Composition and Long-Term Stability of Polyglycidol Prepared by Cationic Ring-Opening Polymerization

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ABSTRACT: Polyglycidol synthesized by cationic ring-opening polymerization of glycidol (boron trifluoride initiation in dichloromethane) was purified of low molecular weight contaminants by centrifugal filtration. The high and low molecular weight fractions were characterized by NMR, GPC, osmometry, viscometry, DSC, and FTIR. The ^{13}C-NMR spectrum of this polymer was completely annotated by proposing a new step in the reaction mechanism. The four thermal dimers of glycidol were also isolated and identified as 2,5-bis(hydroxymethyl)-1,4-dioxane and 2,6-bis(hydroxymethyl)-1,4-dioxane, each of which can exist in *cis* and *trans* configurations. Polyglycidol was found to be hygroscopic, picking up about 5% by weight of atmospheric moisture. It was also found that, over time (ca. 1–2 years), polyglycidol crosslinks into a rubbery, insoluble mass. It is therefore recommended that this polymer be stored dry and used within a few months of synthesis. J Appl Polym Sci 91: 1344–1351, 2004

Key words: crosslinking; cationic polymerization; polyethers.

INTRODUCTION

The ability of glycidol to polymerize has been known[1] since about 1877 ("Glycid . . . condensirt sich zu Polyglyciden"). Polyglycidol (PGly) and glycidol-containing copolymers have been the subject of numerous research studies[2–12] since then. In general, PGly can be considered to be a hyperbranched, polyfunctional analog of the widely used linear polyether, poly(ethylene glycol) (PEG). As such, PGly, with its stable polyether backbone and numerous pendant hydroxyl groups, is a highly attractive substrate for derivatization, possibly allowing its use in many of the applications currently employing PEG.[13] PGly-based materials are also used commercially in the manufacture of chromatographic coatings.[14] This report is the third in a series examining the copolymers of glycidol and the PGly homopolymer.

As usual in cationic ring-opening polymerizations of epoxides, our reaction yields a certain amount of dimeric and oligomeric by-products. Due to the growing importance of PGly, we established a simple method for purifying it from these low molecular weight contaminants. We point out in this article a couple of hitherto overlooked aspects of the reaction mechanism. These are used to complete the annotation of the ^{13}C-NMR spectrum of PGly. The identity of the dimer(s) of glycidol has been the subject of a number of investigations[2,3,5] since at least the 1920s. We have isolated and analyzed the thermal dimers of glycidol and have proposed structures for them based on the "backbiting" mechanism.[15] Finally, some investigations into the long-term stability of this polymer are also described herein.

EXPERIMENTAL

Materials

Glycidol was obtained from the Sigma–Aldrich Co. (Milwaukee, WI). Boron trifluoride diethyl etherate (BF_3:OEt_2), trifluoroacetic anhydride, and HPLC-grade *N*,*N*-dimethylformamide (DMF) were obtained from Acros Organics (Geel, Belgium). Dichloromethane and methanol were obtained from Fisher Chemicals (Rockville, MD). Narrow molecular weight poly(ethylene oxide) (PEO) standards were obtained from Scientific Polymer Products (Ontario, NY). All reaction materials were reagent grade; glycidol and dichloromethane, the reaction solvent, were stored over 4A molecular sieves, with glycidol being kept refrigerated.

Synthesis

Polymerizations were carried out at room temperature (22°C) in a glass three-neck 250-mL round-bottom

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flask fitted with a mechanical stirrer, condenser operating at 5°C with a $CaCl_2$ drying tube, and a thermometer. This reactor was dried with a heat gun under a gentle stream of dry nitrogen. To this dried flask, in air, were added 150 mL dichloromethane and 7 mL (0.11 mol) glycidol. Polymerization was initiated by the addition of 200 μL (1.6 mmol) BF_3:OEt_2. The reaction mixture was stirred vigorously throughout the course of the reaction. CAUTION: HIGHLY EXOTHERMIC REACTION! DO NOT USE HIGHER CONCENTRATIONS OF GLYCIDOL DUE TO DANGER OF VIOLENT OVERHEATING. VIGOROUS MECHANICAL STIRRING IS NEEDED FOR A SAFE POLYMERIZATION.

The progress of the reaction was monitored by GC–MS by periodically withdrawing 100 μL of the reaction mixture. Complete consumption of the monomer generally took about 10 min, although the reaction was allowed to run for 0.5 h. The reaction mixture was then quenched by adding 1–2 mL distilled water, followed by 1–2 h of vigorous stirring. Volatiles were removed by rotary evaporation followed by freeze-drying in a lyophilizer (−50°C trap at 40 mTorr) to give a clear, colorless, viscous polymer **I** in quantitative yield.

This as-prepared PGly **I** was dissolved in water and filtered through centrifugal filters having a nominal molecular weight cutoff of 10,000 g/mol (Amicon YM-10 filters, Millipore Corp., Bedford, MA). This was found to be a very quick and efficient method of removing the low molecular weight contaminants of PGly. The high molecular weight fraction (retentate) and low molecular weight fraction (filtrate) solutions were evaporated in a sand bath at 85°C overnight. The high molecular weight fraction **II** was recovered as a tacky gum (74% by mass), and the low molecular weight fraction **III**, as a slightly viscous liquid (21% by mass), indicating 95% total isolated yield. Both fractions were clear and colorless. All polymers were stored under an ordinary atmosphere at room temperature.

Heating glycidol induces a certain amount of dimerization, oligomerization, and polymerization, and the thermal dimers of glycidol were collected by simple vacuum-distillation of the monomer. After all the glycidol had distilled over, a pale yellow liquid, bp 236–238°C/200 mm, was collected, which was heated to remove traces of glycidol before analysis.

Aged PGly samples were dried on a lyophilizer (as above) for 2 days before thermal analysis. This was necessary because of the hygroscopic nature of the polymer.

Analysis

The GC–MS used to monitor the polymerizations was a Thermoquest (San Jose, CA) Trace 2000 GC with a Trace MS detector, equipped with a Restek Rtx-5MS capillary column of length of 15 m and an i.d. of 0.25 mm. Helium was used as the carrier gas. ^{1}H- and ^{13}C-NMR spectra of the polymers were recorded using a Bruker/IBM (Billerica, MA) WP270SY spectrometer operating at 270.1 and 67.9 MHz, respectively, in CD_3OD (polymer concentration approximately 250 mg/mL). NMR spectra of the glycidol dimers were obtained on a Varian MercuryPlus 300-MHz spectrometer (CD_2Cl_2 or $CDCl_3$ solvent). Solvent peaks were used as internal references in the NMR spectra. Infrared spectra of thin films of the polymer smeared on KBr disks were taken with a Perkin–Elmer (Norwalk, CT) 1760 FTIR. Differential scanning calorimetry (DSC) was performed on a Mettler (Columbus, OH) DSC 30 equipped with a low-temperature cell. Each sample was analyzed from −150 to 25°C, at 10°C/min. Gel permeation chromatography (GPC) provided a relative measure of the polymer molecular weight and was carried out on a Waters (Milford, MA) GPC system (515 HPLC pump, 717plus autosampler, 2410 refractive index detector, column heater module at 50°C, two HR4E columns, and Millennium32 software). HPLC-grade DMF was used as the mobile phase, and narrow molecular weight distribution PEO standards of 834,000, 592,200, 100,600, 11,300, 2890, and 370 g/mol were used for molecular weight calibration. The polymer concentration used for GPC analysis was 5 mg/mL. Aqueous-phase osmometry was used to obtain an independent estimate of the number-average molecular weight and utilized a Precision Systems (Natick, MA) Osmette S osmometer, which actually operates on the basis of freezing-point depression and has a molecular weight limit of M_n = 25,000 g/mol. After standardization with 100 and 500 mmol/kg NaCl solutions, the instrument was calibrated (correlation coefficient 0.999) with PEGs 8000, 3350, and 400 and sucrose (342 g/mol). All sucrose, PEG, and PGly solutions used for the osmometry had a concentration of 25 mg/mL. The intrinsic viscosity was measured at 20°C using a Cannon (Fisher Scientific, Pittsburgh, PA) #75 Ostwald-type viscometer, using about 0.37 wt % (about 3.0 mg/mL) solutions of the different polymers in methanol.

RESULTS AND DISCUSSION

The room-temperature BF_3-catalyzed cationic polymerization of glycidol in dichloromethane is an extremely rapid reaction which produces PGly **I** in quantitative yield as a viscous precipitate. A study of this system was conducted by Tokar et al.,[7] who proposed a simple reaction mechanism and reported molecular weight and other data on the PGly thus obtained. This mechanism has since been refined and extended.[9,16,17]

Purification of PGly

A cursory comparison of as-prepared PGly **I** (viscous liquid) with the two fractions **II** (tacky gum) and **III** (very slightly viscous liquid) showed that their physical properties were quite different. However, all polymers were soluble in water and in other polar solvents such as methanol and DMF, presumably due to the large number of OH groups in the polymers. Gel permeation chromatography (GPC) analyses of polymers **I**, **II**, and **III** in DMF are shown in Figure 1. It is clear from this figure that the as-synthesized polymer **I** was separated into two distinct fractions, **II** and **III**.

The various molecular weight-related properties of the three polymers are summarized in Table I. Average molecular weights obtained from GPC were artificially large, on the order of 10^6 g/mol, due to the formation of hydrogen-bonded aggregates. The high molecular weight peak in the chromatogram of as-prepared PGly (**I**) disappeared upon derivatization of the polymer with trifluoroacetic anhydride,[18] confirming hydrogen bonding. Number-average molecular weights were therefore obtained by aqueous-phase osmometry (the molecular weight of **II** was above the osmometer's limit of 25,000 g/mol). Intrinsic viscosities measured in a methanol solution at 20°C were consistent with these molecular weights for a polymer with extensive chain branching and were higher than those of low molecular weight PGly reported earlier.[10]

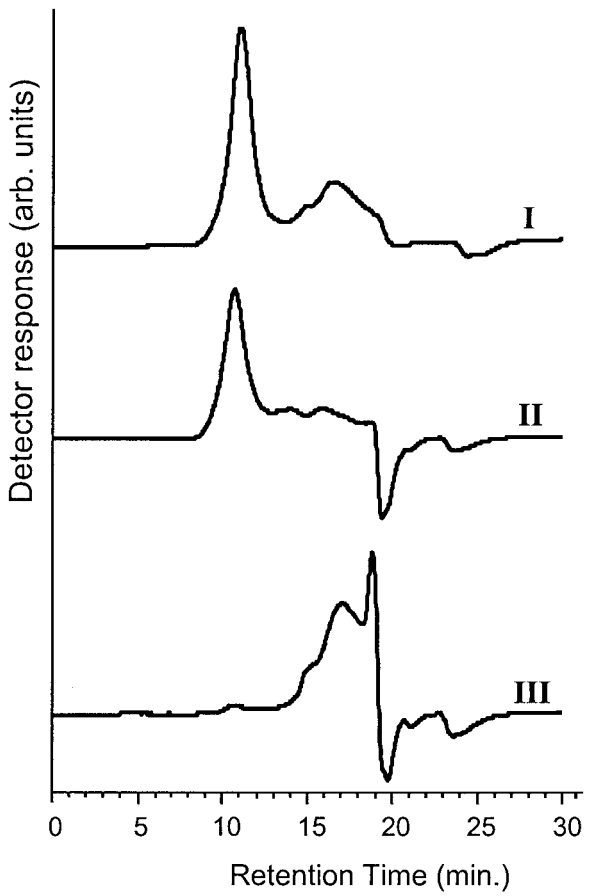


Figure 1 GPC traces of as-synthesized PGly (**I**) showing a bimodal molecular weight distribution, high molecular weight fraction **II**, and low molecular weight fraction **III**.

TABLE I
Molecular Weight-related Properties of the Three fractions of Polyglycidol

Polymer	M_n (g/mol), osmometry	$[\eta]$ (dL/g)
I (as-prepared PGly)	1000	0.143
II (high mol wt fraction)	>25,000	0.175
III (low mol wt fraction)	290	0.0385

In all cases, the properties of **I** are intermediate between those of **II** and **III.** The molecular weight of (*mol wt*) **II** was above the osmometer's limit of measurement.

FTIR spectra of all three polymers showed the expected broad O—H stretch about 3400 cm^{-1} and a strong ether stretch about 1100 cm^{-1}, but were otherwise unremarkable. The complete ^{13}C-NMR spectra of the three fractions in CD_3OD are shown in Figure 2. The spectrum of the high molecular weight fraction **II** is very similar to the published spectrum of hyperbranched PGly prepared by cationic polymerization.[7] The as-prepared polymer **I**, however, shows a number of extraneous peaks, all of which are present more prominently in the spectrum of the low molecular weight fraction **III**. These extra peaks are due to the numerous oligomers which are known to form as by-products in this type of polymerization.[15] The spectrum of **I** is seen to be a combination of the spectra of **II** and **III**, as expected. ^{1}H-NMR was less informative, since all spectra merely showed a large peak due to OH protons at $\delta = 4.83$ and a broad, irregularly shaped peak due to CH and CH_2 protons, spread over the range $\delta = 3.4–4.0$. The above spectral data support the contention that **II** and **III** are clearly different substances and that they constitute separate, isolable fractions of the original PGly polymer **I**.

Polymerization mechanism

An excellent overview of the cationic ring-opening polymerization mechanism of glycidol is found in ref. 16. We present here some previously overlooked facets of this mechanism, in order to complete the annotation of the ^{13}C NMR spectrum of PGly. BF_3-initiated protonation of the epoxide oxygen of glycidol forms the important oxonium ion intermediate, leading to ring-opening polymerization by the active chain-end (ACE) mechanism. Attack on the glycidol molecular oxonium ion at either epoxide carbon by a hydroxyl group of the polymer can lead to ring-opening polymerization by the activated monomer (AM) mecha-

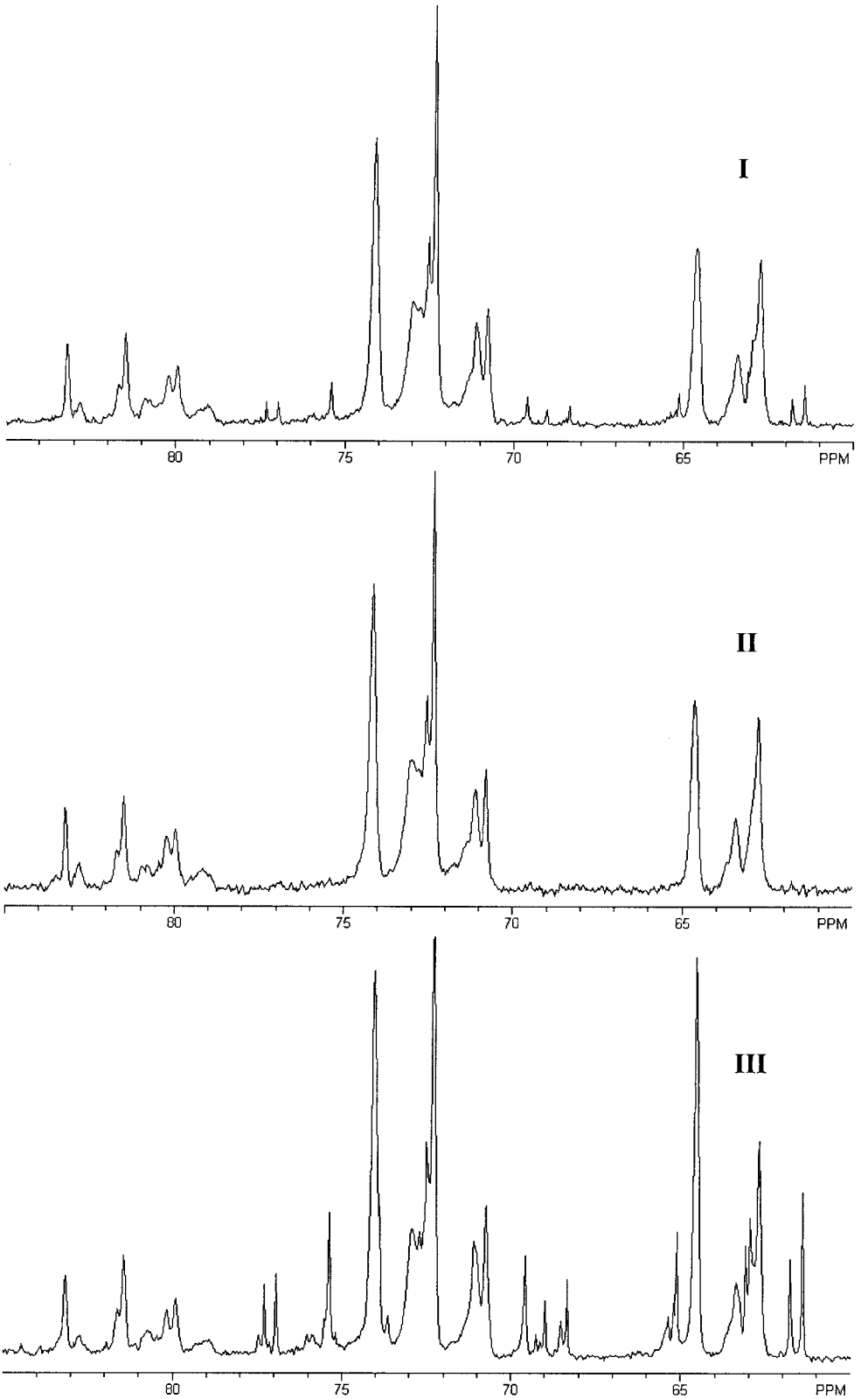


Figure 2 ^{13}C-NMR spectra of (top) **I**, (middle) **II,** and (bottom) **III**.

nism, which generates the same chain structures (repeat units, branching units, and termini) formed by the ACE mechanism. It was noted elsewhere[9,17] that the formation of secondary hydroxyl groups (within so-called linear 1,4 units) along the polymer main chain is possible via the ACE mechanism, as shown in

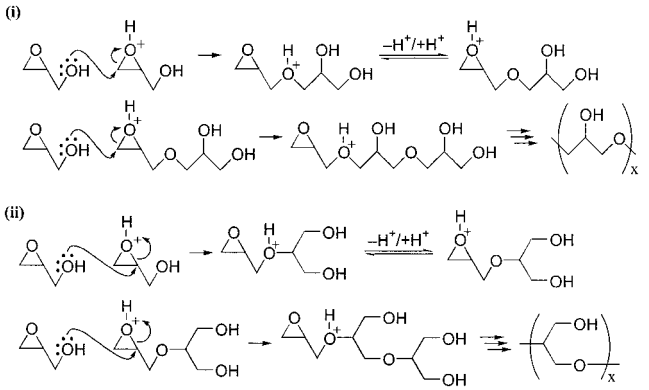


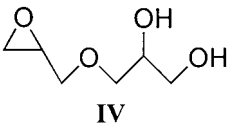
Figure 3 Nucleophilic attack by OH groups in the ACE polymerization mechanism for glycidol forms (i) linear 1,4 units and (ii) chain-end structures of the type —$OCH(CH_2OH)_2$.

Figure 3(i), if the hydroxyl group of glycidol attacks the oxonium ion at the polymer chain end. The processes shown in Figure 3(i,ii) are akin to a chain-transfer process, but they can still contribute to chain growth due to the continued presence of the reactive epoxide moiety at one chain end.

Nucleophilic attack at the hindered carbon of glycidol, in Figure 3(ii), leads to the formation of the dihydroxy end group —$OCH(CH_2OH)_2$. The presence of this end group is manifested in the ^{13}C-NMR spectra of **II** in Figure 2, as a CH_2 peak at 63.4 ppm (similar in position to the other —CH_2OH peaks at 62.8 and 64.6 ppm) and a CH peak at 83.2 ppm (furthest downfield, due to the deshielding effects of two —CH_2OH groups plus the ether oxygen attached directly to the CH carbon). These selfsame peaks were present in the spectra of cationically polymerized PGly,[7] but were not assigned. These peaks were absent in the spectra of anionically polymerized PGly[10] because there is no route to the —$OCH(CH_2OH)_2$ end group in the anionic polymerization mechanism. Addition of this terminal unit to the known structural units[7,10] of PGly completes the annotation of the ^{13}C-NMR spectrum of this polymer.

Glycidol dimers

The formation of dimers during the cationic polymerization of epoxides is a well-understood process,[15] leading to the formation of substituted 1,4-dioxanes. However, it has been proposed, based in part on the elemental analysis of the products of prolonged heating of glycidol[2] and a study of the anionic polymerization of trimethylsilyl glycidyl ether,[5] that the (predominant) dimer is glycidyl glycerin (**IV**), shown in Figure 4. To establish the identity of the glycidol dimers, we collected them directly during vacuum-distillation of the monomer.



IV

Figure 4 Glycidyl glycerin (**IV**).

The high-boiling liquid which distilled well after glycidol was found by GC analysis to consist of no fewer than four components. GC–MS data (mass spectrum shown is that of largest peak in chromatogram) are displayed in Figure 5. Mass spectra of all four components were fairly similar and corresponded to bis(hydroxymethyl)-substituted 1,4-dioxanes of formula $C_6H_{12}O_4$ (MW 148 g/mol), consistent with what would be expected for glycidol dimers. The ^{13}C-NMR spectrum of the dimers in CD_2Cl_2 is shown in Figure 6. A separate spectrum in $CDCl_3$ (not shown, since the solvent peak interfered with the dimer peaks) had no peaks below 60 ppm, indicating a complete absence of epoxide rings in the dimers, thereby eliminating glycidyl glycerin as a possible thermal dimer. The spec-

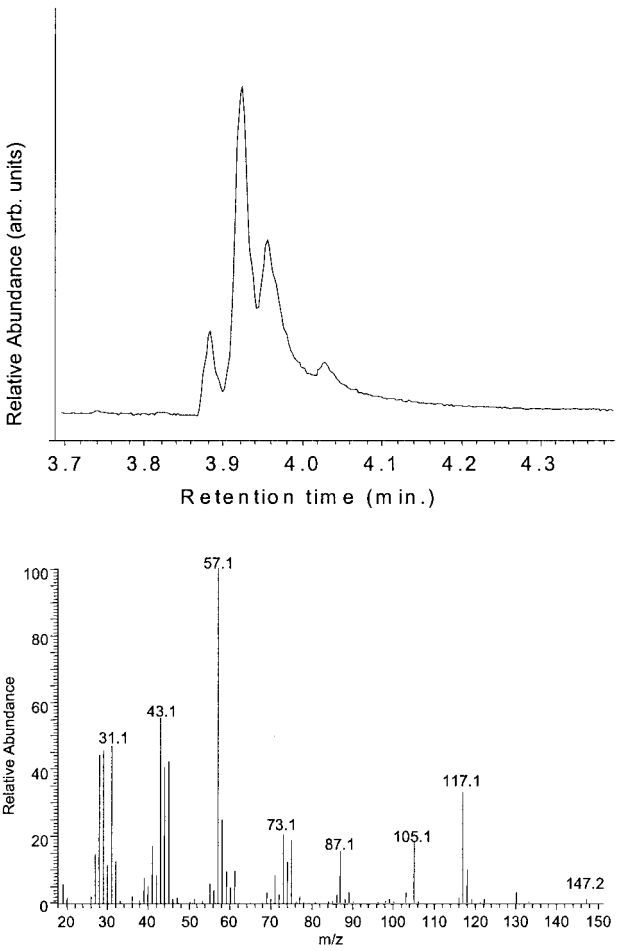


Figure 5 GC–MS analysis of glycidol dimers. Mass spectrum shown is of the tallest peak in the chromatogram.

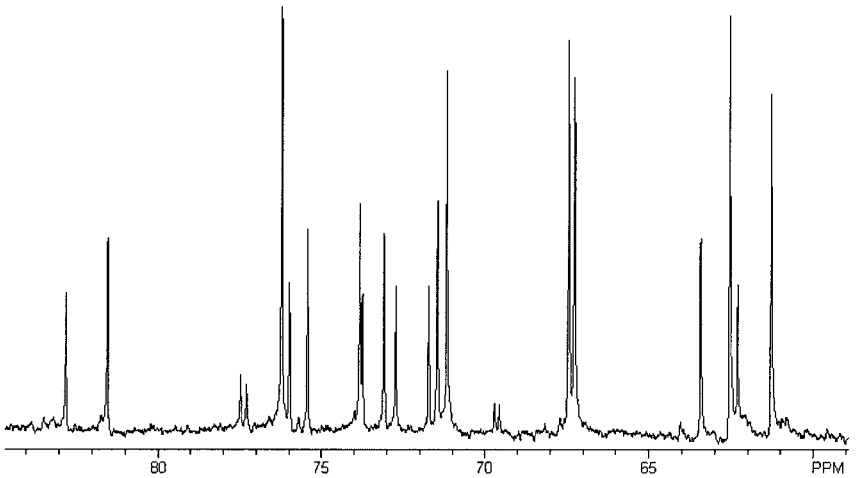


Figure 6 ^{13}C-NMR spectrum of glycidol thermal dimers in CD_2Cl_2.

trum in Figure 6 is seen to contain a large number of peaks, consistent with GC data showing the presence of a mixture of dimers. All the peaks in the spectrum are in the proper range for O-bonded CH and CH_2 carbons. Several of these peaks are also seen in the spectra of **I** and **III** (low molecular weight fraction of PGly) in Figure 2, but not in the spectrum of **II** (high molecular weight fraction), confirming that glycidol dimers constitute a sizable part of the low molecular weight fraction.

The formation of 2,5-bis(hydroxymethyl)-1,4-dioxane (**V**) and 2,6-bis(hydroxymethyl)-1,4-dioxane (**VI**) by the canonical dimerization process is shown in Figure 7. Ether groups in the polymer backbone act as nucleophiles in this process. The hydroxyl groups in PGly are, however, better nucleophiles than are the ether groups, so it is more likely that cyclodimerization involves nucleophilic attack by OH. This process is shown in Figure 8 for the four different diglycidol ions of the ACE mechanism and is found to yield the same dimers **V** and **VI** as before. Larger seven- and eight-membered rings may also be formed, but this is less likely due to the higher ring strain associated with such species.

Each of the dimers **V** and **VI** can exist in *cis* and *trans* configurations (Fig. 9). *cis*-2,5-Bis(hydroxymethyl)-1,4-dioxane (**V-A**) and *trans*-2,6-bis(hydroxymethyl)-1,4-dioxane (**VI-B**) should give rise to six distinct peaks each in the ^{13}C-NMR spectrum, since each has six nonequivalent carbons. *trans*-2,5-Bis(hydroxymethyl)-1,4-dioxane (**V-B**) and *cis*-2,6-bis(hydroxymethyl)-1,4-dioxane (**VI-A**), which are more symmetric, contain three nonequivalent carbons each and should therefore yield only three peaks each. Thus, a total of 18 peaks should be seen in the ^{13}C-NMR spectrum of the dimers, and this is precisely what is observed in Figure 6 (not counting the much smaller peaks at ca. 69.7 and 77.3 ppm, which are probably due to impurities). It is therefore entirely plausible to conclude that the thermal dimers of glycidol are the molecules shown in Figure 9.

Storage and long-term stability

It was noted in our laboratory that freshly prepared PGly stored for a period of a few days in a normal atmosphere increased in weight and decreased in vis-

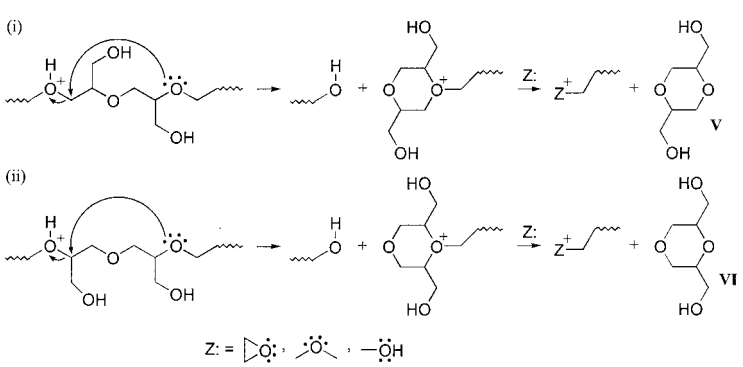


Figure 7 Dimer formation—normal "backbiting" mechanism.

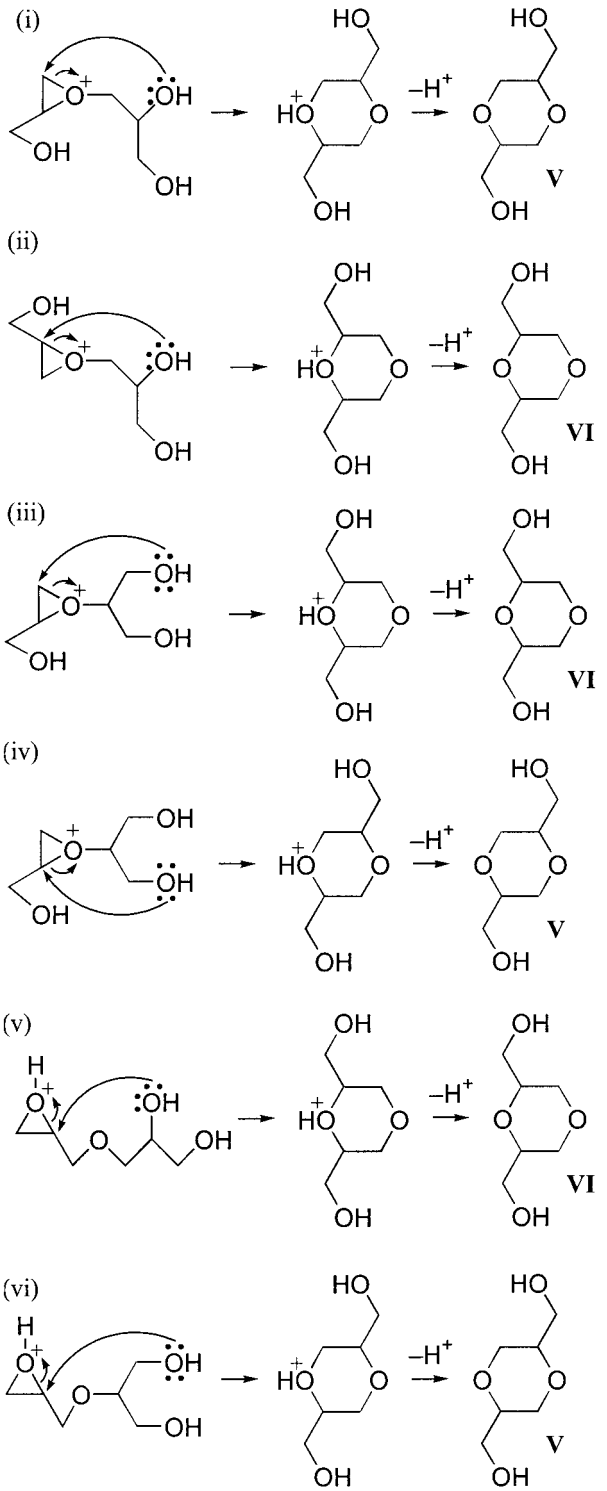


Figure 8 Dimer formation—nucleophilic attack by hydroxyl groups.

cosity. Careful redrying and weighing revealed that PGly had picked up approximately 4–5% of moisture from the air. It is therefore recommended that this polymer be stored in a desiccator and that polymer samples be carefully dried prior to analysis.

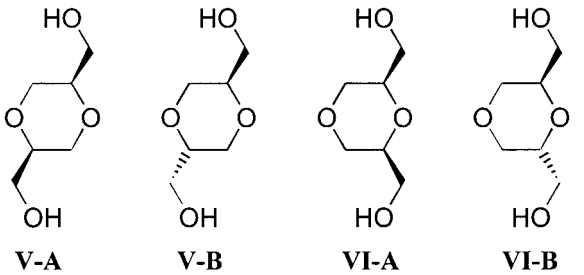


Figure 9 Thermal dimers of glycidol: *cis*-2,5-bis(hydroxymethyl)-1,4-dioxane (**V-A**); *trans*-2,5-bis(hydroxymethyl)-1,4-dioxane (**V-B**); *cis*-2,6-bis(hydroxymethyl)-1,4-dioxane (**VI-A**); and *trans*-2,6-bis(hydroxymethyl)-1,4-dioxane (**VI-B**).

Samples of PGly stored for 1–2 years in our laboratory were found to have turned into insoluble, rubbery masses. These materials, when placed in water, swelled to many times their original volume, but did not dissolve. Glass transition temperatures were found to be very sensitive to the moisture content and were measured by DSC using vacuum-dried samples of newly made and aged polymers. The results are shown in Table II. It is clear that T_g increases with increasing age, and this is suggestive of crosslinking. Heating the freshly made polymer overnight at 110°C also turned the polymer into an insoluble rubber, with a concomitant loss in weight (ca. 10%), probably due to dehydration. We believe that the PGly samples stored for the long term had undergone an acid-catalyzed crosslinking reaction via dehydration, as shown in Figure 10. On the basis of these observations, we believe that cationically polymerized PGly should be used as quickly as possible after synthesis, within a few months at the most.

CONCLUSIONS

We have reported a method for purifying cationically polymerized PGly from the low molecular weight contaminants that are formed during its synthesis. A proposed step (nucleophilic attack by glycidol OH groups in the ACE pathway) in the polymerization mechanism of glycidol helps to annotate fully the ^{13}C-NMR spectrum of PGly. The four different thermal dimers of glycidol have also been isolated and identified for the first time as *cis*- and *trans*-2,5-bis(hydroxymethyl)-

TABLE II
Glass Transition Temperatures of New and Old Samples of PGly

Age of PGly sample (months)	T_g (°C)
1	−41.0
18	−39.3
27	−37.9

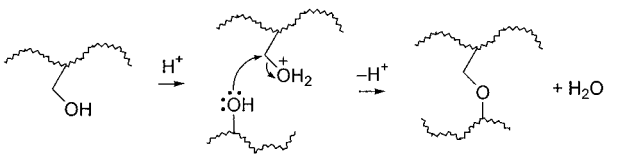


Figure 10 Acid-catalyzed crosslinking of PGly chains, with concurrent dehydration.

1,4-dioxane and *cis*- and *trans*-2,6-bis(hydroxymethyl)-1,4-dioxane. It was found that PGly is hygroscopic and turns into an insoluble, rubbery mass upon long-term (1–2-year) storage. It is therefore recommended that this polymer be stored dry and used within a few months of the initial synthesis.

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