

새로운 폴리아세탈의 합성

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Synthesis of New Polyacetals

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요 약 : 수산화나트륨 존재하에 비스 4-히드록시페닐 술폰과 황화비스 4-히드록시페닐을 할로겐화메틸렌과 반응시켜서, 또 2,2-비스 4'-히드록시시클로헥실 프로판(포화비스페놀 A)을 산 촉매를 사용하여 파라포름알데히드와 직접 축합시켜 새로운 폴리아세탈을 합성하였다. 첫째 방법, 즉 치환반응에 의한 중합체의 합성에서 커다란 용매효과를 볼 수 있었으며, DMF에서 디올의 음이온은 2,2-비스 4'-히드록시시클로헥실 프로판 > 황화비스 4-히드록시페닐 > 비스 4-히드록시페닐 술폰의 순서로 그 반응성이 감소함을 알았다.

합성된 중합체들은 비교적 낮은 분자량을 갖고 있었으며 ($[\eta]=0.05\sim0.06$, $M_n=1150\sim2500$), 구조에 따라 차이는 있으나 $95\sim140^\circ\text{C}$ 의 연화점을 보여 주었다. 이들 중합체의 용해도에 서로 큰 차이가 있음도 관찰하였다.

ABSTRACT: New linear polyacetals were synthesized by reacting bis(4-hydroxyphenyl) sulfone and bis(4-hydroxyphenyl) sulfide with methylene halides in the presence of sodium hydroxide, and also by direct condensation of 2,2-bis(4'-hydroxycyclohexyl) propane with paraformaldehyde. The former reactions revealed strong solvent effect and in N,N-dimethylformamide the reactivity of the anions of diols decreased in the order of 2,2-bis(4'-hydroxyphenyl) propane, bis(4-hydroxyphenyl) sulfide, and bis(4-hydroxyphenyl) sulfone. Polymers obtained were of relatively low molecular weights with their intrinsic viscosity ranging $0.05\sim0.06$ and number average molecular weight of $1150\sim2500$.

INTRODUCTION

Synthesis of new acetal polymers has been pursued by many polymer chemists¹⁻⁶. One of the old methods involves formal exchange reactions by Carothers between dibutylformal and glycols in the presence of acidic catalyst¹ or direct reaction of a glycol with a mixture of aldehyde, alcohol and catalyst under such conditions that the alcohol is continuously removed². The polymerization of formaldehyde to high molecular weight polymers useful for many practical applications is well known⁷.

Perry and Hibbert prepared polyethylene glycols through the reaction of the monosodium salts of polyethylene glycols with the dichloro derivatives of polyethylene glycols⁸. Later Benoit incorporated oxymethylene groups into a polyalkylene glycol by reacting a alkali metal alcoholate of a polyalkylene glycol with a methylene halide at 125 °C under autogenic pressure⁹. Shuto applied similar substitution reactions to obtain polyacetals containing benzene rings in the main chain of the polymers¹⁰. He reacted disodium salts of diphenols with methylene bromide in ethanol solvent at the refluxing temperature and observed the fact that polymer yields were very low (23~41 wt. %) even after 7 hours of reaction.

The present work deals with the synthesis of new polyacetals containing diphenyl sulfone or diphenyl sulfide groups in the main chain by the substitution reactions similar to those above mentioned. Synthesis of polyacetals from 2, 2-bis(4'-hydroxycyclohexyl) propane and paraformaldehyde is also reported in this paper.

EXPERIMENTAL

Materials

Among the aromatic diols used in the present

work 2, 2-bis(4'-hydroxyphenyl) sulfone and 2, 2-bis(4'-hydroxyphenyl) sulfide were obtained from Crown Zellerbach Co. (U. S. A) and used after recrystallization from acetone solution and drying under reduced pressure. Their melting points were 241~242 °C and 151~152 °C, respectively (Lit values^{11,12}, 240~241 °C and 151 °C). 2, 2-Bis(4'-hydroxyphenyl) propane from Dow Chemical also was recrystallized from acetone solution and vacuum dried (m. p., 153~155 °C, lit value¹³, 150~155 °C). 2, 2-Bis(4-hydroxycyclohexyl) propane from Progil Co. (France) were used after being recrystallized from toluene solution and dried (m. p., 139~141 °C).

Other chemicals employed in the present work were of reagent grade and used as received.

General Synthetic Procedure

1. Reaction of Diphenols with Methylene Halides in the Presence of Sodium Hydroxide: In a typical polymerization reaction 0.050 moles of a diphenol and 0.10 moles of sodium hydroxide were dissolved in 75 ml of N, N-dimethylformamide (DMF) or DMF-ethanol mixtures or in ethanol. To this solution 0.050 moles of a methylene halide was added. After a given reaction time at 78 °C the reaction mixture was poured into a large excess of water (800 ml) and the precipitated polymers were collected by filtration. The collected polymers were then washed with dilute (3wt. %) sodium hydroxide solution, water, dilute hydrochloric acid, and finally with methanol. The washed polymers were dried at 40 °C under a reduced pressure (40 mmHg).

2. Direct Condensation of 2, 2-Bis(4-hydroxycyclohexyl) propane with paraformaldehyde: A mixture of 0.050 moles of paraformaldehyde, 0.050 moles of 2, 2-bis(4-hydroxycyclohexyl) propane, 8×10^{-5} moles of p-toluenesulfonic acid, and 20 ml of tetrahydropyran was stirred

at 60 °C for 1 hour. And then the reaction mixture was allowed to reflux for another hour. After refluxing, the azeotropic mixture of tetrahydropyran and water was allowed to slowly distil out for 2 hours. Additional amount (2.5×10^{-3} moles) of paraformaldehyde and 10ml of tetrahydropyran were added to the reaction mixture, and the heating and refluxing procedure were repeated. The mixture, after the catalyst in the solution was neutralized by adding a few drops of ammonium hydroxide, was finally subjected to distillation under reduced pressure (ca. 5mmHg). The polymer obtained was washed with acetone and dried at 40 °C under reduced pressure.

Determination of Molecular Weights of Polymers

Intrinsic viscosities of polymers were measured at 25.0°C using an Ostwald viscometer. The number average molecular weights of polymers were determined by vapor pressure osmometry using a Vapor pressure Osmometer equipped with an electronic universal temperature measuring instrument⁴ of Herbert Knauer & Co. (W. Germany) and an X-Y recorder (Model 27,000) of Griffin & George, Ltd. (England).

Measurement of Softening Points of Polymers

The softening points of polymers were measured by a micro melting point apparatus of Mitamura Riken Corp. (Japan) which is equipped with a hot stage and a microscope.

RESULTS AND DISCUSSION

Polymerization Variables

1. Effect of Solvent Medium: When the reaction between bis(4-hydroxyphenyl) sulfone and dibromomethane was conducted at 78 °C for 10 hours in ethanolic sodium hydroxide solution

following Shuto's experimental procedure, the polymer yield was only 33 wt. %, which was comparable to the results reported for other diphenols by Shuto. The polymer yield was improved to 52.2 wt. % when methylene iodide was employed in place of methylene bromide under the same reaction condition.

One of the possible reasons for such low polymer yield was assumed due to the hydrolysis of methylene halides¹⁰. When excess amount of methylene iodide was used, polymer yields were further improved (Table I), even though the improvement was not so much as desired.

Table I. Polymer Yield (wt. %) for the Polycondensation of Bis (4-hydroxyphenyl) Sulfone and Methylene Iodide*1

reaction time (hr.) \ mole ratio*2	1.00 : 1.00	1.00 : 1.05	1.00 : 1.10	1.00 : 1.25
10.0	50.0	52.7	55.1	58.9
20.0	56.4	59.3	70.3	74.7
30.0	70.6	74.2	78.4	87.1

*1. Reaction conditions were the same as those described in the 'Experimental'.

*2. Molar ratio of diphenol to methylene iodide.

Shuto mentioned that ethanol was the best solvent for this polymerization among the solvents, he tried, such as benzene, chlorobenzene, tetrahydrofuran, monoethyl ether of ethylene glycol, and ethanol. Since the reaction appeared too slow in ethanol, more solvents were examined for the possible improvement of the reaction rate. DMF, among other solvents, was found to be a much better reaction medium than ethanol.

When the sulfone diphenol was reacted with methylene bromide in DMF-ethanol mixtures, polymer yield rapidly increased as the volume fraction of DMF in the mixtures increased (Figure 1). As will be seen later in Figure 2,

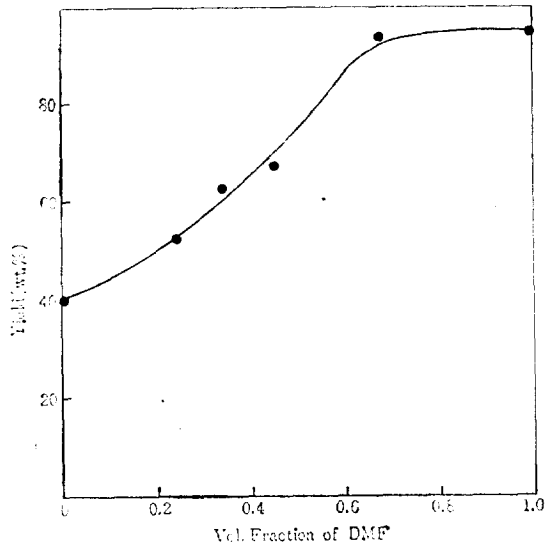


Figure 1. Solvent effect in the preparation of polyacetals (Reactions were conducted in DMF-ethanol mixtures for 10hrs. at 78°C.).

more than 90% yield was obtained in 4 hours of reaction when DMF alone was used as the reaction medium.

The reactions occurring in these syntheses should be of typical S_N2 type ones and an initial charge of the diphenolic anions should be dispersed in the transition states. Therefore, the reactions are expected to be hindered by the protic polar solvents such as ethanol, because the reactant anions would be more efficiently solvated resulting in stabilization, thus decrease in their reactivity. Discussions on such a solvent effect can be found elsewhere¹⁵.

2. Structure vs. Reactivity of Diphenols: The anions of three diphenols, bis(4-hydroxyphenyl) sulfone (I), bis(4-hydroxyphenyl) sulfide (II), and 2,2-bis(4'-hydroxyphenyl) propane (III), were found to react in differing rate with methylene bromide in DMF forming polymers of similar structures (Figure 2.). The anion of III showed the highest reactivity among the three, while that of I revealed the lowest reactivity toward methylene bromide.

Moreover, it can be seen that the reactions

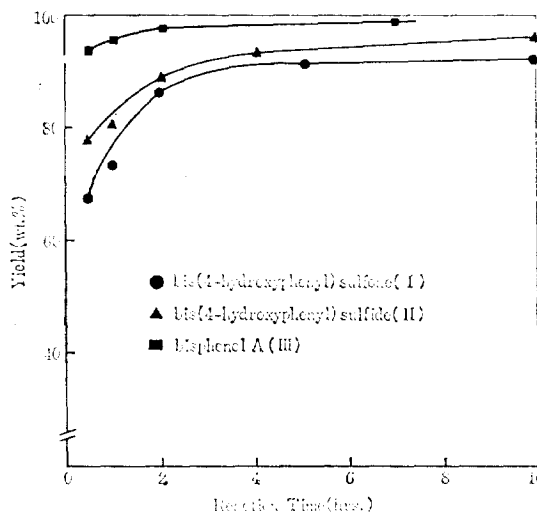
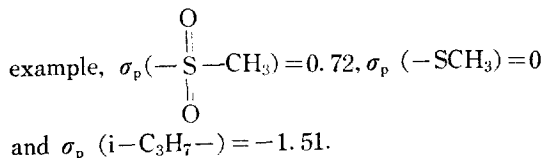


Figure 2. Relationship between the structures of diphenols and their reactivities (Reactions were conducted in DMF at 78°C.).

were practically over in about 4 hours of reaction. The difference in the reactivity of the three anions can be explained in terms of the substituent effect of isopropylidene, sulfide, and sulfone groups between the two benzene rings. Sulfonyl group reduces the nucleophilicity of the diphenolic anion, while isopropylidene group increases it, comparatively speaking. This observation is in parallel with the substituent constant of analogous functional groups¹⁶, for



3. Methylene Chloride as a Reactant: Polymerization with methylene chloride in place of methylene bromide was examined in DMF under the same reaction condition. Dry-ice/acetone filled cold-finger was attached to the reaction vessel in order to prevent the loss of the volatile reactant.

When the correagent was 2,2-bis(4'-hydroxyphenyl) sulfone, the polymerization proceeded too slowly. The polymer yield was only 48.9

% after 10 hours of reaction.

Addition of potassium iodide increased the polymerization rate, but only to a small extent (Figure 3). The low solubility of potassium iodide in the reaction mixture prevented us from using larger amount of the salt.

Catalytic effect of the iodide ion can partly assumed due to its high nucleophilicity and its better leaving property than those of chloride and phenolic anions^{17, 18}.

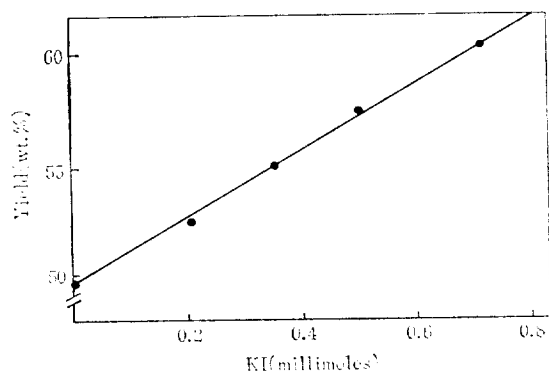


Figure 3. The catalytic effect of KI in the preparation of polyacetals (Reactions were conducted in DMF for 10hrs. at 78 °C.).

4. Direct Condensation of 2,2-Bis(4'-hydroxycyclohexyl) propane (IV) with Paraformaldehyde:

An excess of paraformaldehyde was necessary to obtain polymers with light colors. When diol was present 5 mole % in excess, the polymer was brown. The use of excess amount of paraformaldehyde not only improved the color of the polymers, but also their molecular weights.

Neutralization of catalyst by ammonium hydroxide prevented the acid catalyzed decomposition of polymers when the reaction mixture was subjected to concentration under reduced pressure in the final stage of reaction. When the catalyst had not been neutralized, the polymers obtained had intrinsic viscosity of 0.03. Similar observations were reported earlier by Jackson and Caldwell¹⁹.

o-Dichlorobenzene could also be used as a satisfactory reaction medium for preparing the same polymers. Tetrahydropyran and water, however, was much easier to remove at the end of reaction (refer to the exp. no's 9 and 11 in Table II).

Properties of Polymers

The intrinsic viscosities and the number average molecular weights of polymers obtained under various conditions are summarized in the

Table II. Properties of Polyacetals Prepared

Exp. No.	Reactant		Reaction medium	Reaction time (hrs.)	[η] (solvent)	\overline{M}_n	Softening point (°C)
	diphenol or diol	coreactant					
17	I	CH ₂ Br ₂	ethanol	10.0	0.038(DMF)	—	65~75
90	I	CH ₂ Br ₂	DMF	0.50	0.038(DMF)	—	65~75
87	I	CH ₂ Br ₂	DMF	1.0	0.043(DMF)	—	79~88
74	I	CH ₂ Br ₂	DMF	10.0	0.051(DMF)	1340	130~139
72*1	I	CH ₂ I ₂	DMF	10.0	0.061(DMF)	2140	132~138
84	I	CH ₂ Cl ₂	DMF	10.0	0.031(DMF)	—	—
82	II	CH ₂ Br ₂	DMF	10.0	0.058(DMF)	1138	134~145
96	III	CH ₂ Br ₂	DMF	7.0	0.058(THF)	1410	94~106
11	IV	PF*2	tetrahydropyran	refer to Experimental	—	1800	130~135
9	IV	PF*2	o-dichlorobenzene	"	0.059(THF)	1070	70~80

*1. 1 mole % of KI was present in the reaction mixture.

*2. Paraformaldehyde

Table II. All the polymers prepared were brittle solid and had low molecular weights.

Molecular weight of polymers as well as their softening points increased with reaction time, which is a typical phenomenon usually observed for any step-growth polymerization (refer to experimental no's, 74, 87, and 90)²⁰. The chemical structures of polyacetals were confirmed by IR spectra. A strong absorption band for S=O stretching vibration in polysulfone acetals was observed at 1210 cm^{-1} and a weak but sharp absorptions for C-S stretching vibration were detected at 640 cm^{-1} for both sulfone and sulfide polymers.

The acetal polymer of 2,2-bis(4'-hydroxyphenyl) propane prepared by the present method have significantly higher intrinsic viscosity (0.058) than that (0.040) of the same polymer synthesized by Shuto in ethanolic solution.

All the polymers started to decompose around 250°C when their thermal behaviors were examined in air by DTA method with the heating rate of $18^\circ\text{C}/\text{min}$. When the polymer samples were heated up to 800°C , they left practically no chars.

The softening points of polymers were not too high ranging $95\sim 135^\circ\text{C}$ for higher molecular ones depending on their structures. Polysulfide acetal appeared to have higher softening point than polysulfone acetal, which in turn showed higher softening range than bisphenol A polymer. One can also see from Table II (refer to experimental numbers, 17, 74, 87, 90 and 72) that as the molecular weight of polymers increases, their softening points also increase reaching to a maximum value. For polysulfone the maximum value is about 135°C . Similar trends were also observed for polyacetals from sulfide and bisphenol A. Polysulfone acetal was soluble in dimethylsulfoxide and DMF and insoluble in chloroform, benzene, acetone, and

aliphatic hydrocarbons. Polymer from sulfide was only slightly soluble in DMSO and DMF and insoluble in common solvents above mentioned. Polyacetal of saturated bisphenol A showed high solubility in chloroform and carbon tetrachloride while it was insoluble in diethyl ether, acetone, methanol, DMF, tetrahydrofuran, and cyclohexane.

CONCLUSION

1. New polyacetals could be synthesized i) by simple nucleophilic substitution reactions of the anions of bis(4-hydroxyphenyl) sulfone and bis(4'-hydroxyphenyl) sulfide on methylene halides and ii) by direct polycondensation of 2,2-bis(4-hydroxycyclohexyl) propane with paraformaldehyde.

2. The polymerizations by substitution reactions were found to be strongly effected by the nature of solvent used as reaction medium. In N,N-dimethylformamide the diphenolic anion from bisphenol A (III) was observed to be more reactive than that of diphenol sulfide (II), which in turn was more reactive than that derived from sulfone diphenol (I).

3. Even the polymers with higher molecular weights among the prepared had relatively low molecular weights ($[\eta]=0.05\sim 0.06$) and had the softening range of $95\sim 140^\circ\text{C}$ depending on their structures.

4. Solubility of the polymers obtained widely varied depending on their structures. Polyacetals from the sulfone (I) dissolved in polar solvents, while those of saturated bisphenol A was soluble in chlorinated hydrocarbons. Sulfide polymers showed the lowest solubility in various solvents.

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