

A NEW POLYMERIC POLYOL FOR THERMOSET COATINGS: SUPERACID-CATALYZED COPOLYMERIZATION OF WATER AND EPOXY RESINS

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Abstract

Whereas free-radical emulsion polymerization has been studied extensively, published reports of cationic (i.e., acid-catalyzed) polymerizations of emulsified monomers are rare, and we have found no reported examples of non-reversible emulsion polymerizations catalyzed by Brønsted acids. It was recently discovered that treatment of an emulsion of liquid epoxy resin with select superacid catalysts yields a polymeric polyol. Catalysis with 1% perchloric acid at room temperature yields a product with a number average molecular weight of 1650, and a polydispersity of 5.0 as measured by GPC. The polyol's structure differs from that of conventional high molecular weight epoxy resins prepared by the advancement process in several ways, including the incorporation of two glycidyl units in the repeat unit. In essence, the product is a copolymer of the epoxy resin and water. A similar product can be prepared by solution polymerization, where the molecular weight is controlled by the ratio of water to epoxy resin. The product was shown to have lower levels of residual bisphenol-A diglycidyl ether (BADGE) and bisphenol-A than conventional advanced epoxy resins. The presence of these compounds at current commercial levels is a health concern of great importance to producers of epoxy-based can linings for foods and beverages. Polyols prepared by these processes were crosslinked with melamine-formaldehyde resins in waterborne coating formulations which were free of added cosolvent, as well as solvent-borne coating formulations. The coatings developed excellent solvent resistance at lower bake temperatures than traditional epoxy resins.

Introduction

By crosslinking high molecular weight epoxy resins through the 2° hydroxyl groups on the resin backbone it is possible to prepare thermosetting coatings with excellent mechanical and chemical resistance properties. The crosslinking agents most often employed in these applications are amino resins (primarily melamine-formaldehyde and urea-formaldehyde resins), as well as isocyanates and phenolic resins. Substantial markets for high performance coatings based on these resin systems have been developed, including can, drum and pail linings, and coil coating primers. A particularly large market has developed for water reducible interior beer and beverage can linings. The formulations are often based on blends of epoxy and acrylic resins, or epoxy/acrylic graft copolymers,¹ crosslinked with melamine-formaldehyde and related crosslinkers.

High molecular weight epoxy resins are now commercially prepared by the advancement process, which is the copolymerization of bisphenol-A with excess bisphenol-A diglycidyl ether (BADGE). The process results in relatively high levels of residual starting materials in the final product. Bisphenol-A is a suspect estrogen mimic,² and BADGE is of concern for various health effects³ as are most glycidyl ether compounds. For these reasons, there is considerable desire to develop coatings for

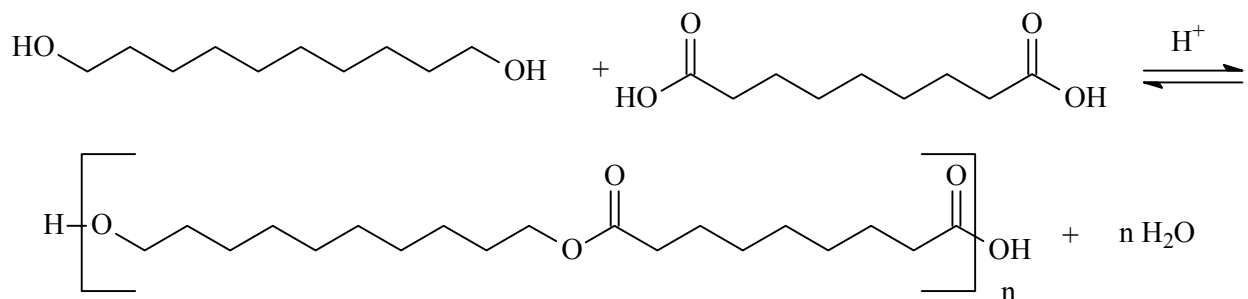
food and beverage containers that have much lower levels of extractable bisphenol-A and BADGE than can be obtained with current commercial technology.

The acid-catalyzed homopolymerization of epoxy resins to form crosslinked final products like coatings, adhesives, and composites is a well-known and commercially important process. It can be affected with a variety of strong Brønsted and Lewis acids, including photochemical processes whereby strong acids are generated by photochemical transformation of nonacidic starting materials.⁴

The acid-catalyzed ring opening polymerization of monofunctional epoxides is also a commercially important process that has been extensively studied.⁵ Brønsted himself⁶ studied the acid-catalyzed hydrolysis of ethylene oxide in 1929. Shortly thereafter, the molecular weight distribution of poly(ethylene oxide) produced in this reaction and its dependence on the ratio of ethylene oxide to water was determined.⁷ However, we have been unable to find any references to the use of acid catalysts to prepare tractable, non-gelled reaction products from multifunctional epoxides.

In contrast to the well-studied and commercially important process of free-radical initiated emulsion polymerization, examples of cationic emulsion polymerizations of any kind in the chemical literature are rare. Perhaps one reason the field remains largely unexplored is that many Lewis acid catalysts commonly employed in cationic polymerizations are unstable in water. Another is that many cationic polymerizations involve intermediates such as carbocations that react with water, terminating chain growth. Adequate molecular weight build is then difficult unless the process is equilibrium driven (*i.e.*, reversible). Saam and Chou⁸ patented the acid-catalyzed polymerization of emulsified, hydrophobic diacids and diols or hydrophobic hydroxy-acids. Catalysts for the process include strong mineral acids and organic sulfonic acids. As shown in Scheme 1, esterification is an equilibrium process. In the present example, it is clear that the starting functional groups, acids and alcohols, are more hydrogen bonding and more polar than the product ester functional groups. Thus, one would expect that there exists in this system a modest thermodynamic driving force to reduce the equilibrium concentration of water in the emulsion, in effect ‘squeezing’ water from the emulsion and moving the equilibrium toward polymerization. Using azelaic acid and 1,10-decanediol as starting materials, a maximum average D_p of 14.8 was achieved. In a similar process, the authors also prepared polyketals from emulsions of mixtures of hydrophobic diols and ketones or aldehydes.⁹

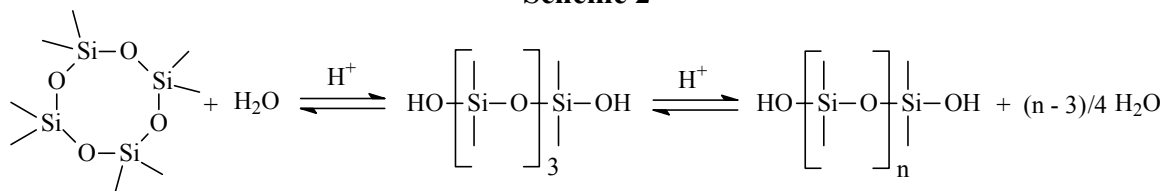
Scheme 1



Weyenberg and coworkers¹⁰ first described the acid-catalyzed emulsion polymerization of octamethylcyclotetrasiloxane as shown in Scheme 2. In this case, polymer molecular weights as high as 172,000 were obtained at 25°C, though molecular weight dropped to 49,000 at 90°C. This process

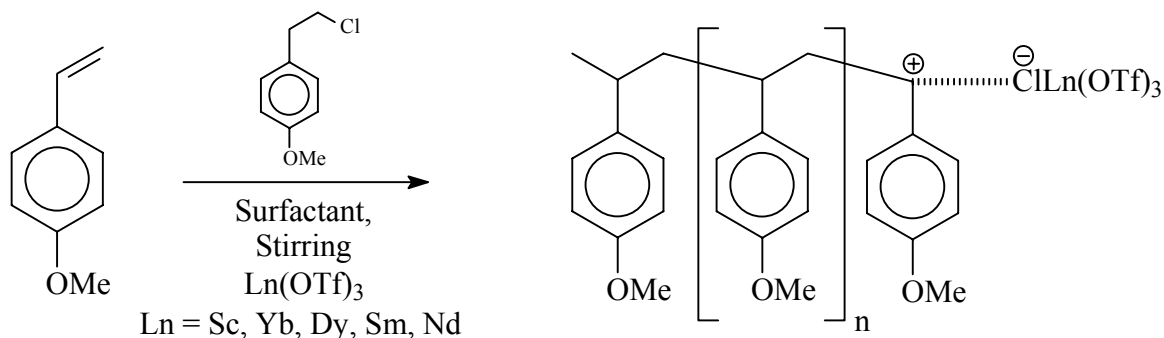
also involves equilibrium reactions¹¹ with water. Presumably, a decrease in equilibrium water concentration in the emulsion particles *vs.* reaction conversion, as well as the thermodynamic preference for siloxanes relative to silanols, combine to drive the reaction to high polymer. Since the Weyenberg publication, there have been several additional papers and patents published regarding this same basic process.¹²

Scheme 2



Quite recently, Satoh, Kamigaito and Sawamoto¹³ described the emulsion polymerization of *p*-methoxystyrene (PMOS) using lanthanide triflate catalysts and PMOS-HCl adduct as a cationic initiator (see Scheme 3). The lanthanide triflates are a unique class of water stable Lewis acid catalysts, initially developed for aqueous acid-catalyzed processes by Kobayashi.¹⁴ This is the first example we have found of a non-equilibrium polymerization of emulsified monomers with acid catalysis. The increase in molecular weight in proportion to conversion, and the low polydispersity of the final product (about 1.4) both lend credence to the assertion that the process is a living polymerization. Unfortunately, the very high cost of lanthanide triflate catalysts limits the commercial utility of this process.

Scheme 3



We have been unable to find any reports of the acid-catalyzed emulsion polymerization of epoxide-containing monomers using any catalyst system. There are also no reports of non-equilibrium-driven emulsion polymerization of *any* monomer using Brønsted acids, or for that matter with any acid catalyst currently available at costs that would be acceptable in the coatings and related industries.

In this paper, we show that emulsified epoxy resins can be polymerized using Brønsted superacid catalysts in a non-reversible process to give a new type of polymeric polyol. A similar product can also be prepared in a solution polymerization process by copolymerizing the epoxy resin with water. The products contain lower levels of residual bisphenol-A and BADGE compared to commercial high molecular weight epoxy resins, and can be crosslinked at relatively low bake temperatures with melamine-formaldehyde resins to yield highly chemical-resistant coatings.

Experimental

Safety Precaution.

The superacids described in this paper are powerful reagents. They are capable of causing severe and rapid damage to skin, and most particularly, eye tissue. Appropriate hand and eye protection should always be worn when handling these reagents, and eye wash fountains and safety showers should be readily available. Dilute acid solutions should be prepared from concentrated acids by addition of the acid *to* the water. The reactions with epoxy resins described below are highly exothermic. Safe reaction conditions should be established using small scale procedures, and workers should be shielded from the reaction mixture with lowered sash hoods or safety shields, particularly when adding the acid reagents to solutions containing epoxy resin.

Procedure for Measuring Extent of Reaction by IR Spectroscopy.

Infrared spectra were obtained on a Nicolet Magna-IR® 550 spectrometer. A few drops of emulsion were placed on an out-of-compartment attenuated total reflectance 45° Zn-Se flat cell, available from Spectra-tech, Inc., Shelton, CT. The emulsion was smeared across the cell surface using a soft cotton pad. Care must be taken to prepare a film thin enough to allow for the rapid evaporation of water, but not so thin that the film thickness is thinner than the depth penetration of the evanescent wave of IR radiation above the crystal (approximately 6.3 μm at 400 cm^{-1}). Water was allowed to evaporate from the resulting thin film, during which time the film changed in appearance from milky white to clear. Typically, this process took about 1 min. The IR spectrum (32 scans) was obtained in absorption mode, and then processed with Nicolet Omnic® software to obtain the 2nd derivative of the spectrum. The height of the *gem*-dimethyl absorbances at 1383 and 1362 cm^{-1} were then measured, and divided into the height of the epoxy ring absorbance at 916 cm^{-1} . This yields a normalized absorbance for the epoxide, since the *gem*-dimethyl group is inert toward the reaction conditions. To estimate the extent of reaction as a function of time, the normalized epoxy absorbance at time *t* was divided by the normalized absorbance at *t*=0. The same procedure can be utilized in some solution polymerizations, as long as the solvent contains no absorbance near the bands of interest in the procedure. If it does, the tendency of the samples to retain solvent, particularly when high molecular weight product is produced, lead to error in the measurement.

Epoxy Equivalent Weight Determination.

To a 100 mL beaker was added 1 g of tetraethyl ammonium bromide and 50 mL of glacial acetic acid, which was stirred with a magnetic stir bar to effect dissolution of the tetraethyl ammonium bromide. The solution was tared on an analytical balance. A sample of a reaction mixture from an acid-catalyzed epoxy resin and water copolymerization was added to the tared solution, and the sample weight recorded to 0.1 mg. The sample size used depended on the expected degree of conversion (at the beginning of the reaction, typically 0.2 – 0.5 g, and toward the end, from 1 – 2 g). A conductometric titration was performed using a Brinkman automatic titrator with 0.1N perchloric acid, after first allowing the electrode to equilibrate with the solution for approximately 5 min. The equivalent weight on solids was calculated as $(\text{Sample Wt.} \times \% \text{NV} \times 1000) / (\text{Adj. mL} \times \text{N})$, where %NV is the theoretical solids of the reaction mixture, Adj. mL is the mL of titrant adjusted for the calculated amount of superacid catalyst in the reaction mixture, and N is the normality of the perchloric acid titrant.

Molecular Weight Determination by Gel Permeation Chromatography.

GPC analyses were performed on a Waters Corporation modular GPC component system consisting of a model 715 autosampler, a model 690 pump controller, a model 410 differential refractometer detector, and a column oven compartment maintained at 35°C. Data collection, data processing, and calibration setups were carried out using PL-Caliber GPC software, version 7.01, from Polymer Laboratories, Amherst, MA. A set of two GPC columns from Polymer Laboratories (Mixed Linear-E type) was used for the GPC analyses. These columns have an upper molecular weight limit of approximately 30,000 D. The flow rate of the system is maintained at 1.0 mL/min. The injection volume was 200 μ L at approximately 0.2% (weight) concentration. The mobile phase utilizes stabilized, HPLC grade tetrahydrofuran (THF). Toluene is used as an internal flow marker. The calculated GPC molecular weights are referenced to polystyrene monodisperse standards obtained from Polymer Laboratories, which ranged in molecular weight from 266 to 70,000 D. Twelve standards were used to construct the calibration curve.

Preparation of Epoxy Resin Emulsion.

In a stainless steel mixing bowl was placed 109 g of deionized (DI) water and 77 g of Hydropalat® 65*. The mixture was placed in a Hobart mixer fitted with a slotted paddle and mixed for 3 min. The mixer was turned off, 350 g of a liquid epoxy resin with a specified epoxy equivalent weight (EEW) of 185 – 192 was added, and the mixture was mixed for 5 min. at speed 1 and another 5 min. at speed 2. An additional 300 g of liquid epoxy resin was added and mixed 5 min. at speed 1 and 5 min. at speed 2. An additional 300 g of liquid epoxy resin was added and mixed 5 min. at speed 1 and 60 min. at speed 2. While continuing to stir, the mixture was then slowly let down with 530.7 g of deionized (DI) water and mixed for an additional hour. The final product had a mean volume averaged particle size of 619 nm and a theoretical solids content of 60.0%.

Representative Polymerization of Emulsified Liquid Epoxy Resin.

Into a glass jar was placed 200 g of the emulsion of liquid epoxy resin described in the above procedure, followed by 20.0 g of 10% perchloric acid in DI water. The mixture was shaken for 1 min., and an IR spectrum was then obtained as described above to establish the epoxide content at $t=0$. After 27 hours of reaction at room temperature, the reaction was quenched with 6.99 g of 10% NaOH solution, which resulted in a pH of 7.0 for the solution. Analysis of the 916 cm^{-1} band normalized to the 1362 cm^{-1} band indicated only 7% of the epoxide remained at this time. A film of this material drawn down on a steel panel also dried tack free to a light touch in about 10 minutes (i.e., after water evaporation), whereas the starting emulsion remained tacky indefinitely. The solids of the product (1 hour, 110°C) was 59.6%.

Representative Batch Solution Polymerization of Epoxy Resin.

In a 1000 mL 4-neck round bottom flask equipped with a mechanical stirrer, thermocouple and reflux condenser was placed 200 g of liquid epoxy resin and 200 g 1,4-dioxane. The temperature was raised to 90°C using a heating mantle, and a mixture of 6.66 g of 60% perchloric acid (0.0398 moles) and 10.33 g of deionized water was added to the reaction mixture. After stirring for 4 hours, it was determined by FT-IR that approximately >99% of the epoxide groups were consumed by the procedure given above. The reaction mixture was diluted with 75 g of 2-butoxyethanol, and immediately neutralized by the addition of 60 mL of Amberlite® IRA-67 weak base ion exchange resin. The final

* Henkel Corporation, a 65% solids nonionic surfactant.

product by GPC had $M_w = 12,300$, $M_n = 2640$, and $M_w/M_n = 4.6$ as measured in THF vs. polystyrene standards.

Representative Gradual Addition Process.

In a 500 mL 4-neck round bottom flask equipped with mechanical stirrer, thermocouple and reflux condenser was placed 24.67 g of liquid epoxy resin, 74.89 g of 1,4-dioxane, and 6.17 g of DI water. The solution temperature was 23°C. Through a constant pressure addition funnel, 3.33 g of 60% perchloric acid was added over the course of 2 minutes. Over the course of the next 30 minutes, the temperature rose to 29°C. Heat was then applied from a mantle to raise the temperature to 65°C, where the temperature was held for 30 min. A mixture of 75.33 g of liquid epoxy resin and 25.11 g of 1,4-dioxane was then gradually added over about 3.25 hours with a Masterflex® peristaltic pump with teflon lines. After completion of the feed, the mixture was held for 3.25 more hours at 65°C, at which time titration for epoxide groups yielded no end point, indicating that epoxide conversion was complete within the limits of detection of the method. The mixture was neutralized with 25 mL of IRA-67 ion exchange resin and cooled to room temperature. The final product had $M_w = 11,200$ and $M_n = 2640$.

Measurement of Bisphenol-A and BADGE Content by HPLC.

Samples were analyzed for bisphenol-A and BADGE by HPLC using a Waters Alliance 2690 HPLC system with Waters 996 photodiode array detector. The HPLC was performed under a gradient of 30% acetonitrile and 70% water to 70% acetonitrile and 30% water in 60 minutes on a Waters Symmetry C18 column (250 x 4.6 mm), at a column temperature of 40°C. Calibration standards used were bisphenol-A 99+% (Aldrich Chemical Co.) and Epon® 826[†] (Resolution Chemical Co.), which was assumed to contain 85% BADGE monomer.

Analysis of Polymeric Epoxy Polyol by MALD/I.

The MALD/I experiments were carried out on a Biflex MALD/I time-of-flight mass spectrometer (TOFMS). A solution of the epoxy polyol prepared by reaction of the above described liquid epoxy emulsion with 0.91% perchloric acid for 24 hours at room temperature and neutralized with NaOH was made in tetrahydrofuran (THF) at a concentration of 8 mg/mL. These solutions were mixed 1:7 with a 0.25 M 2,5-dihydroxybenzoic acid (DHB) matrix solution prepared in THF. About 1 µL of the combined solution was spotted on the target. The samples were irradiated with a nitrogen laser (337 nm) and positive ions were analyzed via TOFMS. The data were collected with 1 ns/bin, 50,000 point record length, and 5000 ns delay from 100 shots.

Results and Discussion

Emulsion Polymerization.

The epoxy resin emulsions used in the initial phase of this work were prepared from 5 parts (solids) of a nonionic surfactant and 95 parts of a commercial liquid epoxy resin (EEW 185 – 192) at 60% solids. Figure 1 shows the FT-IR spectrum obtained from emulsion samples treated with 0.91% perchloric acid (on total solution weight) immediately after mixing and after 28 hours reaction time. The spectra were obtained by wiping a thin film of the emulsion onto a flat out-of-compartment ATR cell and recording the spectrum after allowing water to evaporate from the film. Evaporation of water changed the film from opaque to clear, and usually required less than a minute. The figure demonstrates that there was a large increase in the broad OH band from 3200 – 3600 cm^{-1} . Figure 2 shows the

fingerprint region of the spectrum, with an expanded Y-axis so that fine changes in the spectra can be observed. Clearly there was a dramatic reduction in the oxirane asymmetrical ring stretching absorption at 916 cm^{-1} . The magnitude of the decrease can be qualitatively estimated by comparison with the inert *gem*-dimethyl group on the epoxy resin backbone, which exhibits bending modes observed at 1383 cm^{-1} and 1362 cm^{-1} .

The extent of epoxide conversion was quantified by converting the spectrum to its 2nd derivative, as shown in Figure 3. The 2nd derivative does an admirable job of resolving complex absorbances containing shoulders into individual absorbances. Residual epoxy content was then calculated by measuring the peak height at 916 cm^{-1} , normalizing it by the peak height at 1362 cm^{-1} , and then dividing the value obtained at time t by the value obtained at time zero. In the present case, conversion is calculated to be 93.9% at 28 hours. If instead the 1383 cm^{-1} absorbance is used in the calculation the conversion is 93.6%.

In Table I are given the epoxide conversion results for a variety of acids employed at a concentration of 0.91% after 24 hours of reaction. The table also reports GPC molecular weight data obtained for the same reactions after either 24 or 72 hours of reaction time. In Figure 4, the GPC obtained from the starting emulsion and the GPC obtained after 24 hours reaction with 0.91% perchloric acid are compared. Note that the peak with a nominal log molecular weight of 2.5, which is pure BADGE monomer, has been completely consumed. Furthermore, the first large peak that appears in the final product has a nominal log molecular weight of about 2.8. Despite the rather large change in retention volume, it has been shown by spiking experiments and by GC analysis after derivatization of OH groups with trimethylsilane groups that this peak is due to the bis-glycol hydrolysis product (BADGE•2H₂O).

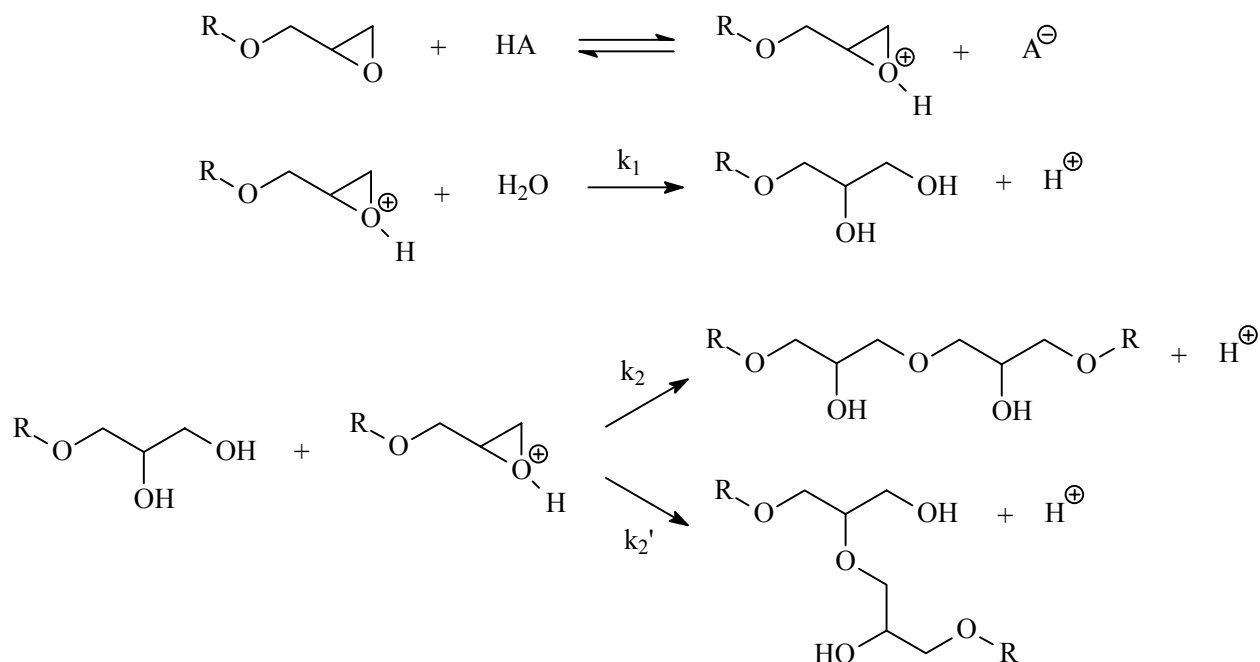
Table I
Epoxide Conversion and Molecular Weight Obtained with Various Catalysts

Catalyst	Extent of Reaction in 24 Hours	M _n	M _w	Reaction Time (Hr.)
None	-	360	565	-
<i>p</i> -CH ₃ C ₆ H ₄ SO ₃ H	2.8%	383	523	72
CH ₃ SO ₃ H	0%	370	500	72
HBF ₄	37.0%	1650	6600	72
HPF ₆	95.3%	1850	12600	72
CF ₃ SO ₃ H	25.3%	1590	6150	72
HClO ₄	91.8%	1755	8250	24

That relatively high molecular weight products are obtained from a process where so much water is present is interesting. As shown in the proposed mechanism in Scheme 4, the initial reaction is hydrolysis of the protonated epoxide by water to yield glycol, which occurs with rate constant k_1 . This is followed by alcoholysis of protonated epoxide, with attack by either 1° hydroxyl with rate constant k_2 , or secondary hydroxyl with rate constant k_2' . (Attack of the alcohols at the tertiary carbon on the protonated epoxides is another possibility not shown in this simplified kinetic scheme.) A bias toward the generation of polymeric products would then result if $k_2[\text{ROH}], k_2'[\text{ROH}] > k_1[\text{H}_2\text{O}]$ such that once a hydrolysis reaction occurs, there is a strong tendency for the resulting glycol unit to participate in a

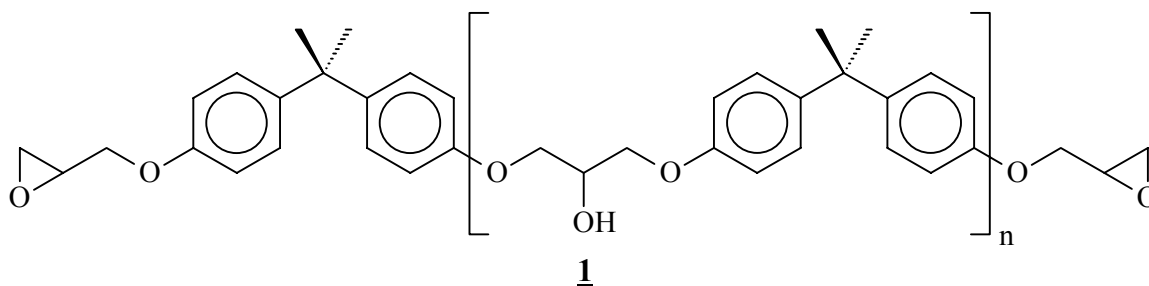
polymerization reaction. It is likely that k_2 and k_2' are greater than k_1 , since alcohols are stronger bases than water, and nucleophilicity usually correlates with basicity for structurally similar reactants.¹⁵ Furthermore, toward the end of the reaction the alcohol concentration within the particles is estimated to be about 7.8 N, based on a calculated OH eq. wt. of 148 and a density of 1.16 (the density of advanced epoxy resins). A 7.8 N concentration of water in resin would be about 14% by weight. This is probably much higher than the solubility of water in the product, though that value has not been measured. Thus, it would appear likely that toward the end of the reaction alcohol concentration should be significantly higher than water concentration. Thus $k_2[\text{ROH}], k_2'[\text{ROH}] > k_1[\text{H}_2\text{O}]$ is most likely true, especially toward the end of the reaction, thereby polymerizing most of the low molecular weight species still present.

Scheme 4

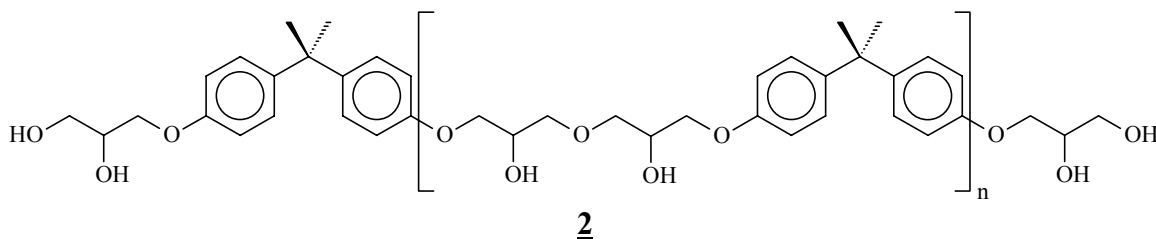


Catalysis by either *p*-toluenesulfonic acid (*p*-TSA) or methanesulfonic acid (MSA) gave little or no epoxy conversion and little or no change in molecular weight. In a separate set of experiments, it was also shown that sulfuric acid and hydrochloric acid under similar conditions also gave little or no epoxy conversion. In contrast, 24 hour conversions with the superacids trifluoromethanesulfonic acid (TFMSA), tetrafluoroboric acid (TFBA), hexafluorophosphoric acid (HFPA) and perchloric acid were 25.3%, 37.0%, 95.3%, and 91.8%, respectively. In all cases there was also a substantial degree of polymerization, with the highest molecular weight obtained with HFPA, closely followed by perchloric acid. Note also that molecular weight correlated with the degree of conversion at 24 hours. (Even though the molecular weight with HFPA was measured at 72 hours vs. 24 hours with perchloric acid, it is likely that at 24 hours reaction time the molecular weight build with HFPA was as high or higher than with perchloric acid.)

Commercial bisphenol-A based epoxy resins have chemical structure **1**. In the liquid epoxy resin used as a starting material in the polymerizations described above, $n \approx 0.15$. Solid epoxy resins have much higher average values of n .



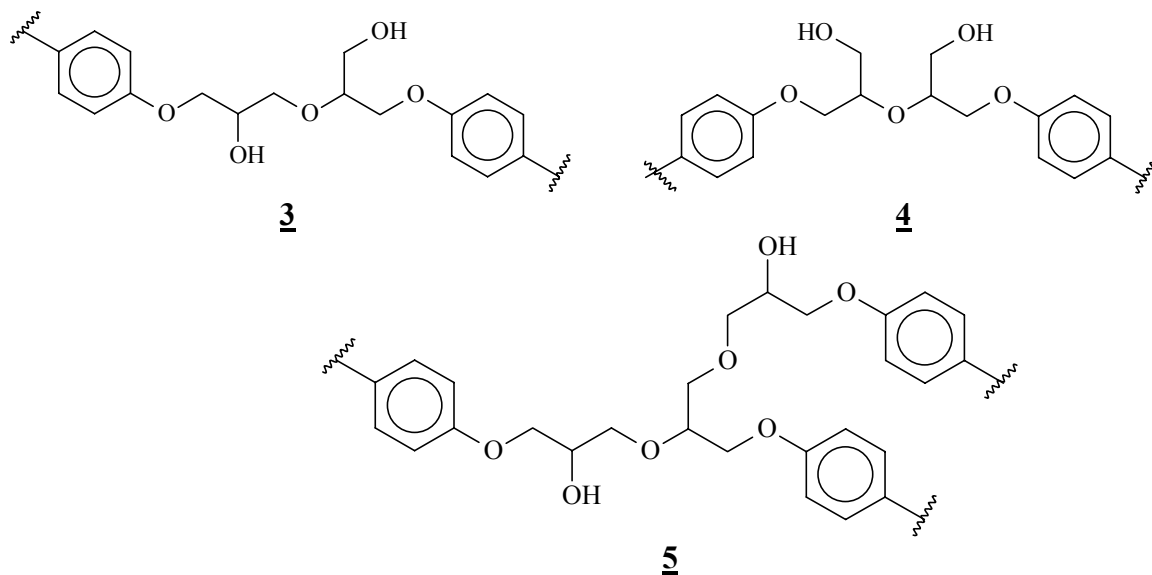
The structure of the polyol was determined by a combination of matrix assisted laser desorption/ionization (MALD/I) mass spectrometry and ^{13}C NMR spectroscopy. The MALD/I spectrum (Figure 5) shows a primary series of peaks starting at a mass of 757 separated by 358 D. These masses are consistent with sodium cations of structure **2**, with $n = 1$ representing the mass at 757. The repeat unit weight of 358 indicates that two glycidyl units are incorporated between bisphenol-A units, in contrast to structure **1** where only one glycidyl unit separates the aromatic moieties. Large quantities of the sodium cation of the monomeric hydrolysis product (399 D) were not detected, which may have been due to matrix effects in the MALD/I experiment, since as mentioned above the presence of this species in the reaction mixture has been confirmed.



The primary series of peaks is associated with progressively smaller peaks 18 and 36 D lower in mass, and with peaks 70, 284, and 568 D higher in mass. This is seen more clearly in the expanded spectrum shown in Figure 6. The structures of 18 and 36 D lower mass are most likely due to oligomers that contain 1 or 2 epoxy end units, respectively, in place of the glycol end groups in **2**. The units 284 D higher in mass are due to incorporation of molecules of **1** where $n = 1$ in the polymerization, and those at 568 D higher mass from incorporation of molecules where $n = 2$, or 2 incorporations of $n = 1$ molecules. (These species are present in the commercial liquid epoxy resin starting material.) At the present time we cannot explain the units at 70 D higher mass. However, we have seen this same series in other polymers analyzed in our laboratories, and it may be an artifact of our instrument or procedure.

Analysis of the ^{13}C NMR spectrum obtained in THF-d_8 in the presence of 0.02M $\text{Cr}(\text{AcAc})_3$ spin relaxation agent (Figure 7) indicates that the polymer structure is significantly more complex than represented by **2**. (The aromatic region, with the expected 1:1:2:2 pattern expected for the *p*-bisphenol-A structure has been omitted). The chemical shift assignments shown in the figure were based on chemical shift additivity principles. The peak at 61 ppm has been assigned to the methylene

of the 1° OH-containing units **3**. (There are presumably also **4** repeat units, but their concentration is so low as to not be detectable by NMR.) The broad peak at 77 – 78 ppm indicates that the polymer is highly branched as in unit **5**, which is consistent with the high polydispersity noted in Table 1. By integration, **2**, **3**, and **5** repeat units are present in a ratio of 19.3 : 34.2 : 46.5. The total ratio of 1° to 2° OH groups, including the glycol end units, is about 1 : 1.6.



The effect of temperature (over the range of 15° to 35°C) and perchloric acid concentration (from 0.48 to 1.66%) on epoxide conversion *vs.* time is shown in Figure 8a. Epoxide conversion was followed using the 2nd derivative FT-IR procedure described above. At 15°C and 0.48% catalyst it required about 215 hours to reach 93.9% conversion, whereas 95.4% conversion was achieved in about 7 hours at 35°C and 1.66% catalyst.

Figure 8b more clearly reveals an interesting aspect to the kinetics of the process. The conversion curves do not exhibit the usual smooth exponential decay typical of most kinetic processes. Rather, the curve has a clear S-shape where initially epoxy conversion is relatively slow, followed by a more rapid conversion rate period, followed by the inevitable slow rate of reaction caused by the low epoxy concentration during the final stages of the process. In other words, during the process there is acceleration in the rate of reaction. As will be shown below, when this reaction is conducted in solution, more traditional conversion *vs.* time curves are obtained, suggesting that the effect is related to the two-phase nature of the emulsion polymerization process. An explanation of the conversion data is that equilibrium water and/or catalyst concentration in the emulsion particles increases during the course of the reaction. This is reasonable, since alcohol group concentration is increasing as hydrolysis reactions occur, thus increasing the hydrophilicity of the polymer.

This brings up an interesting aspect of this polymerization. The molecular weight obtained is a function of the relative rate constants of hydrolysis and alcoholysis, and the concentrations of water and alcohol groups. As shown below, when water and epoxy resin are polymerized in homogeneous solution, it is possible to manipulate the final molecular weight by changing the amount of water charged to the system. In the present two-phase system, decreasing the overall water concentration of the system, (i.e., increasing the solids content), will have little effect upon the equilibrium water

concentration inside the particles, and hence little effect on molecular weight as long as diffusion of water from the continuous phase is much faster than the rate of reaction.

Table II shows the final GPC molecular weights obtained from this series of experiments. Decreasing the temperature and increasing the catalyst concentration both yield higher molecular weight product, though the effect of temperature over the ranges studied is clearly the more potent variable. Due to the highly branched nature of the resin, these parameters both affect the weight average molecular weight more than the number average, and polydispersity also increases. The inverse relationship between temperature and molecular weight may indicate that equilibrium water concentration in the particles increases with temperature, or it may reflect a greater temperature sensitivity of the hydrolysis vs. alcoholysis rate constants to temperature change. That the molecular weight differences are not primarily due to the final % conversions, which ranged from 93.5 to 96.7%, is indicated by lack of correlation with this factor.

Table II
Effect of Temperature and [Catalyst] on Molecular Weight Averages

Temp. (°C)	[Catalyst]	M_w	M_n	M_w/M_n	% Conversion
15.0	0.48%	12,300	1,810	6.8	93.9
15.0	0.91%	15,000	1,880	8.0	94.2
15.0	1.66%	15,500	1,970	7.9	93.5
25.9	0.48%	7410	1,590	4.6	94.5
25.9	0.91%	9130	1,700	5.4	95.1
25.9	1.66%	11,100	1,820	6.1	95.3
35.0	0.48%	5,820	1,530	3.8	96.7
35.0	0.91%	6,520	1,540	4.2	95.6
35.0	1.66%	7,760	1,650	5.5	95.4

Solution Polymerization

It is clear from the repeat unit structure obtained in the emulsion polymerizations that the product obtained is a copolymer of water and epoxy resin. Furthermore, as described above, by conducting the process in solution, it should be possible to control of the molecular weight of the product by manipulating the ratio of epoxy resin to water employed in the process, thus offering the chemist a degree of control over the process that is not available in the emulsion process.

Figure 9 shows the molecular weights obtained for a series of solution polymerizations run in 1,4-dioxane at 90° C. These experiments were all run in batch mode by preparing a 50% solids solution of liquid epoxy resin in the solvent (all solution polymerizations described in this work were conducted using this 1:1 mixture), heating to temperature, then adding 60% perchloric acid to give 2 wt-% catalyst based on epoxy resin. After holding at temperature for approximately one hour, the remaining water was added to give the total water as a percentage of epoxy resin indicated in the figure. This procedure differs from the representative batch solution polymerization given in the experimental section (above), where the perchloric acid and water were added simultaneously. If 6% water was used in the process the reaction mixture gelled. The M_w obtained varied from 4155 D at 12% water, to 21,750 D at 6.5%, whereas the M_n varied to a much lesser extent, from 1580 D to 2985 D. Thus,

polydispersity increases dramatically and eventually leads to gelation as water content is decreased, as would be expected from a polymerization process that leads to a high degree of branching.

A few polymerizations were conducted by adding all of the water at the same time as the perchloric acid. With 6.5% water, M_n was 2640 and M_w was 12,300. These molecular weights, particularly the weight average, are significantly lower than when the water was added an hour after the catalyst, and are undoubtedly the result of initial polymerization in the presence of less water. Nevertheless, the strong dependence of molecular weight on water content was clearly established by these experiments.

As was the case in the emulsion polymerization examples, sulfuric acid and organic sulfonic acids proved to be poor catalysts for the process. For example, in a series of experiments employing 6.5% water on epoxy, the use of the same molar concentration of methanesulfonic acid to replace perchloric acid gave only about 10% conversion of epoxy groups after heating for 14.5 hours at 90° C as estimated by FT-IR. With the same concentration of *p*-TSA, no measurable loss of epoxide was detected after 5 hours at 90° C, and under the same conditions, sulfuric acid gave only 22.4% conversion of epoxide groups after 6 hours, as determined by titration for epoxide end-groups.

Under these conditions with the superacids, however, the reaction proceeds considerably faster than the emulsion polymerizations described earlier, as would be expected based on the higher temperatures employed. For example, in the experiment with 6.5% water described above with all of the water added at the same time as the catalyst, epoxide conversion was estimated by FT-IR to be greater than 99% within two hours. Because of the highly exothermic nature of this reaction, the batch process so far described sometimes led to significant increase in temperature after catalyst addition. The effect was much greater with CF_3SO_2H and HBF_4 than with perchloric acid, and temperature increases of 20°C were observed when working on a scale of only 100 g of epoxy resin diluted in an equal amount of 1,4-dioxane. It was thought that such a large evolution of heat might be difficult to handle in large-scale production. Therefore, a gradual addition process was adopted for further work. In this process, about 25% of the total epoxy resin was dissolved in solvent and then combined with the water and acid catalyst. After allowing the heat of reaction to modestly raise the temperature (typically about 5°C) for a half hour, the temperature was then raised to the desired reaction temperature. The remaining epoxy resin, diluted in a small portion of the solvent so as to make the solution less viscous, was then pumped into the flask over about a 3 hour period.

Table III gives data for a series of experiments conducted with this process, to determine the effects of temperature, catalyst type, and % catalyst (on epoxy) on the molecular weight and polydispersity. With catalysts other than perchloric acid, the catalyst concentration employed was the same molar concentration as 2% perchloric acid. Most of the experiments were conducted using 7.5% water based on epoxy, but two experiments with 8.33% water are also included. Also, two batch experiments are included. In this case, all of the water and catalyst were added concurrently at room temperature as in the gradual addition process, but the heat rise due to the exothermic reaction was considerably larger. After completion of the exotherm, the temperature was raised to the desired reaction temperature, as in the gradual addition process.

By far the largest effect that can be seen in the data is that of % water. It is tempting to conclude that M_w increases with catalyst in the order $CF_3SO_2H > HClO_4 > HBF_4$, that decreasing temperature leads to higher molecular weights, and that batch polymerization leads to slightly higher polydispersity.

However, the effects are small, and it is quite possible that the results are all within experimental error, an interpretation of the data which is supported by the catalyst concentration study, where the results did not correlate with the change in independent variable, and where the results displayed a variability about as large as that observed for these other variables. From a manufacturing point-of-view, this is a fortunate circumstance, as the data would indicate that it should be possible to prepare products with a high degree of reproducibility, despite minor variations in raw material charges, feed rates, and temperature control that are sometimes encountered in a manufacturing environment.

Table III
Effect of Process Conditions on Molecular Weight in Solution Polymerizations

% Water	Temperature	Catalyst	% Catalyst	Process	M _w	M _n	M _w /M _n
7.5	65	CF ₃ SO ₃ H	3	Grad-Add	12,100	2,655	4.50
7.5	65	HF ₄	1.75	Grad-Add	10,700	2,655	4.00
7.5	65	HClO ₄	2	Grad-Add	11,200	2,640	4.30
7.5	65	HClO ₄	2	Batch	11,650	2,520	4.60
7.5	65	HClO ₄	1	Grad-Add	10,500	2,620	4.00
7.5	65	HClO ₄	0.5	Grad-Add	12,600	2,970	4.30
7.5	90	CF ₃ SO ₃ H	3	Grad-Add	11,900	2,740	4.30
7.5	90	HF ₄	1.75	Grad-Add	9,980	2,290	4.40
7.5	90	HClO ₄	2	Grad-Add	11,400	2,590	4.40
7.5	90	HClO ₄	1	Grad-Add	9,910	2,410	4.10
7.5	90	HClO ₄	0.5	Grad-Add	11,000	2,510	4.40
8.83	65	HClO ₄	2	Grad-Add	5,360	1900	2.80
8.83	65	HClO ₄	2	Batch	5,810	1,970	3.00

The rate of epoxide conversion is shown in Figure 10 for a series of four batch processes, conducted at either 90°C or 65°C, and with either 0.5% or 2.0% perchloric acid on epoxy resin solids. In these processes, the catalyst was added at the reaction temperature, and because the heat evolved with perchloric acid is not as great as with the other catalysts, the maximum heat rise obtained was only 2°C. These conversion curves do not show the acceleration evident in the emulsion process discussed above.

Analysis of the polyols by ¹³C NMR reveals interesting differences in the chemical structure obtained in solution and emulsion polymerizations. The data are summarized in Table IV. All of the polymerizations were catalyzed with perchloric acid, at 2% based on epoxy resin for the solution polymerizations, and at 0.91% on total weight for the emulsion polymerization. The epoxide conversion in the emulsion polymer was 95% by FT-IR.

The biggest apparent difference is the much higher level of branching in the emulsion polymerized sample. This is also reflected in the significantly higher polydispersity of the emulsion polymerized product, despite its lower M_n. The solubility of water in epoxy resin is quite low at room temperature. While the solubility of water in the emulsion particles may be somewhat higher than in the bulk, it is unlikely that it approaches the water concentration present at the start of the solution processes, and lower water concentrations clearly should yield higher branching levels. Indeed, were it not for the fact that water in the emulsion particles is constantly replenished by the continuous phase (or perhaps even increases as the product becomes more hydrophilic), it is likely that the emulsion process would

yield microgel. Decreasing molecular weight by increasing the water concentration in the solution process also leads to an even more linear polymer.

The emulsion process also leads to the highest level of primary OH groups. This is partly due to the higher amount of glycol end group in a more branched structure. It is also due to an increase in level of repeat units of structure **3** in the emulsion polymerization. The amount of these repeat units also increases as the solution polymerization product is driven to higher molecular weight. A final difference worth noting is that whereas the solution polymerization process yields a final product that is devoid of epoxide groups, the emulsion process has always yielded a product with a measurable quantity (typically 3 – 7%) of epoxide end groups, even when reaction times were extended to a week or more. It might be possible to drive the reaction to higher conversion using more catalyst and higher temperatures, but the latter approach can lead to difficulties with emulsion stability.

Table IV
Comparison of Emulsion and Solution Polymerized Polyol Structure

Polyol	EP1	SB1	SB2	SB3
% Water on Epoxy	--	6.5	8.83	8.83
Reaction Temp. (°C)	Ambient	90	65	65
Process	Emulsion	Batch	Batch	Grad-add
M _n	1630	2640	1970	1900
M _w	7,250	12,300	5810	5360
Repeat Unit Content				
2 (Bis 2° OH)	19%	42%	70%	71%
3 (1° & 2° OH)	34%	25%	14%	14%
5 (Branched)	47%	33%	16%	14%
1°/2° OH Ratio (excluding glycol end groups)	1.0 : 4.8	1.0 : 6.9	1.0 : 13.3	1.0 : 12.9
1°/2° OH Ratio (including glycol end groups)	1.0 : 1.6	1.0 : 2.6	1.0 : 3.5	1.0 : 3.6
% Epoxide End Groups	3.2	0	0	0

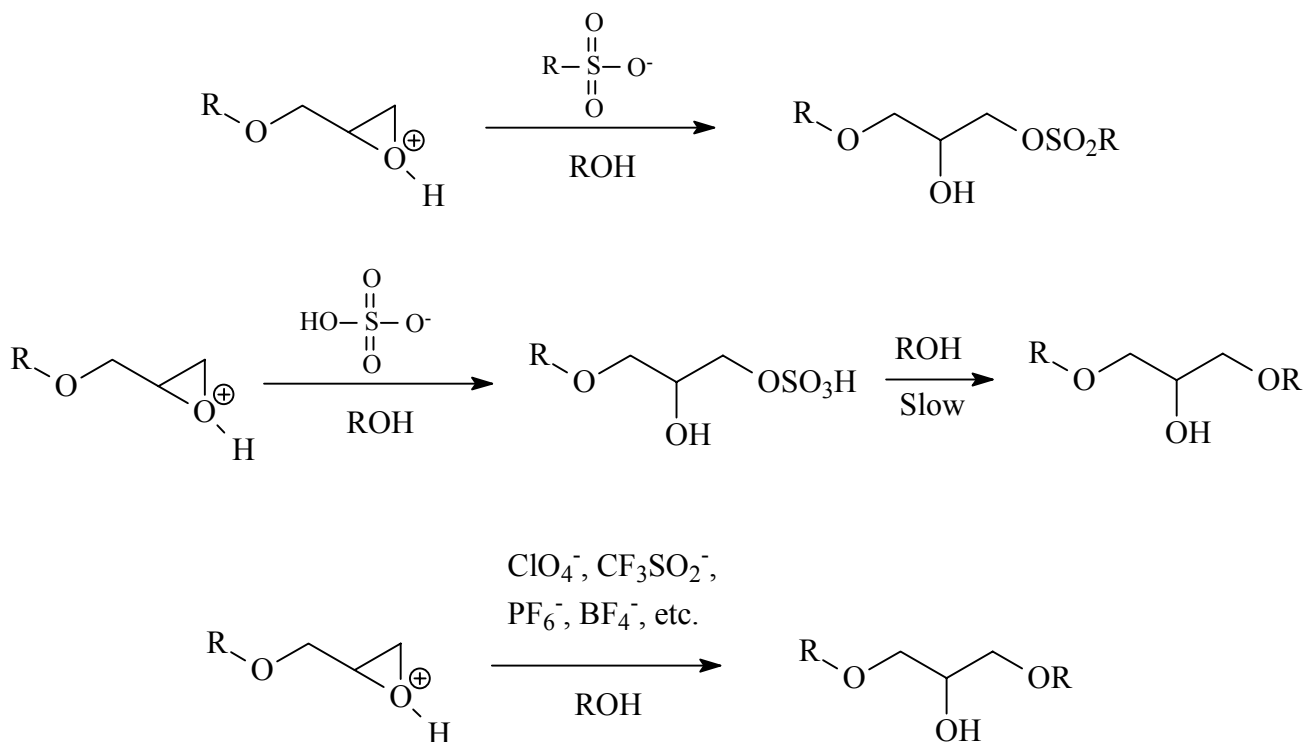
Acid Catalysis

According to Olah¹⁶, a widely accepted though admittedly arbitrary definition of a superacid is any acid system stronger than 100% sulfuric acid, i.e., having $H_0 \geq -12$. Perchloric acid, TFMSA, TFBA and HFPA are all superacids, while sulfuric acid, hydrochloric acid, MSA and *p*-TSA are not. Thus, catalysts with superacidity are seemingly required to polymerize BADGE under these conditions. In dilute aqueous media, the acidity of all strong acids is limited by the basicity of water, and therefore all should be equal to the acidity of the water-solvated proton, commonly denoted as H_3O^+ . Thus, the requirement for superacidity is somewhat unexpected. In a preliminary report¹⁷ on the emulsion polymerization aspects of this work, it was suggested that since the reaction most likely occurs within the emulsion particles, it was possible that in the oil phase where less water is available for solvation higher acid strengths could be obtained, thus explaining the requirement for superacidity. Based on the experiments described below, it is now clear that the extremely weak nucleophilicity of superacid counterions, rather than the acid strength, accounts for whether polymerization occurs.

A solution polymerization containing a 1:1 mixture of liquid epoxy resin and 1,4-dioxane was treated at room temperature with an aqueous solution of methanesulfonic acid to yield a final solution containing 1.91% acid and 7.5% water based on epoxy resin. Free MSA was determined by dissolving samples in methanol followed by titration with KOH to a phenolphthalein end-point. Within the time required to prepare a sample for titration, about 36% of the acid was consumed, and within 1 hr. only a trace of free acid was present. The reaction mixture was stirred at room temperature for 24 hours followed by treatment at 90°C for 6 hours. Analysis of epoxide content by FT-IR and EEW determination indicated that there was only 1% and 2.5% epoxide conversion, respectively. Comparable rapid consumption of catalyst was also obtained with *p*-TSA, with both FT-IR and EEW indicating only about 1% conversion. Sulfuric acid likewise was consumed rapidly, though by the end of this procedure both FT-IR and EEW determination indicated approximately 22% conversion of epoxide functional groups.

The rapid consumption of catalyst with little or no epoxide conversion indicates that the sulfonic acids and sulfuric acid add to the epoxide to form β -hydroxy sulfonate and sulfate esters, respectively, as shown in Scheme 5. This reaction is well known in organic media,¹⁸ having first been studied by Stanger and Criegee in 1936.¹⁹ The sulfonate esters are apparently stable products under these conditions. The sulfate ester, on the other hand, likely undergoes solvolysis reactions with water and alcohols to slowly achieve the conversions indicated. The superacids, however, all have counterions that are much weaker nucleophiles than sulfate or sulfonate. Thus, either water and alcohol add to the protonated epoxide in preference to these counterions (as shown in the scheme), or the products of addition of these counterions are unstable and are rapidly solvolyzed by water and alcohol.

Scheme 5



Interestingly, reaction of sulfuric acid with epoxide as determined by acid titrations in the emulsion polymerization process is much slower than in solution. After stirring at room temperature for 24 hours, less than 5% of the sulfuric acid titer was lost. With *p*-TSA in the emulsion process acid conversion was also much slower than in solution, but it reacted much faster than sulfuric acid. In 5 hours, 25% of the *p*-TSA was consumed, and in 24 hours, about 65% of the acid was consumed. These results are probably due to partitioning of the acids in the aqueous phase in preference to the organic phase.

Residual Bisphenol-A and BADGE Determinations

Based on the general coatings performance properties obtained from the melamine cured coatings described below, it appeared that properties suitable for interior beverage can linings might be attainable. Currently, suppliers of these coatings are facing pressure to reduce extractables from their coatings due to health concerns. Two of the targeted molecules are bisphenol-A, which is a suspect estrogen mimic, and BADGE, which is of concern for various health effects as are most glycidyl ether based compounds. A commercially important resin technology that is currently employed in interior can coatings involves the free-radical grafting of acrylic monomers onto an *in situ* prepared '9-type' (EEW = 2300 – 3800) resin.¹ Since such high molecular weight epoxy resins are prepared by step-growth polymerization of bisphenol-A and BADGE, we thought that they probably would contain relatively high levels of residual starting materials. We also reasoned that our process may yield lower levels of these residuals. The bisphenol-A content should be no higher than whatever is present in the starting liquid epoxy resin, and the final BADGE content should be a function of both degree of polymerization as well as the final extent of epoxide hydrolysis.

An HPLC method using a photodiode array detector, and a solvent gradient of 30% acetonitrile / 70% water to 70% acetonitrile / 30% water, was developed to quantify these residuals. Since we lacked a pure BADGE standard, a commercial liquid epoxy resin[†] was employed as the standard with the assumption that it contained about 85% BADGE, which is a reasonable estimate based on the equivalent weight. For this study, and for the coatings evaluations described below, the emulsion polymerization was conducted on a 60% solids emulsion of liquid epoxy resin stabilized with a different, proprietary nonionic surfactant, by a process, also proprietary, that was quite similar to the one given in the experimental section. Two different batches were prepared, both at 40°C and with 0.91% perchloric acid, but with different reaction times. The solvent-borne polyol (SB-C) was prepared using 7% water and 2% perchloric acid on epoxy resin using a batch process at 90°C and a 24 hour reaction time, and had $M_n = 2820$ and $M_w = 19700$. Prior to this measurement and in preparation for the coatings evaluations described below, the solution was diluted with butoxyethanol and then most of the 1,4-dioxane was removed by distillation at atmospheric pressure to yield a 76.8% solids solution. Residual bisphenol-A and BADGE levels are compared in Table V with those obtained from commercially available '7-type' and '9-type' epoxy resins.

Polyols prepared by acid catalyzed polymerization, whether by an emulsion or solution polymerization process, have levels of bisphenol-A about 20 to 60 times lower than the commercial resins prepared by the advancement process. This probably represents the level of bisphenol-A present in the liquid epoxy resin employed as a starting material, unless trace quantities of bisphenol-A are generated by a side reaction. The BADGE levels are also much lower in the products of cationic polymerization than

[†] Epon® 826, Resolution Chemical Co., EEW 178 – 186.

in the commercial resins. However, there is almost an order of magnitude reduction in BADGE in going from the emulsion process to the solution process, which clearly reflects the ability to drive the reaction to higher degrees of conversion in the latter process. Interestingly, by emulsion polymerization there was little difference in BADGE content in the polyol at 19 hours or 1 week of reaction time.

Table V
Residual Bisphenol-A and BADGE Levels

Sample	Reaction Conditions	Bisphenol-A (ppm)	BADGE (ppm)
EP-A	40°C, 19 hr.	7	769
EP-B	40°C, 144 hr.	6	698
SB-C	90°C, 24 hr.	8.5	88
7-Type Resin [‡]	--	137	4730
9-Type Resin [§]	--	447	3321

Coating Evaluations.

We are still at an early stage in the study of thermosetting coatings prepared from the products of the polymerization processes described above. However, some interesting results have already been obtained.

A polyol prepared by the emulsion process (EP-A) was crosslinked with a hexamethoxymethyl melamine (HMMM) in the waterborne formulation given in Table VI. A comparison formulation was based upon a commercial dispersion of a '7-type' solid epoxy resin which is supplied at 55% solids in a 76/24 blend of water and 2-propoxy ethanol. Thus, the formulation based on EP-A is free of added cosolvent, whereas the formulation based on the commercial resin contains 7.8% cosolvent by weight. Both formulations contain an 80/20 ratio of polyol to melamine, and 0.3% *p*-TSA based on total solids. Note that the catalyst is not blocked, so these formulations are not designed to be storage stable, and coatings were applied within two hours of adding the catalyst to the formulation.

[‡] Epon® 1007, Resolution Chemical Co., EEW 1700 – 2300.

[§] Epon® 1009, Resolution Chemical Co., EEW 2300 – 3800.

Table VI
Waterborne Melamine Cured Clearcoat Formulations

Ingredient	EP-A Dispersion Formulation	Solid Resin Dispersion Formulation
Resin Dispersion	52.53	58.18
Water	0.00	12.94
Hexamethoxymethyl melamine**	8.00	8.00
<i>p</i> -Toluenesulfonic acid (10%)	1.20	1.20
Formulation Properties		
% Solids (calc.)	65.0	50.0
Resin / Melamine	80/20	80/20
Viscosity (cP)	478	72

The formulation based on the commercial dispersion had to be formulated at lower solids due to its relatively high viscosity (7000 – 17000 cP as supplied). The viscosity of the EP-A emulsion, on the other hand, was only 201 cP as measured by a Brookfield cone and plate viscometer (CP41 spindle, 20 rpm). Part of the reason for the large difference in viscosity may be due to swelling of the particles by the cosolvent, although different nonionic stabilizers and particle sizes may also play a role.

As shown in Figure 11, EP-A developed >250 MEK double rubs solvent resistance with a 30 minute bake at 90°C, whereas comparable solvent resistance from the solid dispersion required a 130°C bake. There are several potential explanations for the improved cure response of the cationically polymerized polyol. The OH equivalent weight of EP-A (excluding surfactant) is calculated to be about 148, whereas the conventional resin's is 303. The higher hydroxyl content will yield a faster rate of conversion when formulated on an equal weight ratio basis as is done here. The effect will be more pronounced at higher conversion where solvent resistance is likely to develop, simply because the ratio of unreacted hydroxyl groups to melamine ether groups will be larger. The higher hydroxyl content would also be expected to allow EP-A to react more efficiently in transesterification reactions with the melamine resin, as opposed to melamine self-condensation reactions.²⁰ EP-A is also more branched than the conventional resin, and this will yield higher crosslink density at equivalent degree of melamine conversion. Conventional epoxy resins contain only 2° OH groups, while it was shown above that a polyol prepared under conditions similar to EP-A had a ratio of 1° to 2° OH of about 1 : 1.6. The 1° OH content would be expected to lead to faster cure based on steric effects. Finally, the epoxide content of the conventional resin dispersion is considerably higher than the residual epoxy content left in the cationically polymerized resin. It is also possible that some of the *p*-TSA reacted with the epoxide groups to form the sulfonate esters, which would then have to be released during the bake by alcoholysis reactions or other decomposition processes to yield active catalyst.

Table VII compares the coating performance of EP-A cured at 100 °C to the conventional dispersion cured at 130°C. The coatings were applied to iron phosphate (Bonderite 1000) panels using a #20 roll bar. The higher solids of the EP-A formulation resulted in a slightly higher dry film thickness. Gloss values for the formulations were comparable, as were impact resistances. However, it should be noted

** Resimene® 747, Solutia Inc.

that EP-A gave poorer impact results if baked at a higher temperature. In T-bend testing it also was not as flexible as the '7-Type' formulation, and it appears that EP-A yields films that are somewhat less flexible than those based on conventional epoxy resins. This is probably due to a higher crosslink density in the films based on EP-A, even though they were cured at a lower cure temperature. Hardness was approximately comparable for the two coatings, though EP-A gave somewhat better scratch resistance in the pencil test.

Dry adhesion was excellent for both coatings. Both coatings were also resistant to blistering in condensing humidity at 40°C. However, the coating based on EP-A lost adhesion to all three substrates tested, whereas the conventional resin maintained most or all of its adhesion to iron phosphate treated and cold-rolled steel.

Wet cross-hatch adhesion after 24 hours of DI water immersion is shown in Figure 12. In this series of tests a coating from EP-A cured at 130°C also was included. On iron phosphate treated steel, EP-A yielded 4B adhesion at both temperatures, compared to 5B for the conventional resin. The '7-Type' resin maintained this excellent performance on cold-rolled steel, while EP-A dropped to 3B with a 130°C cure, and 2B with a 100°C cure. All three resins lost all adhesion when cured over zinc phosphate treated steel.

Table VII
Waterborne Coating Performance Data

Test	EP-A Formulation	'7-Type' Dispersion Formulation
Cure Conditions	30', 100°C	30', 130°C
DFT (microns)	15	12.5
Gloss, ASTM D523 (20°/60°)	78 / 117	82 / 118
Pencil Hardness, ASTM D3363 (Scratch / Gouge)	H / 4H	F / 4H
Persoz Hardness, ASTM D4366 (sec.)	383	387
Impact Resistance, ASTM D2794 (fwd. / rev.; in.-lb.)	160 / 160	160 / 160
T-bend, ASTM D4145	3T	1T
Dry Cross-Hatch Adhesion, ASTM D3359	5B	5B
144 Hr. Cleveland Humidity, ASTM D4585 (Blister Rating / Adhesion)		
Fe-Phos Steel	10 / 0B	10 / 4B
Zn-Phos Steel	10, Discoloration / 0B	10, Sl. Discoloration / 0B
Cold-Rolled Steel	10 / 0B	10, Black Corrosion Spots / 5B

A solvent-borne formulation was prepared from resin SB-C, and is compared in Table VIII to formulations prepared from the 7-type and 9-type resins. All the formulations were prepared at an 80/20 ratio of polyol to HMMM, all were catalyzed with 0.3% *p*-TSA immediately before application, and all were at 66.86% solids. Performance properties are compared in Table IX.

Table VIII
Solvent-borne Melamine Cured Clearcoat Formulations

Resin	SB-C		55% Solids '7-Type' Resin		40% Solids '9-Type' Resin	
	Weight	Solids Weight	Weight	Solids Weight	Weight	Solids Weight
Polyol	20.83	16.00	29.09	16.00	40.00	16.00
HMMM	4.08	4.00	4.08	4.00	4.08	4.00
Solvent	41.35	0.00	33.10	0.00	22.18	0.00
10% <i>p</i> -TSA	0.60	0.06	0.60	0.06	0.60	0.06
Total	66.86	20.06	66.87	20.06	66.86	20.06

The temperature required to reach >250 MEK double rub resistance was 90°C, just as in the waterborne formulations. However, the solvent-borne formulations of the higher molecular weight resins cured at 100° and 110°C, not as low as SB-C, but better than the commercial waterborne dispersion of epoxy resin. Gloss was slightly lower for SB-C compared to the solvent-borne epoxies, especially at the higher bake temperature. Persoz hardness, water immersion and humidity resistance results were comparable. Dry adhesion at the lower temperature cure was fairly comparable for all three formulations, whereas at the higher cure the commercial epoxy resins fared better, though far from perfectly. Interestingly, wet adhesion was superior for the '9-type' resin at both cure temperatures, with both the '7-type' and SB-C showing poor results. Reverse impact at the lower cure temperature was better for the commercial epoxy resins, though it must be born in mind that at this temperature these resins have not yet developed good solvent resistance, whereas SB-C has developed enough crosslink density for excellent solvent resistance. With a higher cure temperature, all three formulations lose impact resistance, which is probably adversely affected by their decreased adhesion as well as the higher crosslink density.

The coating formulations described above have not been optimized. Nevertheless, coatings with some excellent properties have been obtained, though there are some performance shortcomings that will need to be addressed for the products to be commercialized in certain markets. It is likely that adjustment of the formulations described above could improve some of the deficiencies noted.

Table IX
Solvent Coating Performance Data

Example	SB-C	'7-Type'	'9-Type'
DFT (microns)	11	12	10
MEK Dbl Rubs			
Cure at 90°C	>250	Fail @ 10	Fail @ 10
Cure at 100°C	--	Fail @ 200	>250
Cure at 110°C	--	>250	--
Performance with 90° Cure			
20° GLOSS	65.0	80.8	67.1
60° GLOSS	102.1	110.6	104.1
Cross-hatch Adhesion, Dry	4B	5B	5B
Water Immersion, 24 Hr.	Pass	Pass	Pass
Cross-hatch Adhesion, Wet	0B	0B	4B
6 Day Humidity, 100°F (Blister/Rust)	10/10	10/10	10/10
Persoz Hardness	358	377	353
Reverse Impact (in-lb)	40	160	160
Performance with 130° Cure			
20° GLOSS	42.0	65.2	60.0
60° GLOSS	91.5	101.6	98.3
Cross-hatch Adhesion, Dry	0B	3B	3B
Water Immersion, 24 Hr.	Pass	Pass	Pass
Cross-hatch Adhesion, Wet	0B	0B	3B
6 Day Humidity, 100°F (Blister/Rust)	10/10	10/10	10/10
Persoz Hardness	360	382	381
Reverse Impact (in-lb)	<4	<4	<4

Conclusions

Cationic epoxide emulsion polymerization, a fundamentally new process for the preparation of polymeric polyols, has been demonstrated. This is one of only a few known examples of acid catalyzed emulsion polymerization. Catalysts with very weakly nucleophilic counterions, which are generally superacids, are required to obtain significant yields of polymer under these conditions. Weaker acids such as sulfonic acids add to the epoxide compound to yield stable products, thus preventing their function as catalysts.

A pleasing aspect of this technology is that the process is inherently straightforward. An emulsion of epoxy resin is simply mixed at ambient or slightly elevated temperature and neutralized when the desired degree of conversion is achieved. Fortuitously, the reaction proceeds at a rate that is also amenable to industrial practice. Heat is not evolved so fast as to create significant difficulties, but the reaction is complete in a reasonable amount of time. Another fortuitous aspect of the process is that the equilibrium concentration of water in the emulsion particles is at the right level to give polymers of useful molecular weight.

The structure of the polyol demonstrates that the product is a copolymer of water and epoxy resin, and it has proved possible to also prepare similar polymeric polyols in solution using solvents such as 1,4-dioxane. The molecular weight is mostly determined by the ratio of water to epoxy resin employed, and this offers the chemist a means to manipulate the process to prepare resins of different molecular weight that is not available in the emulsion process. Molecular weight is little influenced by other variables such as temperature, catalyst, and catalyst concentration over the ranges studied. The solution polymerization process, however, yields a product that is considerably less branched at comparable number average molecular weight than does the emulsion process. This is likely the result of the low concentration of water in the oil phase where polymerization presumably occurs in the emulsion process.

The polyol formed from this process differs in several ways from high molecular weight epoxy resins. The repeat unit structure contains two glycidyl fragments, and two OH groups. The resin contains mostly glycol end-groups instead of epoxy end-groups, and it is considerably branched. The resin also contains significantly lower levels of residual bisphenol-A and BADGE than do commercial advanced epoxy resins, which is desirable for coatings with direct food contact. Because of the ability to drive the polymerization further in the solution process than is practical in the emulsion process, residual levels of BADGE are even lower in the former process, whereas bisphenol-A levels are comparable, most likely representing the bisphenol-A present in the liquid epoxy resin employed in the polymerizations.

Crosslinking with melamine resin gives very chemical-resistant films at lower baking temperatures than conventional epoxy systems. Interestingly, waterborne formulations showed a larger difference in cure temperature necessary to achieve good solvent resistance than did solvent-borne formulations. The waterborne formulations from which these films were derived were free of added cosolvent, though not free of VOCs, since the melamine crosslinkers generate alcohols during cure. There are several possible explanations for the improved cure response, and further experimentation is required in order to understand this effect. The film properties obtained are generally comparable with properties obtained from commercial high molecular weight epoxy resins, both waterborne and conventional, though, as would be expected for any new technology, there are a few performance properties that will require improvement to meet particular market needs. Important among these are improved wet adhesion to various steel substrates, and greater flexibility, especially with overbake conditions. We are optimistic about the potential to solve these technical difficulties, and believe the technology holds significant promise for applications where highly chemical-resistant, baked coatings with low extractables are required.

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