

Epoxide-Substituted Vinyl and Acrylate Copolymers

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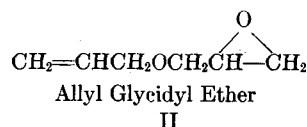
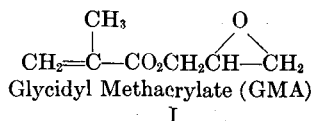
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INTRODUCTION

This paper covers some studies on polymers which are multifunctional in epoxide groups. The work was prompted by a recognition of several limitations in conventional epoxide resins based on phenolic intermediates: (a) they are deficient in color stability in some applications because of yellowing characteristics; (b) they are limited to terminal difunctionality in epoxide groups; (c) they require polar solvents; (d) and they are limited to materials that are below 5000 in average molecular weight.

The polymers which were sought were to have good color stability, be multifunctional in epoxide groups, and be capable of being prepared easily at molecular weights above 5000. These conditions led to the examination of acrylate and vinyl polymers as "backbones" to be substituted with epoxide groups. The simplest route to such epoxide functional polymers appeared to be the introduction of a polymerizable epoxide-containing comonomer into the polymerization.

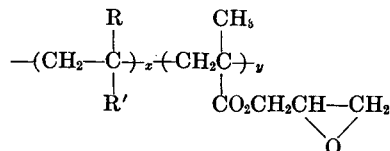
Glycidyl methacrylate (GMA), I, was chosen as the epoxide functional comonomer. Glycidyl methacrylate (b.p. = 75°C./10 mm., $n_D^{25} = 1.4482$) is a product of E. I. du Pont de Nemours and Co., Fabrics and Finishes Department.¹ It has proved to be a versatile intermediate for introducing epoxide groups into vinyl and acrylate copolymers. Parallel studies showed that it polymerized more readily than allyl glycidyl ether, II, an alternate epoxy functional monomer. It was also found that allyl glycidyl ether has a strong tendency to limit polymer molecular weight by chain transfer through the allyl portion of the molecule.



The remainder of this paper will examine the copolymerization characteristics of glycidyl methacrylate, methods of crosslinking the copolymers, and uses for specific copolymers.

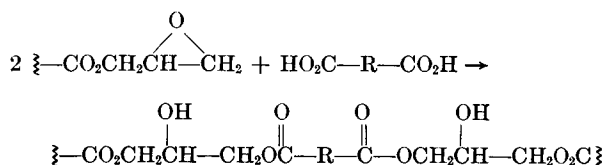
COPOLYMERIZATION

In the free radical-catalyzed copolymerization of glycidyl methacrylate, the epoxide groups are not affected, thus giving rise to epoxide-substituted polymers with the general structure:



where R = H, CH₃, etc., and R' = C₆H₅—, —CO₂CH₃, Cl, CN, etc.

Glycidyl methacrylate is similar to methyl methacrylate in its copolymerization characteristics. The reactivity ratios for the monomer pair styrene (M₁), glycidyl methacrylate (M₂) were determined by the method of Mayo and Lewis² (see Table I). The reactivity ratios, $r_1 = 0.34 \pm 0.05$ and $r_2 = 0.63 \pm 0.1$ (65°C.), are approximately the same magnitude as those reported for styrene-methyl methacrylate and styrene-butyl methacrylate.³ From the definition of r_1 as the rate of addition of styrene-terminated radicals to styrene divided by the rate of addition of styrene-terminated radicals to GMA, it is evident that such radicals tend to add to GMA. Similarly, the r_2 value shows that a GMA-terminated radical tends to add styrene. Thus, the styrene/GMA copolymer is not completely random. These r_1 , r_2 values indicate that a polymer azeotrope is formed when the monomer mixture contains 62 mole-% GMA.



Temperatures of 100–150°C. are needed to cause this reaction to occur. Thermosetting terpolymers containing styrene, GMA, and methacrylic acid have been reported.⁵

Many of the trends found in the reaction of amines with low molecular weight epoxy resins also hold true with GMA copolymers. Aliphatic primary amines cause more rapid crosslinking at room temperature than aromatic amines. With GMA copolymers the multifunctional nature of the epoxide polymer permits it to be cured with primary monoamines. With solutions of copolymers containing 20 mole-% GMA, pot lives of 4–6 hr. are usually obtained with aliphatic amines.

Most of the amine curing agents so far investigated exude from thin films when the polymers are allowed to cure at room temperature. Methanedi-amine is the most satisfactory curing agent located to date from the point of view of pot life and compatibility. The amines that are compatible in the polymer solution will usually give compatible baked (100°C.) films even though the amines exude during room temperature curing.

Specific examples of acid- and amine-cured polymers will be considered in the following section.

END USE EVALUATION OF SPECIFIC GMA COPOLYMERS

I. Thermosetting Finish: Styrene/GMA (85/15 Wt.-%) Copolymer

Appliance finishes with improved hardness and stain resistance, compared to alkyd-nitrogen resin systems, have been a continuing goal of the finishes industry. A crosslinked styrene-based polymer was expected to show these improvements, and the epoxide functional styrene/GMA copolymer offered many possibilities for crosslinking. The polymer was prepared by solution polymerization using 2% di-*tert*-butyl peroxide as the initiator (see experimental section for details). It has a molecular weight of about 5000–10,000. The composition reflects the epoxide content found to be satisfactory for crosslinking with the phosphoric acid curing system. The low molecular weight is needed so that the enamel solids content

will be 40–50% at application viscosity. Assuming a molecular weight of 10,000 the average polymer molecule would have ten pendant epoxide groups.

When the polymer is reacted, in a solvent blend containing methyl isobutyl ketone, with 0.85 moles of phosphoric acid for each mole of epoxide, a room temperature-stable polymer solution is produced. Although the uncured polymer is similar to low molecular weight polystyrene in that it is brittle and readily soluble in xylene, a 30 min. bake at 150°C. converts it to a hard, insoluble, and strongly adhering coating.

In order to compare this new film-forming system with conventional baking enamels, the phosphated styrene/GMA copolymer was pigmented with an equal weight of Ti-Pure (Du Pont registered trademark) R-510 titanium dioxide pigment using the sand grinding technique.⁶ The hardness, stain resistance, and soap resistance are the properties most improved over typical appliance finishes based on alkyd resins. Resistance to discoloration upon heating and upon Florida exposure was excellent.

TABLE II
EA/GMA Copolymers

	Experiment no.			
	42	75	173	92
Recipe				
Ethyl acrylate, parts	97	97	97	94
GMA, parts	3	3	3	6
Water, parts	210	210	210	210
Sodium lauryl sulfate, parts	1.5	1.5	1.5	1.5
α, α' -Azodiisobutyramidine-2HCl (catalyst) parts	0.05	0.05	0.05	0.05
Dodecyl mercaptan, parts	0.025	0.05	0.10	0.05
Reaction time, hr.	1.5	1.5	1.5	1.5
Temperature, °C.	65	65	65	65
Emulsion characteristics				
pH	7.08	6.82	6.0	6.6
Solid, %	31.5	31.9	31.3	31.6
Conversion, %	98	99	97.5	98
Polymer characteristics				
Inherent viscosity (0.5% in ethyl acetate at 25°C.)	2.74	1.76	1.00	2.03

II. Elastomer: Ethyl Acrylate/GMA (97/3 and 94/6)

These polymers were investigated to determine whether more convenient curing systems could be developed for acrylate-based elastomers. The copolymers were prepared in an emulsion system. Polymers having inherent viscosities from 1.0 to 2.74 (0.5% in ethyl acetate) were obtained by using dodecyl mercaptan as the molecular weight regulator (Table II).

Satisfactory curing of the EA/GMA (94/6) elastomer with azelaic acid occurred at 180°C. for 30 min. *m*-Phenylenediamine crosslinked the 97/3 polymer under the same conditions. Trimene base was effective with the 3% GMA copolymer at 150°C. for 30 min.

The initial tensile properties (see Table III) of the compounded polymers are similar to the values found for a commercial acrylate rubber. Ac-

celerated aging tests have not been conducted as yet.

III. Room Temperature Curing System: MMA/GMA (70/30)

This solution copolymer, blended with amines, gave films which crosslinked at room temperature. The 30% solids copolymer solution had a pot life of 4-24 hr., depending on the particular amine used. The films developed excellent resistance to toluene in one week.

As shown in Table IV, only a few amines were compatible. The films from many of the combinations which were compatible in solution showed spewing of the amine. Menthanediamine has proved the most satisfactory material in initial tests from the point of view of pot life, compatibility, and good film color. The same compatibility trends were also observed with butyl methacrylate/GMA and styrene/GMA copolymers. Holding the catalyzed solutions for several hours before casting films did not improve the amine compatibility.

TABLE IIIA

Ethyl Acrylate/GMA Copolymers: Elastomer Recipe

	Parts
EA/GMA copolymer	100
Crosslinking agent	^a
Philblack A ^b	50
Stearic acid (processing aid)	1.0
Catalyst	^a
Processing cycle ^c	3 min., 100°C.
Cure	^a

^a See Table IIIB.

^b High modulus furnace black, Phillips Chemical Co., Philblack Division.

^c Blended at room temperature on a two-roll rubber mill, then given the indicated processing cycle.

EXPERIMENTAL DETAILS

Styrene/GMA (85/15)

The polymers were prepared in aromatic hydrocarbon solvents using di-*tert*-butyl peroxide as the initiator. The reaction flask was fitted with an anchor-type stirrer, a dropping funnel, thermometer, and reflux condenser. A nitrogen atmosphere was maintained during the polymerization.

TABLE IIIB
Ethyl Acrylate/GMA Copolymers as Elastomers

Polymer	Composition	No.	Crosslinking agent	Parts	Catalyst	Parts	Cure		Ultimate elongation, % ^a	Ultimate tensile strength, psi	Initial modulus, psi
							Time, min.	Temp., °C.			
EA/GMA (94/6)	92		None	Uncompounded gum elastomer					2200	170	70
"	92		Azelaic acid	3.62	Dicyandiamide	0.11	30	150	480	270	400
							30	180	250	1120	590
EA/GMA (97/3)	75		<i>m</i> -Phenylenediamine	1.13	Sulfur	1.0	30	150	350	610	690
							30	180	290	940	850
EA/GMA (97/3) ^b	75		Trimene base ^c	4	Sulfur	1.0	30	150	440	1280	480
Hycar No. 4021 ^d	—		Trimene base ^c	4	Sulfur	1.0	30	150	270	1250	650

^a Samples tested at 1 in./min., 77°F., 50% R.H.

^b This composition had a tendency to cure on the mill.

^c Trimethyltrimethylenetriamine, Naugatuck Chemical Division of United States Rubber Co.

^d A commercial acrylic rubber, B. F. Goodrich Chemical Company.

TABLE IV
Amines Tested as Crosslinking Agents for MMA/GMA
(70/30) Copolymer^a

Structural type	Examples	Compatibility ^{a,b}
Straight chain aliphatic	<i>n</i> -Hexylamine	Compatible
	<i>n</i> -Decylamine	Slight surface haze
	Ethylenediamine	Slight surface haze
	Hexamethylenediamine	Haze
	Bis(4-aminocyclohexyl) methane	Slight surface haze
Polyfunctional aliphatic	2-Methylhexamethylenediamine	Oily surface haze
	Diethylenetriamine	Slight surface haze
	Menthanediamine	Compatible
Hindered aliphatic	Bis(aminomethyl)durene	Haze
	Bis(aminomethyl)mesitylene	Haze
	<i>N</i> -(2-phenylethyl)hexamethylenediamine	Oily surface haze
Alkylated aliphatic	<i>N</i> -(2-phenyl-2-hydroxyethyl)diethylenetriamine	Slight surface haze
Hydroxyl-containing	<i>p</i> ' <i>p</i> '-Diaminodiphenylmethane	Compatible
Aromatic		

^a All of the films were crosslinked after 1 week at room temperature. Exposure to 5/1 toluene/butanol for 5 min. did not soften any of the films.

^b One equivalent of N—H used for each equivalent of epoxide in the polymer.

In a typical experiment, a solution of styrene (45.3 parts), glycidyl methacrylate (8.0 parts), and di-*tert*-butyl peroxide (1.1 parts) was added over a 3-hr. period to xylene (22.8 parts) held at 136°C. The solution was then heated for 3 hr. at 136°C. to complete the polymerization (100% conversion). The polymer solution was reduced to 54% solids by the addition of methyl isobutyl ketone (22.8 parts). The styrene/GMA (85/15) copolymer had a relative viscosity of 1.175 (1% in 1,2-dichloroethylene at 77°F.).

Styrene/GMA Phosphate

The S/GMA (85/15, 85.3 parts) prepolymer was blended with a solution of 85% *o*-phosphoric acid (2.3 parts) and 100% *o*-phosphoric acid (2.0 parts) in methyl isobutyl ketone (5.0 parts), xylene (2.7 parts), and butanol (2.7 parts). This blend of phosphoric acid was used to control the water (92.2%) content of the system, and 0.85 mole of phosphoric

acid was used for each mole of epoxide group. The mixture was heated for 1 hr. at 60°C. to yield the phosphated copolymer, which had the following characteristics: solids, 49%; total acid as H₃PO₄, 7.6%; monoester as H₂PO₄, 4.2%; Gardner-Holdt viscosity, X (12.9 poise).

The polymer solution is stable indefinitely at room temperature.

Ethyl Acrylate/Glycidyl Methacrylate Copolymers

These polymers were prepared in an emulsion system. It was important that the pH of the emulsion system be kept between 5 and 7. The inherent viscosity of the polymer was varied over a wide range by the addition of dodecyl mercaptan to the polymerization recipe. The emulsions are covered in detail in Table II. The polymers were obtained in high yield with short polymerization times. The copolymerization characteristics of GMA make it an ideal monomer to use to introduce crosslinking sites into polyethyl acrylate.

Methyl Methacrylate/GMA (70/30)

This polymer was prepared by heating a solution of methyl methacrylate (42 parts), glycidyl methacrylate (18 parts), α,α' -azobisisobutyronitrile (0.6 parts, Eastman Organic Chemicals No. 6400), *n*-butyl alcohol (15 parts), and toluene (75 parts) for 16 hr. at 75°C. A clear, colorless, 40% solids (100% conversion) solution with a Gardner-Holdt viscosity of W was produced.

CONCLUSIONS

1. A variety of multifunctional epoxides can be prepared by copolymerizing GMA with vinyl and acrylate monomers.

2. These epoxides have good resistance to yellowing because of their aliphatic hydrocarbon backbone.

3. In contrast to conventional epoxide resins, many GMA copolymers are soluble in nonpolar solvents.

4. The polymers represent some of the first examples of high molecular weight polyepoxide-containing polymers.

5. The polymers can be crosslinked with diacids, phosphoric acid, and aromatic or aliphatic amines.

The data on phosphated S/GMA copolymers were obtained by J. C. Fang, A. E. Braehmán, C. H. Stolle, J. A. Vasta, D. R. Strehlau, and C. M. Alslys.

References

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Synopsis

Polymers which are multifunctional in epoxide groups were synthesized by copolymerizing glycidyl methacrylate (GMA) with acrylate and vinyl monomers. The reactivity ratios at 65°C. for the monomer pair styrene (M_1)-GMA (M_2) are $r_1 = 0.34 \pm 0.05$ and $r_2 = 0.63 \pm 0.01$. Glycidyl methacrylate (GMA) is similar to methyl methacrylate in its copolymerization characteristics. The copolymers can be crosslinked by the same classes of materials that are useful with conventional epoxide resins based on epichlorohydrin and bisphenol-A. Similar curing conditions and reactant stoichiometry can also be used. Three GMA copolymers are described: (1) a phosphated styrene/GMA (85/15) copolymer which is thermosetting and can be used as an appliance finish vehicle to yield enamels with excellent resistance properties; (2) an ethyl acrylate/GMA (97/3) elastomer which can be vulcanized with amines or diacids; and (3) a methyl methacrylate/GMA (70/30) copolymer which can be crosslinked at room temperature with amines. These polymers have good resistance to yellowing because of their aliphatic hydrocarbon backbone. The molecular weight and epoxide functionality of the polymers can be varied over wide ranges.

Résumé

On a synthétisé par copolymérisation de méthacrylate de glycidyle (GMA) avec de l'acrylate et des monomères vinyliques, des polymères qui sont multifonctionnels avec des groupes époxydes. Les rapports de réactivité à 65°C pour le couple de monomère, styrène (M_1) et GMA (M_2) sont

$r_1 = 0.34 \pm 0.05$ et $r_2 = 0.63 \pm 0.1$. Le méthacrylate de glycidyle (GMA) est semblable au méthacrylate de méthyle quant à ses caractéristiques de copolymérisation. Les copolymères peuvent être pontés par les mêmes matériaux utilisés avec des résines d'époxyde conventionnelles basées sur l'épychlorhydrine et le bis-phénol A. Des conditions similaires de traitement et la stoechiométrie des réactifs peuvent également être employées. On décrit trois copolymères GMA: (1) un copolymère phosphaté styrène/GMA (85/15) qui est thermodurcissable et qui peut être utilisé comme fini avec une excellente résistance; (2) un élastomère d'acrylate d'éthyle/GMA (97/3) qui peut être vulcanisé avec des amines ou des diacides; (3) un copolymère de méthacrylate de méthyle/GMA (70/30) qui peut être ponté à température de chambre avec des amines. Ces copolymères ont une bonne résistance au jaunissement à cause de leur chaîne principale hydrocarbonée aliphatique. Le poids moléculaire et la fonctionnalité de l'époxyde de ces polymères peuvent être variés sur une vaste échelle.

Zusammenfassung

Polymer mit dem Charakter multifunktioneller Epoxyde wurden durch Copolymerisation von Glycidylmethacrylat (GMA) mit Acryl- und Vinylmonomeren dargestellt. Die Reaktivitätsverhältnisse für Styrol (M_1) und GMA (M_2) bei 65°C sind $r_1 = 0,34 \pm 0,05$ und $r_2 = 0,63 \pm 0,1$. Glycidylmethacrylat ist in seinem Copolymerisationsverhalten dem Methylmethacrylat ähnlich. Die Copolymeren lassen sich durch die gleichen Stoffklassen vernetzen, die auch bei den gewöhnlichen Epoxydharzen auf der Grundlage von Epichlorhydrin und Bisphenol A verwendbar sind. Auch ähnliche Härtungsbedingungen und stöchiometrische Verhältnisse der Reagenzien können eingehalten werden. Drei GMA-Copolymere werden beschrieben: (1) ein wärmehärtendes Styrol-Phosphat/GMA-(85/15)-Copolymeres, welches als Finish-Trägersubstanz bei der Erzeugung von Emails mit ausgezeichneter Widerstandsfähigkeit verwendet werden kann; (2) ein Äthylacrylat/GMA-(97/3)-Elastomeres, das mit Aminen oder zweiwertigen Säuren vulkanisiert werden kann und (3) ein Methylmethacrylat-GMA-(70/30)-Copolymeres, das bei Raumtemperatur mit Aminen vernetzt werden kann. Diese Polymeren besitzen eine gute Beständigkeit gegen Vergilbung, da ihre Hauptkette den Charakter eines aliphatischen Kohlenwasserstoffs besitzt. Das Molekulargewicht und die Epoxyd-Funktionalität der Polymeren kann in einem weiten Bereich variiert werden.

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