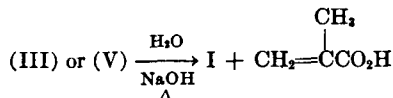
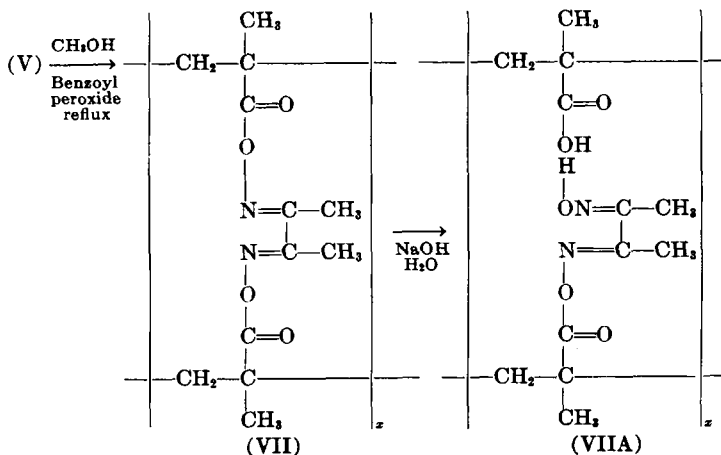
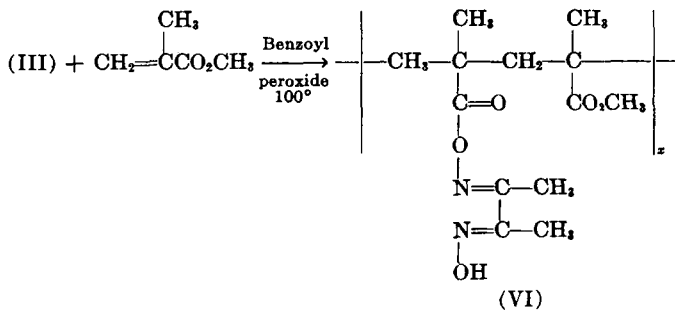


Both compounds (III) and (V) had the correct elemental analyses and expected infrared spectra. Moreover, both were hydrolyzed with aqueous base to yield compound (I) and methacrylic acid. Both gave positive Baeyer tests<sup>5</sup> whereas compound (I) did not.



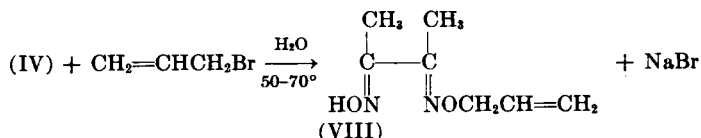
Compound (III) did not homopolymerize readily in the presence of benzoyl peroxide but it did form a copolymer with methyl methacrylate under the same conditions; (V) readily formed a homopolymer.



Compound (III) formed a red-brown nickel chelate which was a mixture of nickel dimethylglyoxime and the Ni(II) chelate of compound (III). It was so hydrolytically unstable that a chelate of constant composition could

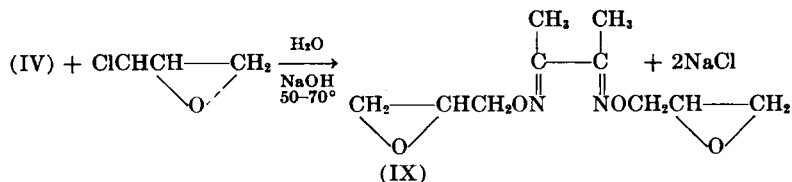
not be obtained from it in aqueous methanol even at pH 5-7. Compound (V), as expected, did not form a Ni(II) chelate. Compound (VI) turned pink in the presence of Ni(II). Compound (VII) did not form a chelate unless it was partially hydrolyzed with hot aqueous alkali before contact with the metal ion (VIIA).

*O*-Allyldimethylglyoxime (VIII) was easily prepared by reaction of allyl bromide with compound (IV):



Compound (VIII) had the correct elemental analysis and the expected infrared spectrum. The near infrared spectrum showed the presence of a terminal methylene group<sup>6</sup> and the compound gave a positive result with the Baeyer test.<sup>5</sup> Compound (VIII) did not polymerize easily either as pure monomer or as a comonomer with conventional monomers such as styrene and methyl methacrylate in the presence of varying amounts of benzoyl peroxide.

Reaction of compound (IV) with epichlorohydrin yielded *O,O'*-diglycidyl dimethylglyoxime.



Compound IX had the correct elemental analysis and a logical infrared spectrum. When heated with conventional epoxy resin curing agents such as *m*-phenylenediamine, ethylenediamine, and hexamethylenediamine, copolymers were formed. In addition to compound (IX) the reaction produced a low molecular weight epoxy resin which could be cured with the same reagents. Neither acid- nor base-catalyzed hydrolysis of the polymers was effective and no products could be obtained which formed Ni(II) chelates.

## EXPERIMENTAL

### Preparation of Monomethacrylyldimethylglyoxime

A 30 g. portion of dimethylglyoxime (0.259 mole) was dissolved in 300 ml. of dry ether. Pyridine (50 ml.) and then 11 g. (0.105 mole) of methacrylyl chloride were added to the rapidly stirred mixture. When the addition was complete, the mixture was allowed to stir for 2 hrs. and the ether evaporated with a nitrogen stream. The residue was extracted with cold chloroform and then with hot chloroform. The combined extracts

were washed with water, dried, and filtered, and the filtrates were evaporated to dryness under vacuum. The residues were extracted with *n*-hexane. The cooled extracts were filtered and the filtrates evaporated to dryness under vacuum. The residues were again extracted with *n*-hexane. The hexane extracts were filtered hot and concentrated. The concentrate was cooled to yield 8 g. (43%) of white crystalline material. The product was recrystallized from *n*-hexane and melted at 110–111°C. The infrared spectrum of the material was consistent with the structure of monomethacrylyldimethylglyoxime.

ANAL. Calcd. for  $C_8H_{12}O_2N_2$ : C 52.10%, H 6.85%, N 15.2%. Found: C 52.10%, H 6.61%, N 15.25% and 15.45.

### Preparation of Dimethacrylyldimethylglyoxime

The disodium octahydrate salt of dimethylglyoxime (60.8 g., 0.2 mole), 20 g. of anhydrous magnesium sulfate, and 200 ml. of ether were placed in a Morton flask and stirred rapidly. To this mixture was added dropwise, slowly, 20.8 g. (0.2 mole) of methacrylyl chloride. The ether refluxed slightly during the addition. When the addition was complete, the mixture was allowed to stir for 1 hr. at room temperature. It was then acidified to below pH 2 and the mixture slurried with chloroform. The slurry was filtered and the solid washed with water and set aside. The chloroform layer of the filtrate was washed with water and dried. The solid from the original filtration was mostly dimethylglyoxime. The solvent was removed from the dry extract under vacuum to leave a white solid. This material weighed 21.7 g. (43.4%); it was filtered and recrystallized from hot *n*-hexane. After one recrystallization the material melted at 80–87° and turned pink when exposed to Ni(II) ions. After another recrystallization from *n*-hexane it melted at 82–87° and did not turn pink when exposed to Ni(II) ions. The melting point range did not decrease after another recrystallization.

ANAL. Calcd. for  $C_{12}H_{16}O_4N_2$ : C 57.1%, H 6.34%, N 11.10%. Found: C 57.54%, 57.3%; H 6.35%, 6.42%; N 11.28%, 11.28.

The infrared spectrum of this material was consistent with the analysis and with the assigned structure of the dimethacrylyl ester of dimethylglyoxime.

### Hydrolytic Cleavage of the Methacrylyl Esters of Dimethylglyoxime

A 2 g. quantity of monomethacrylyldimethylglyoxime was refluxed for 3 hrs. with 25 ml. of 10% sodium hydroxide. At the end of this time, a clear solution had formed. The solution was acidified with concentrated hydrochloric acid, cooled, and filtered. A white solid in 1.5 g. amount was obtained which had an infrared spectrum identical with that of an authentic sample of dimethylglyoxime. The acidic filtrate was extracted with ether and the extract dried. Removal of the solvent from the dry extract left an oil which had an infrared spectrum similar to that of methacrylic acid. The yield of crude methacrylic acid was 0.73 g. In an identical fashion, the

dimethacrylyl ester of dimethylglyoxime was saponified to yield the same products.

### Polymerization of the Methacrylyl Esters of Dimethylglyoxime

Dimethylacrylyldimethylglyoxime (2 g.) was dissolved in 20 ml. of methanol, and 0.2 g. of benzoyl peroxide was added. The mixture was heated to reflux, at which point it foamed violently. When the foaming subsided the polymer started to gel. The mixture was refluxed 15 min. more and the white solid was removed by filtration. This polymer did not become colored red when placed in contact with Ni(II) ions until after it had been slurried with 10% aqueous sodium hydroxide on the steam bath for several minutes. Treatment of the material with 10% sodium hydroxide at room temperature did not degrade the polymer sufficiently to form red complexes with nickel unless it was allowed to stand for several hours.

One gram of monomethacrylyldimethylglyoxime, 5 g. of methylmethacrylate, and 0.1 g. of benzoyl peroxide were mixed and heated in a test tube on a steam bath. After 15 min. of heating, the polymer gelled and was heated 5 min. more. The polymer was boiled with 2½ l. of benzene and then filtered. The filtrate was concentrated and the material dissolved in it precipitated with *n*-hexane to yield a white solid, melting over the range 150–190°. This material became pink when treated with 10% nickelous chloride hexahydrate solution. After dissolving in benzene and reprecipitation with hexane it still became pink in the presence of Ni(II) ions.

ANAL. Calcd. for  $C_{58}H_{96}O_{22}N_2$ : C 59.4%, H 8.18%, N 2.38%. Found: C 59.60%, 59.66; H 8.29%, 8.25; N 2.36%, 2.39.

This analysis calculates for  $C_{58}H_{96}O_{22}N_2$ . On this basis, one monomethacrylyldimethylglyoxime unit per 10 methyl methacrylate units were in the polymer.

### Reaction of Allyl Bromide with Dimethylglyoxime Disodium Salt

A 304 g. quantity (1 mole) of the disodium salt of dimethylglyoxime was dissolved in the minimum amount of water; 1 mole (121 g.) of allyl bromide was added and the mixture was rapidly stirred and heated at 50–70° for 6 hrs. At the end of this time, the mixture was cooled and the solid removed by filtration. The solid product was recrystallized from hexane to yield a compound which melted at 63–65°.

ANAL. Calcd. for  $C_7H_{12}N_2O_2$ : C 53.8%, H 7.7%, N 17.95%. Found: C 53.73%, 53.47; H 7.86%, 7.87; N 17.91%, 17.97.

The infrared spectrum of this material showed bands which could be expected to be present in the spectrum of the monoallyl ether of dimethylglyoxime. The yield of recrystallized material was 71 g. (45%).

### Preparation of Bisglycidyl Ethers of $\alpha$ -Dioximes

The disodium octahydrate salt of dimethylglyoxime, 70 g. (0.23 mole), was dissolved in a minimum amount of water; 207 g. (2.24 moles) of epichlorohydrin was added and the mixture heated to 50°; 18 g. (0.45 mole) of sodium hydroxide was added in small amounts. The temperature of the reaction mixture was never allowed to go over 70°. When the addition was complete, the mixture was allowed to stir until it reached room temperature. The excess epichlorohydrin was pumped off at 50° under full vacuum pump pressure. The solid product was removed by filtration and boiled with a large excess of hexane. The hexane solution was filtered or decanted and the filtrate or decantate concentrated. In this manner, 18 g. (34%) of crude *O,O'*-bis-glycidyl dimethylglyoxime was obtained. After another recrystallization from hexane, the product melted at 91–94° and gave an infrared spectrum consistent with the assigned structure.

ANAL. Calcd. for  $C_{10}H_{16}O_4N_2$ : C 52.6%, H 7.02%, N 12.28%. Found: C 52.2%, 52.11; H 7.16%, 7.24; N 12.13%, 12.02.

The hexane-insoluble material was extracted into chloroform and the extract dried. The solvent was removed under full pump vacuum to leave 29.2 g. (55%) of a yellow-brown oil. The infrared spectrum of the yellow-brown oil was quite similar to that of the bisglycidyl ether of dimethylglyoxime. Light-scattering measurements on solutions of this material in chloroform, acetone, and methyl ethyl ketone indicated that the material was a polymer.

ANAL. Found: C 49.97%, H 6.98%, 7.02; N 10.05%, 10.21.

The products obtained from the reaction of dimethylglyoxime with epichlorohydrin could be copolymerized in a manner similar to that employed for the curing of conventional epoxy resins. The epoxide was melted by gently heating it to 70°, the comonomer was then added, and the mixture was gently heated at 70° or below until a homogeneous mixture was formed; this mixture was then heated in an oven at 70° for 8 to 24 hrs. to yield the copolymer. Hard castings were obtained from the reaction of bis-*O,O'*-glycidyl dimethylglyoxime and *m*-phenylenediamine. Waxlike materials were obtained by treating the bisglycidyl dimethylglyoxime with excess ethylenediamine and hexamethylenediamine. The *m*-phenylenediamine-cured casting did not melt up to 300°. The ethylenediamine- and the hexamethylenediamine-treated materials melted at 100–108° and 119–124°, respectively. The polymeric material which was isolated from the preparation of bis-*O,O'*-diglycidyl dimethylglyoxime was cured with *m*-phenylenediamine to yield a black casting which softened at 104° but did not melt.

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### Synopsis

Monomethacrylyldimethylglyoxime and dimethacrylyldimethylglyoxime were prepared by acylation of dimethylglyoxime with methacrylyl chloride. Monoallyldimethylglyoxime and diglycidyl dimethylglyoxime were prepared by alkylation of dimethylglyoxime sodium salt with allyl bromide and epichlorohydrin, respectively. The monomethacrylyl derivative formed a copolymer with methyl methacrylate and the dimethacrylyl derivative yielded a homopolymer. Nickel chelates could be formed from both polymers. Diglycidyl dimethylglyoxime was easily copolymerized with a number of diamines. A polymer formed as a by-product from the preparation of the diglycidyl dioxime was easily cured with *m*-phenylenediamine.

### Résumé

On a préparé la monométhacrylyldiméthylglyoxime et la diméthacrylyldiméthylglyoxime par acylation de la diméthylglyoxime avec le chlorure de méthacrylyle. La monoalkyldiméthylglyoxime et la diglycidyl diméthylglyoxime ont été préparées par alkylation du sel solide de la diméthylglyoxime avec le bromure d'allyle et l'épichlorhydrine respectivement. Le dérivé monométhacrylyle forme un copolymère avec le méthacrylate de méthyle et le dérivé diméthacrylyle fournit un homopolymère. On a pu former des complexes de nickel à partir des deux polymères. La diglycidyl diméthylglyoxime copolymérise facilement avec bon nombre de diamines. Un polymère formé comme produit secondaire dans la préparation de la diglycidyl dioxime fut facilement insolubilisé par traitement avec la *m*-phénylène diamine.

### Zusammenfassung

Monomethacrylyldimethylglyoxim und Dimethacrylyldimethylglyoxim wurden durch Acylierung von Dimethylglyoxim mit Methacrylylchlorid dargestellt. Monoallyldimethylglyoxim und Diglycidyl dimethylglyoxim wurden durch Alkylierung des Natriumsalzes des Dimethylglyoxims mit Allylbromid bzw. Epichlorhydrin dargestellt. Das Monomethacrylylderivat bildete ein Copolymeres mit Methylmethacrylat und das Dimethacrylylderivat lieferte ein Homopolymeres. Nickelchelate konnten aus beiden Polymeren erhalten werden. Diglycidyl dimethylglyoxim konnte mit einer Anzahl von Diaminen leicht copolymerisiert werden. Ein als Nebenprodukt bei der Darstellung von Diglycidyl dioxim anfallendes Polymeres liess sich mit *m*-Phenylen-diamin leicht härten.

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