

## Phase-Transfer Catalyzed Polycondensation of $\alpha,\alpha'$ -Dichloro-*p*-xylene with 2,2-Bis(4-hydroxyphenyl)propane

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**ABSTRACT:** The phase-transfer catalyzed polycondensation of  $\alpha,\alpha'$ -dichloro-*p*-xylene with 2,2-bis(4-hydroxyphenyl)propane was carried out in the presence of benzyltriethylammonium chloride in a two-phase system of an aqueous alkaline solution and its solution-immiscible organic solvents such as benzene, tetrahydrofuran (THF), and *N*-methyl-2-pyrrolidone. Addition of dimethyl sulfoxide (DMSO) to the system not only enhanced the reaction but also suppressed side reactions to give a completely soluble, high molecular weight polyether. Optimal solvent systems at 60°C were THF–DMSO (3 : 1) or nitrobenzene–DMSO (3 : 1)/50 wt% aqueous sodium hydroxide, which gave the polymer having an inherent viscosity of 0.54 dl g<sup>-1</sup>. The reaction temperature also affected the inherent viscosity of the resulting polymer causing it to become 0.62 dl g<sup>-1</sup> at 100°C in a toluene–DMSO (3 : 1)/50 wt% aqueous sodium hydroxide system.

**KEY WORDS** Phase-Transfer Catalyzed Reaction / Polycondensation / Polyether /  $\alpha,\alpha'$ -Dichloro-*p*-xylene / 2,2-Bis(4-hydroxyphenyl)propane /

Phase-transfer catalyzed (PTC) polycondensation is a novel type of interfacial polycondensation, since it is carried out in the presence of phase-transfer catalysts in a two-phase system of an aqueous alkaline solution and its solution-immiscible organic solvent. Some polymers not get prepared by conventional interfacial or solution methods can be obtained easily by this PTC method without using expensive reagents and/or solvents under fairly mild conditions. Several polymers such as polycarbonates,<sup>1</sup> polysulfonates,<sup>2</sup> polyesters,<sup>3,4</sup> and polyethers<sup>2,5-9</sup> have been prepared from bisphenols by the PTC method.

Synthesis of a polyether by the PTC polycondensation of  $\alpha,\alpha'$ -dichloro-*p*-xylene (DCPX) and 2,2-bis(4-hydroxyphenyl)propane (BPA) was reported independently by N'Guyen and Boileau<sup>5,6</sup> and Cameron and Law<sup>7</sup>; the polyether having a molecular weight of about 4,000 calculated from the chlorine content was obtained.

At the beginning of our studies on the PTC polycondensation of DCPX with BPA in a benzene/aqueous alkaline solution system, we encountered

the problems of the resulting polymer being pale yellow and partially insoluble in polar aprotic solvents. It was confirmed that the polymer contained xylylidene units to some extent in the polymer backbone. This was supported by the homopolymerization of DCPX under the PTC conditions which gave a yellow, insoluble, and infusible xylylidene-containing polymer.<sup>10</sup>

An investigation was then undertaken to overcome the problems of xylylidene formation and other side reactions and to prepare a completely soluble polyether with high molecular weight. It is known that the PTC alkylation of active methylene compounds and the Williamson ether synthesis were greatly enhanced when dimethyl sulfoxide (DMSO) was added to the reaction mixture.<sup>11,12</sup> By doing so, it was found that a solvent system consisting of a mixture of benzene and DMSO could effectively suppress the side reactions. This article deals with the successful synthesis of a soluble polyether with high molecular weight by the PTC polycondensation in organic solvent–DMSO/aqueous alkaline solution systems under a variety of

conditions.

## EXPERIMENTAL

### Materials

Commercial  $\alpha,\alpha'$ -dichloro-*p*-xylene (DCPX) and 2,2-bis(4-hydroxyphenyl)propane (BPA) were recrystallized from methanol and benzene, respectively. Organic solvents were purified by distillation before use. Benzyltriethylammonium chloride (BTEAC) was obtained commercially and used as received. Aqueous alkaline solutions were prepared just before use.

### Model Reaction

*2,2-Bis[4-(4-methylbenzyloxy)phenyl]propane.* In a 200-ml flask equipped with a mechanical stirrer and a condenser, 2.9 g (20 mmol) of  $\alpha$ -chloro-*p*-xylene, 2.3 g (10 mmol) of BPA, 0.45 g (2.0 mmol) of BTEAC, 20 ml of benzene, and 20 ml of DMSO were placed. To this solution, 40 ml of 50 wt% aqueous sodium hydroxide was added all at once with vigorous stirring at 60°C. After 3 h reaction at 60°C, the reaction mixture was neutralized with hydrochloric acid and extracted with benzene. After the benzene solution was dried over sodium sulfate, the benzene was removed by evaporation to obtain the product. It was recrystallized from ethanol to give 4.1 g (94%) of 2,2-bis[4-(4-methylbenzyloxy)phenyl]propane, mp 103–104°C. The infrared (IR) spectrum (KBr disk) exhibited absorptions at 1250 and 1020  $\text{cm}^{-1}$  ( $=\text{C}-\text{O}-\text{C}$ ). *Anal.* Calcd for  $\text{C}_{31}\text{H}_{32}\text{O}_2$ : C, 84.40%; H, 7.34%. Found: C, 84.35%; H, 7.30%.

### Polymerization

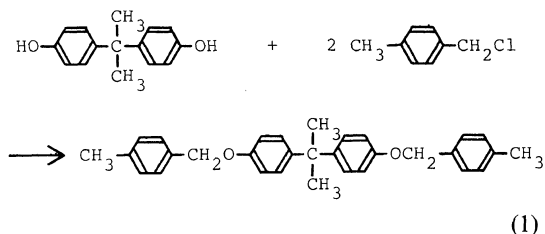
*Polyether from DCPX and BPA.* In a 50-ml flask equipped with a mechanical stirrer and a condenser, 0.88 g (5.0 mmol) of DCPX, 1.14 g (5.0 mmol) of BPA, 0.23 g (1.0 mmol) of BTEAC, 10 ml of benzene, and 10 ml of DMSO were charged. The mixture was heated at 60°C and stirred vigorously, and then 20 ml of 50 wt% aqueous sodium hydroxide was added. After 7 h reaction at 60°C, the reaction mixture was neutralized with hydrochloric acid and the precipitate was filtered off. This crude polymer was washed successively with water, methanol, and acetone to remove inorganic salts, monomers, and oligomers. The polymer was purified by dissolution in *N*-methyl-2-pyrrolidone (NMP)

followed by precipitation in methanol. The inherent viscosity of the polymer in NMP was 0.32  $\text{dl g}^{-1}$ , measured at a concentration of 0.5  $\text{g dl}^{-1}$  at 30°C. The IR spectrum (KBr disk) showed absorptions at 1250 and 1020  $\text{cm}^{-1}$  ( $=\text{C}-\text{O}-\text{C}$ ). *Anal.* Calcd for  $\text{C}_{23}\text{H}_{22}\text{O}_2$ : C, 83.64%; H, 6.67%. Found: C, 82.87%; H, 6.72%.

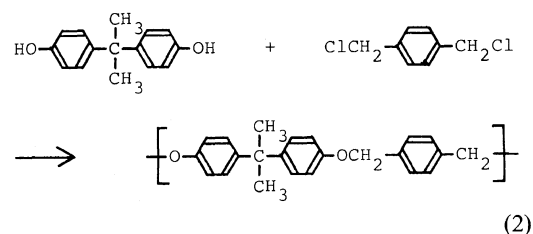
## RESULTS AND DISCUSSION

### Polycondensation in a Benzene–DMSO/Aqueous Alkaline Solution System

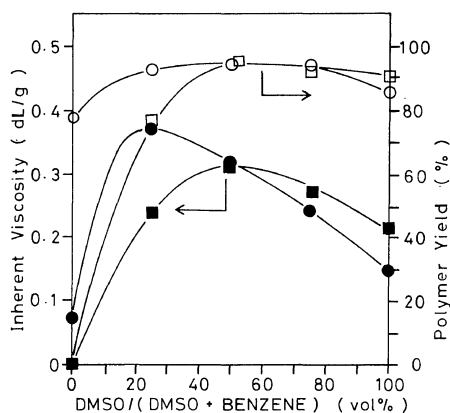
Before going to polymer synthesis, a model-compound study was undertaken to determine the effectiveness of a mixed solvent system, a benzene–DMSO/aqueous sodium hydroxide system, under phase transfer conditions for the Williamson ether synthesis. The PTC reaction of BPA with  $\alpha$ -chloro-*p*-xylene in this system afforded the expected ether compound, 2,2-bis[4-(4-methylbenzyloxy)phenyl]propane, in a quantitative yield [eq 1].



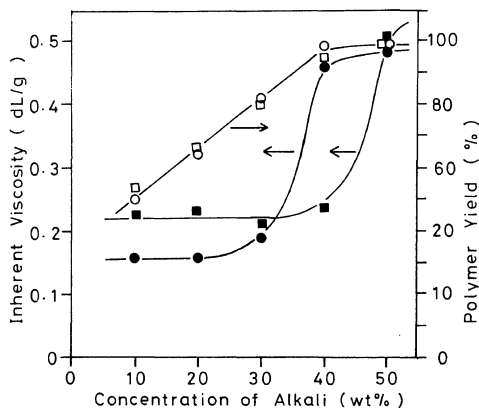
This high yield reaction was then applied to polymer synthesis. The PTC polycondensation of DCPX with BPA leading to the formation of a polyether was carried out in a benzene–DMSO/50 wt% aqueous sodium hydroxide system in the presence of BTEAC as a catalyst [eq 2].



The effects of DMSO and the catalyst on the polycondensation are shown in Figure 1. No polymer was obtained by the uncatalyzed polymerization (without a phase-transfer catalyst) in a benzene/aqueous sodium hydroxide system. It is interesting to note that the uncatalyzed polymeri-



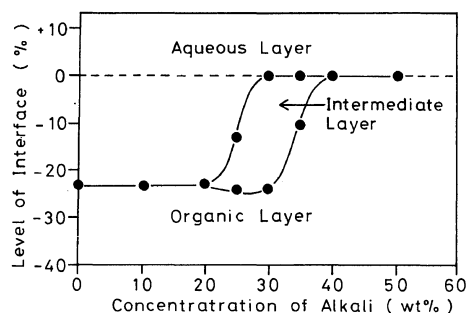
**Figure 1.** The effects of DMSO and catalyst on the polycondensation of DCPX with BPA at 60°C for 7h: presence of BTEAC (●, ○); absence of BTEAC (■, □).



**Figure 2.** The influence of alkaline concentration on the PTC polycondensation of DCPX with BPA in a benzene-DMSO (3:1)/aqueous alkaline solution system with BTEAC at 80°C for 7h: sodium hydroxide (●, ○); potassium hydroxide (■, □).

zation proceeded smoothly when DMSO was added to the organic phase (*cf.* Table I). The inherent viscosity and yield of the polymer increased markedly by using DMSO; the inherent viscosity reached a maximum value of  $0.32 \text{ dl g}^{-1}$  and the yield, 95% by addition of 50 vol% of DMSO (based on the total volume of the organic phase) to the system.

The catalyst was also highly effective for the preparation of a higher molecular weight polymer. The PTC polycondensation in a benzene/aqueous sodium hydroxide system resulted in the formation of the polymer having a inherent viscosity of only

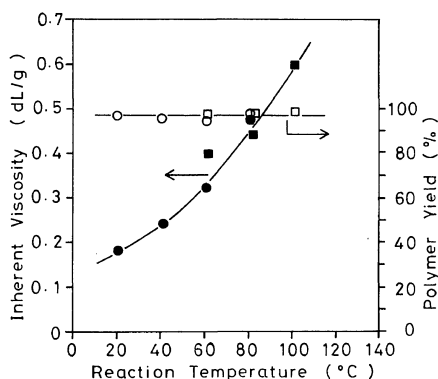


**Figure 3.** Change in the level of the interface between the organic phase and aqueous phase. A mixture of benzene and DMSO (3:1) was shaken well with aqueous sodium hydroxide and set aside for 10 min to determine the level of the interface.

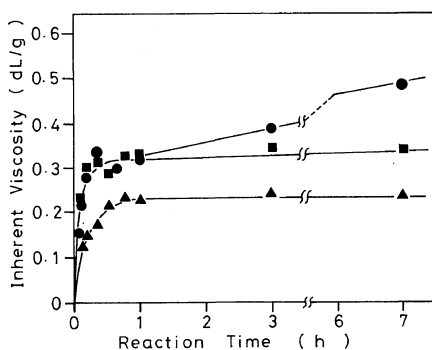
$0.07 \text{ dl g}^{-1}$ , whereas the inherent viscosity reached as high as  $0.38 \text{ dl g}^{-1}$  when 25 vol% of DMSO was added to the system. Although DMSO obviously enhanced both the uncatalyzed and PTC polycondensations, the use of more than 50 vol% of DMSO did not increase the yield of the polymer with high inherent viscosity.

The influence of the sodium hydroxide or potassium hydroxide concentration on the PTC polycondensation in a system of an aqueous alkaline solution and a mixture of benzene and DMSO (3:1) is given in Figure 2. The alkaline concentration greatly affected both yield and inherent viscosity of the resulting polymer. The concentration of sodium hydroxide below 30 wt% afforded only a low molecular weight polymer. The inherent viscosity and yield increased markedly from  $0.18 \text{ dl g}^{-1}$  and 80% at a concentration of 30 wt% to  $0.45 \text{ dl g}^{-1}$  and 99% at 40 wt%. Thus, a concentration higher than 40 wt% is essential for the preparation of the polymer with high molecular weight in quantitative yield. This is also true in the case of potassium hydroxide, which gave somewhat better results.

Figure 3 shows the changes in the level of the interface between the organic and aqueous phases as a function of concentration of sodium hydroxide. DMSO dissolves in dilute aqueous sodium hydroxide (below 20 wt%) rather than in benzene, and a stable two-phase system is formed. At a concentration of sodium hydroxide of 20–40 wt%, three clear layers, benzene, an intermediate, and the aqueous alkaline solution, are obtained. Using a concentrated aqueous alkaline solution (above



**Figure 4.** The effect of reaction temperature on the PTC polycondensation of DCPX with BPA in the presence of BTEAC in a benzene–DMSO (3:1) (○, ●) or toluene–DMSO (3:1) (■, □)/50 wt% sodium hydroxide system.



**Figure 5.** Time dependence of inherent viscosity of the polymer. The PTC polycondensation was carried out at 40 (▲), 60 (■), and 80°C (●) with BTEAC in a benzene–DMSO (3:1)/aqueous sodium hydroxide system.

40 wt%), DMSO moves almost completely into the benzene layer and a stable two-phase system consisting of benzene–DMSO/aqueous sodium hydroxide is again formed. The similarity in shape of Figures 2 and 3 suggests that the benzene–DMSO/50 wt% aqueous sodium hydroxide system plays an important role in enhancing PTC polycondensation.

The effect of the reaction temperature on the polycondensation in benzene–DMSO/ or toluene–DMSO/aqueous sodium hydroxide is shown in Figure 4. The inherent viscosity of the polymer increased markedly with increasing temperature;

the inherent viscosity improved from 0.18 to 0.62 dl g<sup>-1</sup> on raising the temperature from 20 to 100°C.

Figure 5 shows the time dependence of the inherent viscosity of the polymer in the PTC polycondensation at three different temperatures. The polymerization at 40 and 60°C seemed almost completed in 1 h, giving the polymers with inherent viscosities of 0.22 and 0.32 dl g<sup>-1</sup>, respectively. In the case of the polycondensation at 80°C, however, the inherent viscosity continued to increase with increasing reaction time, and the viscosity reached 0.5 dl g<sup>-1</sup> after 7 h reaction.

#### *Polycondensation in Other Mixed Solvent/Aqueous Alkaline Solution Systems*

The polycondensation of DCPX with BPA was carried out in two-phase systems of mixed organic solvents other than benzene–DMSO and 50 wt% aqueous sodium hydroxide. Table I shows the results of the polycondensation in benzene–another organic solvent/aqueous sodium hydroxide system. Organic solvents employed were *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMA), tetrahydrofuran (THF), and 1,4-dioxane (DOX). Although all of these solvents are freely soluble in water, they formed stable two-phase systems with 50 wt% aqueous sodium hydroxide. The combination of benzene and dipolar aprotic solvents such as NMP and DMA resulted in the formation of the polyether in high yield with or without BTEAC as a catalyst, whereas a mixture of benzene and THF or dioxane gave only a low yield of the polymer with low inherent viscosity even in the presence of the catalyst. It is interesting to note that the PTC polycondensation in a NMP or DMA/aqueous sodium hydroxide system yielded a higher molecular weight polymer compared with that in the corresponding benzene-containing system. The combinations of DMSO and these organic solvents resulted in both high yield and fairly high inherent viscosity of the polymer.

In the case of run 1-3 in Table I, a pale yellow, insoluble, and infusible polymer was obtained. The IR spectrum of this polymer was identical with that of poly(*p*-xylylene), indicating that the homopolymerization of DCPX took place. Being insoluble in aqueous alkaline solution, DCPX polymerized in the solid state, probably from crystalline surfaces, by attack of hydroxide ions in the presence

## Phase Transfer Catalyzed Polycondensation

**Table I.** PTC polycondensation of DCPX with BPA in two-phase systems of mixed organic solvent/50 wt% sodium hydroxide<sup>a</sup>

Run No.	Two-phase system			BTEAC	Polymer yield	$\eta_{inh}$
	Organic phase		50 wt% NaOH			
	ml		ml			
1-1	—	—	40	—	0	—
1-2	Bz 20	—	20	—	0	—
1-3	—	—	40	Pres	22.0	Insoluble
1-4	Bz 20	—	20	Pres	78.7	0.07
1-5	Bz 10	DMSO 10	20	Pres	94.1	0.32
1-6	Bz 10	DMSO 10	20	—	96.2	0.32
1-7	—	DMSO 20	20	Pres	86.2	0.15
1-8	—	DMSO 20	20	—	91.2	0.22
2-1	—	THF 20	20	Pres	0	—
2-2	Bz 10	THF 10	20	—	0	—
2-3	Bz 10	THF 10	20	Pres	20.3	0.21
2-4	DMSO 10	THF 10	20	Pres	96.4	0.31
2-5	DMSO 10	THF 10	20	—	96.8	0.29
3-1	—	DOX 20	20	Pres	39.9	0.17
3-2	Bz 10	DOX 10	20	—	0	—
3-3	Bz 10	DOX 10	20	Pres	22.0	0.14
3-4	DMSO 10	DOX 10	20	Pres	95.8	0.25
3-5	DMSO 10	DOX 10	20	—	96.5	0.22
4-1	—	NMP 20	20	Pres	97.6	0.45
4-2	Bz 10	NMP 10	20	—	55.9	0.16
4-3	Bz 10	NMP 10	20	Pres	89.7	0.32
4-4	DMSO 10	NMP 10	20	Pres	95.7	0.30
4-5	DMSO 10	NMP 10	20	—	24.7	0.23
5-1	—	DMA 20	20	Pres	97.5	0.29
5-2	Bz 10	DMA 10	20	—	88.8	0.19
5-3	Bz 10	DMA 10	20	Pres	85.3	0.17
5-4	DMSO 10	DMA 10	20	Pres	94.9	0.23
5-5	DMSO 10	DMA 10	20	—	97.7	0.21

<sup>a</sup> Polycondensation was carried out at 60°C for 7 h. Abbr.: presence, Pres; benzene, Bz; tetrahydrofuran, THF; dioxane, DOX; *N*-methyl-2-pyrrolidone, NMP; *N,N*-dimethylacetamide, DMA; dimethyl sulfoxide, DMSO.

of PTC. The homopolymerization of DCPX by the PTC method will be reported in further detail in the near future.

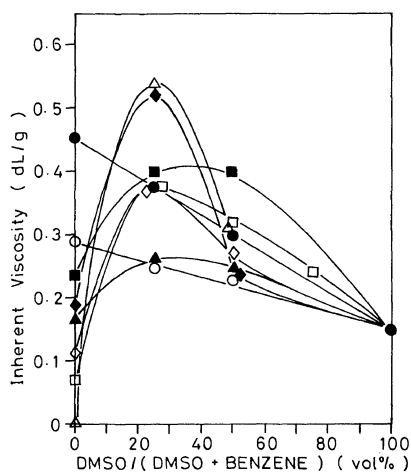
PTC polycondensation was then conducted using a mixture of DMSO and other organic solvents such as toluene, nitrobenzene, anisole, dioxane, THF, NMP, and DMA for the organic phase. Figure 6 gives the curves of inherent viscosity of the polymer as a function of DMSO content. Except for the curves for the polycondensation in NMP–DMSO/

and DMA–DMSO/50 wt% aqueous sodium hydroxide systems, all the curves were similar in shape. The inherent viscosity increased with DMSO content to a maximum at 25 vol% and then decreased monotonically. The most effective solvent systems were found to be nitrobenzene–DMSO (3:1)/ and THF–DMSO (3:1)/50 wt% aqueous sodium hydroxide yielding a polymer of inherent viscosity as high as 0.54 dl g<sup>-1</sup>. Elemental analyses of some of the polymers obtained are listed in Table II.

**Table II.** Elemental analysis of polyether<sup>a</sup>

Polymerization conditions	C	H	Cl	$\eta_{inh}$
	%	%	%	dl g <sup>-1</sup>
Calcd. for C <sub>23</sub> H <sub>22</sub> O <sub>2</sub>	83.64	6.67	0	—
Benzene-DMSO (3:1), 80°C	82.87	6.72	1.21	0.48
Toluene-DMSO (3:1), 100°C	82.05	6.57	1.87	0.60
MMP, 60°C	83.69	6.62	1.09	0.45
THF-DMSO (3:1), 60°C	83.32	6.32	1.93	0.54

<sup>a</sup> PTC polycondensation was carried out in two-phase systems of mixed organic solvent/50 wt% sodium hydroxide in the presence of BTEAC for 7h.



**Figure 6.** The solvent effect on the PTC polycondensation of DCPX with BPA in the presence of BTEAC at 60°C for 7h: benzene (□); toluene (■); nitrobenzene (◆); anisole (◇); dioxane (▲); tetrahydrofuran (△); *N*-methyl-2-pyrrolidone (●); *N,N*-dimethylacetamide (○).

Although the carbon and hydrogen content was in good agreement with the calculated values, some chlorine end groups were detected in these polymers and the chlorine contents were not correlated with the inherent viscosities. The reason for such results is not clear. However, hydrolysis of the chlorine end groups probably took place to some extent during the reaction to possibly prevent formation of a high molecular weight polymer.

From these results, it is evident that the addition of DMSO to the organic phase minimizes the side

reactions, thus permitting the expected polycondensation almost exclusively to give high molecular weight polyether in high yields. This is because the organic phase containing DMSO serves as a reaction medium and DMSO solvates both cations and DCPX, so naked phenolate anions react with DCPX much faster than hydroxide anions.

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