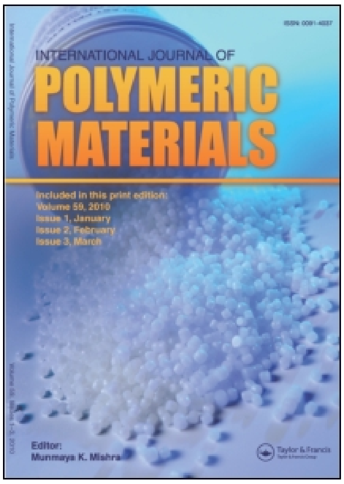

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Polymerization by Phase Transfer Catalysis. 16.[a] Synthesis of Polyestercarbonates and Polyesterthiocarbonates

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Polyestercarbonates and polyesterthiocarbonates were synthesized from the diphenol-esters 4-hydroxyphenyl-4-hydroxybenzoate and 3-hydroxyphenyl-4-hydroxybenzoate and phosgene and thiophosgene respectively, under phase transfer catalysis conditions. The behaviour of the catalysts was evaluated by the yields and the inherent viscosities. Only the polyesterthiocarbonate derived from 3-hydroxyphenyl-4-hydroxybenzoate was soluble in the reaction media, being benzyltriethylammonium chloride (TEBAC) an effective catalyst for this synthesis.

KEY WORDS Polyestercarbonates, polyesterthiocarbonates, phase transfer catalysis, benzyltriethylammonium chloride.

INTRODUCTION

Monomer sequence is a specially important factor for the control of the properties of a polymeric or copolymeric meterial. In this sence there are several studies about the properties of copolymers that have different monomeric sequence but with the same final monomeric composition. An example of this is the study of a series of aromatic copolyesters with thermotropic characteristics, in which there are a great dependence of the thermal properties and the crystalline structure with the monomeric sequence.[1-2]

In this work we present the synthesis of polyestercarbonates and polyesterthiocarbonates from diphenols that content the ester group previously incorporated in the structure, 4-hydroxyphenyl-4-hydroxybenzoate (**I**) and 3-hydroxyphenyl-4-hydroxybenzoate (**II**), with phosgene and thiophosgene respectively. The obtained polymers have a monomeric sequence with two functional groups in the main chain.

As synthetic method, it has been used the technique of phase transfer catalysis,[3] that presents several advantages because offers mild conditions that prevent the change of the sequence of the functional groups because of side reactions or high

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[a] For part 15, see Reference 12.

temperatures. On the other hand, this technique has been used successfully by us in the synthesis of polycarbonates,[4,5] polythiocarbonates,[5,8] copoly(carbonate-thiocarbonate)s,[9] and polyesters.[10–12]

EXPERIMENTAL PART

Reagents and solvents were supplied by Aldrich and Merck. The following catalysts (from Fluka) were used without further purification: benzyltriethylammonium chloride (TEBAC), methyltrioctilammonium chloride (ALIQUAT 336™), tetrabutylammonium bromide (TBAB), hexadecyltrimethylammonium bromide (HDTMAB), benzyltriphenylphosphonium chloride (BTPPC), and hexadecyltributylphosphonium bromide (HDTBPB).

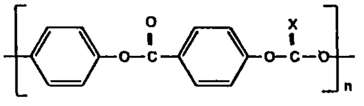
The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^{1}H NMR on a 200 Mz instrument (Bruker) using $CDCl_3$ as solvent and TMS as internal reference. Viscosimetric measurements were made in a Desreux-Bischoff[13] type dilution viscosimeter at 25°C.

4-hydroxyphenyl-4-hydroxybenzoate (**I**) and 3-hydroxyphenyl-4-hydroxybenzoate (**II**) were synthesized from 4-hydroxy-benzoic acid with hydroquinone of resorcinol respectively, according to a method described previously in the literature. Both diphenols were characterized by IR and ^{1}H NMR spectroscopy and melting points.[14–15]

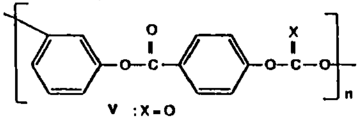
In a typical procedure for polymer synthesis, 5 mmol of **I** or **II** and 0.125 mmol (5%) of the catalyst were dissolved in 20 mL of NaOH 0.5 M solution, and then 20 mL of CH_2Cl_2 were added. Then, 5 mmol of phosgene (from a 20% in toluene solution) or thiophosgene dissolved in 5 mL of CH_2Cl_2 were added at once. The mixture was stirred at 20°C for 60 minutes, and then the organic layer was poured into methanol. The precipitated polymer was filtered, washed with methanol, dried under vacuum at 40°C until constant weight, and characterized.

RESULTS AND DISCUSSION

Polyestercarbonates **III** and **V** and polyesterthiocarbonates **IV** and **VI**, were synthesized in a biphasic system under phase transfer catalysis conditions, according to the procedure described in the experimental part.



III : X=O
IV : X=S



V : X=O
VI : X=S

Polymers were characterized by IR and ^{1}H NMR spectroscopy and quantitative elemental analysis of C and H. The results are shown in Table I and are in agreement with the proposed structures.

Only the nature of the catalyst was considered in the phase transfer process, which was evaluated by the yields and inherent viscosity measurements. Reaction time, solvent, temperature, and catalyst and base concentration remained constant.

The reaction time was determined by evaluating the hydrolysis of the monomer in the reaction media, for which the monomer was dissolved in NaOH 1 M and stirred by several times at 20°C. At 60 minutes the monomer was recovered quantitatively. After this time it was observed hydrolysis of the ester group.

Reaction occurs when the diphenolate is transferred in the form of an ionic pair with the catalyst from the aqueous phase to the organic one according to the general mechanism of phase transfer catalysis proposed by Starks.[16] Normally the ionic pair in the organic phase is highly reactive because the solvation is very low due to the low polarity of this solvent.

Table II shows the yields obtained for polyestercarbonate **III** and polyesterthiocarbonate **IV** derived from monomer **I**, and yields and inherent viscosities obtained for polyestercarbonate **V** and polyesterthiocarbonate **VI** derived from monomer **II**.

Polymers also were obtained without catalyst, therefore an interfacial polycondensation process between the diphenolate dissolved in the aqueous and phosgene or thiophosgene dissolved in the organic phase cannot be discarded.

Polyestercarbonate **III** and polyesterthiocarbonate **IV** were insoluble in all organic solvents, by which it was not possible to obtain the inherent viscosities, and precipitated in the reaction media, which limited the growth of the polymeric chain. In spite of that, a slow increment of the yields can be seen with respect to those

TABLE I

Elemental analyses and spectroscopic data of polyestercarbonates **III** and **V** and polyesterthiocarbonates **IV** and **VI**

	III	**IV**	**V**	**VI**
Elemental analysis	Calc. C: 65.63% H: 3.13%	Calc. C: 61.76% H: 2.94%	Calc. C: 65.63% H: 3.13%	Calc. C: 61.76% H: 2.94%
	Found C: 64.83% H: 3.88%	Found C: 61.46% H: 3.48%	Found C: 65.05% H: 3.29%	Found C: 60.58% H: 3.32%
I.R. (KBr) (cm^{-1})	1750 (C=O carb.) 1720 (C=O est.) 1600 (arom.) 1500 (arom.) 1200 (C—O) 880 (p-sust.)	1680 (C=O est.) 1600 (arom.) 1500 (arom.) 1220 (C=S) 1200 (C—O) 850 (p-sust.)	1770 (C=O carb.) 1730 (C=O est.) 1590 (arom.) 1100 (C—O) 860 (p-sust.)	1730 (C=O est.) 1550 (arom.) 1100 (C—O) 1060 (C=S) 860 (p-sust.)
^{1}H NMR ($CDCl_3$)	—	—	—	7.09 (s, 1H, m-arom) 7.20 (d, 1H, m-arom) 7.39 (t, 1H, m-arom) 7.42 (d, 2H, p-arom) 7.52 (d, 1H, m-arom) 8.33 (d, 2H, p-arom)

TABLE II

Yields and inherent viscosities obtained for polyestercarbonates and polyesterthiocarbonates

Polymer	III	IV	V		VI	
Catalyst	%	%	%	η_{inh}[a]	%	η_{inh}[b]
—	66	71	85	0.26	49	0.13
TEBAC	87	82	88	0.05	84	0.54
ALIQUAT	93	85	57	0.05	97	0.15
TBAB	74	80	84	0.17	71	0.13
HDTMAB	83	80	64	0.05	90	0.13
BTPPC	96	84	88	0.21	86	0.06
HDTBPB	97	79	88	0.13	97	0.19

[a] In *N,N*-dimethyl-formamide at 25°C (c = 0.5 g/dL).
[b] In $CHCl_3$ at 25°C (c = 0.5 g/dL).

obtained without catalyst, which can to be shown as a sign of the efficiency of the phase transfer process.

Polycarbonate **V** also was insoluble in the reaction media, which limited the growth of the polymeric chain. However, after the purification, polycarbonate **V** was soluble in *N,N*-dimethylformamide, solvent in which the inherent viscosities were determined. As can be see in Table II, the best result was obtained without catalyst due to the insolubility in CH_2Cl_2. In fact, when the catalyst is added, the inherent viscosity decreases to very low values due to that the hydrolysis of the polymeric chains is the principal process because the insoluble polymer cannot grow. The influence of the catalysts in the hydrolysis of polycarbonates has been described previously.[4]

Polythiocarbonate **VI** was soluble in the reaction media and the inherent viscosities are shown in Table II. The best catalyst was TEBAC, which has been described as hydrophilic,[17] and suitable for to transport lipophilic dianions as this. On the other hand, TEBAC has Cl^- as counterion which is interchanged more easily that Br^-, that is the counterion of the other catalysts, except ALIQUAT and BTPPC, which are very lipophilic.[6] This behaviour has been described in the synthesis of several polythiocarbonates and polyesters.[6,11-12]

The other catalysts were ineffective to transport the dianion and the polythiocarbonate was obtained principally by an interfacial polycondensation process.

Finally, we can conclude that phase transfer catalysis is a suitable technique for the synthesis of these kinds of polymers, especially for polyesterthiocarbonate **VI**, that was soluble in the reaction media and therefore the synthetic process is affected by the nature of the catalyst.

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