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Glycidyl Esters. III. Reaction of Diglycidyl Esters and Cyclic Carboxylic Anhydrides

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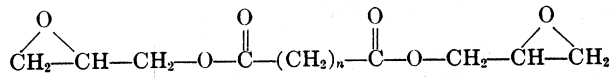
The reactions of glycidyl ethers and cyclic carboxylic anhydrides have been studied in detail, and the resins which result from these reactions have found wide acceptability in many fields of application.[1]

In contrast, the reactions of glycidyl esters have escaped investigation almost entirely, although such esters, especially glycidyl acrylate and glycidyl methacrylate, have been used in resin formulations.

The purpose of our work was to prepare a number of members of the series



and to prepare resinous materials by the reaction of these esters with phthalic anhydride and with other cyclic carboxylic anhydrides. It was anticipated that a relationship between the chemical structure of the diglycidyl esters, i.e., the nominal distance between epoxide functions, and the physical properties of the derived resins could be found.

PREPARATION OF REAGENTS AND POLYMERIZATION PROCEDURE

Phthalic anhydride. Phthalic anhydride (Eastman Organic Chemicals)‡ was dissolved in hot benzene, the solution filtered to remove undissolved *o*-phthalic acid, and the filtrate cooled to obtain recrystallized *o*-phthalic anhydride, m.p. 131–131.5°C.

Maleic anhydride. Maleic anhydride (Eastman Organic Chemicals) was distilled at 49 mm. The main cut melted at 52.0–52.5°C.

Hexahydrophthalic anhydride. Hexahydrophthalic anhydride (National Aniline) was distilled at 4 mm. pressure under nitrogen, and the portion boiling at 122°C. was used for subsequent experiments.

Tetrahydrophthalic anhydride. Tetrahydrophthalic anhydride (Eastman

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‡ Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

Organic Chemicals, Practical Grade) was recrystallized twice from benzene–Skellysolve C (1:2) to obtain purified product, m.p. 98.5–100.5°C.

Diglycidyl sebacate. Diglycidyl Sebacate was prepared from potassium sebacate and epichlorohydrin, as described previously.[2] Oxirane oxygen by the HBr method[3]: 9.64% (theory, 10.18%).

Diglycidyl azelate. Diglycidyl azelate was prepared from sodium azelate and epichlorohydrin, as described previously.[4] Oxirane oxygen: 10.07% (theory, 10.63%).

Diglycidyl pimelate. A one-liter three-necked flask was equipped with stirrer, dropping funnel, reflux condenser, and a universal trap[5] permitting the separation of immiscible condensate layers and return flow of the heavier layer to the reaction flask. Redistilled epichlorohydrin (486 g.) (Eastman Organic Chemicals) was added to the flask and heated to reflux. A hot solution containing 51.1 g. of pimelic acid (American Cyanamid Co.), 31.2 g. of potassium hydroxide, and a mixture of 18.6 g. of benzyltrimethylammonium chloride as 60% aqueous solution (Commercial Solvents Corp.) in 115 ml. water was added to the vigorously agitated, refluxing flask content over a period of 30 min., while water was removed continuously by means of the trap. After addition had been completed, the reaction mixture was allowed to reflux for an additional period of 10 min. The crude product was isolated by a procedure analogous to that described for crude diglycidyl azelate. The distillation residue was crude diglycidyl pimelate, 91.0 g. Oxirane oxygen: 8.82% (theory, 11.75%).

The crude material was extracted repeatedly with warm (80°C.) Skellysolve C, b.p. 88–89°C., the combined extracts were evaporated, and the residue was recrystallized twice from methanol at −50°C., yielding refined diglycidyl pimelate. Oxirane oxygen: 11.22%.

Diglycidyl adipate. To 492 g. of redistilled epichlorohydrin at reflux was added, over a period of 23 min., a hot solution containing 43.8 g. of adipic acid, 31.2 g. of potassium hydroxide, and 18.6 g. of a mixture of benzyltrimethylammonium chloride, as 60% aqueous solution, in 100 ml. of water in the manner described for the preparation of diglycidyl pimelate. After an additional reflux period of 12 min., the crude diglycidyl adipate was isolated in the manner described for diglycidyl azelate, yielding 88.2 g. Oxirane oxygen: 8.45% (theory, 12.39%).

The crude product, on cooling at 0°C., crystallized in part. The liquid portion was decanted, the crystals were washed with Skellysolve C at room temperature, and the washed solids were recrystallized three times from aqueous methanol (90 Vol.-% methanol) at −20°C. Purified product: oxirane oxygen 11.93%, m.p. 48.7–50.8°C.

Diglycidyl succinate. A mixture of 888 g. of redistilled epichlorohydrin and 70.8 g. of succinic acid (Eastman Organic Chemicals) was heated to 102°C. in a two-liter flask equipped with a reflux condenser and efficient stirrer. To this solution 37.3 g. of a 60% aqueous solution of benzyltrimethylammonium chloride was added, and the reaction mixture was heated at 107–109°C. for 20 min. The mixture was then cooled and was

washed twice at 40–45°C. with 250 ml. portions of water. The free epichlorohydrin was then removed by distillation at reduced pressure under nitrogen, as described for the preparation of diglycidyl azelate. Removal of remaining volatiles at 60°C. and 0.5 mm. Hg gave as residue 178.2 g. of crude diglycidyl succinate. Oxirane oxygen: 6.40% (theory, 13.9%). The crude material was distilled in a brush still at 111–112°C. and 0.1 mm. Hg. The distillate was washed with ether at −20°C. and recrystallized twice from ether at −27°C. to obtain purified diglycidyl succinate. Oxirane oxygen: 13.60%.

Diglycidyl oxalate. To 81.0 g. of redistilled triethylamine in 400 ml. of methylene chloride at −20°C. was added 51.8 g. of glycidol (Eastman Organic Chemicals; purity by oxirane determination, 88.7%). The solution was stirred vigorously while 43.2 g. of oxalyl chloride (Eastman Organic Chemicals) in 80 ml. of methylene chloride was added dropwise (68 min.) and the temperature was maintained between −15 and −25°C. The mixture was allowed to warm to 10°C. and was then heated to reflux and refluxed for 30 min. After the organic phase was cooled to 20°C. and washed four times with 250 ml. portions of water, it was dried over calcium sulfate, condensed to 100 ml. volume, and cooled at −20°C. overnight. The deposited solid was washed with some cold methylene chloride and dried to obtain 21.8 g. of crude diglycidyl oxalate. Oxirane oxygen: 15.40 (theory, 15.82%). The filtrate was added to 400 ml. of petroleum ether, the resulting mixture was cooled at −20°C. and filtered, and the cake was dried to give a 14.2 g. of a second, cruder crop. Oxirane oxygen: 14.03%. The first crop of crystals was recrystallized twice from methylene chloride at −20°C. to get purified diglycidyl oxalate. Oxirane oxygen: 15.58%.

Curing of Diglycidyl Esters with Phthalic Anhydride. A Pyrex glass tube 11 in. long, O.D. 9 mm., was sealed at one end, rinsed with methyl oleate (99% purity; used as mold release agent), and allowed to drain for several minutes. Into the tube were weighed 3.50 g. of diglycidyl ester and sufficient *o*-phthalic anhydride to provide one anhydride group per analyzed epoxide function. In some experiments 0.0035 g. of benzyldimethylamine was added as accelerator. The polymerization procedure and test specimen preparation were the same as that described previously.[6] The samples were heated at 150°C. to the gel point and then cured at 150°C. for 3 hrs. or more, and at 120°C. for an additional period. After the physical properties of the test specimen had been measured, the samples were cured at 150°C. for an additional 24 hr. period.

Measurement of Heat Distortion Temperature. The heat distortion temperatures reported in this paper were determined by the torsional modulus method.[7]

RESULTS

Experimental conditions for the preparation of resins from the individual diglycidyl esters are shown in Table I, while in Table II the heat distortion temperatures of the resins are compared with gel times and with the number

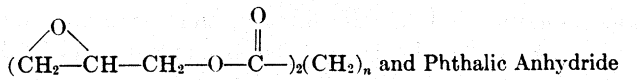
of methylene groups contained in the diglycidyl esters. A number of interesting relationships are apparent from these data.

TABLE I
Preparation of Resins from Diglycidyl Esters and Phthalic Anhydride

Diglycidyl ester		Phthalic anhydride, g.	Gel time, min.	Cure time,[a] hr.	
Name	Amount used, g.			At 150°C.	At 120°C.
Diglycidyl oxalate	3.50	5.05	3	3	24
Diglycidyl succinate	3.50	4.41	5	3	24
Diglycidyl adipate	3.50	3.87	30	3	24
Diglycidyl pimelate	3.50	3.56	15	3	24
Diglycidyl azelate	3.50	3.27	35	3	24
Diglycidyl sebacate	3.50	3.13	2.90[b] min.	17	7

[a] All samples were given an additional cure of 24 hr. at 150°C.
[b] Estimate.

TABLE II
Heat Distortion Temperatures (HDT) of Cured Resins Prepared from Diglycidyl Esters



Diglycidyl ester		Gel time, min.	HDT, °C.	
Name	n		After initial cure	After additional cure
Diglycidyl oxalate	0	3	138	<138[a]
Diglycidyl succinate	2	5	112	111
Diglycidyl adipate	4	30	66	87
Diglycidyl pimelate	5	15	78	82
Diglycidyl azelate	7	35	36	67
Diglycidyl sebacate	8	290	6	40

[a] HDT after additional cure was less than that after initial cure but could not be determined precisely since sample failed.

Relationship of Chain Length and Reactivity

If the assumption is made that the gel time provides a rough measure of reactivity[8] in a series of polymerizations such as the one reported here, it is apparent that the reactivity of diglycidyl esters toward phthalic anhydride is inversely related to chain length. This relationship, however, is not linear, even when minor differences in purity of the esters and the concentration effects are considered. Moreover, the resin formed by diglycidyl adipate does not follow the pattern exactly. An obvious consequence of the finding that chain length influences the reactivity of the diglycidyl esters is that resins formed from these esters have different curing requirements;

i.e., the more reactive esters require milder curing conditions to reach the point of maximum crosslinking than do the less reactive esters.

Relation of Chain Length and Heat Distortion Temperature

Heating of a resin causes interaction of potential crosslinking sites until all available sites have reacted. Simultaneously, the heating is likely to cause some disruption of the three-dimensional network, and this effect counteracts the establishment of new crosslinks. Thus, it can be expected that the degree of crosslinking of the resin first increases, then reaches a maximum point, and finally decreases under continued heating. At the point of maximum crosslinking, the second-order transition temperature of the resin can also be expected to be at a maximum and, since the heat distortion temperature (HDT) is approximately equal to the second-order transition temperature, the former can be used as a measure of maximum crosslinking of a polymeric material. It is apparent that, in order to compare the HDT's of different polymers and thus perhaps derive a relationship between the chemical structure of the monomeric epoxide and the physical properties of the derived resin, it is necessary that all polymers to be compared have reached, but have not exceeded, their maximum degree of crosslinking. The method used by us to prepare and test the resin samples was not suitable for a continuous determination of HDT's during cure. Using a standard cure cycle for resins made from monomers of widely varying reactivity, therefore, resulted in polymers of greatly differing degrees of crosslinking. This is evident from the fact that additional curing raised the HDT's of the polymers prepared from the less reactive esters and decreased (diglycidyl oxalate) or did not change (diglycidyl succinate) the others, as shown in Table II. Although a linear relationship between chain length and HDT could not be expected under these circumstances and was not found, a clear trend exists, showing that the distance between epoxide groups is inversely related to HDT. This is consistent with earlier observations[6] that the distance between crosslink points in epoxy resins is inversely related to the HDT.

Effect of Addition of a Tertiary Amine to the Polymerization Mixture

To test the effect of the addition of an amine accelerator on the gel time and HDT of resins prepared from diglycidyl esters, 0.1 wt.-% (based on ester weight) of benzyldimethylamine was added to mixtures of diglycidyl sebacate or diglycidyl azelate with phthalic anhydride. The sebacate resin had a gel time of 4 min. and an initial cure HDT of 45°C., while the azelate resin gelled in 2 min. and had an HDT of 60°C. after initial cure. It is evident that the effect of a small amount of amine is considerable both in decreasing gel time and in raising the HDT of the resin.

Reaction of Diglycidyl Esters and Miscellaneous Cyclic Anhydrides

As a qualitative test of the behavior of carboxylic anhydrides other than phthalic anhydride toward glycidyl esters, mixtures of tetrahydrophthalic

anhydride, maleic anhydride, hexahydrophthalic anhydride, succinic anhydride, or NADIC* methyl anhydride with diglycidyl sebacate or diglycidyl azelate were heated at 150°C. The reactivity of the anhydrides toward the glycidyl esters, as measured by gel time, decreased in the order in which the anhydrides are listed. NADIC methyl anhydride required more than $2^1/_2$ days to gel and after cure produced a gelatinous resin which on standing returned to the liquid form. Maleic anhydride showed anomalous behavior by evolving a gas before gelling and by forming an extremely hard, dark resin, even when the polymerization was carried out at 120°C. Tetrahydrophthalic anhydride and maleic anhydride, when polymerized with diglycidyl sebacate, had considerably shorter gel times than phthalic anhydride.

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Synopsis

The diglycidyl esters of oxalic, succinic, adipic, pimelic, azelaic, and sebacic acids were prepared and were made to react with *o*-phthalic anhydride to form crosslinked resins. The chain length of the monomeric diglycidyl esters was found to be directly related to the gel time and inversely related to the heat distortion temperatures of the derived resins, although neither relationship was linear. The reaction of diglycidyl sebacate and of diglycidyl azelate with several cyclic carboxylic anhydrides showed the reactivity of the anhydrides toward the esters to decrease in the following order: tetrahydrophthalic anhydride > maleic anhydride > hexahydrophthalic anhydride > succinic anhydride > nadic methyl anhydride.

Résumé

Les esters diglycidiques des acides oxalique, succinique, adipique, azélaique et sébacique ont été préparés et mis en réaction avec l'anhydride phtalique en vue de former des résines pontées. On a trouvé que la longueur de chaîne des esters monomériques diglycidiques est directement liée au temps de gel et inversément liée aux températures de déformation quoiqu'aucune relation ne soit linéaire. La réaction du sébacate diglycidique et de l'azélate diglycidique avec plusieurs anhydrides carboxyliques cycliques a montré que la réactivité des anhydrides envers ces esters diminuait dans l'ordre suivant:

* Methyl bicyclo[2,2,1]heptene-2,3-dicarboxylic anhydride isomers obtained from National Aniline Division, Allied Chemical Corporation.

anhydride tétrahydrophtalique > anhydride maléique > anhydride hexahydrophtalique > anhydride succinique > anhydride méthylnadique.

Zusammenfassung

Diglycidylester von oxal-, Bernstein-, Adipin-, Pimelin-, Azelain- und Sebacinsäure wurden dargestellt und mit *o*-Phthalsäure-anhydrid unter Bildung vernetzter Harze zur Reaktion gebracht. Die Kettenlänge der monomeren Diglycidylester stand in direkter Beziehung zur Gelbildungsdauer und in umgekehrter zur Hitzeverformungsbeständigkeit der gebildeten Harze; allerdings waren diese Beziehungen nicht linear. Die Reaktion von Diglycidylsebacat und Diglycidylazelat mit mehreren cyklischen Carbonsäureanhydriden zeigte, dass die Reaktivität der Anhydride gegen die Ester in folgender Reihe abnimmt: Tetrahydrophthalsäureanhydrid > Maleinsäureanhydrid > Hexahydrophthalsäureanhydrid > Bernsteinsäureanhydrid > Methylnadinsäureanhydrid.