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狀移動重合. Tetrabutylammonium Bromide 존재하에서 Diphenoxides와 1,6-Dibromohexane의 二狀重縮合反應

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Phase Transfer Polymerization. Two Phase Polycondensation of Diphenoxides and 1,6-Dibromohexane in the Presence of Tetrabutylammonium Bromide

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요 약. 수용액상에 존재하는 2,2-비스(4-히드록시페닐)프로판, 황화비스(4-히드록시페닐) 및 비스(4-히드록시페닐)술폰의 음이온과 니트로벤젠속에 존재하는 1,6-디브르모헥산을 브롬화테트라부틸 암모늄을 상이동 촉매로 사용하여 반응시켜 새로운 폴리에테르를 합성하였다. 중합속도는 교반속도와 촉매량에 의존하였으나 어느정도 이상에서는 영향을 받지 않았다. 분배실험으로 부터 친수성 음이온이 촉매에 의하여 니트로벤젠 층으로 상이동함을 확증하였으며 일부 중합체의 본성점성도 (0.09~0.16), 수평균분자량 (2400~4800) 및 열안정성등을 조사하였다. 이와같은 중합 메카니즘은 소위 interfacial polymerization의 메카니즘과 다르며, 이를 구별하기 위하여 "상이동 중합" (phase transfer polymerization)이란 용어를 사용할 것을 제안한다.

ABSTRACT. Linear polyethers were prepared by the reaction of diphenoxide anions from 2,2-*bis*(4-hydroxyphenyl)propane, *bis*(4-hydroxylphenyl)sulfide, and *bis*(4-hydroxyphenyl)sulfone with 1,6-dibromohexane in aqueous/nitrobenzene heterogeneous phases. Tetrabutylammonium bromide was employed as a phase transfer catalyst. The polymerizations were dependent both on stirring speed and catalyst level, but only up to certain maximum values. Distribution studies demonstrated transference of diphenoxide anions from aqueous phase into nitrobenzene in the presence of the catalyst. Some of polymers were characterized with respect to their intrinsic viscosities (0.09~0.16), number average molecular weight (2400~4800), and thermal properties. The use of a new terminology, 'phase transfer polymerization', is proposed to differentiate this type of polymerizations from interfacial polycondensations.

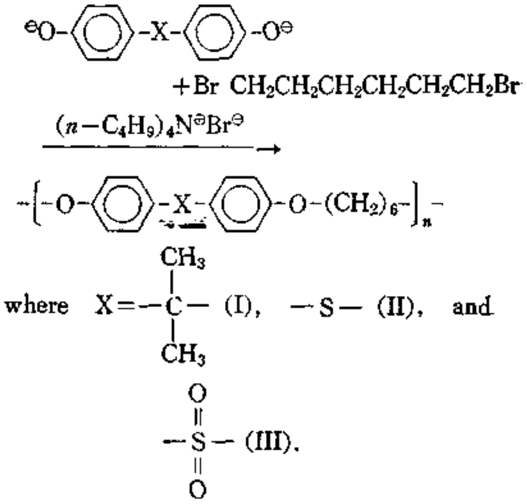
INTRODUCTION

Utilization of two phase heterogeneous polycondensation (step polymerization) methods has been mostly restricted to the so-called interfacial polymerizations mainly involving Schotten-Baumann type reactions, where one reactant residing in a water immiscible organic phase reacts at or near the interface with the other in aqueous solution.[1~4] Synthesis of polyamides from diamines and diacyl halides *via* this method is a well-known example[2]. Recently many heterogeneous reactions, typically in two phases of aqueous and orgainic solutions, have been found to be effectively accelerated by the use of ammonium or phosphonium salts, which are commonly called phase transfer catalysts following Stark's introduction of the terminology.[5~10] It is generally believed that the catalysts are able to bring hydrophilic anions from aqueous phase into organic layer and make them to react homogeneously with another reactant.

Hirose and Imamura[11] reported the polymerization of 2, 4, 6-tribromophenol in H_2O/organic phases by potassium permanganate in the presence of various phase transfer catalysts. Certainly permanganate anions were solubilized in organic solvents by the catalysts and promoted oxidative polymerization of the phenol derivative.

There was also an earlier report by Schnell[12] of the preparation of polycarbonate from quaternary ammonium salts of bisphenol A and phosgene in concentrated aqueous NaOH solution/dichloromethane. Here again the transfer of bisphenol A anions by the quaternary ammonium cation from aqueous phase into dichloromethane must have occurred.

We have applied this novel method for the preparation of polyethers from diphenols and 1, 6-dibromohexane, and the results are presented in this paper. Sodium salts of diphenols in aqueous phase and 1, 6-dibromohexane in nitrobenzene were reacted together in the presence of tetrabutylammonium bromide (QBr):



Synthesis of polyacetals of the same diphenols in homogeneous solutions of N, N-dimethylformamide was previously reported by us[13].

We have used in this report the terminology of 'phase transfer polymerization' to emphasize the distinction between the present and interfacial polymerizations.

EXPERIMENTAL

1. Chemicals and Instruments

Bis(4-hydroxyphenyl)sulfide (diphenol sulfide) and *bis*(4-hydroxyphenyl)sulfone (bisphenol S) obtained from Crown-Zellerbach Co. (U. S. A.) were recrystallized from deionized distilled water and dried at 40 °C under reduced pressure (10 mmHg). 2, 2-*Bis*(4-hydroxyphenyl)propane (bisphenol A) from Dow Chemicals (U. S. A.) was recrystallized from toluene and vacuum dried. The melting points of these purified diphenols were in the same range as those reported in literatures.[13] 1, 6-Dibromohexane was of reagent grade from Merck and used after vaccum fractional distillation. Purity of the distilled material was 99.5 % by gas chromatographic analysis. Tetrabutylammonium bromide and other chemicals used in the present work were of reagent grade and used as received.

Differential scanning calorimeter (Model 1B) and thermogravimetric analyzer (Model TGA-1) of Perkin-Elmer were used for the study of thermal behaviors of polymers. Vapor pressure osmometer from Knaner Co. (W. Germany) equipped with an electronic universal temperature measuring device and an X-Y recorder was employed for the determination of number average molecular weights of polymers. Micro melting point apparatus (MRK, Japan) having a microscope and hot stage was used for melting point determinations.

2. Synthesis of Polyethers

A general procedure for the preparation of polyethers was as follows: A mixture of 20.0 m*l* of nitrobenzene, 20.0 m*l* of distilled water, 5.00 mmoles of a diphenol, 5.0 mmoles of 1, 6-dibromohexane, 10.0 or 12.0 mmoles of sodium hydroxide, and 0.05∼1.0 mmoles of tetrabutylammonium bromide was placed in a 250 m*l* round bottom flask and agitated with a mini stirrer (Model E 1342 of Electrothermal Co, Britain) for 1∼10 hours under nitrogen atmosphere. Reaction temperature was kept constant at 78 °C. Stirring speed was measured by a tachometer. At the end of reaction nitrobenzene layer was separated from aqueous phase and was slowly poured into 100 m*l*. of methanol which had been acidified to pH 1 with concentrated hydrochloric acid. The precipitated polymers were separated by filtration and washed with diluted hydrochloric acid, water, and methanol. Washed polymers were dried at 60 °C under a reduced pressure (10 mmHg).

3. Determination of Distributions of Diphenoxide and Bromide Ions Between Water and Nitrobenzene

A mixture having the same composition as the one described above in 'Synthesis of Polyethers' was taken in a separatory funnel.

The amount of QBr used in this study was kept constant at 2.0 mole % based on diphenols, and 1, 6-dibromohexane was excluded in order to avoid of occurrence of reactions. The mixture was viogorously shaken for 15 minutes and was then placed in a water bath at 78 °C for 24 hours. Nitrobenzene layer was separated and dried over 20 g anhydrous sodium sulfate. To 20.0 m*l* of dry nitrobenzene solution added was 60.0 m*l* of methanol and then diphenoxide concnetration was determined by titrating the solution against a standardized hydrochloric acid solution. The concentration of bromide anion in aqueous phase was determined by potentiometric titration against a standardized silver nitrate solution. Mutual solubility of water and nitrobenzen and adsorption of diphenoxide ions on drying agent were neglected.

RESULTS AND DISCUSSION

1. Polymerization

Nitrobenzene was chosen as an organic phase because it was found in preliminary experiments to be a reasonably good solvent for polymers at the reaction temperature. Preliminary experiments also showed that QBr was capable of transferring diphenoxide anions (I, II, and III) from aqueous solution to nitrobenzene. All the reactions were conducted at 78 °C at which temperature our previous investigation on the synthesis of polyacetals from the same diphenols was performed.[13]

1.1 Effect of Stirring. The effect of stirring speed on polymerization rate for II/1, 6-dibromohexane system was examined under the same conditions to those described in Experimental. As shown in *Table* 1 polymerization rate was dependent on stirring speed, but only to certain rpm. The higher was the amount of QBr used, the lower the critical rpm above which polymerization rate leveled off. Such a phenomenon was reported earlier by others[6, 11]. For the present investigation all the reactions were run at about 900 rpm when 2 mole % or more catalyst based on reactant was used, and at 1600 rpm for the case of 1 mole % QBr. Since the critical stirring speed must vary with reactor shape, quantity of reactant mixture used, the shape and size of the stirrer, *etc.*, we used the same stirrer and reaction flask throughout this work.

1. 2 The Catalytic Effect of Tetrabutylammonium Bromide. When diphenoxide anions (I, II and III) in aqueous phase were allowed to react with 1, 6-dibromohexane in the absence of QBr, practically no polymer was obtained at 78 °C even after 7 hours of reaction (rpm of the stirrer; 2000). However, the addition of even a small quantity of QBr affected the reaction as shown in *Fig.* 1, 2 and 3.

Among the three anions investigated I was most reactive and III least reactive at the same level of QBr (*Fig.* 1). The difference in

Table 1. The effect of stirring speed in the phase transfer polymerization of *bis*(4-hydroxyphenyl)sulfide and 1, 6-dibromohexane[a].

Stirring speed (rpm)	Polymer yield (wt. %)	
	1.0 % QBr	2.0 % QBr
135	—	50.0
370	—	66.3
600	21.5	66.6
1000	25.8	—
1350	29.5	—
1590	29.6	65.7

[a] Reactions were conducted for 7 hours at 78 °C. Concentrations of reactants were the same as described in Experimental. Twenty mole % excess NaOH was employed.

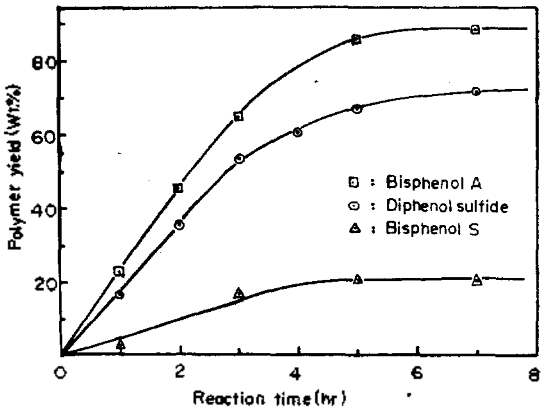


Fig. 1. Polymerization of diphenoxides and 1, 6-dibromohexane in water/nitrobenzene in the presence of tetrabutylammonium bromide (Two mole% QBr and 20 mole% excess of NaOH based on the amount of diphenols were used. The concentrations of diphenol and 1, 6-dibromohexane were the same as described in Experimental. Reaction temperature was 78 °C and rpm of the stirrer 900.).

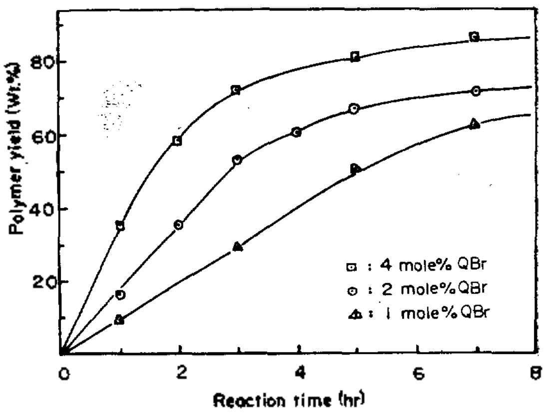


Fig. 2. Polymerization of diphenol sulfide and 1, 6-dibromohexane in water/nitrobenzene at various levels of tetrabutylammonium bromide (QBr) (The concentrations of the two reactants were the same as described in Experimental. Excess (20 mole%) NaOH was used. Reaction temperature was 78 °C and rpm of the stirrer 900 when 2 or 4 mole% QBr was used and 1600 when 1 mole% used.).

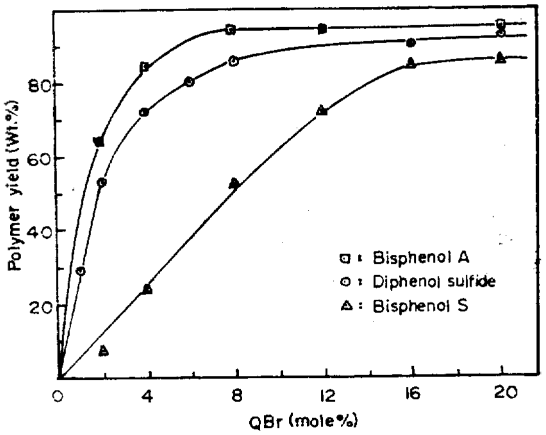


Fig. 3. Dependence of polymer yield on the amount of tetrabutylammonium bromide (QBr) in the phase transfer polymerization of diphenoxides and 1, 6-dibromohexane in water/nitrobenzene (Reactions were run for 3 hours at 78 °C with the stirring speed of 900 rpm. The concentrations of reactants were the same as described in Experimental. Excess (20 mole%) NaOH was used.).

reactivity of these three anions in a similar reaction has been discussed in our earlier paper.[13] The difference, however, is much more pronounced under the present phase transfer polymerization conditions than that under a simple homogeneous reaction conditions. Additional factor to be taken into account, in addition to their inherent differences in nucleophilicity, is the possibility that the three ions (I, II and III) are solubilized by QBr to varing extents into the nitrobenzene layer. This aspect will be further discussed in the following section. Apparently polymerization rate depends on the amount of QBr used (*Fig.* 2), but only up to a certain level where enough concentration of diphenoxide ions are phase-transfered into nitrobenzene. This is clearly illustrated for the three case in *Fig.* 3.

Table 2. Dependence of polymer yield on the amount of sodium hydroxide used[a].

Amount of NaOH[b]	Diphenol		
	Bisphenol A	Diphenol sulfide	Bisphenol
Equivalent	40.2	24.1	11.6
Excess (20 mole%)	64.5	53.1	16.8

[a] Polymerizations were conducted for 3 hours at 78 °C. Values in the table are wt. % of polymers obtained at the concentrations of reactants described in Experimental.

[b] Amount of NaOH used in the synthesis of polymers. Expressed based on the amount of diphenols used.

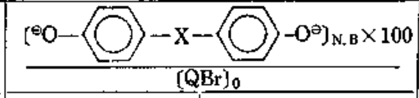
According to *Table* 2 the use of excess amount of sodium hydroxide resulted in higher yields of polymers, which can be explained by the assumption that the presence of higher concentration of hydroxide ion in aqueous phase favors more facile transfer of diphenoxide ions into nitrobenzene, which could be proven by a distribution study to be discussed in the following section (*Table* 3).

2. Distribution of Diphenoxide Anions between Water and Nitrobenzene in the Presence of QBr.

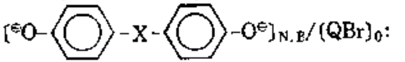
2.1 Distribution of Diphenoxide Anions. The partition of I, II and III between water/nitrobenzene phases determined by the method described in 'Experimental' are tabulated in *Table* 3. We can make two generalizations from these results: 1) partition of diphenoxide anions in nitrobenzene increases in the order of III<II<I and 2) the higher was the concentration of hydroxide used, the higher the distribution of a diphenoxide ion in nitrobenzene. These observations are in perfect parallel with facts above disussed on the dependence of polymerization rate on the structure of anions and concentration of hydroxide used.

2.2 Distribution of Bromide Ions. Since one of reaction products in the present polymerizations is bromide ion, partition of this ion between water and nitrobenzene was also ex-

Table 3. Distribution of diphenoxide and bromide ions between water and nitrobenzene[a].

Distribution[b]				$\frac{[Br^{\ominus}]_w \times 100}{[QBr]_0}$	
NaOH[c]		Equivalent	Excess (20 mole%)	Equivalent	Excess (20 mole%)
Diphenoxides	I	70.2	81.8	96.7	97.5
	II	60.2	64.4	92.8	95.8
	III	26.7	47.3	90.9	91.5

[a] 2 mole% of tetrabutylammonium bromide (QBr) based on moles of diphenols was present in the mixture.

[b] $_{N.B}/[QBr]_0$: moles of diphenoxide ion in nitrobenzene divided by the moles of QBr originally added. $[Br^{\ominus}]_w/[QBr]_0$; moles of bromide ions in aqueous layer divided by the moles of QBr originally added. Determined at 78 °C.

[c] Expressed based on the moles of diphenols used.

amined in the presence of diphenoxide ions. We used QBr as a source of bromide ion. The results (*Table* 3) show that most of the bromide ions resided in aqueous phase. According to the table slightly higher amount of bromide ion was present in water phase when the concentration of hydroxide increased. In other words slightly lower concentration of bromide ion was transferred into nitrobenzene. However, the change in partition of bromide ions between aqueous phase and nitrobenzene is much less dependent on the concentration of hydroxide ion compared with those of diphenoxide anions.

3. Mechanism of Polymerization

Catalytic effects of quatenary ammonium halide in two phase nucleophilic substitution reactions have been widely reported and this effect has been advantageously utilized by Mckillop *et al.*[14] in the synthesis of various phenol ethers. We belive that in light of our experimental results and observations same mechanistic pathways as described by others for simple phase transfer catalytic reactions are applicable to the present phase transfer polymerization.

Phenoxide anions in aqueous solution is transferred by Q^+ to nitrobenzene, where they react with 1,6-dibromohexane producing polyethers. The side product, bromide ion, generated in this reaction is brought by Q^+ from nitrobenzene into aqueous phase. This cycling of Q^+ between aqueous solution and nitrobenzene continues to solubilize the diphenoxide anions in the organic solvent and transporting bromide ions back into water layer

Since polymerization did not proceed to any detectable extent even at a very high rpm (*ca.* 2000) when QBr was absent, interfacial reactions seem to be insignificant.[8] Neglecting the interfacial polymerization and the possibility of reactions occurring in aqueous phase. the present polymerization is believed to proceed mainly in organic phase. This mechanism is completely different from that of interfacial polycondensations where two reactants meet at or near the interface of the two immiscible phases.

4. Properties of Polymers

The number average molecular weights and intrinsic viscosities of polyethers prepared in the presence of 2 mole % QBr (7 hrs. reaction) are presented in *Table* 4. Their melting ranges have been also included in the same table. Poly-

Table 4. Molecular weights and softening points of polyethers.[a]

Diphenols	Properties		
	Intrinsic viscosity[b]	Number average molecular weight[c]	Softening temperature (°C)
Bisphenol A	0.158 (Chloroform)	4830 (Chloroform)	92~98
Diphenol sulfide	0.103 (Chlorobenzene)	2910 (Chlorobenzene)	140~150
Bisphenol S	0.0870 (N, N-Dimethylformamide)	2450 (N, N-Dimethylformamide)	117~123

[a] Polyethers were prepared in the presence of 2 mole% QBr using the reactant concentrations specified in Experimental and 20 mole% excess of NaOH. Reactions were conducted for 7 hours at 78 °C.

[b] Determined at 25° C in the solvents shown in parentheses.

[c] Determined by vapor pressure osmometry using the solvents in parentheses.

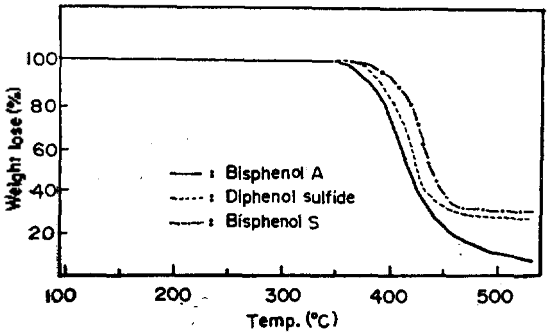


Fig. 4. Thermogravimetric analysis of polyethers prepared from diphenols and 1, 6-dibromohexane (Thermagrams were obtained in air with heating rate of 20°C/min. Polymers used were those listed in *Table* 4.).

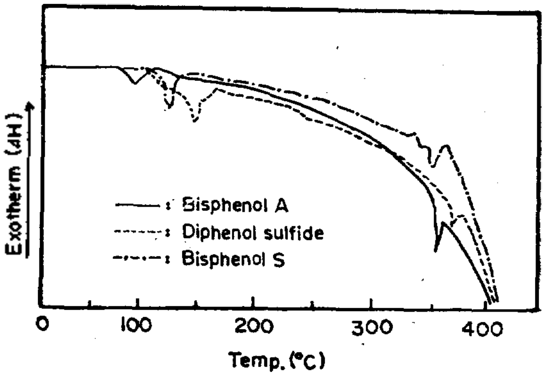


Fig. 5. Differential scanning calorimetric analysis of polyethers prepared from diphenols and 1, 6-dibromohexane (Thermograms were obtained in air with heating rate of 20 °C/min. Polymers used were those listed in *Table* 4.).

ethers from I have the highest molecular weight among the three and those from III the lowest, which is parallel with reactivity of the diphenoxide anions. It is well known that molecular weight of step-reaction polymers increases as the extent of reaction or polymer yield gets higher.[15] Among the three polyethers sulfide polymer has the highest softening point. Same tendency was previously observed by us for the polyacetals prepared from the same diphenoxides and methylene bromide in N, N-dimethylformamide.[13]

Thermal behaviors of the polyethers were examined by thermogravimetric analysis (*Fig.* 4) and differential scanning calorimeter (*Fig.* 5). The thermograms show that the three polymers start to undergo weight loss around 350°C, even though a little differences in their thermal behaviors exist. *Fig.* 5 also shows relatively sharp softening region of the polymers, whose values are in good accord with the microscopically determined ones shown in *Table* 4.

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REFERENCES

1. E. L. Wittbecker and P. W. Morgan, *J. Polymer Sci.*, **40**, 289 (1959).
2. P. W. Morgan and S. L. Kwolek, *J. Polymer Sci.*, **40**, 299 (1959).
3. P. W. Morgan, "Condensation Polymers: By Interfacial and Solution Methods", Wiley-Interscience, New York, 1965.
4. H. Vernaleken, "Interfacial Synthesis", (F. Millich and C. E. Carreher, Jr., Eds.), Marcel Dekker, New York, 1975.
5. C. M. Stark, *J. Amer. Chem. Soc.*, **93**, 195 (1971).
6. C. M. Stark and R. M. Owens, *J. Amer. Chem. Soc.*, **95**, 3613 (1973).
7. E. V. Dehmlow, *Angew. Chem. Int. Ed.*, **16**, 493 (1977).
8. W. P. Weber and G. W. Gokel, *J. Chem. Educ.*, **55**(6), 350 (1978); **55**(7), 429 (1978).
9. A. W. Herriot and D. Picker, *J. Amer. Chem. Soc.*, **97**, 2345 (1975).
10. H. Kise and M. Seno, *Yuki Gosei Kagaku Kyokaishi* (*Japan*), **35**(6), 448 (1977).
11. M. Hirose and Y. Imamura, *Nippon Kagaku Zasshi*, **1**, 113 (1977).
12. H. Schnell, *Angew. Chem.*, **20**, 633 (1956).
13. J.-I. Jin and Y.-D. Choi, *Polymer* (*Korea*), **2**(5), 249 (1978).
14. A. McKillop, J.-C. Fiaud and R. P. Hug, *Tetrahedron*, **30**, 1379 (1974).
15. G. Odian, "Principles of Polymerization", P. 56, McGraw-Hill Book Co., New York, 1970.