

# An Application of Polyalcohols Prepared from Diols. I. Elastic Polymers with Functional Groups Prepared by Chemical Modifications

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## Synopsis

An elastic polymer with hydroxymethyl side chains, which contains some crosslinked structure, has been prepared by treating its prepolymer with maleic anhydride and styrene in the presence of an initiator. Its mechanical properties were varied largely by the molar ratio of the hydroxyl group: maleic anhydride: styrene. A typical example of the polymer showed elongation 69%, tensile strength 0.85 kgf/mm<sup>2</sup>, and Young's modulus 9.4 kgf/mm<sup>2</sup>. Some other modifications are also examined.

## INTRODUCTION

We reported the novel synthesis of elastic polyalcohols having hydroxymethyl side groups pendant from the hydrocarbon main chain.<sup>1</sup> A typical polymer was prepared by polycondensation of 1,10-decanediol in the presence of potassium phenoxide at 300°C for 4 h in an autoclave, and by heating the resulting mixture at 250°C in a flask under vacuum, and then by pressing it at 250°C under vacuum. The film obtained exhibited a tensile strength of approximately 0.2 kgf/mm<sup>2</sup>. Under such conditions, however, the catalyst was retained in the polymer.

In this report, we applied a two-step polymerization for this polymer. We interrupted the polymerization in an earlier stage to obtain a prepolymer. The prepolymer was subjected to chemical modifications (as well as further polymerization) after removal of the catalyst.

The modifications to be studied include the treatments (i) with maleic anhydride and either styrene or divinylbenzene in the presence of an initiator [azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO)], (ii) with an acid anhydride (such as maleic, succinic, or isophthalic anhydride) in the presence (or absence) of *p*-toluenesulfonic acid, (iii) with allyl glycidyl ether in the presence of an initiator, and (iv) with a diisocyanate.

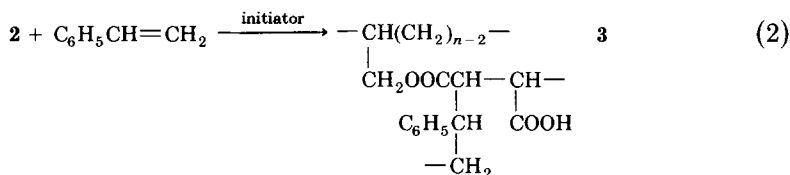
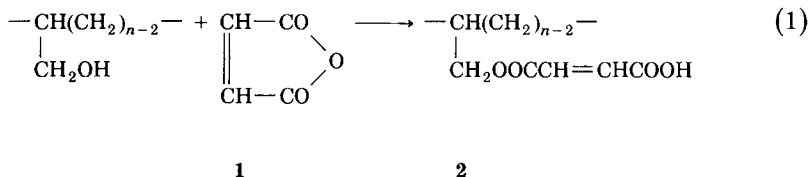
The purpose of this study is to obtain a polymer with various functional groups as well as with a tensile strength high enough for practical applications.

## RESULTS AND DISCUSSION

The tensile strength of commercially available low density polyethylene ranges from 0.4 to 1.6 kgf/mm<sup>2</sup> (600–2300 psi).<sup>2</sup> We planned the preparation of a polymer with various functional groups and having practical tensile strength of at least 0.4 kgf/mm<sup>2</sup>. Heating of a diol in the presence of potassium phenoxide gave an elastic polymer as reported before.<sup>1</sup> In order to make a film with practical tensile strength, some chemical modifications of this prepolymer were performed, and its mechanical properties were determined as a form of film.

Modification 1 ( $n = 10$  in the Structure 1)

The results are listed in Table I. A prepolymer prepared from the diol, HO(CH<sub>2</sub>)<sub>n</sub>OH, is mixed with maleic anhydride and either styrene or divinylbenzene, and the resulting mixture is heated in the presence of AIBN or BPO. The reaction will proceed as follows:



The polymerization generally goes through three steps: (a) half-ester formation of the prepolymer at 50°C by the acylation with maleic anhydride as shown in eq. (1), (b) the copolymerization of the acylated prepolymer with styrene (or divinylbenzene) in the film-processing device as shown in eq. (2) (typically at 90°C for 6 h), and (c) the heat treatment of the polymer film at the elevated temperature in a vacuum oven (typically at 150°C for 3 h).

It is well known that maleic anhydride copolymerizes with styrene in an alternate fashion.<sup>3</sup> Based on this fact, the structure of **3** is depicted. The molar ratio of maleic anhydride:the hydroxyl group in the prepolymer was varied over the range of 1:1–1:4, where the mole of the hydroxyl group is calculated on the assumption that the molecular weight of the prepolymer is infinite. If the molar ratio is 1:1, all the hydroxyl groups in the prepolymer will be theoretically replaced with the carboxyl groups [see eq. (1)]. If the ratio is 1:2, half of the hydroxyl groups will remain unreacted, but at elevated temperatures may react with the carboxyl groups to form the corresponding ester linkages, leading to a condensed network structure. To obtain a polymer containing functional groups, however, the formation of this network structure is undesirable due to disappearance of all the functional groups when the reaction proceeds completely.

TABLE I  
 Treatment of the Prepolymer by the Modification 1<sup>a</sup>

No. <i>n</i>	Maleic anhydride (mol)	Ratio <sup>b</sup>	2nd olefin (mol) <sup>c</sup>	Initiator <sup>d</sup>	Conditions <sup>e</sup> (°C/h)	Elongation at break (%)	Tensile strength at break (kgf/mm <sup>2</sup> )	Sub. no.
1	0.0641	1/1	S 0.0641	AIBN BPO	*90/6	9	3.1 4	-1
					*90/1, *90-120/3, *120/1, & 150/3	10	0.5 2	-2
2	0.0481	3/4	S 0.0481	AIBN BPO	*90/6	20	0.2 3	-1
					*90/1, *90-120/3, *120/1, & 150/3	13	0.3 2	-2
3	0.0321	1/2	S 0.0321	AIBN AIBN BPO	*90/6 <sup>f</sup>	30	0.1 5	-1
					*90/6 & 150/3 <sup>f</sup> *90/1, *90-120/3, *120/1, & 150/3	23 23	0.6 9 0.3 1	-2 -3
4	0.0160	1/4	S 0.0641	AIBN AIBN AIBN	*90/6	98	0.1 5	-1
					*90/6 & 150/3	69	0.8 5	-2
					*90/6, 150/3, & 200/3	10	3.4 0	-3
5	0.0160	1/4	S 0.1282	AIBN AIBN	*90/6	17	0.5 7	-1
					*90/6 & 150/3	13	1.5 0	-2
6	0.0641	1/1	D 0.0321	AIBN	*60/2.5, *60-90/1, *90-150/1.5, & *150/1 <sup>f</sup>	12	2.1 4	
7	0.0321	1/2	D 0.0160	AIBN	*60/2.5, *60-150/2.5, *150/1.5, & 150/3	21	0.2 8	
8	0.0641	1/1	None	AIBN	*150/3 & 150/3	50	0.4 1	

<sup>a</sup>The prepolymer (10.0 g, 0.0641 mol of OH) obtained from 1,10-decanediol was used.

<sup>b</sup>Maleic anhydride/OH in Prepolymer (mol/mol).

<sup>c</sup>S = styrene; D = divinylbenzene.

<sup>d</sup>AIBN = azobisisobutyronitrile; BPO = benzoylperoxide. Maleic anhydride/Initiator = 100/1 (mol/mol).

<sup>e</sup>Under the condition with \*, the heating was carried out in the film-processing device and under other conditions in the vacuum oven.

<sup>f</sup>See Experimental.

Introduction of styrene into the prepolymer increased the tensile strength of the resulting polymer. For example, as shown in Table I (no. 1-1), the tensile strength was 3.1 kgf/mm<sup>2</sup> (Young's modulus, 51.0 kgf/mm<sup>2</sup>) when maleic anhydride and styrene were used in a molar ratio of 1 : 1 to the mole of the hydroxyl group in the prepolymer. However, a sample, after being processed to a film, lost elasticity to be very brittle. This may be due to the introduction of stiff phenyl groups into the polymer chains. Heat treatment of a film at 150°C under vacuum was also effective to increase the tensile strength, the reason of which will be discussed later.

Divinylbenzene (*m*- and *p*-isomers mixture, bp 87°C) was used in place of styrene. Difunctional divinylbenzene may be more effective than styrene in terms of nonbrittleness, longer elongation, elasticity of the resulting polymer, and formation of the network structure. The modification with divinylbenzene, because of its low boiling point, was carried out by a method slightly different from that with styrene. As shown in Table I (nos. 6 and 7), the result supports this expectation.

Another attempt was made to form a loose network structure in the polymer in order to increase elasticity. For this purpose we decreased the amount of maleic anhydride, though the mechanical properties of the polymer are sacrificed. However, if the addition of styrene (or divinylbenzene) in a much larger amount improves the mechanical properties, this modification should be desirable. Because a lot of hydroxyl side groups remain unreacted even if all the carboxyl groups derived from maleic anhydride have reacted with hydroxyl groups in the prepolymer. As shown in Table I (nos. 4-1, 4-2) and Figure 1, both films had a larger elongation, a higher strength, and a better elasticity, and had a good clarity. The Young's modulus of 0.6 and 9.4 kgf/mm<sup>2</sup> was obtained for these films. These values were lower than those for low-density polyethylene (9.8–26.7 kgf/mm<sup>2</sup>).<sup>2</sup> However, these films were heated at 200°C under vacuum to increase Young's modulus up to 43.4 kgf/cm<sup>2</sup> and tensile strength to 3.4 kg/cm<sup>2</sup>, whereas the elongation decreased markedly with addition of a larger amount of styrene (see nos. 5-1 and 5-2). In nos. 4-1 and 4-2, at least half of the hydroxyl groups in the prepolymer theoretically remains, and they are available for conversion into other groups by chemical modification.

If styrene copolymerizes effectively with half-ester of maleic acid, the size of the network will be determined by the molar ratio of maleic anhydride:the hydroxyl group in the prepolymer, and the residual styrene polymerizes to remain as the polystyrene branches, which harden the polymer. The results in Table I show that the mechanical properties (elongation and tensile strength) depend on the size of the network (compare no. 1-1 with no. 4-1) as well as the conditions of heat treatment. The amount of styrene also had a substantial effect on the mechanical properties (compare 4-1 or 4-2 with 5-1 or 5-2).

These observations indicate that the mechanical properties of the polymer are able to be satisfactorily modified by depending upon various applications.

When styrene was absent, both the tensile strength (see no. 8) and Young's modulus (0.8 kgf/mm<sup>2</sup>) of the resulting polymer were lower than those of the polymer prepared in the presence of styrene. Therefore, step (b) shown in eq. (2) should be indispensable.

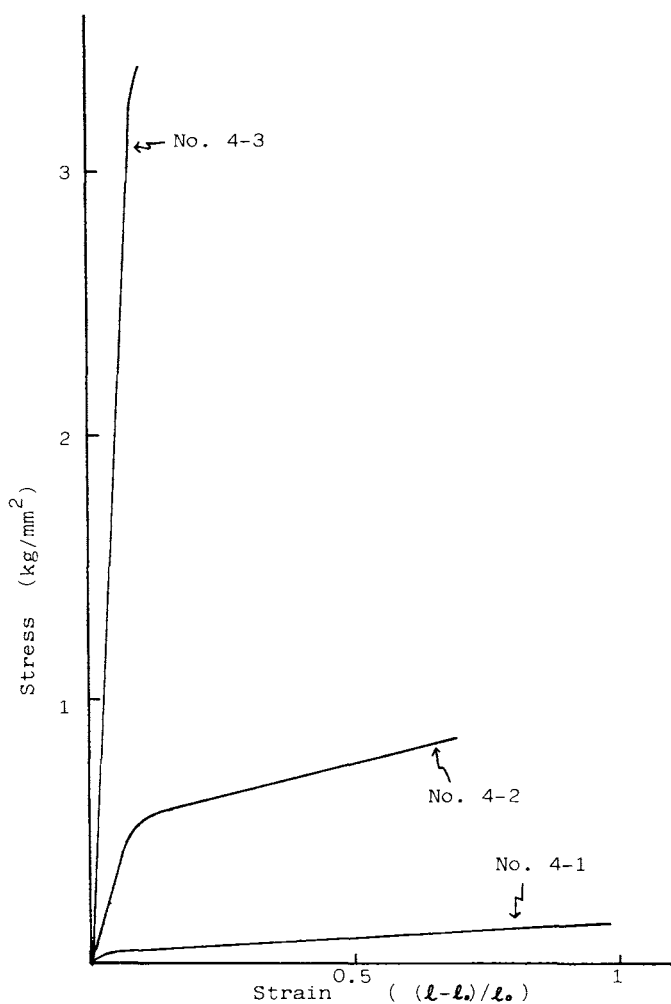


Fig. 1. Stress-strain curve of the film of no. 4 in Table I.

### IR Study

The IR spectroscopic analysis was conducted to reveal the mechanism of the reaction course.

Absorptions characteristic of maleic anhydride, 1850 and 1790  $\text{cm}^{-1}$ ,<sup>4</sup> disappeared at an earlier stage of the modification but a strong and broad absorption with shoulders appeared at 1730  $\text{cm}^{-1}$ , indicating half-ester formation. For a film of no. 5 series (in Table I), a medium absorption at 1630  $\text{cm}^{-1}$  (due to the C = C of styrene) completely disappeared under the condition of no. 5-1. And a strong and broad absorption centered at 3300  $\text{cm}^{-1}$  with two shoulders between 2700 and 2500  $\text{cm}^{-1}$ , which was characteristic of carboxyl group, still remained without considerable changes even when the film was heated at 200°C. Therefore, the heat treatment, step (c), may cause the

partial formation of ester linkage to affect the mechanical properties of the polymer.

### Hydrolysis of the Polymer

The film specimen (no. 3-1 in Table I) was hydrolyzed by aq. KOH-pyridine and the hydrolysate was divided into three types of the product depending on the solubility (see Experimental). Of these, the pyridine-soluble part which was supposed to contain polystyrene, if any, was analyzed by  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectroscopies. No detection of any aromatic components indicated the starting styrene is all consumed for the copolymerization with maleic acid (or its half-ester).

### Modification 1 ( $n = 8$ or $6$ in the Structure 1)

The prepolymers from 1,8-octanediol and from 1,6-hexanediol were attempted to be crosslinked under the comparable conditions for the prepolymer from 1,10-decanediol. Then, the mixture of the prepolymer (from 1,8-octanediol or 1,6-hexanediol) and maleic anhydride (1:1 molar ratio) was stirred at  $50^\circ\text{C}$  for 20 min. These IR spectra clearly showed two absorptions at  $1850$  and  $1790\text{ cm}^{-1}$ , indicating the presence of unreacted maleic anhydride. An equimolar amount of styrene was added to each mixture with stirring, but a uniform mixture was not obtained, especially when 1,6-hexanediol was used, due to increasing hydrophilicity of the prepolymer (the prepolymer from 1,6-hexanediol is substantially soluble in water).

### Modification 2

Maleic, succinic, and phthalic anhydrides were heated with the prepolymer in the presence or absence of *p*-toluenesulfonic acid (see Experimental). The polymer obtained was inferior in the tensile strength (less than  $0.06\text{ kg/mm}^2$ ). The main reason revealed by the IR studies was that the ester-linkage formation corresponding to step (c) in the modification 1, leading to the network structure, occurred only partially.

### Modification 3

The prepolymer was treated with allyl glycidyl ether (AGE) and then heated in the presence of an initiator in the film-processing device in the hope of forming a polymer with network structure without loss of the hydroxyl groups. When BPO was used as an initiator, the resulting film was spongelike, too soft, and weak to test. This polymer was not soluble in pyridine or dimethyl sulfoxide, indicating possible formation of the network structure. To contrast, no film was obtained from the product when AIBN was used as an initiator.

### Modification 4

An attempted crosslinkage formation in the prepolymer by using toluenediisocyanate (2,4- and 2,6-mixture) was carried out. The mixture coagulated immediately after the addition of toluenediisocyanate.

## EXPERIMENTAL

### Prepolymers from 1,10-Decanediol and 1,8-Octanediol

A mixture of 1,10-decanediol (52.3 g, 0.300 mol) and potassium phenoxide (4.0 g, 0.030 mol) was heated at 300°C for 2.5 h in an autoclave. The mixture was transferred into a flask and washed with 100 mL of water for five times (to remove potassium phenoxide), and then with 50 mL of hot benzene for three times (to remove unreacted 1,10-decanediol). Water contained was removed by the azeotropic distillation with benzene by the use of the water separator.<sup>5</sup> The prepolymer obtained is a highly viscous liquid. Its average molecular weight was about 2250 by the hydroxyl number determination. The prepolymer from 1,8-octanediol was also prepared according to this method.

### Prepolymer from 1,6-Hexanediol

Polymerization was carried out according to the method used in the preparation of the prepolymer from 1,10-decanediol, but in the post-treatment both phenol and unreacted 1,6-hexanediol were removed by washing the reaction mixture with water because the diol is readily soluble in water.

### Method of Modification 1

Two typical examples are shown.

(1) A mixture of prepolymer (10.0 g), maleic anhydride (3.15 g, 0.0321 mol), styrene (3.34 g, 0.0321 mol), and AIBN (0.05 g, 0.000321 mol) was stirred rapidly at 50°C for 20 min and vacuum (about 5 mmHg) was applied to degas. The resulting mixture was poured into the film-processing device and heated at 90°C for 6 h, and a film was obtained (see no. 3-1 in Table I). The film was heated at 150°C for 3 h under vacuum (see no. 3-2 in Table I).

(2) In the above procedure, styrene was replaced by divinylbenzene (4.17 g, 0.0321 mol; Tokyo Kasei). After the mixture was stirred at 60°C for 2.5 h, the temperature was raised to 90°C in 1 h, and then to 150°C in 1.5 h and kept there for 1 h (see no. 6 in Table I).

### Method of Modification 2

The procedure was similar to the modification 1 except that styrene or divinylbenzene and an initiator were absent.

Reaction conditions examined are listed in the order of a kind of acid anhydride, molar ratio of acid anhydride/OH in the prepolymer (mol/mol), heating temperature (°C) in the film-processing device/time (h), heating temperature (°C) in the vacuum oven/time (h): (a) maleic anhydride, 1/1, 150/3, 150/3; (b) maleic anhydride, 1/2, 150/3, 150/3; (c) succinic anhydride, 1/2, 90/3, 150/3; (d) phthalic anhydride, 1/2, 250/2, —. In the experiments of (b), (c), and (d), 1/100 mol of *p*-toluenesulfonic acid was added.

### Method of Modification 3

(1) The mixture of prepolymer (10.0 g), allyl glycidyl ether (AGE, 7.31 g, 0.0641 mol), and BPO was stirred at 90°C for 20 min and heated to 150°C.

Then, the temperature was raised from 150 to 180°C in 3 h and the heating was continued for 1 h. Under similar conditions, AIBN was used in place of BPO.

#### Method of Modification 4

To the prepolymer (10.0 g), toluenediisocyanate (a mixture of 2,4- and 2,6-isomers, 5.58 g, 0.0321 mol) was added and stirred at room temperature, but the mixture coagulated immediately. Similarly, 4,4'-diphenylmethanediisocyanate was used in place of toluenediisocyanate, but the coagulation again took place.

#### Determination of Hydroxyl Group

The number of the hydroxyl group in the prepolymer was determined according to the method described by Sorenson and Campbell.<sup>6</sup>

#### Method of the Hydrolysis of the Polymer

A mixture of the prepolymer (10.0 g), maleic anhydride (3.15 g), and styrene (3.34 g) was heated by the method of no. 3-1 (see Table I) in the presence of AIBN (0.05 g). The film (2.23 g) obtained was refluxed for 24 h in pyridine (65 mL), containing 15 mL of 5% aq. KOH solution. After cooling, 1.20 g of the pyridine-insoluble product was obtained by filtration. From the filtrate, pyridine was evaporated off to leave 0.70 g of the methanol-soluble product and the residue. The residue was acidified with concd. aq. HCl after pulverization with a mortar and pestle and washed with water after the filtration (weight, 0.20 g).

#### Film Processing

The device produced by Shibayama Kagaku, SS-VP-50, was used.

#### Stress-Strain Curve

All stress-strain curves were obtained by a form of film. A sample film (width 5.0 mm; length, 20.0 mm; thickness, about 2.5 mm depending on the sample) was subjected to a stress-strain test (Toyo Baldwin Co., Ltd., STM-100BP). Elongation speed was 20 mm/min.

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