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POLYMERIZATION BY PHASE-TRANSFER CATALYSIS. 8. SYNTHESIS AND CHARACTERIZATION OF POLYTHIOCARBONATES FROM DIPHENOLS WITH METHYL GROUPS[†]

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ABSTRACT

Polythiocarbonates were synthesized from five different diphenols and thiophosgene under phase-transfer catalysis conditions, with quaternary ammonium and phosphonium salts as catalysts and dichloromethane as solvent. The polythiocarbonates were characterized by IR, ^{1}H NMR, and elemental analysis. Viscosity-average molecular weights were estimated from inherent viscosity measurements. The influence of the catalysts and the structure of the diphenols both exert an important effect on the molecular weight. The hydrolysis of the polythiocarbonates was studied by observing the variation of η_{inh}. The polymer undergoes a hydrolytic process in the organic phase, and this is influenced by the catalysts.

[†] For Part 7, see Ref. 4.

INTRODUCTION

In previous papers [1-4] we described a systematic study of the synthesis of polythiocarbonates from diphenols and thiophosgene with several catalysts and solvents.

In one of those papers [1] we studied the synthesis of Bisphenol A polythiocarbonate, and analyzed the influence of the solvent and the nature of the catalyst, as well as several modes of thiophosgene addition, concluding that the best solvent was dichloromethane, and the best mode of thiophosgene addition was in one portion. Several of the catalysts were effective for obtaining high yields and molecular weights. In other work [2], we studied the synthesis of several polythiocarbonates, using the best conditions determined previously.

Polycarbonates also were synthesized [5] under the same conditions, and we studied the influence of the catalysts on the hydrolysis of the polymer chains, concluding that there is not only a phase-transfer process but also a hydrolytic process which occurs in the organic phase and is influenced by the nature of the catalyst and the interface of the system.

On the other hand, phase-transfer catalysis [6, 7] (PTC) has had a great impact on organic chemistry and has been used satisfactorily in the synthesis of several kinds of polymers, such as polycarbonates [8], polyethers [9, 10], polythioethers [11, 12], and others [13]. This technique offers mild conditions and technical advantages which should make it a suitable method for polythiocarbonate synthesis.

Continuing our work on the application of PTC to polymer synthesis, we describe here the synthesis of polythiocarbonates from diphenols with methyl groups in the aromatics rings and thiophosgene, with several catalysts and reactions times and dichloromethane as solvent. We also studied the effect of the aqueous medium on the hydrolysis of the polymers.

EXPERIMENTAL

Materials

Diphenols were synthesized from *o*-cresol and the corresponding ketone according to the procedure described by McGreal et al. [14]. Thiophosgene and solvents (from Merck) were used without further purification. The following catalysts (from Fluka) were used: tetrabutylammonium bromide (TBAB), methyltrioctylammonium chloride (Aliquat 336, MTAC), hexadecyltrimethylammonium bromide (HDTMAB), tributylhexadecylphosphonium bromide (TBHDPB), and benzyltriethylammonium chloride (BTEAC).

Measurements

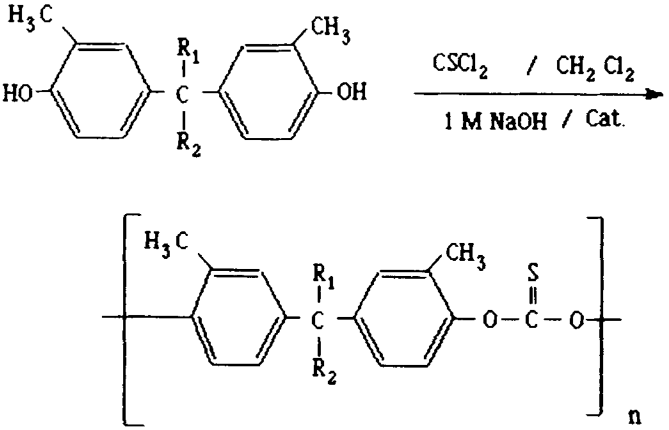
The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, the ^{1}H NMR on a 100-MHz instrument (Varian XL-100), with $CDCl_3$ as solbent and TMS as internal standard. Viscometric measurements were made in a Desreux-Bischoff [15] type dilution viscometer in $CDCl_3$ at 25°C.

Polymerizations

In a typical polycondensation reaction, 5 mmol monomer and 0.25 mmol catalyst were dissolved in 20 mL of 1 *M* NaOH and mixed with 20 mL CH_2Cl_2. Then, 5 mmol thiophosgene dissolved in 15 mL CH_2Cl_2 was added. The mixture was stirred at 20°C and then the organic layer was separated and poured into methanol. The precipitated polymer was filtered, washed with methanol, and dried under vacuum at 40°C.

RESULTS AND DISCUSSION

Poly[oxythiocarbonyloxy-(3-methyl)-1,4-phenylene-2,2-propyl-(3-methyl)-1,4-phenylene] (I), poly[oxythiocarbonyloxy-(3-methyl)-1,4-phenylene-2,2-butyl-(3-methyl)-1,4-phenylene] (II), poly[oxythiocarbonyloxy-(3-methyl)-1,4-phenylene-1-phenyl-ethyl-(3-methyl)-1,4-phenylene] (III), poly[oxythiocarbonyloxy-(3-methyl)-1,4-phenylene-1,1-cyclohexyl-(3-methyl)-1,4-phenylene] (IV), and poly[oxythiocarbonyloxy-(3-methyl)-1,4-phenylene-1,1-(4-methyl)-cyclohexyl-(3-methyl)-1,4-phenylene] (V) were obtained according to the following reaction:



where

	R_1	R_2
I	$-CH_3$	$-CH_3$
II	$-CH_3$	$-CH_2-CH_3$
III	$-CH_3$	$-C_6H_5$
IV	$-(-CH_2-)-_5$	
V	$-(-CH_2-)-_2-CH(CH_3)-(-CH_2-)-_2-$	

All the polythiocarbonates were characterized by IR and ^{1}H-NMR spectroscopy and elemental analysis, and they showed an absorption band at 1200 cm^{-1} corresponding to C=S stretching. The ^{1}H NMR and the elemental analyses, shown in Table 1, are in agreement with the proposed structures.

In order to study the polycondensation reaction, two variables were considered: the structure of the catalyst and the reaction time. The concentration of catalyst and base, as well as the reaction time, were kept constant.

Table 2 shows the yields and inherent viscosities of the polythiocarbonates obtained without catalyst. Without a catalyst, low η_{inh} values were obtained although the yields were between 68 and 82%, probably due to an interfacial polycondensation between thiophosgene dissolved in the organic phase and the alkaline diphenolate in the aqueous phase.

Table 3 shows the yields and inherent viscosities obtained for polythiocarbonate I. BTEAC and TBHDPB were ineffective as catalysts, and the results obtained could be due to an interfacial polycondensation. In fact, BTEAC has been described, according to its chemical structure, as a hydrophilic catalyst, particularly so in dilute aqueous media [16], and we would expect a low efficiency for the transport process of the diphenolate anion from the aqueous to the organic phase. The low yields obtained with BTEAC, specially at short reactions times, confirm this behavior. At 150 min the yield was similar to that obtained without catalyst. Similar results were observed with this catalyst in the Bisphenol A polythiocarbonate synthesis [1].

TBHDPB is a lypophilic catalyst residing mainly in the organic phase, and as a result it does not form ion pairs easily. Hence, interfacial reaction is favored, resulting in good yields at all reactions times but low inherent viscosities.

Good yields were obtained with MTAC and TBAB at all reaction times, but there were low inherent viscosities except at 120 and 150 min. While

TABLE 1. Elemental Analysis and ^{1}H-NMR Spectra of Polythiocarbonates

Polythiocarbonate	Elemental analysis		Chemical shifts δ, ppm
	Found, %	Calc, %	
I	C: 71.50	C: 72.48	1.64 (s, 6H, CH_3); 2.2 (s, 6H, Ar–CH_3); 7.14 (m, 6H, Ar–H)
	H: 6.82	H: 6.04	
II	C: 73.12	C: 73.06	0.71 (t, 3H, CH_3); 1.3 (c, 2H, CH_2); 1.64 (s, 3H, CH_3); 2.2 (s, 6H, Ar–CH_3); 7.12 (m, 6H, Ar–H)
	H: 6.46	H: 6.41	
III	C: 76.53	C: 76.65	2.24 (s, 9H, CH_3); 7.03 (s, 5H, Ar–H); 7.29 (m, 6H, Ar–H)
	H: 5.76	H: 5.55	
IV	C: 74.51	C: 74.54	1.5 (s, 6H, Ar–CH_3); 2.25 (s, 10H, CH_2); 7.13 (m, 6H, Ar–H)
	H: 6.72	H: 6.50	
V	C: 75.13	C: 74.99	0.83 (d, 3H, CH_3); 1.51 (m, 8H, CH_2); 2.23 (m, 6H, Ar–CH_3); 2.58 (d, H, CH); 7.12 (m, 6H, Ar–H)
	H: 6.77	H: 6.81	

TABLE 2. Yields and Inherent Viscosities Obtained without Catalyst[a]

Polythiocarbonate	Yield, %	η_{inh}, dL/g[b]
I	76	0.12
II	82	0.06
III	79	0.05
IV	68	0.11
V	74	0.08

[a] Reaction time, 150 min.
[b] In $CHCl_3$ at 25°C (c = 0.3 g/dL).

both catalysts have been described as effective for other systems [1, 2], steric hindrance due to the CH_3 groups in the diphenol rings probably prevents the formation of ion pairs. On the other hand, HDTMAB gave the best results. This catalyst has a long chain and three methyl groups bonded to the N atom, and, as a consequence, the formation of ion pairs is probably not subject to steric encumbrances. Thus the inherent viscosities increase with the reaction time.

TBAB, TBHDPB, and MTAC have long chains bonded to the central atom and, because of this, no ion pairs are formed, favoring interfacial polycondensation. TBAB was an excellent catalyst for the synthesis of the polythiocarbonate of Bisphenol A which has no methyl groups in the aromatic rings, and high yields and inherent viscosities were obtained [1].

HDTMAB is a catalyst known to form micelles [17]. Micellar, as opposed to phase-transfer catalysis, cannot be ruled out. However, Yamazaki and Imai [18] have demonstrated that the mechanism of polymerization in polyether synthesis is the same with HDTMAB and TBAB, which is not a micellar agent.

As the inherent viscosities were not high, we postulated that a hydrolytic process in which the catalyst can transfer the OH^- anion to the organic phase takes place in competition with polymerization. To check this, we allowed Polythiocarbonate I to react in the same medium with and without catalyst (see Table 4). Without a catalyst, the yield was 53%, and η_{inh} decreased to 0.41 dL/g, probably due to interfacial hydrolysis. With HDTMAB, the yield was the same, but η_{inh} decreased to 0.33 dL/g. With the other catalysts, yields and η_{inh} decreased, and that confirms their effect on the hydrolysis process,

TABLE 3. Yields and Inherent Viscosities Obtained for Polythiocarbonate I[a]

	Time, min													
	10		20		30		60		90		120		150	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}
TBAB	76	0.05	91	0.05	75	0.11	92	0.12	85	0.07	77	0.39	79	0.10
MTAC	76	0.02	88	0.07	73	0.03	77	0.05	89	0.08	81	0.13	76	0.41
HDTMAB	76	0.15	87	0.18	89	0.34	79	0.28	91	0.40	77	0.53	84	0.64
TDBDPB	87	0.13	67	0.13	67	0.10	63	0.13	70	0.13	81	0.15	89	0.13
BTEAC	4	0.05	7	0.08	18	0.05	29	0.08	45	0.11	58	0.05	56	0.06

[a] η_{inh} in dL/g in chloroform at 25°C (c = 0.3 g/dL).

TABLE 4. Effect of the Catalysts on the Hydrolysis of Polythiocarbonate I[a]

Catalyst	η_{inh}, dL/g[b]	Yield, %
None	0.41	53
HDTMAB	0.33	52
TBAB	0.25	26
MTAC	0.10	40

[a] At 20°C for 150 min; η_{inh} 0.53.
[b] In $CHCl_3$ at 25°C (c = 0.3 g/dL).

which is more extensive when the catalyst is more lypophilic, as can be seen with MTAC. A similar behavior was shown in polycarbonate synthesis [5].

Table 5 shows the results obtained for Polythiocarbonate II. BTEAC was ineffective as catalyst and shows a behavior similar to that for Polythiocarbonate I, probably due to their structural similarity. TBAB, MTAC, and TBHDPB were ineffective as catalysts due to steric hindrance of the methyl groups in the aromatic rings, and the results obtained can be due to an interfacial polycondensation process.

Only HDTMAB is an effective catalyst. The η_{inh} value increases when the reaction times increase up to 90 min and then decreases, probably due to a hydrolytic process. To check this, we allowed a sample of this polythiocarbonate (η_{inh} 0.61 dL/g) to react in the same medium, with and without catalyst. Without catalyst, the yield was 77% and η_{inh} was 0.52 dL/g, whereas with the catalyst there was considerable hydrolysis, giving a yield of 37% and η_{inh} of 0.25 dL/g.

Table 6 shows the results obtained for Polythiocarbonate III. TBAB, TBHDPB, BTEAC, and MTAC were ineffective as catalysts, and the results obtained can be due to an interfacial polycondensation process. In a previous paper [2] we described the synthesis of the polythiocarbonate derived from the same monomer but without the methyl groups in the main rings, and MTAC was an effective catalyst. This behavior indicates that the steric hindrance caused by the methyl groups interferes with the ion pair formation, and the polythiocarbonate obtained with these catalysts results from an interfacial polycondensation process.

HDTMAB was effective as a catalyst for this monomer. The η_{inh} value increases up to 30 min and then decreases due to hydrolysis. When we caused

TABLE 5. Yields and Inherent Viscosities Obtained for Polythiocarbonate II[a]

	Time, min													
	10		20		30		60		90		120		150	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}
TBAB	66	0.07	69	0.09	69	0.08	59	0.07	70	0.09	55	0.06	81	0.09
MTAC	64	0.05	61	0.05	69	0.07	66	0.05	70	0.07	77	0.09	83	0.09
HDTMAB	88	0.19	88	0.23	88	0.17	84	0.09	84	0.61	94	0.47	91	0.49
TBHDPB	71	0.17	70	0.07	67	0.06	66	0.07	74	0.06	75	0.08	83	0.09
BTEAC	7	0.07	21	0.04	56	0.06	52	0.08	65	0.07	59	0.08	65	0.08

[a] η_{inh} in dL/g in chloroform at 25°C ($c = 0.3$ g/dL).

TABLE 6. Yields and Inherent Viscosities Obtained for Polythiocarbonate III[a]

	Time, min													
	10		20		30		60		90		120		150	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}
TBAB	91	0.09	94	0.13	78	0.05	89	0.10	81	0.08	76	0.11	79	0.07
MTAC	84	0.05	86	0.07	87	0.06	94	0.10	87	0.09	89	0.10	89	0.09
HDTMAB	94	0.56	92	0.51	90	0.76	93	0.72	89	0.33	90	0.33	94	0.32
TBHDPB	94	0.13	95	0.16	96	0.11	94	0.10	92	0.10	88	0.13	89	0.26
BTEAC	79	0.07	85	0.08	85	0.05	83	0.08	80	0.09	80	0.07	76	0.07

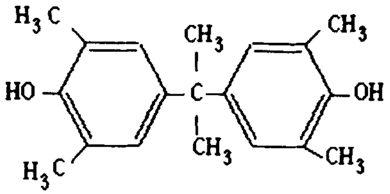
[a] η_{inh} in dL/g in chloroform at 25°C ($c = 0.3$ g/dL).

a sample of this polythiocarbonate (η_{inh} 0.51 dL/g) to react under the same conditions, the yield was 71% and η_{inh} was 0.27 dL/g without catalyst, and 22% and 0.12 dL/g, respectively, with catalyst. This result is similar to that reported for the analogous polycarbonate [5].

Table 7 shows the results obtained for Polythiocarbonate IV. Only HDTMAB was an effective catalyst at 20 min, and then the η_{inh} values decreased to the value obtained without catalyst due to hydrolysis. The resulst obtained with the other catalysts can be due to interfacial polycondensation. In a previous paper [2], when we synthesized the analogous polythiocarbonate without the methyl groups in the aromatic rings, TMAC was an acceptable catalyst, which provides evidence about the influence of these groups.

Table 8 shows the results obtained for Polythiocarbonate V. All the catalysts were ineffective, and the results can be due to interfacial polycondensation. It is conjectured that the highly lypophilic character of this dianion makes it difficult to transfer to the organic phase.

To verify the influence of the methyl groups in the aromatic rings, we synthesized the following diphenol with two methyl groups on each aromatic ring:



When this monomer was polymerized with thiophosgene under the same conditions used for the others, and with HDTMAB as catalyst, we obtained a yield of only 7% at 120 min and η_{inh} of 0.08 dL/g. This result shows that when two methyl groups are present in each aromatic ring, the steric hindrance is increased and no ion pair is formed.

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, because thiophosgene is highly reactive, and the catalyst and the monomer structure are important factors in this transfer process. Moreover, the hydrolysis of the polymeric chains, which occurs principally in the organic phase, depends rather more on the nature of the catalyst than on an interfacial process.

Finally, we conclude that PTC is a suitable method for polythiocarbonate synthesis if one considers the monomer structure and the hydrolytic process produced by the catalyst in an alkaline medium.

TABLE 7. Yields and Inherent Viscosities Obtained for Polythiocarbonate IV[a]

	Time, min													
	10		20		30		60		90		120		150	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}
TBAB	61	0.06	61	0.07	68	0.08	66	0.09	71	0.08	69	0.09	71	0.09
MTAC	90	0.11	70	0.09	68	0.08	74	0.09	84	0.11	77	0.09	75	0.09
HDTMAB	56	0.10	92	0.70	77	0.13	72	0.15	85	0.16	78	0.16	89	0.19
TBHDPB	78	0.04	91	0.05	76	0.08	79	0.08	88	0.05	87	0.07	86	0.08
BTEAC	63	0.08	75	0.11	77	0.06	74	0.08	77	0.07	80	0.06	74	0.08

[a] η_{inh} in dL/g in chloroform at 25°C (c = 0.3 g/dL).

TABLE 8. Yields and Inherent Viscosities Obtained for Polythiocarbonate V[a]

	Time, min													
	10		20		30		60		90		120		150	
Catalyst	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}	%	η_{inh}
TBAB	68	0.05	63	0.05	73	0.07	76	0.07	71	0.07	81	0.08	80	0.07
MTAC	61	0.07	68	0.07	72	0.07	79	0.07	77	0.05	86	0.07	90	0.09
HDTMAB	60	0.09	61	0.06	76	0.06	80	0.08	81	0.07	96	0.10	87	0.09
TBHDPB	69	0.09	57	0.10	69	0.09	72	0.08	67	0.07	84	0.08	75	0.10
BTEAC	61	0.09	67	0.08	59	0.08	52	0.06	68	0.08	68	0.09	71	0.10

[a] η_{inh} dL/g in chloroform at 25°C ($c = 0.3$ g/dL).

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