

Polymerization by phase transfer catalysis

10. Polycarbonates and polythiocarbonates from diphenols with chlorinated aromatic side groups*

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SUMMARY

Polycarbonates and polythiocarbonates from phosgene and thiophosgene respectively, were synthesized from diphenols with chlorinated aromatic side groups under phase transfer conditions using several quaternary ammonium and phosphonium salts and dichloromethane as solvent. Polymers were characterized by IR and ^1H NMR, and the molecular weights estimated by viscosity measurements. The influence of the catalysts and the structure of the diphenols were studied.

INTRODUCTION

Phase transfer catalysis^[1-2] is a widely used technique in organic synthesis, and can be applied to reactions between dissolved salts in an aqueous media and substrates in an organic media. Thus, the catalyst form an ion pair with the salt and is transferred to the organic phase due to its organic character. In the organic phase, and as is normally of low polarity, the ion pair reacts rapidly.

Both, the nature of the catalyst and the organic solvent are the two most important factors that affect the transfer process. An increase of the number of carbon atoms around the central atom of the onium salt, increase the lipophilicity of the catalyst and increase the extraction constant in the organic solvent^[3].

This technique has been used in polymer synthesis. In our laboratory we have synthesized a great number of polycarbonates^[4],

*for part 9, see ref. 9

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polythiocarbonates^[5-8] and copoly(carbonate-thiocarbonate)s^[9] from several diphenols and phosgene or thiophosgene. In these works we have studied the influence of the nature of the catalyst and the structure of the diphenols. Also we have studied the influence of the catalyst on the hydrolysis of the polycarbonate or polythiocarbonate, finding that the nature of the catalyst exerts an important effect, in the sense that the higher its lipophilic character the higher the possibility of hydrolysis of the polymer since the possibility of transport OH^- ions is greater^[4,10].

Continuing our work on polymer synthesis under phase transfer conditions^[9], in this work we describe the synthesis of polycarbonates and polythiocarbonates from diphenols with chlorinated aromatic side groups and phosgene or thiophosgene, respectively, using several ammonium and phosphonium salts as catalysts and the conditions previously described^[5].

EXPERIMENTAL PART

Diphenols 2,2-bis(4-hydroxy-phenyl)-2-(4-chloro-phenyl)-ethane; 2,2-bis(4-hydroxy-phenyl)-2-(3-chloro-phenyl)-ethane; and 2,2-bis(4-hydroxy-phenyl)-2-(3,4-dichloro-phenyl)-ethane were synthesized from phenol and 4-chloro-acetophenone; 3-chloro-acetophenone; and 3,4-dichloro-acetophenone respectively, according to the procedure described by McGreal^[11]. Phosgene, thiophosgene, and solvents (from Merck) were used without purification. The following catalysts (from Fluka) were used: tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), benzyltriethylammonium chloride (BTEAC), hexadecyltributylphosphonium bromide (HDTBPB), and methyltrioctylammonium chloride (Aliquat 336™).

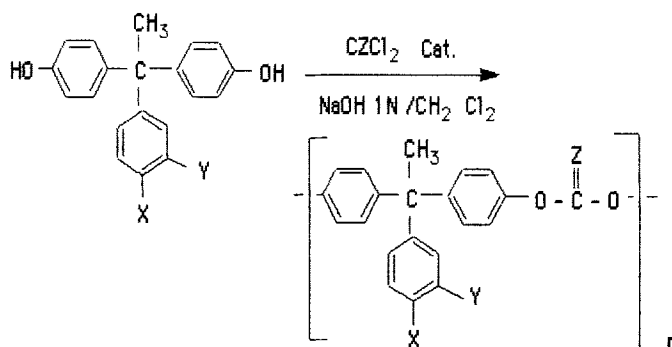
The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, the ^1H NMR on a 100 Mz instrument (Varian XL-100), using CDCl_3 as solvent and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischoff^[12] type dilution viscosimeter in CHCl_3 solution at 25°C.

In a typical polycondensation reaction, 5 mmol of the diphenol and 0.25 mmol of the catalyst dissolved in 30 mL of 1 M NaOH were mixed with 20 mL of CH_2Cl_2 . Then, 5 mmol of phosgene or thiophosgene dissolved in 10

mL of CH_2Cl_2 were added at once. The mixture was stirred at 20°C for 30 or 60 minutes. The organic layer was separated and poured into methanol. The precipitated polymer was filtered, washed with methanol, and dried under vacuum until constant weight. The polymers were characterized by IR, ^1H NMR, and elemental analysis.

RESULTS AND DISCUSSION

Polycarbonates and polythiocarbonates were obtained according to the following reaction:



where

Ia:	X = Cl	Y = H	Z = O
Ib:	X = Cl	Y = H	Z = S
IIa:	X = H	Y = Cl	Z = O
IIb:	X = H	Y = Cl	Z = S
IIIa:	X = Y = Cl		Z = O
IIIb:	X = Y = Cl		Z = S

and the structures were confirmed by IR, ^1H NMR, and elemental analysis. Polycarbonates showed the adsorption band at 1780 cm^{-1} corresponding to the $\text{C}=\text{O}$ group, and polythiocarbonates the absorption at 1200 cm^{-1} corresponding to the $\text{C}=\text{S}$ group. The ^1H NMR signals and the elemental analysis are shown in Table I and are in agreement with the proposed structures.

Two variables were considered: the nature of the catalyst and the reaction time. Solvent, temperature, and catalyst and base concentrations remained constant.

TABLE I.- Elemental analysis and ^1H NMR signals of polycarbonates (**Ia** - **IIIa**) and polythiocarbonates (**Ib** - **IIIb**)

	Ia	IIa	IIIa
^1H RMN δ (ppm) (CDCl_3)	2.17(s,3H, CH_3); 6.94- 7.36(m,12H,Ar-H)	2.19(s,3H, CH_3); 6.86 -7.4(m,12H,Ar-H)	2.2(s,3H, CH_3); 6.82- 7.44(m,11H,Ar-H)
Elemental Analysis	Calc.: C: 71.90% H: 4.28% Found: C: 71.71% H: 4.43%	Calc.: C: 71.90% H: 4.28% Found: C: 71.69% H: 3.99%	Calc.: C: 65.45% H: 3.64% Found: C: 65.70% H: 3.90%
	Ib	IIb	IIIb
^1H RMN δ (ppm) (CDCl_3)	2.2(s,3H, CH_3); 6.94- 7.38(m,12H,Ar-H)	2.2(s,3H, CH_3); 6.86-7.34 (m,12H Ar-H)	2.2(s,3H, CH_3); 6.86- 7.46(m,11H,Ar-H)
Elemental Analysis	Calc.: C: 68.76% H: 4.09% Found: C: 68.40% H: 4.65%	Calc.: C: 68.76% H: 4.09% Found: C: 68.92% H: 4.60%	Calc.: C: 62.84% H: 3.49% Found: C: 62.80% H: 3.80%

Table II shows the yields and η_{inh} obtained for polycarbonate **Ia** and polythiocarbonate **Ib** with and without catalyst. Without catalyst, low values of η_{inh} and acceptable yields were obtained, due to an interphasial polycondensation process between the alkaline diphenolate in the aqueous phase and phosgene or thiophosgene dissolved in the organic phase.

Only BTEAC at 60 minutes was effective as catalyst for polythiocarbonate **Ib**, and the polymers obtained with the other catalysts are due to an interphasial polycondensation process. This catalyst has been considered as hydrophilic^[13], even more in aqueous dilute systems as this; therefore it has affinity to form ionic pairs with lipophilic dianions as this.

For polycarbonate **Ia**, TBAB was ineffective as catalyst. BTEAC showed a

TABLE II.- Yields and inherent viscosities obtained for polycarbonate **Ia** and polythiocarbonate **Ib**

Cat.	Ia				Ib			
	30'		60'		30'		60'	
	%	η^a	%	η^a	%	η^a	%	η^a
—	66	0.09	88	0.14	87	0.14	72	0.14
TBAB	70	0.08	78	0.12	87	0.12	81	0.14
HDTMAB	93	0.31	93	0.32	82	0.13	75	0.10
BTEAC	78	0.22	93	0.26	78	0.15	86	0.25
HDTBPB	88	0.23	83	0.22	94	0.18	89	0.15
ALIQAT	89	0.29	88	0.18	71	0.10	60	0.07

a: inherent, in CHCl_3 at 25°C ($c = 0.5 \text{ g dl}^{-1}$)

similar behaviour to that with the polythiocarbonate **Ib**. The best results were obtained with HDTMAB, which has the characteristics of a micellar agent and a process of this kind is impossible to rule out. However, Yamazaki and Imai^[14] have demonstrated in polyether synthesis that the mechanism of polymerization is the same with HDTMAB and TBAB, which is not a micellar agent.

With Aliquat we obtained a good value of η_{inh} at 30 minutes, which then decreases by a hydrolytic process due to the lipophilic nature of this catalyst, which has been described in the synthesis of other polycarbonates^[4].

Table III shows the results obtained for polycarbonate **IIa** and polythiocarbonate **IIb** with two catalysts: HDTMAB and BTEAC. Without catalyst only one attempt was made at 60 minutes, and we cannot discard an interphasial polymerization process.

For polythiocarbonate **IIb** the results were poor and could be due mainly to an interphasial process. On the other hand, is also probably that a hydrolytic process exists specially with HDTMAB.

For polycarbonate **IIa** the yields were very low, but with both catalysts good values of η_{inh} were obtained. With HDTMAB there is an increase of

TABLE III.- Yields and inherent viscosities obtained for polycarbonate **IIa** and polythiocarbonate **IIb**

Cat.	IIa				IIb			
	30'		60'		30'		60'	
	%	η^a	%	η^a	%	η^a	%	η^a
—	—	—	51	0.14	--	--	--	--
HDTMAB	52	0.24	66	0.46	89	0.24	69	0.11
BTEAC	41	0.56	43	0.47	80	0.18	77	0.19

a: inherent, in CHCl_3 at 25°C ($c = 0.5 \text{ g dl}^{-1}$)

η_{inh} with the reaction time, and with BTEAC the value slightly decreases probably due to a hydrolytic process.

The results obtained for polycarbonate **IIIa** and polythiocarbonate **IIIb** are shown in Table IV. Without catalyst low values of η_{inh} were obtained due to an interphasial polycondensation process.

For polythiocarbonate **IIIb** all the catalysts were effective at 30 minutes, and then at 60 minutes, the η_{inh} values decrease due to a hydrolytic process. With BTEAC the decrease is very small because its hydrophilic structure is not capable to transport hydrophilic anions as OH^- , necessary for the hydrolysis.

For polycarbonate **IIIa** the tendency of the catalysts was the same as that obtained for polycarbonate **Ia**. The best catalysts were HDTMAB, BTEAC, and Aliquat. Aliquat was effective at 30 minutes and then the η_{inh} value decreases due to a hydrolytic process. With BTEAC the η_{inh} value increases as the reaction time increases, showing that with this hydrophilic catalyst the hydrolysis of the polymer is less favoured. Furthermore, BTEAC has Cl^- as counterion, which is exchanged more easily than Br^- .

When we compare the behaviour of the catalysts with the three monomers, it can be seen that the tendency of the η_{inh} values is the same with all of

TABLE IV.- Yields and inherent viscosities obtained for polycarbonate **IIIa** and polythiocarbonate **IIIb**

Cat.	IIIa				IIIb			
	30'		60'		30'		60'	
	%	η^a	%	η^a	%	η^a	%	η^a
—	63	0.12	80	0.12	66	0.09	68	0.14
TBAB	80	0.13	84	0.14	81	0.23	84	0.16
HDTMAB	92	0.31	87	0.29	82	0.23	70	0.14
BTEAC	90	0.16	90	0.25	78	0.36	78	0.34
HDTBPB	79	0.17	91	0.24	86	0.23	84	0.17
ALIQAT	92	0.30	92	0.22	82	0.47	83	0.19

a: inherent, in CHCl_3 at 25°C ($c = 0.5 \text{ g dl}^{-1}$)

them. However, we note some differences when comparing the absolute values. As phosgene and thiophosgene are the same in all reactions, these differences can be attributed to the nature of the dianion, which is only different in the number and position of the chlorine atoms in the side ring. So, the nature of the dianion which is transferred from the aqueous phase to the organic phase, seems to play an important role in these polycondensations.

In general, it seems that the limiting step of the polymerization process is the transfer of the dianion rather than the reaction in the organic phase, since phosgene and thiophosgene are highly reactive species. Finally, phase transfer catalysis is a suitable technique for the synthesis of this kind of polymers.

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