. In this case the change of the methyl group by ethyl in the ester group made the polymers insoluble. In spite of this, the phase-transfer process was effective because polymers were not obtained without catalysts.

It is necessary to point out that BTEAC, described as a hydrophilic catalyst [3, 23], has been effective for the synthesis of polycarbonates [9] and polythiocarbonates [16] derived from lipophilic diphenols. This fact was not observed in this work, and BTEAC was less effective in the synthesis of polymer **Va**, with a longer side chain, than in the synthesis of polymer **Ia**, which showed the higher η_{inh} value. There is no good reason for the behavior of BTEAC either with the poly(ester-carbonate)s or the poly(ester-thiocarbonate)s; it is effective for the first but ineffective for the second, with the only difference the nature of one substrate, phosgene and thiophosgene, which have similar reactivities.

For all polymers it can be seen that there is a similar trend in the behavior of the catalysts which have a limited action due to the insolubility of the polymers in the reaction media. Also, it can be observed that when the organic character of the monomer is increased, either by an increase of the side chain or by a change of the methyl group by ethyl in the ester group, the η_{inh} values decrease due to the fact that the insolubility of the polymers increases.

On the other hand, comparison of the polymer having methyl bonded to the ester group with that having ethyl, shows that there are not important differences, and the trends in yields and η_{inh} are similar. The exceptions were polymers **VIa** and **VIb** which were insoluble and whose η_{inh} s were not determined but whose yields showed the same trend.

In general, the limiting step of phase-transfer-catalyzed polymerizations is the transfer of the dianion to the organic phase rather than the reaction in that phase due to the high reactivity of phosgene or thiophosgene. Nevertheless, in the synthesis of these polymers the principal limitation was their insolubility in the reaction media, which hindered the growth of the polymeric chain. However, it is possible to conclude that phase-transfer catalysis is a suitable method for the synthesis of these poly(ester-carbonate)s and poly(ester-thiocarbonate)s because these polymers cannot be obtained with a catalyst.

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