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Polymerization by phase transfer catalysis

7. Effect of the catalyst on the hydrolysis of bisphenol A polythiocarbonate*

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Summary

The hydrolysis of bisphenol A polythiocarbonate is studied under phase transfer conditions, and occurs principally in the organic phase, influenced by the catalysts according to their structure.

Introduction

In a previous paper (1) we described the synthesis of the polythiocarbonate from bisphenol A and thiophosgene under phase transfer conditions, and the influence of the nature of the catalyst in the yield and molecular weight.

Considering that polythiocarbonates are polyesters, and that the reaction is carried out in a biphasic system which has an organic solvent and an alkaline aqueous solution, it is impossible to rule out a hydrolytic process parallel to the polymerization, which can occur in the interphase or in the organic phase influenced by the catalyst.

Continuing our works on the applications of phase transfer catalysis to polymer synthesis, in this note we report the results obtained in the influence of the nature of the catalyst on the hydrolysis of the bisphenol A polythiocarbonate.

Experimental part

Bisphenol A polythiocarbonate was synthethized and characterized as described in a previous paper (1). Solvents and reactives (from Merck) were used without further purification. The following catalysts (from Fluka) were used: TBAB, tetrabutylammonium bromide; BTEAC, benzyltriethylammonium chloride; HDTMAB, hexadecyltrimethylammonium bromide; TBHDPB, tributylhexadecylphosphonium bromide; and Aliquat, methyltrioctylammonium chloride.

Viscosimetric measurements were made in a Desreux-Bischoff (2) type dilution viscosimeter in $CHCl_3$ at 25°C.

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* For part 6, see the preceding paper

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In a typical reaction 500 mg of bisphenol A polythiocarbonate dissolved in 30 mL of CH_2Cl_2 were mixed with 20 mL of 1M NaOH and 0.5 mmol of the catalyst. The mixture was stirred at 20°C for 2.5 h. The organic layer was separated and poured into methanol. The precipitated polymer was filtered, washed with methanol, and then dried under vacuum at 40°C.

Results and Discussion

Table I shows the results obtained with and without catalyst, using a sample of bisphenol A polythiocarbonate of 0.67 $dL \cdot g^{-1}$ as η inh ($CHCl_3$ at 25°C, c= 0.5 g/dL.

TABLE I. Effect of the Catalyst on the hydrolysis of bisphenol A polythiocarbonate.

Catalyst	Yield (%)	η inh[a]
None	95	0.54
TBAB	69	0.18
BTEAC	74	0.42
HDTMAB	46	0.20
TBHDPB	62	0.18
Aliquat	71	0.15

a: $dL \cdot g^{-1}$ in $CHCl_3$ at 25°C (c= 0.5 g/dL)

Without catalyst the recovery was 95% and the η inh decreases to 0.54 $dL \cdot g^{-1}$, probably due to an interphasial hydrolysis. On the other hand with TBAB, HDTMAB, TBHDPB, and Aliquat, the recovery, and specially the η inh values decrease to a very low values, and that confirms their effect on the hydrolysis process. BTEAC, which is a more hydrophilic catalyst, present a smaller effect than the others, as can be see in the recovery and the higher η inh value than those obtained with other catalysts more lypophilic, which might transfer OH^- anions for the polymeric chain hydrolysis.

Finally we can conclude that the hydrolysis of the polymeric chains of bisphenol A polythiocarbonate, occurs principally in the organic phase, and depends rather on the nature of the catalyst that on an interphasial process. This behaviour has also been described for the hydrolysis of polycarbonates (3).

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