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Phase Transfer Catalysis

Polymerization by Phase Transfer Catalysis

1. Polyethers Synthesis

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Summary

Polyethers from 1,4-bis(chloromethylene)-2,5-dimethoxybenzene and 4,4'-biphenol were obtained by phase transfer catalysis, using different catalysts and solvents. The molecular weights and yields were determined, showing a solvent effect and a influence of the catalysts used.

Introduction

Phase transfer catalysis (PTC) has been used widely in organic synthesis since it was reported by STARKS (1-2). Nevertheless its application to polymer synthesis is more reduced. However, this technique has been used satisfactorily in polyether synthesis (3-5), polycarbonates (6), polythioethers (7), polyesters (8) and others polymers (9).

It has been shown that PTC offers mild conditions and technical advantages, and would be a suitable method for polyethers synthesis, normally prepared at high temperatures and in polar solvents (10).

In order to apply PTC's technique to polymer synthesis, in this first work we report the synthesis of dimethoxylated polyethers from 1,4-bis(chloromethylene)-2,5-dimethoxybenzene and 4,4'-biphenol, using several catalysts and solvents under PTC conditions.

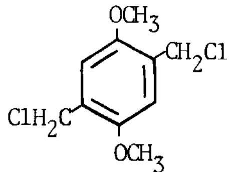
Experimental Part

1,4-bis(chloromethyelene)-2,5-dimethoxy benzene was obtained according to the method of WOOD and GIBSON (11). Solvents and reagents were purchased from Aldrich and Merck. The following catalysts (Fluka) were used: TBAB, tetrabutylammonium bromide; TEBAC, triethylbenzylammonium chloride; HDTMAB, hexadecyltrimethylammonium bromide; HDTBPB, hexadecyltributylphosphonium bromide and BTPPB, benzyltriphenylphosphonium bromide.

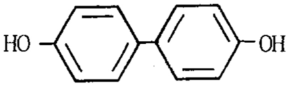
In a typical polycondensation reaction, 4,26 mmoles of dihalide (I) and 5% mmol of catalyst dissolved in 30 ml of solvent were mixed with 4,26 mmols of 4,4'biphenol (II) in 30 ml of NaOH 3N. The mixture was stirred at 70°C (40°C in CH_2Cl_2) for 48 hours, cooled and poured into methanol. The precipitated polymer was filtered, washed with water to remove inorganic salts, benzene to remove unrreacted dihalide and methanol, then was dried under vacuum at 40°C. The polymers were characterized by IR spectroscopy (Perkin-Elmer Model 1310) and elemental analysis (Hareaus).

Results and Discussion

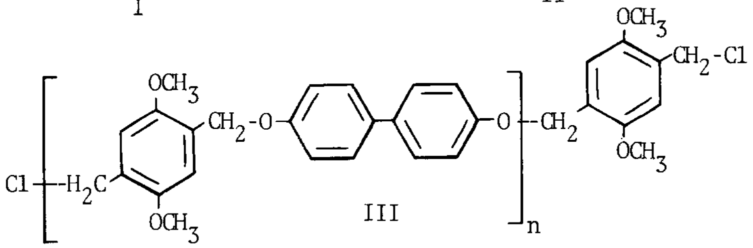
The IR spectrum of the polymer showed characteristics bands at 1600 and 1500 cm^{-1} (aromatic rings), 1210 cm^{-1} (aromatic ether) and 1040 cm^{-1} (aliphatic ether). This data and elemental analysis (C: calcd. 75,86%, found 75,84%; H. Calcd. 5,75%, found 5,76%) are consistent with structure III.



I



II



III

Polyether III was insoluble in all organic solvents and the molecular weights were determined by halogen content analysis.

Table I shows the results obtained with several solvents using different catalyst. A well-known solvent effect in the obtained molecular weights can be observed, for example in a high polar solvent such as nitrobenzene, the molecular weights are higher, probably due to a greater solubility of the polymeric growing species. In CH_2Cl_2 this effect is small, due to the low work temperature (40°C) caused by the high volatility of this solvent.

In all solvents, the polymer precipitate in the course of the reaction and that produce an obvious limitation to obtain high molecular weights because there are low concentrations of polymer in the organic phase. Clearly this happened when benzene was used as the solvent, and the molecular weights were very similar and they are not influenced by the catalyst's structure.

However, in nitrobenzene and chlorobenzene, were obtained the highest molecular weights, and we note an influence of the catalyst structure. Catalysts such as TBAB and TEBAC, which by their structure are partitioned mainly in the aqueous phase, and BTPPB which is partitioned in the organic phase due to its more lipophilic structure, give low molecular weights. HDTBPB is the best catalyst in these solvents, evidenced not only by the higher molecular weight but also by the yields obtained, and seem to confirm Dehmlow's (12) statement that not only interest the number of carbon atoms but also the distribution of them around the central atom of the catalyst. We have confirmed this in other systems (13) too. With HDTMAB we can not discard its action as miscellar agent due to the structure of this catalyst.

TABLE I. Molecular weights and yields of polyether III obtained under PTC conditions at 70°C in 48 hours.

Cata-	C_6H_6		CH_2Cl_2[a]		$C_6H_5NO_2$		C_6H_5Cl	
lyst	M.W.x10^{-3}	Yield %	M.W.x10^{-3}	Yield %	M.W.x10^{-3}	Yield %	M.W.x10^{-3}	Yield %
TBAB	9.2	68.1	1.7	79.6	49.0	89.8	47.3	63.4
TEBAC	14.9	45.9	17.8	45.9	47.3	45.8	45.8	53.2
HDTMAB	13.9	68.1	28.4	34.4	94.7	86.1	47.3	36.6
HDTBPB	12.6	50.6	—	3.4	93.4	94.9	92.2	80.9
BTPPC	11.0	31.0	16.3	35.8	24.5	56.6	65.6	29.3

[a] 40°C.

Finally it is clear that in polymer synthesis under PTC conditions, to obtain high molecular weights the organic phase must support high concentrations of polymer and monomer, and the reactions must be clear and relatively fast (CAMERON and LAW, 1982). There are few systems that fulfill these conditions in polyether synthesis.

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