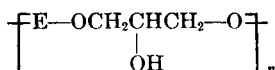


Polyhydroxyethers. III. Ester Derivatives*

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INTRODUCTION

The recent development of methods for preparing high molecular weight thermoplastic polyhydroxyethers from dihydric phenols and epichlorohydrin has resulted in a new family of tough, stable, transparent polymers. The structure of these polymers can be represented by the generalized repeating unit



where E is a radical residuum from a dihydric phenol.

An earlier paper in this series¹ described the properties common to this family of polymers and discussed the effect of structure of the dihydric phenol moiety on certain physical properties. The repeating unit in these polymers possesses reactive sites which make possible rather extensive chemical modification. In addition to the aromatic rings of the dihydric phenol, there is a secondary hydroxyl group which undergoes many of the reactions characteristic of monomeric secondary alcohols, e.g., esterification, etherification, salt formation, oxidation, reduction, and chlorination, thus making possible entire series of modifications based on the parent polyhydroxyethers. These derivatives, through changes in hydrogen bonding, polarity, bulk and symmetry factors and by introduction of other reactive groups, show pronounced differences in chemical and physical properties.

In studying these new polyhydroxyether resins, one of the objectives has been to investigate and evaluate, systematically, the large number of derivatives which are possible. The present paper deals with the preparation and evaluation of ester derivatives based on monohydric organic and inorganic acids.

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EXPERIMENTAL

Ester derivatives of the polymers were prepared by many of the methods commonly used for preparing esters of monomeric secondary alcohols. Thus acid halides, anhydrides, esters, and free acids were employed successfully. Examples of the use of these reagents are included in the following preparations. As a matter of convenience, the esterifications were usually carried out in solution, although a bulk esterification with benzoic acid on a heated 2-roll mill demonstrated that a solvent is not always necessary. An inert solvent such as dioxane or an acid acceptor, e.g., pyridine, was generally used in the solution esterifications. Also a catalyst was employed in those cases involving a transesterification reaction.

Preparation of Ester Derivatives

Via Acid Halides. The polyhydroxyether of 2,2-bis(4-hydroxyphenyl) propane (bisphenol A), 50.0 g. (0.176 mole OH), and pyridine, 31.6 g. (0.400 mole), were dissolved in 500 ml. of dry dioxane. To this reaction mixture was gradually added 29.8 g. (0.264 mole) of chloroacetylchloride. An exothermic reaction was observed during the addition. After addition of chloroacetylchloride, the mixture was refluxed 1.5 hr. to insure complete reaction. The chloroacetylated polymer was isolated by pouring the reaction mixture into propanol-2 containing a small amount of ice. The precipitated polymer was filtered and washed several times with successive portions of propanol-2, dilute hydrochloric acid, and water. The thoroughly washed polymer was dried for 16 hr. in a vacuum oven at 50–60°C. and 10–20 mm. Hg pressure. In this manner, a 61 g. (96% of theory) yield of polymer containing 9.4% chlorine (96% esterification) was obtained.

By using less than one equivalent of acid chloride, partially esterified polyhydroxyethers were obtained.

Via Acid Anhydrides. Bisphenol A polyhydroxyether, 50.0 g. (0.176 mole OH), was dissolved in 327 g. (4.10 moles) of pyridine. To this solution was added 184 g. (1.80 moles) of acetic anhydride and the mixture was heated 4 hr. on a steam bath (temperature 85°C.) with stirring. The acetylated polymer was isolated, washed, and dried as described in the preceding experiment. In this manner, 50 g. (88% of theory) of acetylated polymer was obtained.

By using less acetic anhydride partially acetylated polyhydroxyethers were obtained.

Via Ester Exchange. Bisphenol A polyhydroxyether, 25.0 g. (0.088 mole OH), and 0.50 g. (0.021 mole) of lithium hydroxide were dissolved in 250 ml. of dioxane. The system was dried by azeotropically distilling off water through a fractionating column until a head temperature of 101°C. was reached. The reaction mixture was then allowed to cool to room temperature, and 30.5 g. (0.335 mole) of ethyl nitrate was added. The reaction mixture was slowly heated until a head temperature of 101°C. was reached, indicating the removal of all of the dioxane-ethanol azeotrope.

The esterified polymer was recovered, washed, and dried as described in the first experiment. In this manner, 23 grams (80% of theory) of polymer containing 1.25% nitrogen (29.4% esterification) was obtained.

In a similar manner the mercaptoacetyl ester of bisphenol A polyhydroxyether was prepared from ethyl mercaptoacetate.

Via Free Acids. Bisphenol A polyhydroxyether, 25.0 g. (0.088 mole OH), and 0.50 g. (0.021 mole) of lithium hydroxide were dissolved in 250 ml. of dioxane. To this solution was added 22.5 g. (0.443 mole) of 90% formic acid in water. The reaction mixture was distilled through a fractionating column until the head temperature reached 100°C. indicating the removal of all of the dioxane-water azeotrope boiling at 88°C. The formylated polymer was recovered, washed, and dried as described in the first experiment. In this manner 22 g. (82% of theory) of formylated polyhydroxyether was obtained. A saponification analysis indicated 78% formylation.

Analyses of Ester Derivatives

Determinations of per cent esterification of polyhydroxyether esters containing a hetero atom, such as P, S, N, or Cl, in the acid portion, were readily carried out by analyzing for the hetero atom. In the absence of such convenient labels, the comparative absorption of the OH (2.85 μ) and C = O (5.75 μ) groups in the infrared spectrum afforded a convenient qualitative measure of the degree of esterification. In addition, for those esters not containing a hetero atom, a determination of saponification equivalent was used to measure the degree of esterification. Comparison of the hetero atom analysis and saponification equivalent is shown in Table I for several esters.

TABLE I
Saponification Equivalent as a Measure of Degree of Esterification in Bisphenol A Polyhydroxyether Esters

Ester derivative	Esterification, %	
	Hetero atom analysis	Saponification equivalent
Chloroacetyl	5.8	6.0
Chloroacetyl	52.6	56.7
Chloroacetyl	95.6	100.0
<i>o</i> -Chlorobenzoyl	98.0	100.0
<i>p</i> -Toluenesulfonyl	19.2	19.7

Determination of T_g and Barrier Properties

The methods used for determination of major glass transition temperatures (T_g) and barrier properties have been described previously.¹ In all cases, the hydroxyether polymers and ester derivatives were of sufficient molecular weight so that no influence of molecular weight on T_g could be detected.

RESULTS AND DISCUSSION

Glass Transition Temperatures

Polyhydroxyethers, like polycarbonates,² exhibit two glassy state transitions. The major or glass I transitions of the polyhydroxyethers of all dihydric phenols investigated are well above room temperature and appear to result from the presence of the rigid phenylene links in the polymer chain. The minor or glass II transition, which occurs at about $-70^{\circ}\text{C}.$, is thought to be associated with the mobility inherent in the glyceryl ether segment of the molecule.

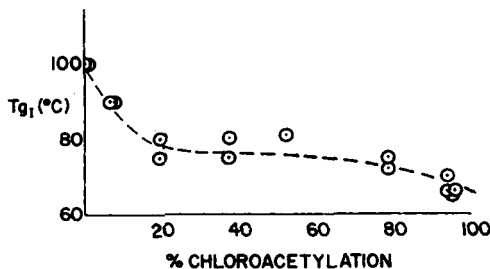


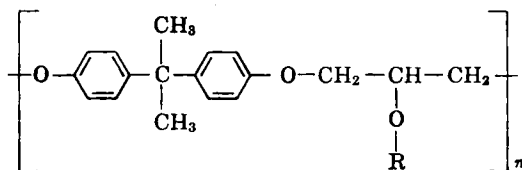
Fig. 1. T_{g_1} as a function of degree of chloroacetylation for bisphenol A polyhydroxyether.

In general, esterification of a given polyhydroxyether resulted in a lowering of the major glass transition temperature of the polymer. This was true at all levels of esterification. This effect is illustrated in Table II for a series of esters of the polyhydroxyether of 2,2-bis(4-hydroxyphenyl) propane, bisphenol A, and in Figure 1 which pictures in more detail the effect of degree of esterification for the chloroacetyl derivative of the bisphenol A polymer. As shown, a gradual decrease in T_{g_1} was observed with increasing degrees of esterification. This effect on T_{g_1} appears to be due to (1) the bulky ester groups which decrease chain symmetry and increase the intermolecular distance between polymer chains and (2) decreased hydrogen bonding. Experimental evidence points to the former or bulk factor, as being the dominating factor. Thus, the larger stearyl group shows a greater effect on T_{g_1} than the acetyl or benzoyl groups. Also, hydroxyethylation (87% etherification), which should not appreciably affect hydrogen bonding, causes a decrease in T_{g_1} comparable to that observed with acetylation.

As indicated earlier, the minor glass transition at $-70^{\circ}\text{C}.$, is attributed to mobility of the glyceryl ether portion of the repeating unit. It is believed that the inherent toughness of the polyhydroxyether family of polymers is the result of this mobility. On esterification, the minor transition at $-70^{\circ}\text{C}.$ becomes much less pronounced or disappears altogether. This has been interpreted as meaning that the presence of the bulky ester groups inhibit motion about the hydroxyether linkage. Consistent with this

interpretation is the observation that the toughness of the polymers (as measured by impact resistance and tensile elongation) decreases with esterification.

TABLE II
Effects of Esterification on Properties of Bisphenol A Polyhydroxyether



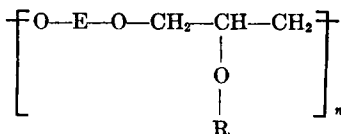
R	Esterification, % ^a	T_{g1} °C.	Oxygen permeability, cc.-mil/ 100 in. ² / 24 hr./atm.	Moisture vapor transmission, g.-mil./ 100 in. ² /24 hr ^b
H	0	100	5	3
Formyl	80	80	10	7
Acetyl	10	90	9	4
	50	80	14	5
	100	60	41	6
Chloroacetyl	10	90	7	7
	50	78	8	—
	100	65	8	8
Mercaptoacetyl	25	80	4	7
Propionyl	100	60	47	9
Stearyl	30	60	23	6
	75	25	>100	10
Benzoyl	10	85	8	4
	50	80	18	5
	100	65	30	6
<i>o</i> -Chlorobenzoyl	100	66	9	8
<i>p</i> -Toluenesulfonyl	95	80	16	9
Diphenylphosphinyl	25	80	11	8
Nitryl	25	80	6	9

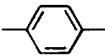
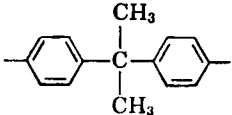
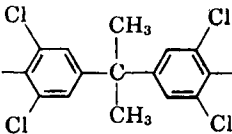
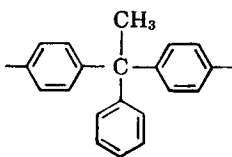
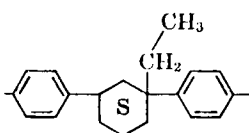
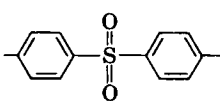
^a Determined either by hetero atom analysis or measurement of saponification equivalent.

^b At 100°F., 90% R.H.

In addition to the bisphenol A polymer, polyhydroxyethers prepared from a number of other dihydric phenols have been studied. Property data for the ester derivatives of several of these polymers are shown in Table III. Of the various polyhydroxyethers investigated, that from α,α -diphenylol ethylbenzene afforded the only exception to the rule that esterification lowers the T_{g1} . Acetylation of this polyhydroxyether resulted in essentially no change of T_{g1} while benzoylation actually resulted in a slight increase of T_{g1} . This is in agreement with the theory that the bulk factor has a dominating influence on T_{g1} since this polymer might be ex-

TABLE III
Effects of Esterification on Properties of Polyhydroxyethers from Various Diphenols



Dihydric phenol residue (E)	Ester (R)	T_{g1} , °C.	Oxygen permeability, cc.-mil./100 in. ² /24 hr./atm.	Moisture vapor transmission, g.-mil./100 in. ² /24 hr. ^a
	H	60	0.5	3
	Acetyl	49	3	6
	H	100	5	3
	Acetyl	60	23	6
	Benzoyl	65	30	6
	H	115	4	3
	Acetyl	100	21	6
	H	115	8	7
	Acetyl	110	25	6
	Benzoyl	126	20	6
	H	140	15	7
	Acetyl	107	41	9
	H	155	2	9
	Acetyl	130	9	—

^a At 100°F., 90% R.H.

pected to accommodate the bulky ester groups because of the pendant phenyl rings already present in the polymer.

Barrier Properties

Collectively, the polyhydroxyethers of dihydric phenols exhibit good to excellent gas barrier properties and only fair moisture barrier characteris-

tics. As indicated in Tables II and III, the replacement of the hydroxyl groups in these polymers by less hydrophilic ester groups did not improve the moisture barrier properties as might be expected. Apparently, the increased branching and decreased symmetry caused by esterification counteracts any beneficial result of decreasing hydroxyl group concentration and, generally, moderate increases in moisture vapor permeability were observed on esterification. The stearyl group, for example, is large enough so that, despite its hydrophobic nature, this effect appeared even at low degrees of esterification. On the other hand, benzylation of the polyhydroxyether from α,α -diphenylol ethylbenzene apparently does not appreciably alter chain symmetry and/or branching and the moisture vapor transmission actually decreased slightly as a result of decreasing the concentration of hydroxyl groups.

In general, the permeability of the polymers to oxygen, as shown in Tables II and III, was increased by esterification. This increase was found to correlate well with the degree of esterification and the bulk of the attached acyl radical. The introduction of a polar substituent on the acyl radical materially reduced oxygen transmission. This is shown in Table II, for example, by a comparison of the values for the acetyl, chloroacetyl, and mercaptoacetyl esters and, also, for the benzoyl and chlorobenzoyl derivatives.

Other Physical and Chemical Properties

Wide variations in the properties of modified polyhydroxyethers are observed with changes in the ester group and degree of esterification. Thus, the stearyl derivative of bisphenol A polyhydroxyether, with a T_g below room temperature, produces an extremely low modulus, waxy film which recovers slowly on being stretched. In contrast, the acetyl derivative is a rigid, high modulus material quite similar to the unmodified polymer. The diphenylphosphinyl and chloroacetyl esters are self-extinguishing when ignited. The mercaptoacetyl ester crosslinks in the presence of peroxides or on extended exposure to atmospheric oxygen. With respect to solvent resistance, esterification markedly improves resistance of the base polymer to most hydroxylic solvents and reduces resistance to nonpolar solvents.

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References

1. Reinking, N. H., A. E. Barnabeo, and W. F. Hale, *J. Appl. Polymer Sci.*, **7**, 2135, 2145 (1963).
2. Reding, F. P., J. A. Faucher, and R. D. Whitman, *J. Polymer Sci.*, **54**, 556 (1961).

Synopsis

The esterification of high molecular weight hydroxyether polymers, derived from dihydric phenols and epichlorohydrin, has been studied. The esters of an assortment of

monobasic acids, both organic and inorganic, were prepared by reaction of acid halides, anhydrides, esters or free acids with the secondary hydroxyl group in the polymer repeating unit. The effects of the structure of the acid radical and the degree of esterification on polymer properties were determined. In general, esterification resulted in a lowering of the major glass transition temperature of the polymer. This was true at all levels of esterification. Decreased chain symmetry and decreased hydrogen bonding appeared to be the major causes of the observed effect. Permeability of the polymers to oxygen and water vapor was increased by esterification. The increase was found to correlate well with the size and polarity of the acid radical. Some additional properties of the ester derivatives were examined in less detail.

Résumé

On a étudié l'estérification de polyhydroxyéthers de haut poids moléculaire, dérivés de diphénoles et l'épichlorhydrine. Par réaction des chlorures d'acides, de anhydrides, des esters ou des acides avec les groupes hydroxyliques secondaires dans le polymère, on a préparé les esters d'une série d'acides monobasiques, organiques et inorganiques. On a déterminé l'effet de la structure du radical de l'acide et du degré d'estérification sur les propriétés du polymère. Généralement, l'estérification abaisse la température de transition vitreuse du polymère. Ceci est vrai pour n'importe quel degré d'estérification. La diminution de la symétrie de la chaîne et de la quantité des ponts hydrogène, semblent être les causes principales. La perméabilité des polymères pour l'oxygène et la vapeur d'eau augmentent par l'estérification. On a trouvé que l'augmentation est liée aux dimensions et à la polarité du radical de l'acide. Certaines autres propriétés des dérivés estérifiés sont étudié moins en détail.

Zusammenfassung

Die Veresterung hochmolekularer, von zweiwertigen Phenolen und Epichlorhydrin abgeleiteten Hydroxyätherpolymerer wurde untersucht. Die Ester einer grossen Zahl organischer und anorganischer, einbasischer Säuren wurden durch Reaktion von Säurehalogeniden, Anhydriden, Estern oder freien Säuren mit der sekundären Hydroxylgruppe im Polymerbaustein dargestellt. Der Einfluss der Struktur des Säureradikals und des Veresterungsgrades auf die Polymereigenschaften wurde bestimmt. Im allgemeinen führte die Veresterung zu einer Erniedrigung der Haupt-Glasumwandlungstemperatur des Polymeren. Das galt für alle Veresterungsgrade. Verringerung der Kettensymmetrie und der Wasserstoffbindung schien die Hauptursache des beobachteten Effektes zu sein. Die Permeabilität der Polymeren für Sauerstoff und Wasserdampf wurde durch Veresterung erhöht. Die Erhöhung stand in einer vernünftigen Korrelation zur Grösse und Polarität des Säureradikals. Einige zusätzliche Eigenschaften der Esterderivate wurden in geringerer Ausführlichkeit untersucht.

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