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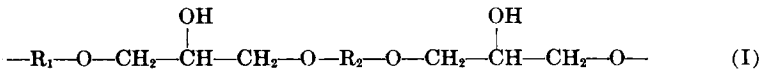
Polyhydroxyethers. II. Effect of Structure on Properties of High Molecular Weight Copolymers from Dihydric Phenol Mixtures and Epichlorohydrin*

N. H. REINKING, A. E. BARNABEO, and W. F. HALE, *Research Department, Union Carbide Plastics Company, Division of Union Carbide Corporation, Bound Brook, New Jersey*

INTRODUCTION

A previous paper described the properties of stable, thermoplastic polyhydroxyethers prepared from selected dihydric phenols and epichlorohydrin.[1] The relationship of structure to physical properties for these novel, high molecular weight polymers has been discussed. In order to elaborate further on the structure–property relation and to gain additional useful information, a series of hydroxyether copolymers derived from mixtures of two dihydric phenols and epichlorohydrin have been evaluated.

The copolymer system can be illustrated by the following generalized structure:



(I)

where R_1 and R_2 represent the dihydric phenol moieties. Structure I, as written, would indicate that the copolymers are characterized by a regular alternating sequence of dihydric phenol units. In practice, it has been found that both a random and an alternating distribution can be achieved.

The available literature on hydroxyether copolymers of high molecular weight is quite limited. One patent[2] describes some of the properties of a copolymer from 2,2-bis(4-hydroxyphenyl)propane and bis(3,5-dimethyl-4-hydroxyphenyl)sulfone. Another patent[3] reports a copolymer from 4,4′-dihydroxydiphenyl and hydroquinone.

As part of a comprehensive study of polyhydroxyethers, a variety of copolymers have been prepared and some observations of physical behavior recorded. This paper describes the glass transition temperatures and gas barrier properties of the copolymers and relates these properties to copolymer composition.

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EXPERIMENTAL

The methods for the determination of major glass transition temperatures (T_{gI}) and gas barrier properties have been described previously.[1] In all cases, the hydroxyether copolymers were of sufficient molecular weight so that no influence of molecular weight on T_{gI} could be detected. The experimental error for transition temperatures was found to be ±2.5°C.

RESULTS AND DISCUSSION

Random and Alternating Copolymers

As indicated previously, two types of copolymer systems are available depending on the method of synthesis. If a mixture of two bisphenols is employed in direct reaction with epichlorohydrin, a nonuniform copolymer is isolated. The method is shown in eq. (1).

$$m\text{HO—R}_1\text{—OH} + n\text{HO—R}_2\text{—OH} + (m+n)\text{CH}_2\text{—CH—CH}_2\text{—Cl} \rightarrow$$

$$\text{—(—R}_1\text{—O—CH}_2\text{—CH(OH)—CH}_2\text{—O—)}_m\textit{ir}\text{—(—R}_2\text{—O—CH}_2\text{—CH(OH)—CH}_2\text{—O—)}_n\text{—} + (m+n)\text{HCl} \quad (1)$$

R_1 and R_2 represent the structurally different dihydric phenol moieties. The *ir* indicates that the sequence of units in the copolymer chain is probably irregular.[4] Of course, if the difference in the reaction rates of the two dihydric phenols with epichlorohydrin is sufficient, a block copolymer can result. No evidence has been obtained which would confirm or negate this possibility.

Table I identifies, by structure and by common name, a number of bisphenols which have been used to prepare copolyhydroxyethers by this method. A representative listing of some of these random copolymers is shown in Table II.

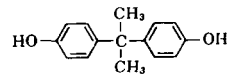
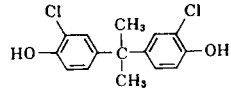
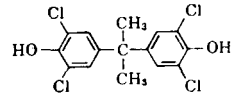
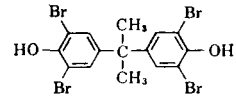
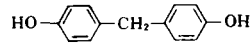
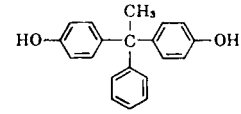
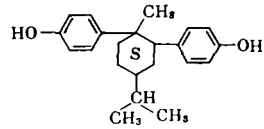
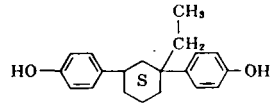
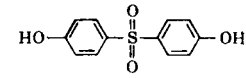
Alternatively to the direct reaction just described, if a dihydric phenol and the diglycidyl ether (monomeric) of another dihydric phenol are employed as reactants, the product should be a regular, alternating hydroxyether copolymer.

$$\text{HO—R}_1\text{—OH} + \text{CH}_2\text{—CH—CH}_2\text{—O—R}_2\text{—O—CH}_2\text{—CH—CH}_2 \rightarrow$$

$$\text{—(—R}_1\text{—O—CH}_2\text{—CH(OH)—CH}_2\text{—O—R}_2\text{—O—CH}_2\text{—CH(OH)—CH}_2\text{—O—)}_n\text{—} \quad (2)$$

Table III lists some of the alternating hydroxyether copolymers which have been prepared according to this scheme.

TABLE I
Names and Structures of Various Bisphenols

Bisphenol	Structure
Bisphenol A	
Dichlorobisphenol A	
Tetrachlorobisphenol A	
Tetrabromobisphenol A	
Bisphenol F	
Bisphenol ACP	
Bisphenol L	
Bisphenol V	
Bisphenol S	

Glass Transition Temperatures

Glass transition temperatures were determined for many of the copolymers. Primarily, a correlation between copolymer composition and major transition temperature (T_{gI}) was sought. In addition, the effect of alternating versus random systems on the thermal behavior of these unique, thermoplastic polymers was of interest. Table IV indicates the major glass transition temperatures of several hydroxyether copolymers and includes for comparison the values for some homopolymers.[1]

It has been observed[5] that many amorphous copolymers have T_g values intermediate between the transition temperatures of the corresponding homopolymers. The present series of copolymers is, in general, no excep-

TABLE II
Random Hydroxyether Copolymers

Source of R_1[a]	Source of R_2[a]	Mole ratio of R_1/R_2 in monomer feed	Reduced viscosity[b]
Bisphenol A	Tetrachlorobisphenol A	9/1	0.30
		4/1	0.22
		2/3	0.15
Bisphenol A	Bipshenol V	1/3	0.54
		1/1	0.55
		3/1	0.60
Bisphenol A	Bisphenol L	1/1	0.64
Bisphenol A	Dichlorobisphenol A	1/1	0.52
Bisphenol S	Tetrachlorobisphenol A	1/1	0.10
Bisphenol V	Tetrachlorobisphenol A	1/1	0.29
Bisphenol V	Bisphenol ACP	1/1	0.33
Bisphenol V	Dichlorobisphenol A	1/1	0.40

[a] Equivalent to R_1 and R_2 of eq. (1).
[b] Measured in tetrahydrofuran, 0.2 g. of polymer/100 ml. of solution at 25°C.

TABLE III
Alternating Hydroxyether Copolymers

Source of R_1[a]	Source of R_2[a]	Reduced viscosity[b]
Tetrachlorobisphenol A	Hydroquinone	0.45
Bisphenol V	Tetrachlorobisphenol A	0.21
Bisphenol A	Tetrachlorobisphenol A	0.67
Bisphenol F	Tetrachlorobisphenol A	0.65
Dichlorobisphenol A	Bisphenol A	0.43
Tetrabromobisphenol A	Bisphenol A	0.30

[a] Equivalent to R_1 and R_2 of eq. (2).
[b] Measured in tetrahydrofuran, 0.2 g. of polymer/100 ml. of solution at 25°C.

tion to this observation. In Table IV only the tetrachlorobisphenol A–bisphenol F and the tetrachlorobisphenol A–bisphenol A copolymers deviate from this general rule.

Fox[6] has proposed a modification of the Gordon-Taylor equation[7] for the prediction of glass transition temperatures of amorphous random copolymers. In simplified form,[6] this may be written as eq. (3), where T_g is the major or glass I transition temperature of the copolymer; T_{g_a} and T_{g_b} the glass transition temperatures of homopolymers a and b, respectively, and W_a and W_b the weight fractions of homopolymer components a and b, respectively.

$$1/T_g = (W_a/T_{g_a}) + (W_b/T_{g_b}) \quad (3)$$

Thus a plot of $1/T_g$ versus weight fraction of either component should be a straight line. The experimental values of T_g for the bisphenol A–bisphenol

TABLE IV
Glass Transition Temperatures of Some Hydroxyether Copolymers

Source of R_1[a]	Source of R_2[a]	Mole Ratio of R_1/R_2 in monomer feed	Copolymer type	T_{g1}, °C.
Bisphenol A	—	1/0	—	100
Bisphenol A	Bisphenol V	3/1	Random	105
Bisphenol A	Bisphenol V	1/1	Random	110
Bisphenol A	Bisphenol V	1/3	Random	130
—	Bisphenol V	0/1	—	140
Bisphenol ACP	Bisphenol V	1/1	Random	130
Bisphenol ACP	—	1/0	—	115
Bisphenol L	Bisphenol A	1/1	Random	140
Bisphenol L	—	1/0	—	175
Dichlorobisphenol A	Bisphenol A	1/1	Random	90
Dichlorobisphenol A	Bisphenol A	1/1	Alternating	90
Dichlorobisphenol A	—	1/0	—	85
Bisphenol A	Tetrachlorobisphenol A	1/1	Alternating	100
—	Tetrachlorobisphenol A	0/1	—	115
Bisphenol A	Hydroquinone	1/1	Alternating	95
—	Hydroquinone	0/1	—	60
Bisphenol F	Tetrachlorobisphenol A	1/1	Alternating	80
Bisphenol F	—	1/0	—	80
Tetrabromobisphenol A	Bisphenol A	1/1	Alternating	117

[a] R_1 and R_2 of eqs. (1) and (2) depending on polymer type.

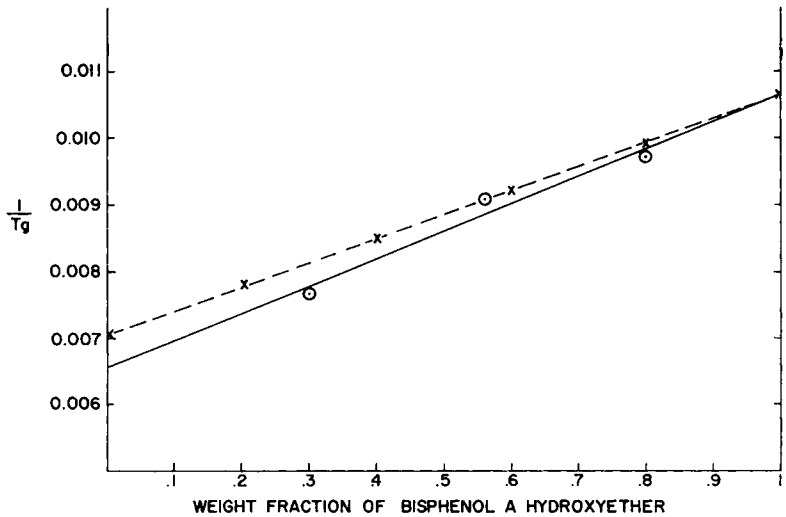


Fig. 1. Reciprocal of glass transition temperature vs. weight fraction of bisphenol A hydroxyether for some bisphenol A–bisphenol V hydroxyether copolymers: (⊙) experimental data; (×) calculated from eq. (3).

V copolymers given in Table IV have been employed to calculate T_{g_a} and T_{g_b}. Figure 1 shows a plot of $1/T_g$ versus weight fraction of bisphenol A component. From the observed values, a T_g of 94°C. would be predicted for bisphenol A polyhydroxyether (observed T_g = 100°C.) and a T_g of 152°C. for bisphenol V polyhydroxyether (observed T_g = 140°C.). Thus, the agreement between the experimental data (solid line of Fig. 1) and the calculated glass transition temperature (dotted line of Fig. 1) is reasonably good.

To test the effect of an alternating versus a random copolymer on glass transition temperature, the 1:1 dichlorobisphenol A–bisphenol A copolymer was prepared by each of the routes described in eqs. (1) and (2). The two copolymers exhibited the same T_{g_I}.

Barrier Properties

Table V lists the oxygen permeability and moisture vapor transmission of some hydroxyether copolymers. In general, the copolymers exhibited

TABLE V
Permeability Properties of Some Hydroxyether Copolymers

Source of R_1[a]	Source of R_2[a]	Mole ratio of R_1/R_2	Copolymer type	Oxygen permeability, cc.-ml./100 in.²/24 hr./atm.	Moisture vapor transmission, g.-ml./100 in.²/24 hr.[b]
Bisphenol A	—	—		5	3
Bisphenol A	Bisphenol V	3/1	Random	6	4
Bisphenol A	Bisphenol V	1/1	Random	8	4
Bisphenol A	Bisphenol V	1/3	Random	12	5
—	Bisphenol V	—	—	15	7
Bisphenol ACP	Bisphenol V	1/1	Random	8	5
Bisphenol ACP	—	—	—	8	7
Dichlorobisphenol A	—	—	—	3	3
Dichlorobisphenol A	Bisphenol A	1/1	Random	6	7
Dichlorobisphenol A	Bisphenol A	1/1	Alternating	4	—
Tetrachlorobisphenol A	—	—	—	4	3
Tetrachlorobisphenol A	Bisphenol A	1/1	Alternating	8	6
Hydroquinone	—	—	—	0.5	3
Hydroquinone	Tetrachlorobisphenol A	1/1	Alternating	5	6
Bisphenol F	Tetrachlorobisphenol A	1/1	Alternating	4	4
Tetrabromobisphenol A	Bisphenol A	1/1	Alternating	7	4

[a] R_1 and R_2 of eq. (1) or (2) depending on polymer type.
[b] At 100°F., 90% R.H.

barrier properties which are intermediate in value between those for the corresponding homopolymers. In a few instances, copolymers exhibited poorer barrier characteristics than either of the two homopolymers. One explanation of this phenomenon is that the decrease in regularity along the polymer chain reduces chain–chain interactions and thus causes an increase in the rate of gas diffusion through the film. This theory is supported to some extent by the observation that a regular, alternating dichlorobisphenol A–bisphenol A copolymer has a somewhat lower oxygen permeability than the corresponding random copolymer.

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Synopsis

The glass transition temperature and gas barrier properties of a number of high molecular weight thermoplastic hydroxyether copolymers have been determined. These copolymers were derived from mixtures of two dihydric phenols and epichlorohydrin. The property data are analyzed in terms of copolymer composition and the random or alternating distribution of monomer units in the polymer chains. In general, the glass transition temperatures of the copolymers were found to be intermediate between the values for the two homopolymers. In one system, good agreement between the experimental data and a simplified equation for the prediction of glass transition temperatures of amorphous, random copolymers was obtained. No differences in the glass transition behavior of random and alternating hydroxyether copolymers could be detected. Gas barrier properties, in general, were found to be intermediate in value between those of corresponding homopolymers. The exceptions are discussed in terms of polymer structure variations.

Résumé

On a déterminé la température de transition vitreuse et les propriétés de barrières vis-ä-vis des gaz d'un nombre de copolymères d'hydroxyéther thermoplastiques de haut poids moléculaire. Ces copolymères résultent des mélanges de deux phénols dihydroxylés et d'epichlorohydrine. Les données sur les propriétés s'expriment en composition du copolymère et la statistique ou la distribution alternante des unités de monomère dans les chaînes de polymère. En général, les températures de transition vitreuse des copolymères sont intermédiaires entre les valeurs pour les deux homopolymères. Dans un systéme, on obtient un bon accord entre les données expéri-

mentales et une équation simplifiée pour la précision des températures de transition vitreuse des copolymères amorphes statistiques. On ne décele aucune différence dans le comportement des copolymères d'hydroxyéther statistiques et alternants. Les propriétés de barrière vis-a-vis des gaz sont en général intermédiaires en valeur entre les homopolymères correspondants. On discute les exceptions en rapport avec les variations de structure du polymère.

Zusammenfassung

Die Glasumwandlungstemperatur und die Undurchlässigkeit für Gase einer Anzahl hochmolekularer, thermoplastischer Hydroxyäthercopolymerer wurden bestimmt. Diese Copolymeren wurden aus Mischungen zweier zweiwertiger Phenole und Epichlorhydrin gewonnen. Eine Analyse der Ergebnisse in Abhängigkeit von der Copolymerzusammensetzung und der "statistischen" oder abwechselnden Verteilung der Monomereinheiten in den Polymerketten wird durchgeführt. Im allgemeinen liegt die Glasumwandlungstemperatur der Copolymeren in der Mitte zwischen den Werten für die beiden Homopolymeren. In einem System wurde gute Übereinstimmung zwischen den Versuchsergebnissen und einer vereinfachten Gleichung zur Ermittlung von Glasumwandlungstemperaturen von amorphen, statistischen Copolymeren erhalten. Zwischen dem Verhalten von statitischen" und alternierenden Hydroxyäthercopolymeren bei der Glasumwandlung konnte kein Unterschied festgestellt werden. Die Undurchlässigkeit für Gase lag im allgemeinen in der Mitte zwischen den Werten für die entsprechenden Homopolymeren. Die Ausnahmen von diesem Verhalten werden in Zusammenhang mit Änderungen der Polymerstruktur diskutiert.

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