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Preparation of Polyethers by Phase Transfer Catalyzed Polycondensation

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ABSTRACT

Polyethers have been prepared by solution polycondensation of bisphenol A with an aromatic or an aliphatic dichloride, using phase transfer catalysis method.

INTRODUCTION

A large number of polyethers have been prepared by reacting a dialkaline metal salt of a bisphenol with a dihalide in polar solvents at high temperatures (Morgan, 1965 ; Johnson et al., 1967 ; Rose, 1974 ; Robeson et al., 1977 ; Attwood et al., 1977 ; Hashimoto et al., 1977). It has been recently shown that phase transfer catalysis method offers several practical advantages over earlier procedures, in many cases, for known organic syntheses (Dockx , 1973 ; Dehmlow, 1974 and 1977 Weber and Gokel, 1977). Particularly, increasing interest is shown in polymer synthesis using phase transfer catalysts (Soga et al., 1977 a, b and 1979 ; Imai et al., 1978 a, b, and 1979). We wish to report our results concerning the preparation of polyethers from bisphenol A (BPA) and 1,4 -dichloro-2 butene (DCB) or 1,4 - bis (chloromethyl) benzene (BCB), by phase transfer catalyzed polycondensation.

EXPERIMENTAL

Bisphenol A was purified by recrystallization

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from toluene. DCB was redistilled before use. BCB, phase transfer catalysts : tetrabutylammonium hydrogen sulfate (TBAH), Kryptofix [222] , and dicyclohexyl-18 crown-6 (DCHE) as well as solvents (toluene and DMSO) were pure grade commercial products and were used without further purification.

Typically, a heterogeneous mixture containing BPA (3.07 mmol) dissolved in NaOH 3N (10 ml), toluene (10 ml) and a phase transfer catalyst (TBAH : 0.61 mmol) was stirred at 65°C under nitrogen.DCB (3.07 mmol) was added and the mixture was stirred at 65°C for 5 h. After cooling the organic layer was diluted with toluene (20 ml), separated, washed with slightly acidic aqueous solution (30 ml of HCl 0.0I N) and with water. The polymer was recovered by precipitation in methanol and purified by dissolution in $CHCl_3$ followed by precipitation in methanol. It was dried under high vacuum. A 98% yield of a white powder was obtained (based on starting materials).

RESULTS AND DISCUSSION

The results of the polycondensation of bisphenol A with DCB and with BCB are shown in Tables 1 and 2.

Analysis of polymers was done by infrared and NMR spectroscopy. The infrared spectrum of the polyether prepared from bisphenol A and DCB displays characteristic absorption bands at 1640 cm^{-1} (C = C stretching), 1600 and 1500 cm^{-1} (phenyl ring vibrations), 1235 cm^{-1} (phenyl ether stretching), and 1015 cm^{-1} (aliphatic ether stretching). The ^1H NMR spectrum of this polyether, in $CDCl_3$ at room temperature, exhibits strong peaks at 1.60 ppm (CH_3), 4.50 ppm ($\underline{CH_2}$-O), 6.02 ppm ($C\underline{H}$ = $C\underline{H}$), 7.20-6.67 ppm (aromatic protons), and a weak peak at 4.25 ppm ($\underline{CH_2}Cl$). No trace of phenolic end groups is detected whereas chloromethyl end groups can be seen in the ^1H NMR spectrum as well as well as in the ^{13}C NMR spectrum.

TABLE 1

Preparation of polyethers from bisphenol A and DCB in toluene-aqueous Na OH system at 65°C

Run	Catalyst (mol %)[a]	Na OH	Time h	Yield %	Elemental analysis C,	H,	O,	Cl	$\overline{M}_n$ [b]
1	-	3 N	18	0			-		-
2	TBAH (10)	3 N	5	98	79.1,	6.9,	10.8,	3.5	2000
3	TBAH (30)	6 N	5	93	80.3,	7.1,	11.2,	0.8	8400
4	TBAH (100)	3 N	5	100	80.9,	7.1,	10.8,	1.5	4600
5	TBAH (30)	25 N	5	92	80.0,	7.1,	12.0,	~0	c
6[d]	TBAH (10)	25 N	5	58	79.5,	7.3,	11.1,	3.2	2200
7	[222] (5)	3 N	17	85	79.5,	7.2,	10.9,	2.6	2700

[a] mol% of the chlorine content of DCB. [b] calculated from the chlorine content of polymer according to formula I. [c] traces of phenolic end groups were found in this sample.

[d] polycondensation was carried out with 3.07 mmol of BPA and 2.05 mmol of DCB.

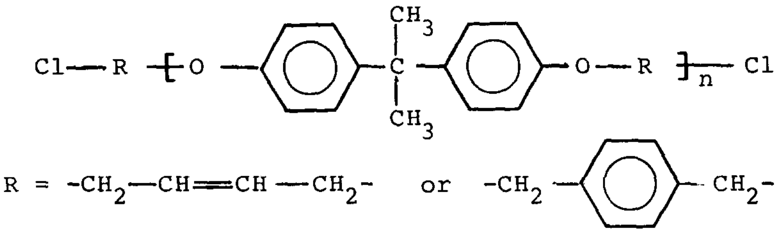
TABLE 2

Preparation of polyethers from bisphenol A and BCB in DMSO - aqueous Na OH 25 N system at 70° C with 5% mol. of DCHE.

Run	Time	Yield	Elemental analysis				$\overline{M}_n$ [a]
	h	%	C,	H,	O,	Cl,	
8	5	63	81.6,	6.6,	9.4,	1.5	4500
9	40	87	80.7,	6.7,	10.1,	0.1	63000

[a] calculated from the chlorine content of polymer according to formula I.

From these results, the following structure can be assumed for the polyether prepared by phase transfer catalyzed polycondensation :



I

Absence of phenolic end groups in polymers was confirmed by spectrophotometric analysis after conversion of the phenolic groups to phenolates via quaternary ammonium hydroxide according to Shchori and Mc Grath (1978). Only traces of phenolic groups could be detected in the case of run 5 (Table 1).

Polyethers from bisphenol A with DCB or BCB are prepared in a similar way as that described for the synthesis of phenol ethers using phase transfer catalysis conditions (Mc Killop et al. 1974). Polycondensation takes place via the alkylation of phenoxide ions with chloromethyl groups in the organic phase. A phase transfer catalyst is necessary for transport of the phenoxide ions between the two phases. It should be noticed that no polymer can be obtained in the absence of catalyst even after 18 h of reaction at 65°C (run 1, Table 1).

As can be seen in Table 1 (run 6), stoechiometric amounts of bisphenol A and DCB are not necessary in order to obtain a polymer since in this case the ratio [bisphenol A] / [DCB] is equal to 1.5. This is an advantage of the phase transfer catalyzed polycondensation.

Polyethers prepared from DCB are soluble in organic solvents such as benzene, toluene, THF, and chlorinated hydrocarbons whereas those prepared from BCB are partly soluble in DMSO.

Molecular weights of the polymers were calculated from the chlorine content by assuming the structure I except for run 5. Analysis of the molecular weight distribution has been examined by GPC in THF at 30°C. The chromatogram of the sample 2 (Table 1) is shown in figure 1. By taking the calibration curve of polyethers formed from bisphenol A and diglycidyl ether, it is possible to estimate $\overline{Mn}$ and $\overline{Mw}$ which are equal to 2000 and 3400 respectively ($\overline{Mw}/\overline{Mn} = 1.7$)

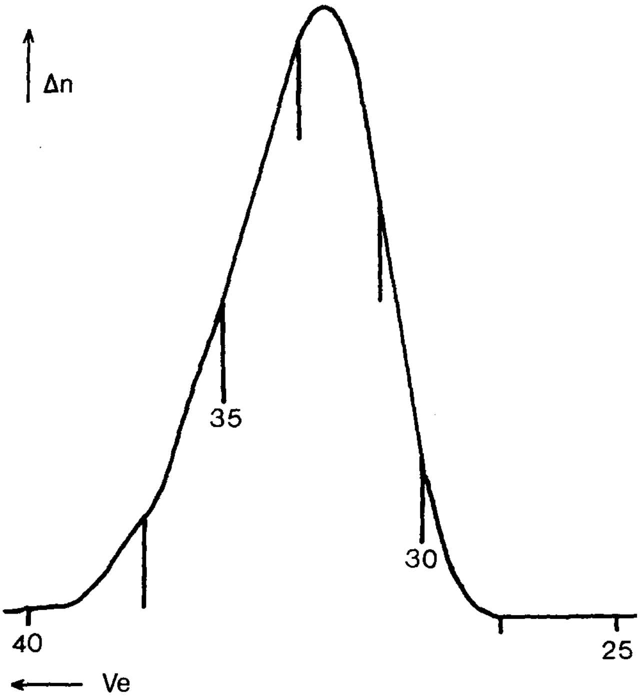


Fig. 1 Chromatogram of polyether prepared from bisphenol A and DCB

A detailed study of this new type of polycondensation is presently being carried out and will be reported in a subsequent paper.

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