

상이동중합 2. 디벤조-18-크라운-6 존재하에서 비스페놀 음이온과 1,6-디브로모헥산의 2상 중축합

진정일, 이광섭, 장진해, 김시중

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(1981년 12월 10일 접수)

Phase Transfer Polymerization 2. Two Phase Polycondensation between Bisphenolate Anions and 1,6-Dibromohexane in the Presence of Dibenzo-18-Crown-6.

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(Received December 10, 1981)

요약 : 수용액 중에 존재하는 몇가지 비스페놀 음이온과 니트로벤젠속에 녹아 있는 1,6-디브로모헥산을 디벤조-18-크라운-6을 상이동 촉매로 사용하여 폴리에테르를 합성하였다. 사용한 알칼리 금속이온(Li^+ , Na^+ , K^+ 및 Cs^+)중에서 비스페놀음이온의 짝이온이 K^+ 일때 상이동성이 가장 좋았으나, 브롬화 테트라부틸 암모늄보다 상이동 촉매성은 뒤떨어짐을 알았다. 사용한 비스페놀 음이온의 반응성은 2,2-비스(4-히드록시페닐)프로판 > 황화비스(4-히드록시페닐) > 비스(4-히드록시페닐)케톤 > 비스(4-히드록시)술폰 순으로 감소하였으며, 이는 이 음이온들의 반응성 및 크라운에테르 촉매에 의한 상이동성의 차이로 설명할 수 있었다. 과량의 KOH를 사용하면 비스페놀음이온의 상이동을 촉진시켜 중합속도를 증가시키기도 알았다.



Abstract : A series of polyethers were prepared by polycondensation reaction between bisphenolate anions and 1,6-dibromohexane in the two phase, heterogeneous system of water and nitrobenzene. Dibenzo-18-crown-6 was employed as a phase transfer catalyst. Of the alkali metal salts examined (Li^+ , Na^+ , K^+ , and Cs^+) phase transfer activity was found to be at a maximum when the counter cation of bisphenolate was K^+ . Activity of dibenzo-18-crown-6 appeared to be less effective for this particular reaction than that of tetrabutylammonium bromide. Reactivity of bisphenolate anions decreased in the order: 2,2-bis (4-hydroxyphenyl) propane > bis (4-hydroxyphenyl) sulfide > bis (4-hydroxyphenyl) ketone > bis (4-hydroxyphenyl) sulfone. Employment of excess amount of potassium hydroxide facilitated the transfer of bisphenolate anions from the aqueous to the nitrobenzene phase, thus increasing the polycondensation rate.

INTRODUCTION

The novelty of phase transfer reactions has been beneficially utilized in many different organic reactions since Stark's detailed report about 10 years ago on the phase transfer activity of quaternary ammonium halides.¹⁻⁴ Earlier we reported the synthesis of linear polyethers by the reaction of bisphenolate anions of 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A; BPA), bis(4-hydroxyphenyl) sulfide (thiodiphenol; TDP), and bis(4-hydroxyphenyl) sulfone (sulfonyldiphenol; SDP) with 1,6-dibromohexane in the two phase heterogeneous system of water and nitrobenzene⁵. The tetrabutyl ammonium ion was used as a phase transfer catalyst. In the same paper, we proposed that the term "phase transfer polymerization" should be used to differentiate this type polymerization from the conventional interfacial polymerization, because to distinguish the reaction mechanisms applicable in these two polymerization methods.

Another type of phase transfer agents used very often for organic synthesis are crown ethers of various cavity sizes.^{6,7} The phase transfer polymerization technique has been utilized in recent years for the preparation of many different polymers. Poly(phenylene oxide)⁸, polythiocarbonates⁹, polycarbonates¹⁰, polysulfonates¹¹ and polysulfides^{12,13} are some of the examples.¹⁴ Catalytic activity of crown ethers, however, has not been established in relation to their phase transfer capability of transporting species from one phase to another, especially in polycondensation reactions.

In the present study we conducted polycondensation reaction between various bisphenolate

anions(O^- --X-- O^- , X being $\text{C}(\text{CH}_3)_2$, SO_2 , S or $\text{C}=\text{O}$) dissolved in the aqueous

phase and 1,6-dibromohexane in nitrobenzene, with 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (dibenzo-18-crown-6) serving as a phase transfer catalyst. We have examined the catalytic effect of the crown ether, counter-ion effect, and the relationship between the reactivity of bisphenolate anions and their structures.

EXPERIMENTAL

Chemicals

All of the bisphenols obtained from commercial sources were purified by recrystallization. 1,6-Dibromohexane and nitrobenzene were purified by fractional distillation before use. Dibenzo-18-crown-6 was synthesized from 1,2-dihydroxybenzene (catechol) and bis(2-chloroethyl) ether following Pederson's method⁶.

Instruments

A differential scanning calorimeter (Perkin-Elmer, Model 1B) and a thermogravimetric analyzer (Perkin-Elmer, Model TGA-1) were used for thermal analysis of polymers. Quantitation of K^+ in solutions was determined by a flame emission spectrophotometer (Pye Unicam). Molecular weights of polymers were measured using a vapor pressure osmometer (Knauer Co.) equipped with an electronic universal temperature measuring device and X-Y recorder. IR spectra of polymers were obtained by a diffraction grating infrared spectrophotometer (Jasco, Model DS-70 1G).

Synthetic Reactions

A general procedure for the synthetic reactions employed in this study was as follows: Bisphenol (10.0 m mole) and alkali hydroxide (24.0 m mole) were dissolved in 20ml of deionized distilled water. 1,6-Dibromohexane (10.0 m

mole) and dibenzo-18-crown-6 (0.2 m mole) were dissolved in 20ml of nitrobenzene. These two solutions were placed in a 250ml round bottom flask equipped with a nitrogen inlet, a water-cooled condenser, and a stirrer.

The reaction mixture was vigorously stirred at 88°C under a nitrogen atmosphere. To avoid any effect of its variations the stirring rate was maintained at 1,500rpm throughout the present study⁵.

At the end of the reaction, the nitrobenzene layer was separated and poured into 100ml of acidified (pH=1) methanol. The precipitated polymers were thoroughly washed with diluted hydrochloric acid, water, and then ethanol. The washed polymers were dried at 60°C in a vacuum oven. Polymer yields were calculated from the weights of polymers obtained.

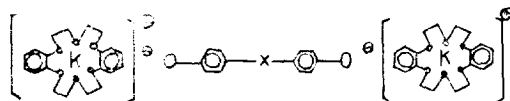
Characterization of Polymers

Intrinsic viscosities of polymer solutions were measured using a Cannon Ubbelohde type viscometer at 25°C or 50°C depending on the solubility of the polymer. Since the polymers showed different solubility characteristics, either chloroform, chlorobenzene, 1,2-dichlorobenzene or N,N-dimethylformamide was used as a solvent for the solution viscosity measurements (see Table VI and VII). Number average molecular weights of polymers were determined by vapor pressure osmometry, using benzil as a standard. The thermal behavior of polymers was examined using DSC and TGA methods.

Study of the Phase Transfer phenomenon

The fraction of bisphenolate anions distributed between aqueous and nitrobenzene phases in the presence of dibenzo-18-crown-6 was estimated by the determination of K⁺ in the two phases, assuming that all of K⁺ ions transferred into nitrobenzene were present in the ne-

utral salt form with bisphenolate anions:



A mixture formulated with the same amounts of each ingredients as described in „Synthetic Reactions” above, excluding 1,6-dibromohexane, was placed in a 250ml separatory funnel and agitated vigorously for 15 minutes. The mixture was then kept in a constant temperature bath at 88°C for 24 hours. One ml of nitrobenzene was taken by a pipet and transferred to a platinum crucible. The solution in the crucible was combusted in an electric furnace and the combustion products were dissolved in a measured amount of distilled water. The determination of potassium ions was performed by the usual flame emission spectrophotometry. Cesium was used as an ionization retarder. Distribution of Br⁻ ion between the phases at 60°C was also studied in a similar manner. Potassium bromide (5 m mole) was distributed between water and nitrobenzene (20ml of each) and the concentration of Br⁻ in the aqueous phase was determined using a bromide ion selective electrode.

RESULTS AND DISCUSSION

1. Polymerization

1.1. Effect of alkali metal cations, and hydroxide and bromide ions on polymerization.

Since it is well known that stability of a complex between a crown ether and an alkali metal cation greatly depends on the size of the inner cavity of the former and of the latter and that of all the alkali metal ions dibenzo-18-crown-6 forms the most stable complex wi-

Table I. Dependence of Polymerization rate on alkali metal cations*

Alkali metal hydroxide	BPA polyether yield, wt. %
LiOH	No reaction
NaOH	5.3
KOH	60.9
CsOH	1.2

*Polymerization of BPA and 1,6-dibromohexane at 88°C for 3 hours with stirring speed of 1,500rpm. The amounts of reactant and solvent were the same as described in "Experimental" section. Excess (20mole%) LiOH, CsOH, NaOH and KOH were used.

th K^{+15} , it was interesting to see whether these facts in a parallel way influence the present polymerization reactions. We conducted a series of polymerizations under the same condition as described in "Synthetic Reactions", using various alkali hydroxides (LiOH, NaOH, KOH, and CsOH); the results are tabulated in Table I. The results strongly imply that phase transfer of the nucleophiles, bisphenolate anions, from the aqueous to the nitrobenzene phase was most efficient when the metal ion was K^{+} . This in turn, indicates that the crown ether- K^{+} complex is the most stable among the complexes expected to be formed with the alkali metals examined, as has been amply demonstrated by others¹⁵.

The tremendous increase in polymer yield with K^{+} strongly emphasizes the importance of selecting the proper complexing cation when a crown ether is employed as a phase transfer

Table II. Dependence of polymer yield on the amount of potassium hydroxide used*

Ratio of KOH to reactants	Polymer yield, wt. %			
	BPA	TDP	KDP	SDP
1 : 1	49.5	38.9	30.7	18.8
1.2 : 1	79.4	68.1	51.2	27.2

*Polymerization of bisphenolate anions and 1,6-dibromohexane at 88°C for 3 hours with stirring speed of 1,500rpm. Amount of the DBC used was 6 mole% of diphenoxide.

catalyst.

As can be seen from Table II, polymerization was very much accelerated by the use of the excess amount of KOH. The presence of higher concentration of K^{+} in the aqueous phase must have favored the formation of complexes between K^{+} and the crown ether at the interface, increasing the transfer of bisphenolate anions from the aqueous to the nitrobenzene phase. This point will be discussed more fully in later part of this paper.

In order to examine the effect of presence of bromide ion together with higher concentration of K^{+} in aqueous phase, the excess KOH was replaced by KBr leaving a 1 : 1 mole ratio of KOH:reactant. The increased polymerization rate observed in the presence of excess KOH was significantly reduced, as shown in Table III. This can be ascribed to the possible partial transference of bromide ions by K^{+} -crown ether complex from the aqueous to the nitrobenzene phase, causing competition with bis-

Table III. The effect of bromide ion concentration on the reaction rate*

Salt concentration.	KOH, mole				KOH+KBr, mole			
	0.020	0.025	0.030	0.035	0.020 +0.000	0.0200 +0.005	0.020 +0.010	0.020 +0.015
BPA polymer yield, wt. %	49.5	77.5	77.9	79.0	49.5	68.8	70.0	75.2

*Polymerization of BPA and 1,6-dibromohexane at 88°C for 3 hours in the presence of 4mole% DBC. 0.020 moles of bisphenolate anions and of 1,6-dibromohexane were used throughout these experiments.

phenolate anions in their reaction with 1,6-dibromohexane and also less facile transport into water of bromide ions produced from the reaction between bisphenolate anions and 1,6-dibromohexane in the nitrobenzene phase. Indeed we could qualitatively detect the dissolution of KBr by the crown ether in nitrobenzene.

1.2. Catalytic effect of dibenzo-18-crown-6

When the reaction was conducted in the absence of the crown ether, only trace amount of polymers was obtained even after 8 hours of reaction at 88°C. Addition of the crown ether in the reaction mixture, however, greatly accelerated the polymerization rate as shown in Figure 1. Increasing the amount of the catalyst used raised the polymer yields up to a certain level above which reaction rate appeared to be independent of quantity of the catalyst. At or above this threshold level the supply of bisphenolate anions to the organic phase by the crown ether apparently becomes equal to or greater than their consumption rate by polymerization. The threshold value for the crown ether is very much dependent on the nature of the bisphenol. Results were approximately 8, 10, 14 and 16 mole% of the bisphenolate for BPA, TDP, KDP, and SDP, respectively. we have earlier observed the same tendency when tetrabutylammonium bromide was used as a catal-

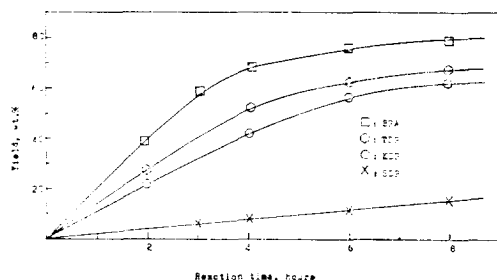


Figure 1. Relationship between the polymer yield and reaction time; polymerization was conducted in the presence of 2mole% DBC and excess (20mole%) KOH.

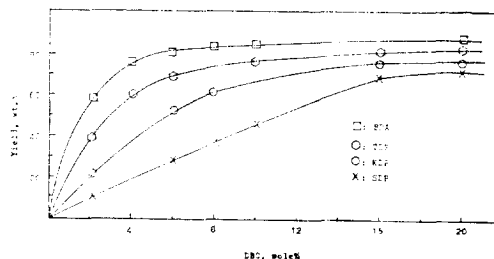


Figure 2. Relationship between polymer yield and concentration of DBC; polymerization was performed at 88°C for 3 hours in the presence of excess (20mole%) KOH.

yst. This difference in the threshold values is considered to be due to the difference in the transferability by the K^+ -crown ether complex of the bisphenolate anions from the aqueous to the nitrobenzene phase and in intrinsic reactivities of the bisphenol anions. The results shown in Figure 1 clearly demonstrate that the overall reactivity of the bisphenolate anions examined was $BPA > TDP > KDP > SDP$.

The same order of reactivity was also observed when the polymerization was performed at a fixed level (2mole%) of catalyst while varying the reaction time (see Figure 2). The order of reactivity parallels the basicity of the anions derived from these bisphenols, i.e. the electron-donating capabilities of the substituents

($-C(CH_3)_2$, $-S-$, $-\overset{\overset{O}{||}}{C}-$ and $-\overset{\overset{O}{||}}{S}-$) between the phenolic rings.

2. Distribution of Potassium Ions Between Water and Nitrobenzene

Distribution of potassium ions between water and nitrobenzene in the presence of dibenzo-18-crown-6 was determined as described in the „Experimental” section. It is strongly dependant on the nature of counter bisphenolate anions, see Table IV. The observed solubilization capability of anions is $BPA > TDP > KDP > SDP$. This appears to be in accord with their lyophilic-

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Table IV. Distribution of potassium ions between aqueous and organic phases^{a)}

Bisphenolate	$2[\text{DBC-K}^{\oplus}\text{O}^{\ominus}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{O}^{\ominus}\text{K}^{\oplus}-\text{DBC}]_{\text{N.B.}}$	
	$[\text{DBC}]_0^{\ominus}$	
	KOH:bisphenolate = 1:1	KOH:bisphenolate = 1.2:1
BPA	74.8%	80.9%
TDP	63.1%	65.3%
KDP	23.7%	31.4%
SDP	9.5%	14.4%

a) Distribution was studied at 88°C using 2mole % crown ether. Determined by flame emission spectrophotometer.

b) $2[\text{DBC-K}^{\oplus}\text{O}^{\ominus}-\text{C}_6\text{H}_4-\text{X}-\text{C}_6\text{H}_4-\text{O}^{\ominus}\text{K}^{\oplus}-\text{DBC}]_{\text{N.B.}}$ is the concentration of potassium ions in the organic phase.

c) $[\text{DBC}]_0$ is the original amount of dibenzo-18-crown-6 added.

ies. The combination of the two factors, greatest nucleophilicity and highest degree of transferability into nitrobenzene makes the BPA anion the most reactive among the bisphenolate anions examined. The opposite is true for SDP. The exact same trend was earlier observed by us when tetrabutylammonium bromide was used as a phase transfer catalyst⁵.

Another point of interest is that, regardless the structure of bisphenolate anions, more K^+ was solubilized in nitrobenzene when excess KOH was used. Since the counter ion of K^+ -crown ether complex should preferably be bisphenolate anions, it is safe to say that higher concentration of bisphenolate anions was transferred into the nitrobenzene phase. In a separate experiment we found that practically no hydroxide ion was solubilized into nitrobenzene even in the presence of the crown ether. This phenomenon can be directly related to the faster polymerization rate observed at higher

concentration of KOH as described earlier (Table III).

3. Comparison of Catalytic Activities of Dibenzo-18-Crown-6 and Tetrabutylammonium Bromide

As we reported earlier, tetrabutylammonium bromide exhibited a proficient catalytic effect in the phase transfer polymerization between the same bisphenolate anions as in the present study and 1,6-dibromohexane under the similar reaction conditions⁵. Comparing these results with the previous data, tetrabutylammonium bromide clearly is a better phase transfer catalyst than dibenzo-18-crown-6.

We have also conducted a series of polymerization using the two catalysts under the same reaction conditions in order to compare directly their catalytic activities (see Table V). As can be seen from the table, tetrabutylammonium bromide is a much better catalyst in these polymerization than dibenzo-18-crown-6. This can be attributed to at least three different factors:

1) greater transfer capacity of tetrabutylammonium toward the bisphenolate anions from the aqueous to the nitrobenzene phase as evidenced by distribution studies, 2) higher solubility of $(\text{K}^+-\text{crown ether})\text{Br}^-$ in nitrobenzene than $(\text{C}_4\text{H}_9)_4\text{N}^+\text{Br}^-$ resulting in less efficient

Table V. Catalytic ability of DBC and TBAB^{a)}

Bisphenolate Catalyst	BPA	TDP	KDP	SDP
DBC ^{b)}	79.4%	63.1%	51.2%	27.2%
TBAB ^{c)}	98.5%	97.1%	85.4%	70.7%

a) Polymerization of bisphenolates and 1,6-dibromohexane at 88°C for 3 hours and stirring speed of 1,500rpm. Amounts of DBC and of TBAB used were 6 mole% of bisphenolates.

b) Dibenzo-18-crown-6

c) Tetrabutylammonium bromide

removal of bromide ions generated during reaction from the nitrobenzene into the aqueous phase, and 3) higher dissociation of phase transferred tetrabutylammonium-bisphenolate ion pairs in nitrobenzene making the bisphenolate ions freer and thus more reactive.

Even though we have qualitative as well as quantitative data supporting 1) and 2), direct evidence for the 3) remains to be shown.

4. Properties of Polymers

Properties of polymers prepared under two different reaction conditions are tabulated in Table VI and VII. The polyether derived from BPA was soluble in chloroform, N,N-dimethylformamide, and nitrobenzene, while TDP polymer was soluble in chlorobenzene and ortho-dichlorobenzene. The KDP and SDP polyethers were soluble in ortho-dichlorobenzene and DMF, respectively. As expected high conversion polymers had higher molecular weights than low conversion polymers.

All the polymers showed rather sharp melting endotherms on the DSC heating runs in the order of KDP > SDP > TDP > BPA (Table VI). Po-

Table VI. Intrinsic viscosity and number average molecular weight of polyethers^{a)}

Bisphenols	Yield wt. %	Intrinsic viscosity ^{b)}	Number average molecular weight ^{c)}
BPA	79.4	0.102 (chloroform)	3,500 (chloroform)
TDP	68.1	0.097 (chlorobenzene)	2,540 (chlorobenzene)
KDP	51.2	0.091 (1,2-dichlorobenzene)	2270 (1,2-dichlorobenzene)
SDP	27.2	0.081 (DMF)	1860 (DMF)

a) Polymerization was conducted for 3hrs. at 88°C using 6mole% DBC.

b) Those of polyethers of BPA, TDP, SDP were determined at 25°C and that of KDP at 50°C in the solvents shown in parentheses.

c) Determined by vapor pressure osmometer.

Table VII. Intrinsic viscosity, number average molecular weight and melting temperature of polyethers^{a)}

Bisphenols	Yield, wt. %	Intrinsic viscosity ^{b)}	Number average molecular weight ^{c)}	Melting temperature °C
BPA	97.6	0.230	6750	100
TDP	97.5	0.211	4990	140
KDP	97.4	0.170	4670	195
SDP	97.5	0.153	3340	165

1) Polymerizations were conducted for 7hrs. (BPA), 15hrs. (TDP), 20hrs. (KDP) and 24hrs. (SDP) at 110°C with 10mole% DBC. For SDP polymer, concentrations of starting materials were as twice as others.

2) Those of polyethers of BPA, TDP and SDP were determined at 25°C and that of KDP at 50°C using chloroform, chlorobenzene, 1,2-dichlorobenzene and DMF, respectively.

3) Determined by vapor pressure osmometer.

lar substituents between the two aromatic rings seem to have raised the melting temperature of the resulting polymers.

Acknowledgement

Authors are grateful to the Ministry of Education of Korea for the support of this work. They are also grateful to Dr. Robert Ausubel for his many valuable suggestions in the preparation of this report.

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