

Phase Transfer Catalysis in Polymerizations and Organic Reactions: Phase Transfer Polycondensation between Bisphenolate Anions and 1,6-Dibromohexane in the Presence of Tetrabutylphosphonium Bromide

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(Received February 3, 1983; Accepted March 20, 1983)

Abstract: Polyethers were synthesized by the reaction of various bisphenols with 1,6-dibromohexane in NaOH (aq)-nitrobenzene using tetrabutylphosphonium bromide as a phase transfer catalyst. The effects of catalyst, bisphenol structure, and base concentration were studied and compared with our earlier results. The catalytic activity of the catalysts in the present polymerization was in the order of tetrabutylphosphonium bromide > tetrabutylammonium bromide > dibenzo-18-crown-6. The reactivity of the bisphenols decreased in the order, 2,2-bis(4-hydroxyphenyl)propane > bis(4-hydroxyphenyl)sulfide > bis(4-hydroxyphenyl)ketone > bis(4-hydroxyphenyl)sulfone. The polymer yield increased when excess NaOH was used. A distribution study revealed that there is a reasonable correlation between the degree of anion partitioning into nitrobenzene and the polymer yield.

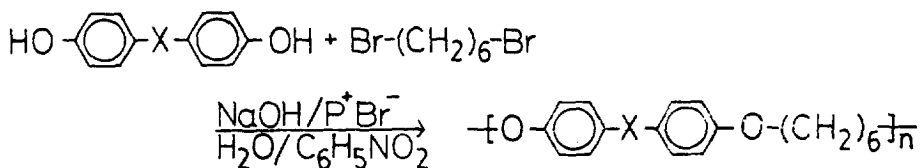
INTRODUCTION

Phase transfer catalysis has been used extensively in organic synthesis^{1,2}, but only recently has it been applied to polymer chemistry³⁻⁹. This aqueous-organic biphasic heterogeneous system offers several advantages over conventional single-phase step-growth polymerization especially of nucleophilic displacement⁷. These include the substitution of dipolar aprotic solvents such as DMSO, DMA, etc., with inexpensive solvents, lower reaction temperature, and shorter reaction time.

We reported earlier the synthesis of linear polyethers by the reactions of various bisphe-

nolate anions with 1,6-dibromohexane (DBH) in the two phase system of water and nitrobenzene using tetrabutylammonium bromide (Q^+Br^-)⁸ and dibenzo-18-crown-6 (DBC)⁹ as phase transfer catalysts. We have also proposed that the term "phase transfer polymerization" should be used to differentiate this type of reaction from the conventional interfacial polymerization⁸.

As an extension of our work we have conducted an investigation on biphasic heterogeneous polymerizations of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), bis(4-hydroxyphenyl)sulfide (thiodiphenol; TDP), bis(4-hydroxyphenyl)ketone (ketone diphenol; KDP), bis(4-hydroxyphenyl)sulfone (sulfone diphenol; SDP),



X=C(CH₃)₂ (BPA), S(TDP), CO(KDP), SO₂ (SDP), O(ODP), CH₂(MDP), none(BDP)

4, 4'-oxydiphenol(ODP), bis(4-hydroxyphenyl) methane (methane diphenol; MDP), and pp'-biphenol (BDP) with 1,6-dibromohexane in the presence of tetrabutylphosphonium bromide (P⁺Br⁻).

We have compared the catalytic activity of P⁺Br⁻ with that of Q⁺Br⁻ and DBC in the present phase transfer polymerization. The structure reactivity relationship of the bisphenolate anions and the properties of the polymers are also discussed.

EXPERIMENTAL

Instruments and Reagents

Melting points, uncorrected, were determined on a Electrochemical melting point apparatus. Infrared spectra were recorded on a Jasco DS-701G spectrophotometer.

All of the bisphenols were obtained from commercial source and purified by recrystallization from water. 1,6-Dibromohexane and nitrobenzene were distilled before use. Tetrabutylphosphonium bromide was prepared according to the literature procedure¹⁰.

Synthetic Reactions

The reaction between various bisphenols and 1,6-dibromohexane were conducted in H₂O-C₆H₅NO₂ using P⁺Br⁻ as described earlier⁹.

Study of the Phase Transfer Phenomenon

The fraction of bisphenolate anions transferred to the nitrobenzene phase by P⁺Br⁻ was determined by titration as described earlier⁹.

Characterization of Polymers

To determine the solution viscosities of the

polyethers 0.2-0.5g of the polymers were dissolved in a suitable solvent and diluted to 100.0 ml. The relative viscosity and inherent viscosity were measured using an Ostwald viscometer in a constant temperature bath at 70.0°C. The structures of polymers were confirmed by their IR spectra.

RESULTS AND DISCUSSION

Catalytic Effect of Tetrabutylphosphonium Bromide

When the polymerizations between bisphenols and DBH were conducted in the water-nitrobenzene system without P⁺Br⁻, no reaction was observed at 78°C even after 7 hours of reaction. However, the addition of a small amount of the catalyst greatly affected the reaction as shown in Fig. 1, 2 and 3.

The effect of P⁺Br⁻ concentration upon the yield of polymerization between TDP and DBH is depicted in Fig. 1.

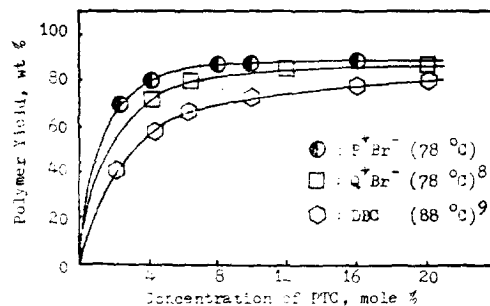


Fig. 1. Effect of PTC concentration on the polymerization of thiodiphenol with 1,6-dibromohexane. Reactions were conducted for 3 hours in the presence of excess (1.2 equiv.) NaOH or KOH.

The yield increases with the catalyst concentration but only up to a certain level, above which the yield remained almost constant. The same trends were observed when Q^+Br^- and DBC were used as catalysts^{8,9}. This result indicates that the supply of bisphenolate anions to the reaction site at this threshold level of catalyst concentration apparently becomes equal to or exceeds their consumption rate through polymerization. The activity of the catalysts based on the polymer yield is in the order, $P^+Br^- > Q^+Br^- > DBC$. The same order of catalytic activity was also observed when the polymerizations were performed at a fixed level (2mol %) of catalyst while varying the reaction time (see Fig. 2 and 3).

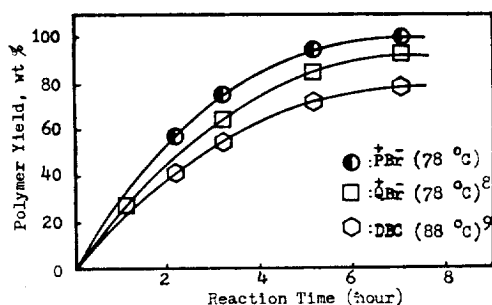


Fig. 2. Phase transfer polymerization between bisphenol A and 1,6-dibromohexane in the presence of 2mole % catalyst and excess (1.2 equiv.) NaOH.

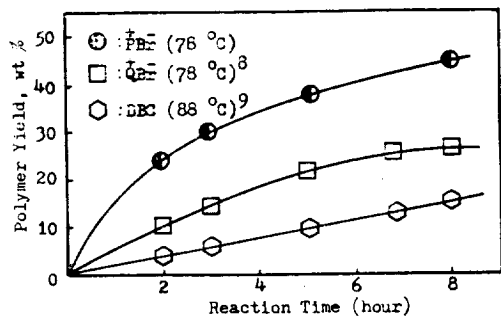


Fig. 3. Phase transfer polymerization between sulfone diphenol and 1,6-dibromohexane in the presence of 2mole% catalyst and excess(1.2 equiv.) NaOH.

The relationship between inherent viscosity of the resulting polymers and the reaction time for the reaction of BPA and TDP with DBH is shown in Fig. 4.

Molecular weight of the polymers, as reflected by their solution viscosity, appears to increase with reaction time. Thus, a step-growth mechanism could be operating for this type of polymerization⁷.

Effect of Bisphenol Structure upon the Reactivity

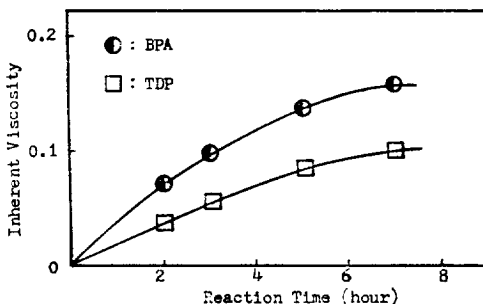


Fig. 4. Dependence of solution viscosity of polymers on the reaction time. Polymerizations were conducted at 78°C in the presence of 2mole % P^+Br^- and excess (1.2 equiv.) NaOH.

Table 1. Effect of Bisphenol Structure upon the Polymer Yield

Bisphenol	Yield (%)		
	P^+Br^- ^a	Q^+Br^- ^{a,b}	DBC ^{c,d}
BDP	79.4	—	—
BPA	73.2	64.5	79.4
TDP	69.9	53.1	68.1
ODP	69.4	—	—
MDP	64.2	—	—
KDP	50.0	—	51.2
SDP	31.6	16.8	27.2

a) Polymerized for 3hrs. at 78°C using 2mole % of catalyst and 1.2 equiv. of base

b) Ref. 8

c) Polymerized for 3hrs. at 88°C using 6mole % of catalyst and 1.2 equiv. of base

d) Ref. 9

The yield of polymerization between various bisphenols and DBH with the three catalysts is listed in Table 1.

The yield decreases with the bisphenol structure in the descending order in the Table. This order of reactivity is in parallel with the nucleophilicity of the anions, except for BPA.

The high reactivity of BPA is attributed to its good phase transferability into the reaction site (see below). Thus, it appears that both the substituent effect and the lyophilicity of the groups between the aromatic rings are important in determining the reactivity of the anions in the phase transfer polymerization.

The catalytic activity of the catalysts can also be compared from Table 1. For the reactions of various bisphenols with DBH, it is again in the order of $P^+Br^- > Q^+Br^- > DBC$.

Effect of Base Concentration

The effect of NaOH concentration upon the polymer yield in the phase transfer polymerization of BPA with DBH is recorded in Table 2.

The yields were always higher when excess NaOH was used. This result can be explained by the increased partitioning of bisphenolate anions in the organic phase (see below). An increase in ionic strength in the aqueous phase seems to salt out the large bisphenolate anions and increase their partitioning into the organic

Table 2. Effect of Base Concentration upon the Polymer Yield

Ratio of NaOH to Bisphenol	Yield (%)		
	P ⁺ Br ^{-a}	Q ⁺ Br ^{-a,b}	DBC ^{c,d}
1 : 1	65.8	40.2	49.5
1.2 : 1	73.2	64.5	79.4

a) Polymerization of BPA with DBH for 3hrs. at 78°C in the presence of 2mole % of catalyst.

b) Ref. 8

c) Polymerization of BPA with DBH for 3hrs. at 88°C in the presence of 6mole % of catalyst

d) Ref. 9

phase, resulting in enhanced polymer yield.

Distribution of Bisphenolate Anions between Water and Nitrobenzene

In order to evaluate the relative catalytic efficiency of the phase transfer polymerizations, the distribution of the bisphenolate anions between water and nitrobenzene in the presence of P⁺Br⁻ was examined. Table 3 includes a comparison with our earlier results^{8,9}.

The partitioning of the bisphenolate anions into nitrobenzene depends strongly on the base concentration, anion structure, and the nature of catalyst. The use of excess NaOH increased the solubilization of the anions in the organic layer. Increasing the base concentration in aqueous layer ties up additional water of hydration, and reduce the amount of water available for the hydration of bisphenolate anion. This would in turn facilitate the transfer of the anions into the organic phase. For a given base concentration, the phase transferability of the anions decreases in the order, BPA > TDP > KDP > SDP. This is not unexpected considering the relative lyophilicity

Table 3. Solubilization of Bisphenolate Anions by PTC's into Nitrobenzene^a

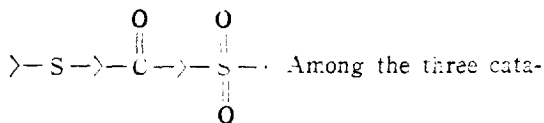
Bisphenol	P ⁺ Br ⁻		Q ⁺ Br ^{-b}		DBC ^c	
	1 : 1	1 : 1.2	1 : 1	1 : 1.2	1 : 1	1 : 1.2
B P A	78	88	70	82	75	81
T D P	71	78	60	64	63	65
K D P	64	68	—	—	24	31
S D P	43	61	27	47	10	14

a) Data presented are mole % bisphenolate anions dissolved into nitrobenzene and expressed as mole % of catalysts used, i.e., 2x moles of bisphenolate in nitrobenzene divided by moles of catalyst initially added. Distribution was studied at 78°C (P⁺Br⁻ and Q⁺Br⁻) and 88°C (DEC) using 2mole % catalysts of bisphenols. The ratios of 1 : 1 and 1 : 1.2 designate the mole ratios of bisphenols to NaOH (P⁺Br⁻ and Q⁺Br⁻) and KOH (DBC).

b) Ref. 8

c) Ref. 9

of the bisphenol substituents, i.e., $-\text{C}(\text{CH}_3)_2-$



Among the three catalysts P^+Br^- was the most efficient in phase transfer capacity, as shown in the table.

There appears to be a reasonable correlation between the anion distribution and the polymer yield, when the effects of catalyst, bisphenol structure, and base concentration are compared. This is not without precedent. From the phase transfer reaction of thiophenol with 1-bromooctane, a linear relationship was noted between the anion concentration in organic phase and the rate¹¹.

Properties of Polymers

The properties of polyethers prepared under two different reaction conditions are tabulated in Table 4 and 5.

The inherent viscosity of the polymers prepared after 3 hours of reaction with 2mole% P^+Br^- decreases in the descending order in

Table 4. Inherent Viscosity of Polyethers*

Bisphenols	BPA	ODP	MDP	TDP	KDP	SDP
	0.105	0.0767	0.0684	0.0652	0.0602	0.0525

* Polymers were obtained after 3 hours of reaction at 78°C using 2 mole % P^+Br^- . Inherent viscosities of polyethers were measured for 1,1,2,2-tetrachloroethane solution at 70°C.

Table 5. Yield, Inherent Viscosity and Melting Point of Polyethers.

Properties	Diols	Yield, % ^{a)}	η inh ^{b)}	Tm, °C
	BPA	99.8	0.340	113
	TDP	99.8	0.338	150
	MDP	99.7	0.339	144
	SDP	99.8	0.333	161

a) Polymers were obtained after 24 hours of reaction at 100°C using 10 mole % P^+Br^- .

b) All of the inherent viscosities were measured on 0.4g/100ml solution of the samples in 1,1,2,2-tetrachloroethane at 70°C.

Table 4.

This, as expected, almost parallels the yields of each polyethers. When the reaction was forced to higher conversion, the viscosity of the resulting polyethers increased accidentally to a similar value regardless of the bisphenol structure (Table 5).

Further study on the relationship between the solution viscosity and absolute molecular weights of the polymers is deemed necessary to explain this observation.

All of the high conversion polymers showed rather sharp melting points in the order, $\text{SDP} > \text{TDP} > \text{MDP} > \text{BPA}$, reflecting that they are semi-crystalline in nature. Polar substituents between the two aromatic rings seem to increase the melting point, while the nonpolar bulky ones decrease it.

CONCLUSION

Following conclusions can be drawn from the results of the present investigation:

- 1) Tetrabutylphosphonium bromide (P^+Br^-) is the best phase transfer catalyst among those examined; P^+Br^- , Q^+Br^- and DBC.
- 2) Phase transfer polymerization seems to follow step-growth polymerization mechanism.
- 3) The use of excess alkali accelerates polymerization rate.
- 4) Catalytic efficiency parallels the phase transfer capacity of anions from aqueous to the organic phase.
- 5) Reactivity of bisphenol anions depends not only their nucleophilicity, but also their transferability by the catalysts into the organic phase.

Acknowledgement: The authors are grateful to Korean Traders Scholarship Foundation for the support of this work.

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