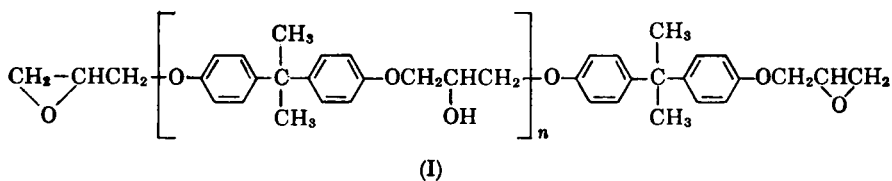


## Polyhydroxyethers. I. Effect of Structure on Properties of High Molecular Weight Polymers from Dihydric Phenols and Epichlorohydrin\*

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### INTRODUCTION

The reaction of dihydric phenols with epoxy compounds is well known. For example, 2,2-bis(4-hydroxyphenyl)propane, bisphenol A, reacts with epichlorohydrin and base to form epoxide-terminated polyhydroxyethers of the following structure (I):



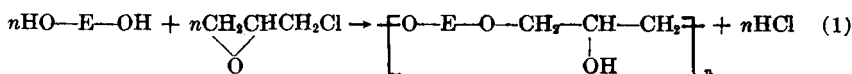
where  $n$  ranges from zero to approximately twenty in the familiar, commercially available series of resins. These relatively low molecular weight epoxy resins have found considerable utility as components of thermosetting structural plastics and organic coatings.

The preparation of epoxy resins of this type generally requires the use of an excess of epichlorohydrin. The value of  $n$  in I, as is well known, can be controlled to some degree by the amount of excess epichlorohydrin employed in the reaction. Theoretically, a 1:1 molar ratio of dihydric phenol and epichlorohydrin should lead to very high molecular weight polyhydroxyethers, and, in fact, some intermediate molecular weight polymers obtained in this manner have been reported.<sup>1</sup> Only limited property data have been made available on these materials, however. In addition, a high molecular weight, epoxy-terminated, bisphenol A-epichlorohydrin polymer, useful as a solution applied surface coating, has been described by Marshall and Somerville.<sup>2</sup>

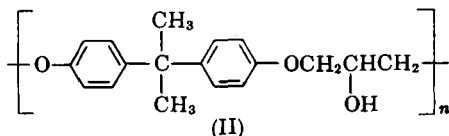
Recently, methods for the preparation, control of the degree of polymerization, and stabilization of very high molecular weight thermoplastic

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polyhydroxyethers have been found in these laboratories. These methods, which involve the reaction summarized in eq. (1), are generally applicable to the preparation of a class of completely amorphous, thermoplastic high polymers corresponding to the structure shown,



where E is a radical residuum from a dihydric phenol. As employed here, the term polyhydroxyether will refer to members of this general class of polymers. The polyhydroxyether of bisphenol A, for example, has the following repeating unit (II):



This polymer differs from the well known commercial epoxy coatings resins in two important aspects: first, it is much higher in molecular weight, (45,000 versus a maximum of about 8000); second, it does not contain terminal epoxide functionality. As a result of the latter, the polymer is thermally stable and can be fabricated by conventional thermoforming techniques.

A study has been made of a number of polymers in this family; of particular interest is the effect of the structure of the dihydric phenol on the (a) glass transition temperature and (b) barrier properties of the resulting polyhydroxyether. A summary of these data is presented in the Results section. In addition, a more complete characterization of a single polyhydroxyether, considered representative of this general class of polymers, is included.

## EXPERIMENTAL

Measurements of transition temperature  $T_g$  and barrier characteristics were carried out on compression-molded films 0.002–0.010 in. in thickness. The films were prepared from dried (24 hr. in vacuum at 60°C.) polymer powders. Molding conditions were 2000 psi pressure and temperatures at least 30°C. above the major  $T_g$ . All of the polyhydroxyethers were sufficiently high in molecular weight so that no influence of molecular weight on  $T_g$  could be detected.

Major glass transition temperatures were determined by measuring resiliency as a function of temperature. The experimental method was essentially the same as that described by Brown.<sup>3</sup> An Instron tensile tester adapted to measure tensile modulus over a wide temperature range was employed. All film samples were 2 in. long and  $\frac{1}{8}$  in. wide. The samples were stretched 1% at a rate of 10%/min. and allowed to return

to gage length at the same rate. From the stress-strain curve, a resiliency value was determined. The minimum of the per cent resiliency versus temperature plot was taken as the glass transition temperature. The experimental error in the determination of this value was found to be  $\pm 2.5^\circ\text{C}$ .

Moisture vapor transmission data were obtained by ASTM procedure E-96-53T. Oxygen permeability was determined by ASTM procedure D-1434-58. Mechanical properties of bisphenol A polyhydroxyether were determined by standard methods noted in Table V. Impact strengths recorded in Figure 1 were obtained by a modification of ASTM test D-256-56.

## RESULTS AND DISCUSSION

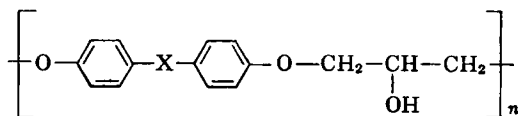
### Glass Transition Temperatures

Glass transition temperatures were measured for a series of polyhydroxyethers prepared from various dihydric phenols. As has been found for polycarbonates,<sup>4</sup> the polyhydroxyethers exhibit two glassy state transitions. A minor or glass II transition,<sup>5</sup> in the neighborhood of  $-70^\circ\text{C}$ ., is attributed to the flexible glyceryl ether portion, and the major or glass I transition, appearing above room temperature in all cases, results from the rigid phenylene linkages in the polymer chain. In the case of bisphenols, it was found that the nature of the connecting link between aromatic rings had considerable influence on the major  $T_g$  of the resulting polymer. This effect is illustrated in Table I. Other investigators have found a similar qualitative order with thermosetting epoxy resins<sup>6</sup> and thermoplastic polysulfonates.<sup>7</sup>

Some general observations can be derived from the data of Table I. The presence of polar groups, such as the sulfone link, tend to increase the  $T_{g_1}$  over the acyclic groups, possibly by hydrogen bonding with the hydroxyls. Alicyclic groups also tend to raise the glass transition temperature. The added rigidity of these substituted, saturated rings and the accompanying restricted rotation of the aromatic rings is presumably responsible for the observed increase. In the acyclic cases and polymer 5 it is considered likely that the amount of restricted rotation of the aromatic rings (producing stiffer polymer chains) is responsible for the observed variations.

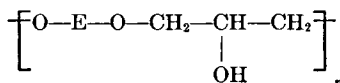
The influence of the type of dihydric phenol on the major  $T_g$  of the corresponding polyhydroxyether is summarized in Table II. It has been shown<sup>8</sup> that the glass transition temperature is a linear function of the number of *p*-phenylene linkages per unit chain length. Therefore, it is not surprising that the polyhydroxyether derived from hydroquinone has the lowest  $T_{g_1}$ . Dichlorobisphenol A polyhydroxyether has a somewhat lower  $T_{g_1}$  than the bisphenol A polymer, while that based on tetrachlorobisphenol A is somewhat higher. The lowering effect may be due to the

TABLE I  
Influence of Connecting Group in Bisphenol on the Glass I Transition Temperature of Polyhydroxyethers



Polymer No.	X	$T_{g1}$ , °C.
1	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{CH}_2-\text{CH}- \\   \\ \text{CH}_3 \end{array}$	75
2	$-\text{CH}_2-$	80
3	$\begin{array}{c} -\text{CH}- \\   \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	95
4	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{CH}_2 \end{array}$	100
5	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{C}_6\text{H}_5 \end{array}$	115
6	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}-\text{C}_6\text{H}_4\text{S}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2 \\   \\ \text{CH}_3 \end{array}$	135
7	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_4\text{S}-\text{C}_6\text{H}_4-\text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	140
8	$\begin{array}{c} \text{O} \\    \\ -\text{S}- \\    \\ \text{O} \end{array}$	155
9	$\begin{array}{c} \text{C}(\text{CH}_3)_2 \\   \\ \text{C}_6\text{H}_4\text{S}-\text{C}_6\text{H}_4-\text{CH} \\   \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$	175

TABLE II  
Influence of the Type of Dihydric Phenol on the Glass I Transition Temperature of Polyhydroxyethers




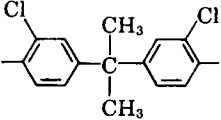
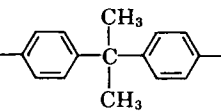
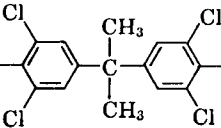
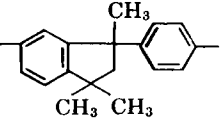
Polymer no.	E	$T_{g1}$ , °C.
1		60
2		85
3		100
4		115
5		120

TABLE III  
Comparison of the Barrier Properties of Some Polymeric Films

Polymer no.	Gas permeability, cc.-mil/100 in. <sup>2</sup> /24 hr./atm.		Moisture vapor Transmission, g.-mil/100 in. <sup>2</sup> /24 hr. <sup>a</sup>
	Oxygen	Carbon dioxide	
1 Vinylidene chloride-vinyl chloride copolymer	<1	2	0.25
2 Polyethylene terephthalate	5	6	2
3 Bisphenol A polyhydroxyether	5	8	3
4 Polyvinyl chloride	15	55	2.5
5 Polyethylene (high density)	107	450	0.6
6 Polypropylene	200	750	0.6
7 Bisphenol A polycarbonate	200	1000	10
8 Polyethylene (low density)	439	1900	1
9 Polystyrene	530	2300	6

<sup>a</sup> At 100°F., 90% R.H.


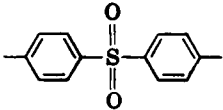
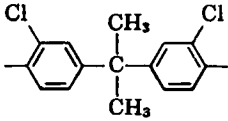
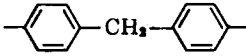
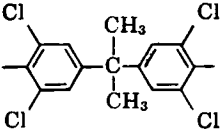
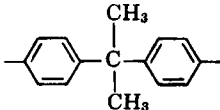
possibility that a random polymer (having less symmetry) is produced from dichlorobisphenol A.

### Barrier Properties

A comparison of the barrier properties of several commercial polymers with those of bisphenol A polyhydroxyether is shown in Table III. As a barrier to oxygen and carbon dioxide, this polyhydroxyether appears to be about equivalent to polyethylene terephthalate. However, as a water vapor barrier, it compares somewhat less favorably with many of the polymers which are commonly employed as moisture barriers. This relatively high moisture vapor permeability appears to be due primarily to the presence of an hydrophilic secondary hydroxyl group in the polymer.<sup>9</sup> Also, it should be reiterated that all of the polyhydroxyether films are completely amorphous, whereas many of the commercial resins listed have

TABLE IV  
Influence of the Type of Dihydric Phenol on Barrier Properties of Polyhydroxyethers

$$\left[ \text{O}-\text{E}-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2 \right]_n$$

Polymer no.	E	Oxygen permeability <sup>a</sup>	Moisture vapor transmission <sup>b</sup>
1		0.5	3
2		2	9
3		3	3
4		4	—
5		4	3
6		5	3

(continued)

at least some degree of crystallinity. It has been demonstrated<sup>10</sup> that the presence of a crystalline structure has a profound effect on barrier properties. No attempt has been made to equate the degree of crystallinity for the polymers shown in Table III.

The effect of the structure of the dihydric phenol on the oxygen permeability and moisture vapor transmission of polyhydroxyethers is shown in Table IV. It can be seen that structural variations produce only a fivefold change in moisture vapor transmission (due, no doubt, to the predominating influence of the hydroxyl group<sup>9</sup>). These same variations, however, result in more than a one hundredfold change in oxygen permeability. In general, the effect of structure on both oxygen and moisture barrier properties correlates well with the observations of others.<sup>9-13</sup> Thus, a small connecting link between aromatic rings produces the maximum in barrier properties in a polyhydroxyether film. The increased polarity of the diphenyl sulfone polymer improves the oxygen barrier properties,<sup>12</sup> but adversely affects the moisture vapor barrier characteristics.<sup>9</sup> Bulky nonsymmetrical groups in the polymer chain decrease both oxygen and moisture barrier properties.

TABLE IV (continued)

Polymer no.	E	Oxygen permeability <sup>a</sup>	Moisture vapor transmission <sup>b</sup>
7		8	7
8		8	7
9		15	7
10		75	15

<sup>a</sup> cc.-mil/100 in.<sup>2</sup>/24 hr./atm.

<sup>b</sup> g.-mil/100 in.<sup>2</sup>/24 hr.—100°F., 90% R.H.

TABLE V  
Properties of Various Polymers

Property	Bisphenol A polyhydroxyether	Bisphenol A polycarbonate	Cellulose acetate butyrate	Chlorinated polyether <sup>a</sup>	Poly-styrene
Tensile strength, psi <sup>b</sup>	9,000	9,000–10,000	5,000	6,000	7,000
Tensile modulus, psi <sup>b</sup>	380,000	320,000	—	160,000	400,000–500,000
Elongation, % <sup>a</sup>	50–100	50–100	60	60–160	1–2.5
Tensile impact, ft. lb./in. <sup>3c</sup>	200–400	200–400	—	—	—
Izod impact, ft. lb./in. <sup>3d</sup>	6	12–16	1.1–2.3	0.4	0.3–0.4
Heat distortion temp. (264 psi), °C. <sup>e</sup>	88	135	65–75	80–90	85
Specific gravity <sup>f</sup>	1.18	1.20	1.21	1.40	1.06

<sup>a</sup> Poly [3,3-bis-(chloromethyl)trimethylene ether]. ASTM test procedures.

<sup>b</sup> D638-58T. <sup>c</sup> D1822-61T. <sup>d</sup> D256-56. <sup>e</sup> D648-56. <sup>f</sup> D792-50.

### Mechanical Properties

The mechanical properties of these polymers are, of course, molecular weight dependent. This is illustrated in Figure 1, which shows the variation of impact, measured on 0.01-in. unoriented film, with weight-average molecular weight for a series of bisphenol A polyhydroxyether samples. In this respect, the bisphenol A polymer shows a behavior typical of most polymers.

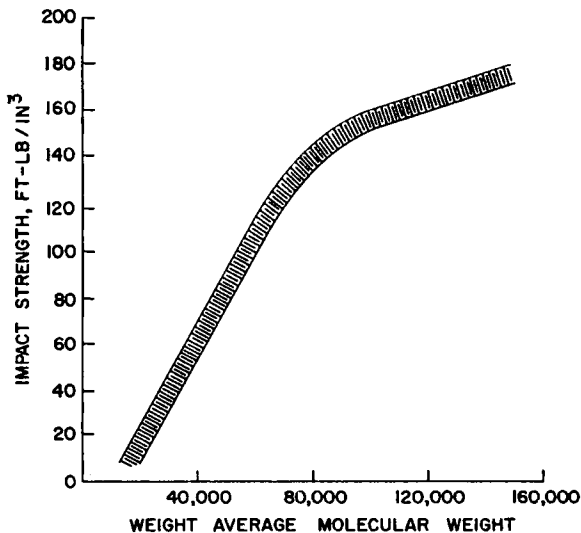


Fig. 1. Effect of molecular weight on impact strength of the polyhydroxyether of bisphenol A.



Some additional properties of bisphenol A polyhydroxyether, considered to be representative of this general class of polymers, are given in Table V together with comparative average data for several commercial resins. In addition to the properties listed, these new materials display the well known stability of the ether linkage to chemical and thermal attack. A high degree of secondary valence attraction, characteristic of the ether and hydroxyl functions, results in excellent dimensional stability. Due to the polar nature of the molecule, these materials exhibit excellent adhesion to most substrates. Also, the presence of the pendant secondary hydroxyl group on the repeating unit provides a site for modification and crosslinking.<sup>14</sup> Furthermore, the preparative methods are readily adaptable to copolymerization with combinations of dihydric phenols.<sup>15</sup>

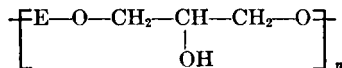
The authors are indebted to G. E. Ingraham, C. N. Merriam, and J. A. Stenstrom of the Union Carbide Plastics Company for the determination of the physical properties of these polymers.

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### Synopsis

An interesting series of high molecular weight thermoplastic polymers, based on dihydric phenols and epichlorohydrin, have been prepared. The polymers have, in common, a structure which can be represented by the general repeating unit

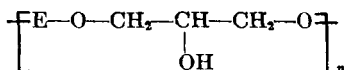


where E is a radical residuum from a dihydric phenol. Certain properties appear characteristic of this class of polymers. All contain some chain branching through the secondary hydroxyl group. They are amorphous, noncrystallizable, transparent, tough, and thermally stable. They show two glassy state transitions, a minor transition at

about  $-70^{\circ}\text{C}$ . and a major transition at a considerably higher temperature. This family of polymers provides an excellent means for studying structure-property correlations. Data are reported showing the effect of the structure of the dihydric phenol moiety (E) on the major glass transition temperature and on certain barrier properties of a series of these polymers. The polymer prepared from 2,2-bis(4-hydroxyphenyl) propane, bisphenol A, is considered typical of this series; its mechanical and physical properties are described in somewhat more detail and compared with properties of certain commercial polymers.

### Résumé

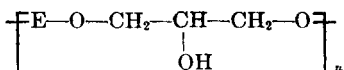
On a préparé une série intéressante de polymères thermoplastiques de haut poids moléculaire, basés sur les dihydrophénols et l'épichlorhydrine. Les polymères ont une structure qui peut, de façon générale, être représentée par l'unité de répétition suivante:



où E est le radical provenant du dihydrophénol. Certaines propriétés apparaissent comme caractéristiques de cette classe de polymères. Tous contiennent certaines ramifications de chaîne à l'endroit du groupement hydroxyle secondaire. Ils sont amorphes, non-cristallisables, transparents, coriaces, et thermiquement stables. Ils ont deux points de transition vitreuse, une transition peu importante à  $-70^{\circ}\text{C}$  et une transition importante à une température considérablement plus haute. Cette famille de polymères constitue un excellent moyen pour l'étude des corrélations structure-propriétés. Les données reportées montrent l'effet de la structure de la partie dihydrophénolique sur la température de transition vitreuse la plus élevée et sur certaines propriétés limitées d'une série de ces polymères. Le polymère préparé au départ de 2,2-bis(4-hydroxyphényl)propane, bisphénol A, est considérée comme typique de cette série; leurs propriétés mécaniques et physiques sont décrites avec quelques détails et comparées avec les propriétés de certains polymères commerciaux.

### Zusammenfassung

Eine interessante Reihe hochmolekularer, thermoplastischer Polymerer wurde ausgehend von zweiwertigen Phenolen und Epichlorhydrin dargestellt. Die gemeinsame Struktur der Polymeren kann durch den allgemeinen Grundbaustein



wiedergegeben werden, wo E der Rest des zweiwertigen Phenols ist. Gewisse Eigenschaften scheinen für diese Klasse von Polymeren charakteristisch zu sein. Alle besitzen eine gewisse Verzweigung über die sekundäre Hydroxylgruppe. Sie sind amorph, nicht kristallisierbar, transparent, zähe und thermisch stabil. Sie besitzen zwei Glasumwandlungen, eine Nebenumwandlung bei etwa  $-70^{\circ}\text{C}$  und eine Hauptumwandlung bei einer beträchtlich höheren Temperatur. Diese Polymerfamilie liefert eine ausgezeichnete Möglichkeit zum Studium von Beziehungen zwischen Eigenschaften und Struktur. Ergebnisse über den Einfluss der Struktur des zweiwertigen Phenolbausteins (E) auf die Haupt-Glasumwandlungstemperatur und gewisse Undurchlässigkeitseigenschaften einer Reihe dieser Polymeren werden mitgeteilt. Das aus 2,2-Bis(4-hydroxyphenyl)propan, Bisphenol A, dargestellte Polymere wird als typisch für diese Reihe betrachtet; seine mechanischen und physikalischen Eigenschaften werden in etwas grösserer Ausführlichkeit beschrieben und mit den Eigenschaften gewisser handelsüblicher Polymerer verglichen.

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