Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization by Phase-Transfer Catalysis. 18.‡ Polycarbonates and Polythiocarbonates from Chlorinated Diphenols

L. H. Tagle[a]; F. R. Diaz[a]; R. Fuenzalida[a]
[a] Organic Synthesis Department, Faculty of Chemistry Catholic University of Chile, Santiago, Chile

To cite this Article Tagle, L. H. , Diaz, F. R. and Fuenzalida, R.(1994) 'Polymerization by Phase-Transfer Catalysis. 18.‡ Polycarbonates and Polythiocarbonates from Chlorinated Diphenols', Journal of Macromolecular Science, Part A, 31: 3, 283 — 290

To link to this Article: DOI: 10.1080/10601329409351518

URL: http://dx.doi.org/10.1080/10601329409351518

J.M.S.—PURE APPL. CHEM., A31(3), pp. 283–290 (1994)

POLYMERIZATION BY PHASE-TRANSFER CATALYSIS. 18.† POLYCARBONATES AND POLYTHIOCARBONATES FROM CHLORINATED DIPHENOLS

L. H. TAGLE,* F. R. DIAZ, and R. FUENZALIDA

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

ABSTRACT

Polycarbonates and polythiocarbonates were synthesized from diphenols with chlorine atoms in the phenyl rings, and phosgene or thiophosgene under phase-transfer catalysis conditions with quaternary ammonium salts as catalysts, at three reaction times. The polymers were characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis. The influence of the nature of both diphenol and catalyst was estimated by yields and inherent viscosity measurements. The steric hindrance exerted by chlorine atoms in the ortho position to the phenolate group was analyzed in relation to the chains bonded to the central atom of the catalyst when the ionic pair is formed.

INTRODUCTION

In previous papers we described the synthesis of polycarbonates and polythiocarbonates derived from several diphenols using phase-transfer catalysis as the polymerization technique [1–6]. In one of these works [3] we described the synthesis of polythiocarbonates derived from diphenols with methyl groups in the ortho position to the phenolic groups, showing that the methyl groups exert a steric hindrance to

---

†For Part 17, see Reference 12.

the formation of the ionic pair with the catalyst. In fact, when the groups bonded to the central atom of the catalyst are large, the efficiency of the catalysts was poor, except for hexadecyltrimethylammonium bromide (HDTMAB) which has three small groups bonded to the N atom. When we used a diphenol with two methyl groups in each aromatic ring, HDTMAB was ineffective as a catalyst, showing an increase of steric hindrance due to the influence of the substituent in the formation of the ionic pair.

On the other hand, we have used phase-transfer catalysis (PTC) [7, 8] as an effective tool for the synthesis of other kinds of polymers such as polyesters [9–12], polyethers [13], and polythioethers [14]. PTC offers mild conditions and technical advantages which should make it a suitable method for polymer synthesis.

Continuing our work in the application of PTC to polymer synthesis, we describe here the synthesis of polycarbonates and polythiocarbonates from diphenols with chlorine atoms in the ortho position to the phenolic group, and phosgene or thiophosgene with several catalysts and reaction times and dichloromethane as solvent. We also study the effect of the chlorine atom on the formation of the ionic pair with several catalysts by determining the yields and the inherent viscosities (η_{inh}) of the polymers.

EXPERIMENTAL

Reagents and solvents were provided by Aldrich and Merck and were used without further purification. The following catalysts (from Fluka) were used: benzyltriethylammonium chloride (BTEAC), tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), and methyltrioctylammonium chloride (Aliquat 336).

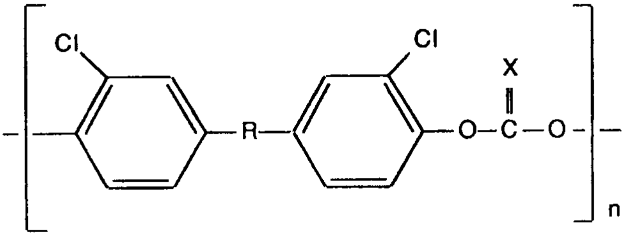
The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, and the ^{1}H-NMR on a 100 MHz instrument (Varian XL-100) using $CDCl_3$ as the solvent and TMS as the internal reference. Viscometric measurements were made in a Desreux–Bischoff [15] type dilution viscometer in $CHCl_3$ solution at 25°C.

Diphenols 1,1-bis(4-hydroxyphenyl)-cyclohexane and 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A) were synthesized according to McGreal et al. [16]. Both diphenols were chlorinated with sulfuryl chloride and thioglycolic acid according to a procedure described in the literature [17]. Monomers 1,1-bis(3-chloro-4-hydroxyphenyl)-cyclohexane and 2,2-bis(3-chloro-4-hydroxyphenyl)-propane were recrystallized from $CHCl_3$ and characterized by IR and ^{1}H-NMR spectroscopy and their melting points: 1,1-bis(3-chloro-4-hydroxyphenyl)-cyclohexane, mp 144–146°C (145–146°C [17]); 2,2-bis(3-chloro-4-hydroxyphenyl)-propane, mp 90–91°C (89–91°C [17]).

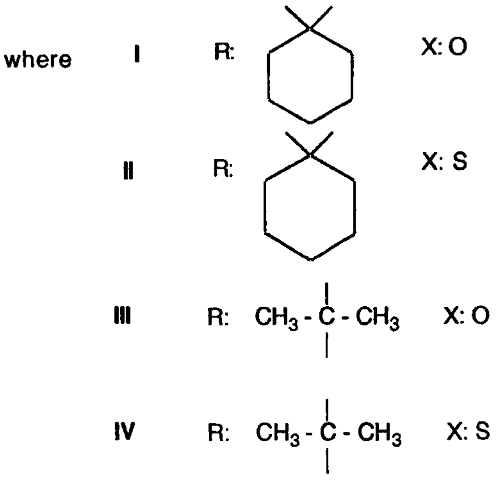
Polymers were synthesized according to the following general procedure: 5 mmol of the diphenol and 0.25 mmol (5%) of the catalyst were dissolved in 20 mL of 1 M NaOH and mixed with 20 mL CH_2Cl_2. Then 5 mmol phosgene or thiophosgene dissolved in 15 mL CH_2Cl_2 was added at once. The mixture was stirred at 20°C for 30, 60, or 150 minutes, and then the organic layer was poured into methanol. The precipitated polymer was filtered, washed with methanol, dried under vacuum at 40°C, and characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis.

RESULTS AND DISCUSSION

Polycarbonates and polythiocarbonates with the following structure



I - IV



were synthesized in a two-phase system (CH_2Cl_2/1 M NaOH) and characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis. The results are summarized in Tables 1 and 2 and are in accord with the proposed structures.

Two variables were considered in the phase-transfer process: the nature of the catalyst and the reaction time. Solvent, temperature, and catalyst and base concentrations remained constant. The reaction occurs when the diphenolate is transferred in the form of an ionic pair with the cation of the catalyst from the aqueous to the organic phase where the reaction occurs according to the mechanism proposed by Starks [7, 8]. Normally the ionic pair is highly reactive in the organic phase due to the low solvation by the low polarity solvent.

Experiments without catalyst were made for polycarbonates and polythiocarbonates at reaction times of 30, 60, and 150 minutes. As seen in Tables 3–6, only at 150 minutes was a polymer with low η_{inh} obtained due to an interfacial polycondensation process between the diphenolate dissolved in the aqueous phase and phosgene or thiophosgene dissolved in the organic phase. Therefore, an interfacial polycondensation process, parallel to phase transfer, cannot be discarded at 150 minutes.

Table 3 shows the yields and η_{inh} obtained for polycarbonate I. This polycarbonate was obtained with all catalysts and at the three reaction times with acceptable yields but with low η_{inh} values. All catalysts showed similar behaviors, and the η_{inh}

TABLE 1. Spectroscopic Data and Elemental Analysis of Polycarbonates **I** and **III**

	I	**III**
IR (cm^{-1}), KBr	2860 (CH$_2$) 1770 (C=O) 1580 (Ar) 1500 (Ar) 1220 (C—O) 810, 920 (1,2,4-substitution)	2960 (CH$_3$) 1760 (C=O) 1500 (Ar) 1200 (C—O) 840, 870 (1,2,4-substitution)
^{1}H NMR (δ) (ppm), CDCl$_3$	1.50 (s, 6H, CH$_2$) 2.20 (s, 4H, CH$_2$) 7.30 (m, 6H, ArH)	1.7 (s, 6H, CH$_3$) 7.3 (m, 6H, ArH)
Elemental analysis	Calculated. C: 62.81% H: 4.41% Found. C: 62.90% H: 4.84%	Calculated. C: 59.44% H: 3.72% Found. C: 59.50% H: 4.31%

values were only slightly higher than that obtained without catalyst. In spite of the low values of η_{inh}, the phase-transfer process was effective since the polycarbonate was obtained at the three reaction times, including the 30 and 90 minutes of reaction at which the polycarbonate was not obtained without catalyst.

Table 4 shows the yields and η_{inh} obtained for polythiocarbonate **II**. BTEAC was effective as catalyst, especially at 30 and 90 minutes. This catalyst has been described as hydrophilic [18] and suitable to transfer lipophilic dianions such as those derived from 1,1-bis(3-chloro-4-hydroxyphenyl)-cyclohexane. At 150 minutes

TABLE 2. Spectroscopic Data and Elemental Analysis of Polythiocarbonates **II** and **IV**

	II	**IV**
IR (cm^{-1}), KBr	2960 (CH$_2$) 1500 (Ar) 1200 (C=S) 810, 870 (1,2,4-substitution)	2960 (CH$_3$) 1500 (Ar) 1260 (C=S) 820, 870 (1,2,4-substiution)
^{1}H NMR (δ) (ppm), CDCl$_3$	1.60 (s, 6H, CH$_2$) 2.30 (s, 4H, CH$_2$) 7.30 (m, 6H, ArH)	1.7 (s, 6H, CH$_3$) 7.3 (m, 6H, ArH)
Elemental analysis	Calculated. C: 60.16% H: 4.22% Found. C: 59.84% H: 4.49%	Calculated. C: 56.64% H: 3.54% Found. C: 56.42% H: 3.67%

TABLE 3. Yields and Inherent Viscosities of Polycarbonate I

	Time (minutes)					
	30		60		150	
Catalyst	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]
—	—	—	—	—	49	0.07
BTEAC	73	0.12	73	0.11	65	0.10
TBAB	76	0.12	80	0.10	70	0.12
HDTMAB	66	0.10	81	0.08	51	0.14
Aliquat	78	0.11	86	0.09	70	0.08

[a] ($dL \cdot g^{-1}$), in $CHCl_3$ at 25°C at $c = 0.5\ g \cdot dL^{-1}$.

there is a decrease of η_{inh}, probably due to a hydrolytic process which is more important when all the diphenolate is transferred to the organic phase. HDTMAB was also effective at 30 and 90 minutes, but at a higher reaction time there was a decrease of η_{inh} due to a hydrolytic process promoted by this catalyst which is more lipophilic than BTEAC.

On the other hand, both BTEAC and HDTMAB exert a low steric hindrance to the formation of the ionic pair due to its structural characteristics. In fact, in a previous work [3] in which a similar diphenol had methyl groups ortho to the phenolic groups, only HDTMAB was effective as a catalyst. This has three methyl groups bonded to the central N atom and exerts a low steric hindrance to the formation of the ionic pair. Other catalysts were ineffective, and polymers were obtained only by an interfacial polycondensation process. In this work, the diphenols have chlorine atoms ortho to the phenolic groups instead of methyl groups, which are larger. For this reason, BTEAC was also effective as a catalyst.

Aliquat and TBAB, which have larger groups bonded to the central N atom, had low efficiencies as catalysts due to the steric hindrance exerted on these groups. Also, these catalysts are lipophilic and less suitable to transport a lipophilic dianion

TABLE 4. Yields and Inherent Viscosities of Polythiocarbonate II

	Time (minutes)					
	30		60		150	
Catalyst	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]
—	—	—	—	—	87	0.12
BTEAC	90	0.22	85	0.24	81	0.08
TBAB	91	0.16	78	0.11	89	0.11
HDTMAB	86	0.22	85	0.16	88	0.06
Aliquat	93	0.15	93	0.15	90	0.08

[a] ($dL \cdot g^{-1}$), in $CHCl_3$ at 25°C at $c = 0.5\ g \cdot dL^{-1}$.

such as this, which has been described in other works [2], and promote hydrolysis of the polymeric chains [4].

For the synthesis of the polythiocarbonate, phase-transfer catalysis was a more efficient process than interfacial polycondensation in which the polymer was obtained only at 150 minutes. However, the polythiocarbonate was obtained with catalysts at all reaction times, although in most cases with low η_{inh} values.

Table 5 shows the yields and η_{inh} obtained for polycarbonate **III**. HDTMAB and Aliquat showed a very low efficiency as catalysts, and the η_{inh} values were similar to that obtained without catalyst at 150 minutes. However, the polycarbonate was obtained at short reaction times, in contrast to the reactions without catalyst. This is evidence of the efficiency of the phase-transfer process.

The poor behavior of Aliquat as a catalyst was expected because the steric hindrance exerted by the three octyl groups with the chlorine atoms of the phenyl rings precluding the formation of the ionic pair with the diphenolate dianion.

HDTMAB is effective as a phase-transfer catalyst probably due to its structure and the more hydrophilic nature of the diphenolate compared with that of the polycarbonate **I**. In fact, HDTMAB, which has three small groups bonded to the N atom, was capable of forming the ionic pair with a similar diphenolate as described in a previous paper [3]. On the other hand, it is probable that hydrolysis of the polymeric chains can be promoted and competition between the diphenolate and OH^- anions can arise. This explains the low values of η_{inh} and the regular yields due to its lipophilic nature.

BTEAC was the best catalyst for this polycarbonate, especially at 30 minutes. At longer times the η_{inh} values decrease, probably due to a hydrolytic process. This catalyst has hydrophilic characteristics [18] and should not be effective in the synthesis of this polycarbonate due to the characteristics of the diphenolate. However, it is probable that chlorine atoms provide the diphenolate with more lipophilic characteristics, which makes the catalyst more effective in the synthesis of this polycarbonate. In spite of the hydrophilic characteristic of this catalyst, it is probable that at higher reaction times there is competition between the diphenolate and the OH^- anion, especially when the diphenolate is completely transferred to the organic phase. As a consequence, the polymeric chains can hydrolyze and the η_{inh} value decreases.

TABLE 5. Yields and Inherent Viscosities of Polycarbonate **III**

	Time (minutes)					
	30		60		150	
Catalyst	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]
—	—	—	—	—	62	0.09
BTEAC	89	0.63	93	0.45	85	0.26
TBAB	97	0.32	74	0.09	61	0.11
HDTMAB	72	0.09	69	0.08	65	0.10
Aliquat	74	0.09	84	0.05	63	0.10

[a] $(dL \cdot g^{-1})$, in $CHCl_3$ at 25°C at $c = 0.5\ g \cdot dL^{-1}$.

TBAB, which has more lipophilic character, has a behavior intermediate between BTEAC and the other catalysts. In fact, it was effective only at 30 minutes, and at higher reaction times the η_{inh} value decreases to values similar to that obtained without catalyst. It is probable that with TBAB there is steric hindrance to forming the ionic pair due to the chlorine atoms in the aromatic rings. At longer reaction times there are more possibilities for a hydrolytic process.

The phase-transfer process was effective for the synthesis of this polycarbonate since the polymer was obtained at all reactions times instead of at 150 minutes as was the case without catalyst. Also, we obtained higher η_{inh} values for this polycarbonate than for polycarbonate **I**, and the catalysts were more effective.

Table 6 shows the yields and η_{inh} values obtained for polythiocarbonate **IV**. BTEAC was practically ineffective as a catalyst for the synthesis of this polycarbonate, although the polymer was obtained at short reaction times, giving η_{inh} values similar to that obtained without catalyst. The other catalysts were effective at all reaction times. TBAB presented the best behavior; this catalyst has a symmetrical structure and has been described as very effective in the synthesis of the polythiocarbonate of Bisphenol A [1]. However, for this polythiocarbonate the η_{inh} values were lower than those obtained for Bisphenol A, probably due to steric hindrance of the chlorine atoms bonded to the aromatic rings.

Aliquat was effective at 30 minutes and then, at higher reaction times, the η_{inh} values decrease due to the fact that the lipophilic character of this catalyst can promote hydrolysis of the polymeric chains. On the other hand, it is also possible that there is steric hindrance of this catalyst which has three C_8 chains bonded to the N atom with the chlorine atoms of the aromatic rings.

With HDTMAB, the η_{inh} values are intermediate between those obtained with the other catalysts, and it is probable that the steric hindrance will be lower due to the small groups bonded to the N atom of the catalyst.

For the synthesis of this polythiocarbonate, the phase-transfer process was effective, depending on the results, yields, and the η_{inh} values of the nature of the catalysts which show a behavior according to the structure.

In general, it seems that the limiting step of polymerization is the transfer of the dianion rather than the reaction in the organic phase, since phosgene and

TABLE 6. Yields and Inherent Viscosities of Polythiocarbonate **IV**

	Time (minutes)					
	30		60		150	
Catalyst	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]	Yield (%)	η_{inh}[a]
—	—	—	—	—	82	0.11
BTEAC	56	0.07	80	0.12	88	0.18
TBAB	95	0.42	91	0.32	95	0.43
HDTMAB	94	0.29	92	0.37	84	0.31
Aliquat	90	0.37	83	0.29	84	0.20

[a] $(dL \cdot g^{-1})$, in $CHCl_3$ at 25°C at $c = 0.5\ g \cdot dL^{-1}$.

thiophosgene are highly reactive species, with the monomer and catalyst structure being the most important factors in the transfer process. Also, it is possible that there is hydrolysis of the polymeric chains, principally due to the lipophilicity of the catalysts which can transport OH^- ions to the organic phase, as was described in other work [4]. On the other hand, the steric hindrance exerted by the chlorine atoms bonded to the aromatic rings to form the ionic pair is smaller than that exerted by methyl groups in analogous monomers [3]. This is why only HDTMAB was effective as a catalyst.

CONCLUSION

We conclude that the phase-transfer process is suitable for the synthesis of these polycarbonates and polythiocarbonates, since these polymers are obtained at all reaction times and with all the catalysts used, in contrast to the experiments without catalyst in which polymer was only obtained at 150 minutes and with low η_{inh}.

REFERENCES

[1] L. H. Tagle, F. R. Diaz, J. C. Vega, and P. F. Alquinta, *Makromol. Chem.*, *186*, 915 (1985).
[2] L. H. Tagle, F. R. Diaz, and P. Riveros, *Polym. J.*, *18*, 501 (1986).
[3] L. H. Tagle, F. R. Diaz, and P. Salas, *J. Macromol. Sci.—Chem.*, *A26*, 1321 (1989).
[4] L. H. Tagle and F. R. Diaz, *Eur. Polym. J.*, *23*, 109 (1987).
[5] L. H. Tagle, F. R. Diaz, and C. Margozzini, *Polym. Bull.*, *25*, 319 (1991).
[6] L. H. Tagle, F. R. Diaz, R. Concha, and H. Cisternas, *Int. J. Polym. Mater.*, In Press.
[7] C. M. Starks, *J. Am. Chem. Soc.*, *93*, 195 (1971).
[8] C. M. Starks and R. M. Owens, *Ibid.*, *95*, 3613 (1973).
[9] L. H. Tagle, F. R. Diaz, and M. A. Vargas, *Acta Polym.*, *42*, 398 (1991).
[10] L. H. Tagle, F. R. Diaz, and S. Roncero, *Polym. Int.*, *29*, 265 (1992).
[11] L. H. Tagle, F. R. Diaz, and M. De La Fuente, *Ibid.*, *29*, 269 (1992).
[12] L. H. Tagle, F. R. Diaz, and W. Campbell, *Eur. Polym. J.*, *29*, 1069 (1993).
[13] L. H. Tagle, F. R. Diaz, and A. M. Muñoz, *Polym. Bull.*, *11*, 493 (1984).
[14] L. H. Tagle, F. R. Diaz, M. P. De La Maza, and J. C. Vega, *J. Polym. Sci., Polym. Chem. Ed.*, *24*, 495 (1986).
[15] V. Desreux and F. Bischoff, *Bull. Soc. Chim. Belg.*, *59*, 93 (1950).
[16] M. McGreal, V. Niederl, and J. B. Niederl, *J. Am. Chem. Soc.*, *61*, 345 (1939).
[17] I. M. Bilkik et al., British Patent 1,047,058 (1966); *Chem. Abstr.*, *66*, 10737k (1967).
[18] R. Bar, L. Karpug-Bar, J. Sasson, and J. Blum, *Anal. Chim. Acta*, *154*, 203 (1983).

Received January 15, 1993
Revision received May 17, 1993