

## Polymerization by phase transfer catalysis

### 13. Polymer synthesis from 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-4-indanol\*

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#### SUMMARY

Polycarbonates, polythiocarbonates, and polyesters from 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-4-indanol were synthesized using phase transfer conditions. The effects of several catalysts and reactions times were evaluated by the yields and inherent viscosities. Phase transfer catalysis was not an efficient technique due to the rigid structure of the diphenol with the indanic group. The results were compared with that obtained with a diphenol having the same number of carbon atoms but forming an aliphatic side chain.

#### INTRODUCTION

Polyesteres and polyamides have been synthesized from diamines, diols and diacids that have in their structure an indane type group, so that the introduction of unsymmetrical and bulky group into polymer backbones, make polymers soluble and without extreme loss of the high thermal stability, specially when are compared with wholly aromatic polymers<sup>[1]</sup> Also soluble polyamides, polyesters, and polyimides with an indanic structure in the polymer chain exhibit high glass transition temperatures<sup>[2-3]</sup>

On the other hand, we have used the phase transfer catalysis (PTC) technique, in the synthesis of several kind of polymers, as polycarbonates<sup>[4-5]</sup>, polythiocarbonates<sup>[5-6]</sup> and polyesters<sup>[7]</sup>, obtaining high yields and molecular weights.

Continuing our work on the application of PTC to the synthesis of

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polymers<sup>[7]</sup>, in this article we describe the synthesis of polycarbonates, polythiocarbonates and polyesters derived from 1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-4-indanol and several PTC catalysts at four reaction times, we also compare the results with that obtained with a diphenol with the same number of carbon atoms but forming an aliphatic side chain.

## EXPERIMENTAL PART

Reagents and solvents were from Aldrich and Merck, and used without further purification. The following catalysts (from Fluka) were used: triethylbenzylammonium chloride (TEBAC), methyltrioctylammonium chloride (ALIQAT™), hexadecyltrimethylammonium bromide (HDTMAB), and tetrabutylammonium bromide (TBAB).

The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer, the <sup>1</sup>H NMR on a 100 MHz instrument (Varian XL-100) and the <sup>13</sup>C NMR on a 300 MHz (Varian XL-300) using CDCl<sub>3</sub> as solvent and TMS as internal reference. Viscosimetric measurements were made in CHCl<sub>3</sub> at 25°C.

1,1,3-trimethyl-3-(4'-hydroxy-phenyl)-4-indanol (**I**) was synthesized according to the following procedure: 4-methyl-3-en-2-pentanone (1 mol), phenol (3.7 mol), and acetic acid (30 mL), were mixed and HCl gas was passing by three hours. The solid was filtered, recrystallized in methanol and characterized. M.p.: 159-161°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (δ): 0.92 (s,3H,CH<sub>3</sub>), 1.36 (s,3H,CH<sub>3</sub>), 1.62 (s,3H,CH<sub>3</sub>), 2.22 (q,2H,CH<sub>2</sub>), and 7.08 (m,7H,Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (δ): 27.5 (CH<sub>3</sub> in C<sub>3</sub>), 30.1 (CH<sub>3</sub> gem in C<sub>1</sub>), 33.0 (C<sub>1</sub>), 39.3 (CH<sub>2</sub>), 50.4 (C<sub>3</sub>), 115.5 (C<sub>3</sub>-Ar), 118.6 (C<sub>5</sub>-Ar), 120.6 (C<sub>3</sub>-<sub>5</sub>-Ar), 128.3 (C<sub>1</sub>-Ar), 128.7 (C<sub>6</sub>-Ar), 129.0 (C<sub>2</sub>-<sub>6</sub>-Ar), 130.1 (C<sub>1</sub>-Ar), 141.6 (C<sub>2</sub>-Ar), 154.6 (C<sub>4</sub>-Ar), and 156.1 (C<sub>4</sub>-Ar). C: calc.: 80.86%; found: 80.80%. H: calc.: 7.46%; found: 7.60%.

Polycarbonates and polythiocarbonates were synthesized by the following general procedure: 5 mmol of **I** and 0.25 mmol (5%) of the catalyst were dissolved in 25 mL of KOH 1M and mixed with 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. Then, 5 mmol of phosgene or thiophosgene dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> were added and the mixture stirred at 20°C. After the reaction time, the organic

layer was poured into methanol and the solvents evaporated. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with water. The organic layer was dried and evaporated, and the residue characterized.

Polycarbonate **II**: IR (KBr) ( $\text{cm}^{-1}$ ): 1760 (C=O), 1600 (Ar), 1250 and 1200 (C-O), and 840 (Ar p-sust).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.92 (s,3H, $\text{CH}_3$ ), 1.36 (s,3H, $\text{CH}_3$ ), 1.68 (s,3H, $\text{CH}_3$ ), 2.22 (q,2H, $\text{CH}_2$ ), and 7.00 (m,7H,Ar).

Polythiocarbonate **III**: IR (KBr) ( $\text{cm}^{-1}$ ): 1600 (Ar), 1200 (C=S) and 840 (Ar p-sust).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.92 (s,3H, $\text{CH}_3$ ), 1.30 (s,3H, $\text{CH}_3$ ), 1.72 (s,3H, $\text{CH}_3$ ), 2.24 (q,2H, $\text{CH}_2$ ), and 7.04 (m,7H,Ar)

Polyesters were synthesized by the following general procedure: 5 mmol of **I** or 2,2-bis(4-hydroxy-phenyl)-4-methyl-pentane **VI**<sup>[6]</sup> and 0.25 mmol (5%) of the catalyst were dissolved 25 mL of KOH 1M and mixed with 25 mL of  $\text{CH}_2\text{Cl}_2$ . Then, 5 mmol of the diacid chloride in 15 mL of  $\text{CH}_2\text{Cl}_2$  were added and the mixture stirred at 20°C for 60 minutes. After the reaction time, the organic layer was poured into methanol and the precipitated polyester filtered, washed, dried under vacuum at 40°C, and characterized.

Polyester **IV**: IR (KBr) ( $\text{cm}^{-1}$ ): 1720 (C=O), 1580 (Ar), 1200 (C-O), and 820 (Ar p-sust).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.86 (s,3H, $\text{CH}_3$ ), 1.38 (s,3H, $\text{CH}_3$ ), 1.76 (s,3H, $\text{CH}_3$ ), 2.28 (q,2H, $\text{CH}_2$ ), 7.14 (m,7H,Ar), and 8.30 (s,4H,Ar).

Polyester **V**: IR (KBr) ( $\text{cm}^{-1}$ ): 2850 ( $\text{CH}_2$ ), 1720 (C=O), 1600 (Ar), 1420 ( $\text{CH}_2$ ) and 1200 (C-O).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.92 (s,3H, $\text{CH}_3$ ); 1.38 (s,3H, $\text{CH}_3$ ), 1.66 (s,3H, $\text{CH}_3$ ), 2.30 (q,2H, $\text{CH}_2$ ), 3.70 (s,8H, $\text{CH}_2$ ), and 7.02 (m,7H,Ar).

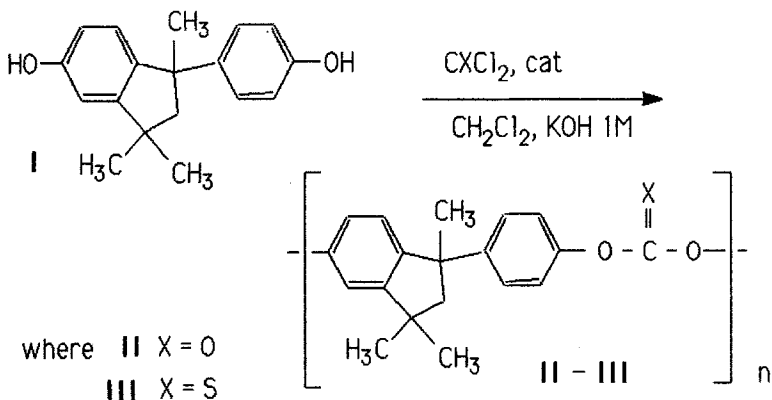
Polyester **VII**: IR (KBr) ( $\text{cm}^{-1}$ ): 2900 ( $\text{CH}_3$ ), 1720 (C=O), 1600 (Ar), 1200 (C-O), and 820 (Ar p-sust).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.72 (d,6H, $\text{CH}_3$ ), 1.72 (d,2H, $\text{CH}_2$ ), 3.50 (s,3H, $\text{CH}_3$ ), 7.02 (m,8H,Ar), and 8.26 (s,4H,Ar).

Polyester **VIII**: IR (KBr) ( $\text{cm}^{-1}$ ): 2980 ( $\text{CH}_2$ ), 1740 (C=O), 1600 (Ar), 1480 ( $\text{CH}_2$ ), 1200 (C-O), and 840 (Ar p-sust).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) ( $\delta$ ): 0.68

(d,6H,CH<sub>3</sub>), 1.98 (d,2H,CH<sub>2</sub>), 3.44 (s,3H,CH<sub>3</sub>), 3.68 (q,8H,CH<sub>2</sub>), and 7.00 (m,8H,Ar).

## RESULTS AND DISCUSSION

Polycarbonates and polythiocarbonates were obtained according to the following reaction:



and characterized by IR and <sup>1</sup>H NMR. The results are summarized in the experimental part and are in accord with the proposed structures.

Polymerizations were carried out at four reaction times (60, 120, 180, and 240 minutes), in a biphasic system KOH 1M/CH<sub>2</sub>Cl<sub>2</sub> at 25°C with the catalysts described in the experimental part. In most cases polymers were soluble in methanol, the organic solvent was evaporated, the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dried, and the solvent evaporated.

Tables I and II show the results obtained for polycarbonate II and polythiocarbonate III, respectively. Without catalyst polycarbonate and polythiocarbonate were not obtained, therefore an interphasial polycondensation process can be discarded. When catalysts were used, low values of  $\eta_{inh}$  were obtained with all of them. For both polymers, the highest values of  $\eta_{inh}$  were obtained with TEBAC as catalyst, which was described as hydrophilic<sup>[8]</sup> and suitable for the transfer of lipophilic dianions such as this. Also with this hydrophilic catalyst the hydrolysis of

Table I.- Inherent viscosities and yields obtained for polycarbonate II

Time	60'		120'		180'		240'	
Catalyst	%	$\eta^a$	%	$\eta^a$	%	$\eta^a$	%	$\eta^a$
---	--	--	--	--	--	--	--	--
TEBAC	65	0.03	31	0.03	69	0.05	64	0.09
ALQUAT	37	0.05	38	0.05	35	0.05	37	0.03
HDTMAB	43	0.03	55	0.08	44	0.04	41	0.03
TBAB	91	0.03	65	0.08	93	0.08	97	0.12

a: inh., in  $\text{CHCl}_3$  at 25°C (c=0.5 g/dL)

Table II. Inherent viscosities and yields obtained for polythiocarbonate III

Time	60'		120'		180'		240'	
Catalyst	%	$\eta^a$	%	$\eta^a$	%	$\eta^a$	%	$\eta^a$
---	--	--	--	--	--	--	--	--
TEBAC	99	0.05	98	0.05	96	0.03	64	0.09
ALQUAT	87	0.04	87	0.04	88	0.03	40	0.04
HDTMAB	74	0.05	81	0.04	79	0.03	39	0.04
TBAB	95	0.05	97	0.04	88	0.05	96	0.04

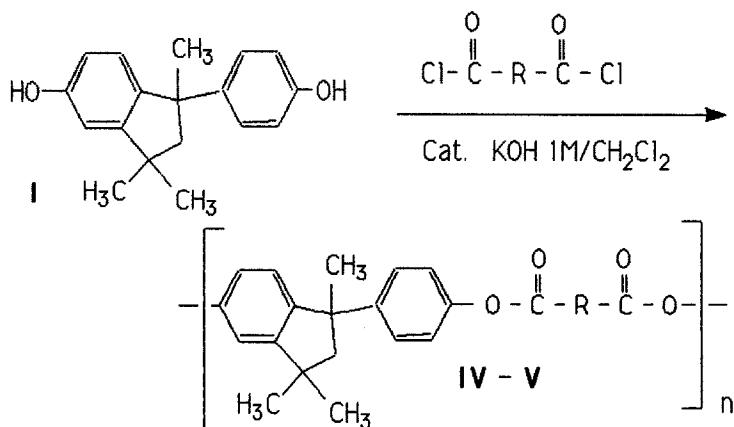
a: inh., in  $\text{CHCl}_3$  at 25°C (c=0.5 g/dL)

the polymeric chains in the organic phase or in the interphase is not favoured<sup>[4]</sup>

For polythiocarbonate III TBAB was also effective. This is probably due to the symmetry of this catalyst; there is an adequate separation of the ionic pair which contributes to a higher reactivity. With the other catalysts the results were the same for both polymers at all the reaction times.

In spite of these results, phase transfer catalysis seems to be an adequate technique to obtain these polymers, because without catalysts neither polycarbonate nor polythiocarbonate were obtained.

In order to explain the poor results obtained with diphenol **I**, we synthesized the polyesters derived from it and terephthaloyl or adipoyl dichloride in the same conditions used for polymers **II** and **III**, according to the following reaction:



where **IV**  $\text{R} = \text{p}-\text{C}_6\text{H}_4-$   
**V**  $\text{R} = -(\text{CH}_2)_4-$

Table III shows the results obtained. Without catalyst and with ALIQUAT and HDTMAB very low yields were obtained of the insoluble polyester **IV**. It is probable that the polymeric chains be very short and with many carboxylic as terminal groups and therefore insoluble in  $\text{CHCl}_3$ . With the other catalysts the yields were higher but with very low  $\eta_{\text{inh}}$ .

For polyester **V** the polymer was not obtain without catalysts and with TEBAC. With HDTMAB and TBAB very low values of yields and  $\eta_{\text{inh}}$  were obtained. Only with ALIQUAT the yield and  $\eta_{\text{inh}}$  were higher.

Also in the synthesis of polyesters from two very different diacid chlorides, the results obtained with diphenol **I** were very poor, probably

Table III. Yields and inherent viscosities obtained for polyesters **IV** and **V**

Catalyst	<b>IV</b> (R=-C <sub>6</sub> H <sub>4</sub> -)		<b>V</b> (R= -( -CH <sub>2</sub> - ) <sub>4</sub> -)	
	%	$\eta^a$	%	$\eta^a$
---	11	i	--	--
TEBAC	40	0.07	--	--
ALIUQUAT	17	i	87	0.13
HDTMAB	17	i	23	0.09
TBAB	34	0.07	19	0.06

a: inherent, in CHCl<sub>3</sub> at 25°C (c= 0.5 g dl<sup>-1</sup>), i: insoluble.

Table IV. Yields and inherent viscosities obtained for polyesters **VII** and **VIII**

Catalyst	<b>VII</b> (R=-C <sub>6</sub> H <sub>4</sub> -)		<b>VIII</b> (R= -( -CH <sub>2</sub> - ) <sub>4</sub> -)	
	%	$\eta^a$	%	$\eta^a$
---	33	i	83	0.11
TEBAC	82	0.31	91	0.17
ALIUQUAT	71	0.14	63	0.10
HDTMAB	43	0.11	47	0.10
TBAB	47	0.13	58	0.09

a: inherent, in CHCl<sub>3</sub> at 25°C (c= 0.5 g dl<sup>-1</sup>), i: insoluble.

due to the rigidity of the structure of the indanic residue, which does not permit an efficient transfer process.

On the other hand, we synthesized polyesters from the same diacid chlorides and the diphenol 2,2-bis(4-hydroxy-phenyl)-4-methyl-pentane **VI** which has the same number of carbon atoms as side chain, but does not form the indanic ring, being a more flexible molecule, and with which we obtained the respective polythiocarbonate in good yield and high  $\eta_{inh}$  with

several catalysts<sup>[6]</sup>.

Table IV shows the results obtained for polyesters **VII** and **VIII**. Without catalyst, polyester **IV** was insoluble in  $\text{CHCl}_3$ , probably because of the very short chains, which means a higher number of carboxylic as terminal groups. When TEAC, of hydrophilic characteristics<sup>[8]</sup> was used, we obtained a good yield and  $\eta_{inh}$ . With the other catalysts, of more lipophilic characteristics, there was a decrease of these variables, according to the behaviour reported with diphenols which also have lipophilic characteristics<sup>[4]</sup>.

For polyester **VIII**, also the best results were obtained with TEAC. With the other catalysts there was only an interphasial polycondensation process. Furthermore, these lipophilic catalysts can promote the hydrolysis of the diacid chloride and/or the polymeric chains, hydrolysis that can occur in the interphase or in the organic phase<sup>[4]</sup>. Then, there is a decrease of the yield and  $\eta_{inh}$ .

Finally, we can conclude that the structure of the diphenol can have an important influence in the transfer process, specially when its structure has a rigidity that makes the transfer of the ionic pair inefficient.

## ACKNOWLEDGEMENTS

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