

# POLYMERIZATION BY PHASE TRANSFER CATALYSIS—17.\* POLYESTERS SYNTHESIS FROM 2,2-BIS(4-CHLOROFORMYLPHENYL)-PROPANE AND 4,4'-BIPHENYL-DICARBOXYL CHLORIDE WITH DIPHENOLS

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(Received 12 October 1992)

**Abstract**—Polyesters from 2,2-bis(4-chloroformylphenyl)-propane (**I**) and 4,4'-biphenyl-dicarboxyl chloride (**II**) as diacid chlorides, and 2,2-bis(4-hydroxyphenyl)-propane (bisphenol-A) (**a**), 1,1-bis(4-hydroxyphenyl)-4-methyl-cyclohexane (**b**), and 4,4'-dihydroxy-biphenyl (**c**) as diphenols, were synthesized under phase transfer conditions using several ammonium and phosphonium salts as catalysts in a dichloromethane/NaOH system for two reaction times. Polyesters were characterized by i.r. and <sup>1</sup>H-NMR spectroscopy and elemental analysis; the molecular weights were estimated by viscosity measurements. The influences of the nature of the catalysts and the reaction time were evaluated by the yields and the inherent viscosities. Lipophilic catalysts were effective at short reaction times but, when the reaction time is increased, there is a decrease of the inherent viscosity due to the hydrolysis of the polymeric chains. This effect is not observed when the catalyst has a more hydrophilic character.

## INTRODUCTION

Polyesters are widely known polymers because of important industrial applications. Particularly, aromatic polyesters derived from bisphenol-A [2,2-bis(4-hydroxyphenyl)propane] and related diphenols and aromatic acid chlorides, have been commercialized and used as high-performance engineering plastics [1]. The introduction of modifications in their structure, such as the incorporation of flexible moieties in the polymer backbone, leads to new materials and applications.

In general, polyesters have been synthesized by interfacial polycondensation between an organic solution of the diacid chloride and an aqueous solution of the diphenolate, or by solution polycondensation at low temperature. Phase transfer catalysis polycondensation has also been used for the synthesis of several kinds of polyesters. Several authors have published on the synthesis of polyesters derived from bisphenol-A using phase transfer conditions [2-4], because of the advantages of this technique.

Phase transfer catalysis [5, 6] is a technique in which an anion forms with a catalyst (normally an ammonium or phosphonium salt) an ionic pair, which is transferred to the organic phase in which it reacts rapidly with the substrate because it has low solvation due to the normally low polarity of the solvent. In this technique, the nature of the catalyst is one of the most important factors. An increase of the number of carbon atoms around the central atom of the onium salt increases the lipophilicity of the

catalyst and increases the extraction constant in the organic solvent [7].

Phase transfer catalysis has been used in our laboratory for the synthesis of polyesters [8, 9] and poly(ether-ester)s [10]. We studied the influence of the nature of the catalysts and the structure of the diphenols. Also we have studied the influence of the catalysts on the hydrolysis of the polymeric chains, finding that the nature of the catalysts exerts an important effect, in the sense that the higher its lipophilic character the greater is the possibility of hydrolysis of the polymeric chains since the possibility of transport of OH<sup>-</sup> ions is greater [11].

Also we have used this technique for the synthesis of polycarbonates [11-14], polythiocarbonates [13-17] and copoly(carbonate-thiocarbonate)s [18, 19]; we studied the influence of the nature of the catalysts in the yields and inherent viscosities.

Continuing our work in the application of phase transfer catalysis in the synthesis of polymers, we now describe the synthesis of polyesters derived from 2,2-bis(4-chloroformylphenyl)-propane and 4,4'-biphenyl-dicarboxyl chloride with bisphenol-A and other diphenols, using several ammonium and phosphonium salts and two reaction times, and evaluating the results by the yields and inherent viscosities.

## EXPERIMENTAL PROCEDURES

### Materials

Reagents and solvents (Aldrich) were used without further purification. The following catalysts (Fluka) were used: benzyltriethylammonium chloride (BTEAC), tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), methyltriocetylammonium chloride (Aliquat 336<sup>TM</sup>) and hexadecyltributylphosphonium bromide (HDTBPB).

\*Part 16 see L. H. Tagle, F. R. Diaz, R. Concha and H. Cisternas. *Int. J. Polym. Mat.* (in press).

## *Measurements*

The i.r. spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, the  $^1\text{H-NMR}$  on a 100 MHz instrument (Varian XL-100) using  $\text{CDCl}_3$  or acetone- $d_6$  as solvent and TMS as internal reference. Viscometric measurements were made using a Desreux-Bischoff [20] type dilution viscometer with  $\text{CHCl}_3$  solutions at  $25^\circ$ .

### *Monomer synthesis*

2,2-Bis(4-hydroxyphenyl)-propane (**Bisphenol-A**) (**a**) and 1,1-bis(4-hydroxyphenyl)-4-methyl-cyclohexane (**b**) were synthesized according to a procedure described by McGreal *et al.* [21], and 4,4'-dihydroxy-biphenyl (**c**) was obtained commercially.

2,2-Bis(4-chloroformylphenyl)-propane ([bd(I)] was synthesized by the following procedure: 5.1 g of 2,2-bis(4-carboxyphenylene)-propane, obtained by a procedure described previously [22-24], were mixed with thionyl chloride and refluxed for 2 hr. Then, the excess of thionyl chloride was distilled off and the product was recrystallized from *n*-hexane and characterized. m.p. 95-96° (Ref. [24] 95-96°).

4,4'-Diphenyl-dicarboxyl chloride was synthesized from commercial 4,4'-dicarboxy-biphenyl and thionyl chloride by the same procedure. The product was recrystallized from n-hexane and characterized. m.p. 187-189° (Ref. [25] 184°).

### *Polymer synthesis*

Polyesters were synthesized according to the following general procedure: 2.5 mmol of the diphenol and 0.125 mmol (5%) of the catalyst were dissolved in 25 ml of 0.3 M NaOH and 20 ml of H<sub>2</sub>O and mixed with 20 ml of CH<sub>2</sub>Cl<sub>2</sub>. Then 2.625 mmol of the diacid chloride dissolved in 5 ml of CH<sub>2</sub>Cl<sub>2</sub> were added. The mixture was stirred at 20°, and then the organic layer was separated and poured into methanol. The precipitated polymer was filtered, washed with methanol, dried under vacuum at 40°, and characterized.

## RESULTS AND DISCUSSION

Polyesters were synthesized according to the following reaction:

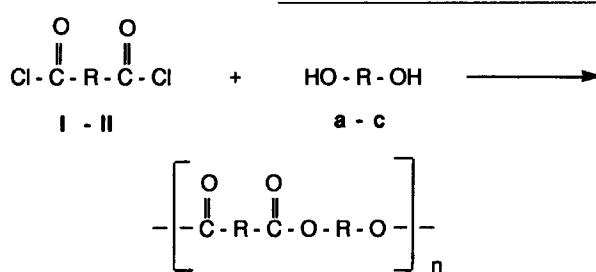
and were characterized by i.r. and  $^1\text{H-NMR}$  and elemental analysis. The results are summarized in Tables 1 and 2, and are in accord with the proposed structures. Polyesters **Ib** and **IIb** were insoluble in  $\text{CDCl}_3$  and acetone- $d_6$ , and the  $^1\text{H-NMR}$  spectra were not obtained.

Two variables were considered in the phase transfer process, viz. the nature of the catalyst and the reaction time. Solvent, temperature and catalyst and base concentration remained constant.

Polycondensation occurs when the diphenolate is transferred, in the form of an ionic pair with the catalyst, from the aqueous phase to the organic, according to the general mechanism of phase transfer catalysis proposed by Starks [6, 7]. Normally the ionic pair in the organic phase has very low solvation and therefore is highly reactive.

Without catalyst, good yields but low values of inherent viscosities were obtained for polyesters derived from I and II; therefore an interfacial polycondensation between the diphenolate dissolved in the aqueous phase and the diacid chloride dissolved in the organic phase cannot be discarded.

Table 3 shows the yields and inherent viscosities obtained for polyesters I(a-c). For polyester Ia, there is an increase of the inherent viscosity and the yield when the reaction time is increased, except for ALL-QUAT in which both values are the same, and for HDTMAB with which there is a decrease in the inherent viscosity. BTEAC had poor behaviour as catalyst with this diphenolate in dilute solution because of its hydrophilic nature [26], unsuitable to transport a dianion that also is hydrophilic. The same behaviour of BTEAC with bisphenol-A has been described for the syntheses of other kinds of polymers [11, 15].



where

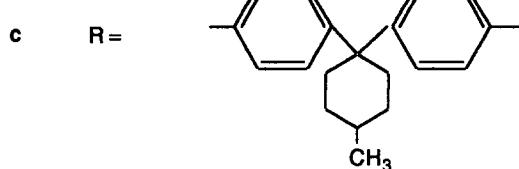
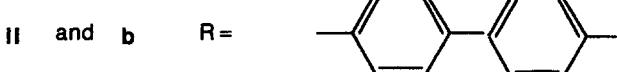
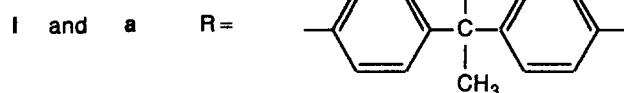


Table 1. Spectroscopic data and elemental analyses of polyesters I(a-c)

	Ia	Ib	Ic
i.r.(cm <sup>-1</sup> ) KBr	2980(CH <sub>3</sub> ) 1730(C=O) 1600(Ar) 1500(Ar) 1260(C—O) 1170(C—O) 860( <i>p</i> -subs.)	2980(CH <sub>3</sub> ) 1740(C=O) 1600(Ar) 1500(Ar) 1270(C—O) 1160(C—O) 860( <i>p</i> -subs.)	2920(CH <sub>3</sub> ) 1730(C=O) 1600(Ar) 1500(Ar) 1260(C—O) 1170(C—O) 850( <i>p</i> -subs.)
<sup>1</sup> H-NMR ( $\delta$ ) (ppm) CDCl <sub>3</sub>	1.68(s,6H,CH <sub>3</sub> ) 1.74(s,6H,CH <sub>3</sub> ) 7.42-7.08(m,12H,ArH) 8.16(d,4H,ArH)	—	0.86(d,3H,CH <sub>3</sub> ) 1.74(s,6H,CH <sub>3</sub> ) 2.74-0.86(m,9H,CH <sub>2</sub> ) 7.5-7.04(m,12H,ArH) 8.16(d,4H,ArH)
Elemental analyses	Calc. C: 80.67% H: 5.88% Enc. C: 79.19% H: 5.97%	Calc. C: 80.18% H: 5.07% Enc. C: 80.82% H: 5.78%	Calc. C: 81.51% H: 6.42% Enc. C: 80.11% H: 6.79%

With TBAB, there is an important increase of the inherent viscosity when the reaction time is increased. In fact, this catalyst has a symmetric structure and therefore the ion pair has a suitable separation between the anion and the cation making it highly reactive, as described previously for the synthesis of the polythiocarbonate of bisphenol-A, in which this catalyst showed the best behaviour [15].

ALIQUAT and HDTBPB, both of lipophilic nature, showed good behaviour, being adequate to transport a hydrophilic dianion of this type.

The decrease of the inherent viscosity with HDTMAB can be due to a hydrolytic process because the special structure of this catalyst, which is capable of forming micelles [11] and a process of this kind is impossible to rule out.

Polyester Ia was insoluble in all solvents and precipitated in the reaction media. For this reason, the inherent viscosities were not obtained. In spite of this, it can be seen an increase of the yield over those obtained without catalyst, which is evidence for the efficiency of the phase transfer process.

ALIQUAT, TBAB and HDTBPB surprisingly were effective for polyester Ic because they are lipophilic catalysts, especially ALIQUAT and HDTBPB, and ineffective for transporting lipophilic dianions such as that from c. However polyesters showed a decrease of the inherent viscosity when the reaction time was increased, due probably to a hydrolytic process promoted by these lipophilic catalyst, as described for the synthesis of polycarbonates [11].

HDTMAB was practically ineffective as catalyst and the polyester was obtained principally by an interfacial polycondensation process. BTEAC was effective especially at 120 min. This catalyst has been described as hydrophilic [26], so allowing transport of more lipophilic dianions such as this. On the other hand, this catalyst has Cl<sup>-</sup> as counterion, which is exchanged more easily than Br<sup>-</sup>, the counterion of the other catalysts [27].

Table 4 shows the yields and inherent viscosities obtained for polyesters II(a-c). There was a similar tendency in the behaviour of the catalysts as that observed for polyesters I(a-c).

For polyester IIa all the catalysts were effective. With BTEAC, we obtained lower values of inherent viscosity, especially at 60 min of reaction, but there is an increase at 120 min, due to the hydrophilic character of this catalysts [26] as mentioned previously. With TBAB also, there is an increase of the inherent viscosity when the reaction time is increased, due the symmetry of this catalyst which produces an adequate separation between the anion and the cation in the ionic pair with this diphenolate [15].

With ALIQUAT and HDTBPB, decrease of the inherent viscosity was observed when the reaction time was increased, due principally to a hydrolytic process. When all the diphenolate was transferred and reacted in the organic phase, it is possible that the lipophilic catalysts can transfer OH<sup>-</sup> anions that promote hydrolysis of the polymeric chains, and therefore the inherent viscosity will decrease.

Table 2. Spectroscopic data and elemental analyses of polyesters II(a-c)

	IIa	IIb	IIc
i.r.(cm <sup>-1</sup> ) KBr	2780(CH <sub>3</sub> ) 1730(C=O) 1600(Ar) 1500(Ar) 1260(C—O) 1160(C—O) 850( <i>p</i> -subs.)	1720(C=O) 1600(Ar) 1480(Ar) 1260(C—O) 1180(C—O) 840( <i>p</i> -subs.)	2920(CH <sub>3</sub> ) 1720(C=O) 1600(Ar) 1500(Ar) 1250(C—O) 1160(C—O) 840( <i>p</i> -subs.)
<sup>1</sup> H-NMR ( $\delta$ ) (ppm) CDCl <sub>3</sub>	1.76(s,6H,CH <sub>3</sub> ) 7.38-7.2(c,8H,ArH) 7.82(d,4H,ArH) 8.36(d,4H,ArH)	— — — —	0.87(d,3H,CH <sub>3</sub> ) 2.7-0.87(m,9H,CH <sub>2</sub> ) 7.54-7.08(m,8H,ArH) 7.8(d,4H,ArH) 8.34(d,4H,ArH)
Elemental analyses	Calc. C: 80.18% H: 5.07% Enc. C: 78.74% H: 5.38%	Calc. C: 79.59% H: 4.08% Enc. C: 78.29% H: 4.34%	Calc. C: 81.14% H: 5.74% Enc. C: 80.42% H: 5.92%

Table 3. Yields and inherent viscosities of polyesters I(a-c)

Time(min):	Polymer											
	Ia				Ib				Ic			
	%	$\eta$	%	$\eta$	%	$\eta$	%	$\eta$	%	$\eta$	%	$\eta$
—	28	0.09	67	0.12	—	—	37	—	71	0.10	97	0.14
BTEAC	48	0.11	89	0.25	65	—	81	—	88	0.14	90	0.40
TBAB	81	0.17	89	0.41	86	—	90	—	92	0.47	96	0.39
HDTMAB	84	0.46	90	0.36	86	—	62	—	94	0.22	80	0.15
ALIQUAT	90	0.50	90	0.50	80	—	71	—	89	0.23	80	0.18
HDTBPB	88	0.45	93	0.49	88	—	69	—	96	0.68	95	0.33

$\eta$ , inherent ( $\text{dl g}^{-1}$ ), in  $\text{CHCl}_3$  at  $25^\circ$ ,  $c = 0.5 \text{ g dl}^{-1}$ .

Table 4. Yields and inherent viscosities of polyesters II(a-c)

Time (min):	IIa				IIb				IIc			
	60		120		60		120		60		120	
	%	$\eta$										
—	67	0.10	78	0.16	49	—	64	—	98	0.23	97	0.26
BTEAC	91	0.30	98	0.53	76	—	79	—	99	0.51	98	0.54
TBAB	96	0.63	96	0.90	88	—	80	—	99	0.65	99	0.65
HDTMAB	98	0.60	95	0.58	94	—	96	—	96	0.45	97	0.36
ALIQUAT	99	1.00	96	0.33	90	—	93	—	99	1.36	91	0.53
HDTBPB	99	0.56	66	0.12	92	—	95	—	99	1.31	80	0.44

$\eta$ , inherent ( $\text{dl g}^{-1}$ ), in  $\text{CHCl}_3$  at  $25^\circ$ ,  $c = 0.5 \text{ g dl}^{-1}$ .

Polyester IIb was insoluble in all organic solvents and in the reaction media, and therefore we cannot obtain the inherent viscosities. However, we can observe an increase of the yields when the catalysts were used, even that when the catalyst were not used.

For polyester IIc, the best catalysts were ALIQUAT and HDTBPB at 60 min. Although both catalysts and diphenolate have lipophilic character, these catalysts showed good behaviour as transfer agents for this polyester, because of that their great volume causes the positive and negative charges of the ionic pair to have a wider separation and so a higher reactivity with the diacid chloride. When the reaction time is increased, there is an important decrease of the inherent viscosity due to a hydrolytic process, which is favoured with these lipophilic catalysts [10, 11].

With BTEAC and TBAB, there is no influence of the reaction time because these catalysts did not favor a hydrolytic process due their more hydrophilic character [26]. HDTMAB showed the worst behaviour and some hydrolysis can be seen when the reaction time is increased.

In general, for these polyesters, we obtained good yields and inherent viscosities, which are strongly influenced by the nature of the catalysts. The limiting step of the polymerization process is the transfer of the dianion rather than the reaction in the organic phase because both diacid chlorides and diphenolate, are highly reactive species. However a hydrolytic process, also influenced by the nature of the catalyst, can be observed especially when the catalyst has lipophilic nature.

Finally, it can be concluded that the phase transfer polymerization is a more suitable technique for the synthesis of polyesters of this kind than the interfacial process.

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