Z-Protected Glutamic Acid-Based Biodegradable Thermoplastic and Thermosetting Polyesters: Synthesis and Characterization

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ABSTRACT: Biodegradable polymers were formed from *N*-benzyloxycarbonyl-L-glutamic acid with the comonomers ethylene glycol, diglycidyl ether of 1,4-butanediol, and diglycidyl ether of bisphenol A. The three polymers were a linear and a crosslinked heterochain polyester and a crosslinked polyester that contained aromatic units within its network chains. The thermoplastic resin and the soluble fractions for the thermosetting resins were characterized by gel permeation chromatography. Conversions for carboxylic acid were determined by titrations. A quality, 22,000 molecular weight thermoplastic resin was formed. The two thermosets were cured past their gel points. Gelation analysis revealed that the relative rate constants for the sequential oxirane/acid and alcohol/acid reactions were distinct. With diglycidyl ether of 1,4-butanediol, the ratio of the respective rate constants was 3; with diglycidyl ether of bisphenol A, the ratio approached 200. The resins hydrolyzed to monomers in the presence of lipase, but in the presence of a mixed microbial culture, only the first two resins decayed to biomass, respiratory gases, and water. The third resin was inert during the period of observation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 869–879, 1999

Key words: amino-protected glutamic acid; biodegradable polymers; gelation; polymer networks; polyesters

INTRODUCTION

The development of biodegradable polymers using value-added, renewable agricultural resources was a prime motivation for this research. Annually, an enormous tonnage of plastics is sent to waste-disposal systems, such as landfills. Synthetic, organic polymers resist natural degradation due to variables that include a low surface area per unit mass, chemical structure, and high molecular weight. Degradation may be initiated through environmentally induced changes which transform the polymer into smaller segments. To be classified as biodegradable, these fragments should decay via microorganisms into biomass, respiratory gases, and water. In tertiary recycling, polymers decay to monomers.[1] Potential uses of biodegradable polymers include controlled release formulations for drugs, the preparation of surgical implants, agricultural chemicals, and agricultural mulch. In this article, the synthesis and characterization of three quality polymers with distinct chain configurations is addressed. Companion articles discuss the results of biodegradation studies.

Soybean protein and its derivatives were a focus of polymer research in the 1930s and 1940s. Today, proteins are used to form grafted, syn-

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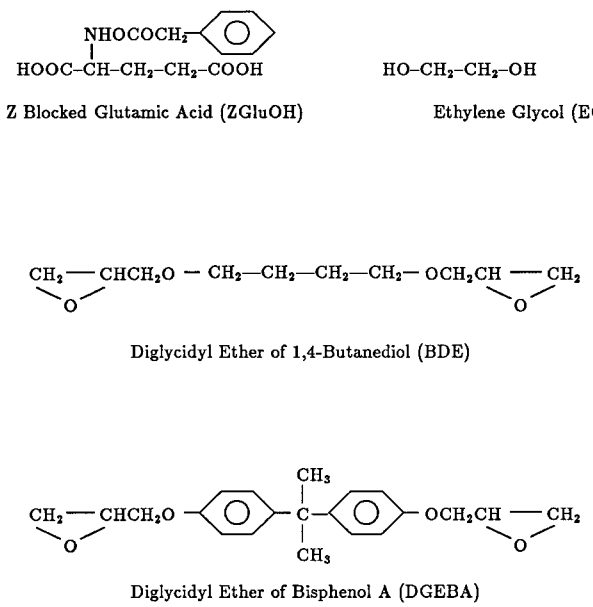

Figure 1 Chemical formulas for monomers.

thetic copolymers as well as protein-based biodegradable plastics.[2] In general, mixed monomers reduce a plastic's physical properties. Therefore, instead of using complex protein molecules, glutamic acid was selected to produce resins with regular chain configurations. Glutamic acid is a major component of oil-seed proteins, representing the order of 20% of their amino acid content. Several methods are available for separating glutamic acid from hydrolyzed amino acids.[3–5] It is also produced by fermentation. In addition, poly(L-glutamic acid) is a biodegradable material[6] and a block copolymer between poly(γ-ethyl-L-glutamate) and polybutadiene is biocompatible as well as biodegradable.[7] A review of the literature regarding biodegradability further directed the research toward the chemical design and synthesis of polyesters.[8]

Glutamic acid is an α-amino acid containing two carboxylic acids and one amino group. Heating glutamic acid with a diol can result in the formation of a cyclic amide, a five-member lactam. In addition, dipeptides easily cycle to six-member diketopiperazines. These are major side reactions encountered in peptide synthesis.[9,10] In our work, oligomeric-forming side reactions were observed to occur in abundance. Cyclization was controlled through protection of the α-amino group using benzyloxycarbonyl (Z) (see Fig. 1). Different amino-protecting groups were discussed by Jones.[9] Since polyesterifications are acid-catalyzed reactions, the benzyloxycarbonyl group (Ar—CH_2—O—CO—) was selected due to its stability under acidic conditions.[11] Comonomer structures also appear in Figure 1.

Glutamic acid is amphoteric, that is, it can act as an acid or as a base in an aqueous medium of different pH. The suitable pH for activating the acid form of the amino acid is lower than the isoionic point for each ionization group. In acidic aqueous media, the amino acid is an active acid and thus directs a synthesis toward forming polyesters with dioles. Pramanick and Rey[12] reported the formation of a 4000 molecular weight polymer with ethylene glycol in an aqueous acidic medium. Since our goal was to synthesize higher molecular weight resins, we did not explore this avenue. Bulk polymerizations with protected amino acids were selected.

For the second monomers, a diol and diepoxies were chosen. The diol yields a thermoplastic; diepoxies yield thermosets. An epoxy moiety initially opens during the polymerization, forming a hydroxyl group and an ester linkage. The hydroxyl site then couples with a second carboxyl group, forming a second ester bond and water. The functionality for a diepoxy monomer is four, and networks form (see Fig. 2). In this sketch, functionality is emphasized. The diepoxy branch node is represented by a tetrafunctional chain link. The amino acid is expressed by a bifunctional chain link. The order for reactions is labeled 1st and 2nd, arbitrarily, for discussion. On the upper right, an unreacted epoxy is represented by two unreacted branches; at the lower right, an unreacted alcohol is indicated by one unreacted branch. In the interior of the sketch, both the oxirane and formed alcohol have reacted. Variables appearing on the sketch will be discussed in the section on gelation. The Z-protecting group is not indicated but is pendent to the bifunctional chain links.

EXPERIMENTAL

Materials

Benzyloxycarbonyl-L-glutamic acid (ZGluOH) and L-glutamic acid (HGluOH) (Aldrich), ethylene glycol (EG; Fisher), diglycidyl ether of 1,4-butanediol (DGEB; Ciba Chemical), and diglycidyl ether of bisphenol A (DGEBA; Shell Chemical) were used as received. Tetrahydrofuran (THF; Quaker Oats) was the mobil phase during GPC fractionations. In studies designed to address the thermal stabil-

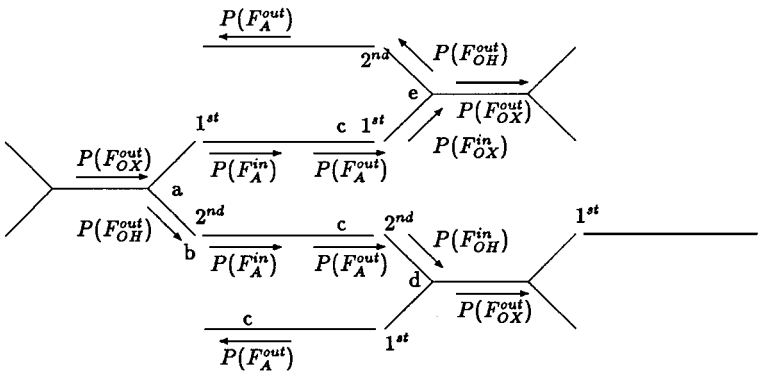

Figure 2 A cluster of network chain segments: stochastic gel-structural parameters related to rubber elasticity for arbitrary oxirane 1st and hydroxyl 2nd reactions.

ity of the *Z* protection, the monofunctional 1-nonanol (Aldrich) was reacted with ZGluOH. Fractionations used reversed-phase high-performance chromatography (HPLC). The mobil phase was a gradient of acetonitrile (Aldrich) and water. The catalyst was *p*-toluene sulfonic acid (PTS).

Thermal Stability of the Amino Protection

In discussing the thermal stability of urethanes, Stevens[13] stated that a polycarbamate derived from aliphatic-based monomers can be melt-processed at 180°C, but warns that the higher temperatures needed for melt polymerization of resins formulated with aromatic diisocyanates tend to cause dissociation into alcohol and isocyanate or degradation into amines, olefins, and carbon dioxide. In our formulations, alcoholysis was of concern. To examine the stability of the *Z*-protecting group, a carbamate, the reaction between ZGluOH and the monofunctional alcohol 1-nonanol was studied using HPLC. Batch reactions with formulations based on stoichiometry ratios of acids/alcohols at 170°C and atmospheric pressure were conducted. The condensation product water was allowed to escape from the reactor. If appreciable levels of alcoholysis occurred, esters of varying chemical composition would be observed through fractionations. In a 2-h interval, the formation of mono- and diesters was readily observed. Similar compounds formed in the presence of alcoholysis were not observed. Therefore, we concluded that the major polymerization site would be the carboxylic acid moiety. A Waters chromatograph was used with a μ-bondapak C_{18} column, 3.9 $\times$ 300 mm. The gradient of 40–90% acetonitrile/water was conducted over 1 h. An ultraviolet detector at 280 nm was used. The reaction was catalyzed with PTS.

Polymerization Procedures

Thermoplastic Resin

In an initial polymerization, HGluOH/EG/PTS was melt-mixed with a molar ratio of 1/1/0.01. The polymerization proceeded by amidization/esterification reactions. Water was stripped under a vacuum (400 mmHg) from a batch reactor to shift the chemical equilibrium toward higher conversions.[1,14] A slow stream of inert gas (N_2) was bubbled through the molten mix to assist with moisture removal and to limit resin oxidation. The reaction temperature was maintained within 1°C of the set point, 170°C. This procedure was then modified by melt-mixing ZGluOH/EG/PTS with a stoichiometric ratio of 1/1.08/0.01. In latter stages of the cure, excess ethylene glycol was stripped from the reactor during transesterification reactions.[1] Isothermal cure temperatures were 110 and 170°C. Samples ($\simeq$0.1 g) were analyzed through end-group analysis and gel permeation chromatography (GPC).[15,16]

The reactor apparatus consisted of a 100-cc round, Pyrex glass flask. A glass tube about 10 cm long was used to admit a stream of nitrogen to bubble through the molten resin. Another tube was used for removing samples. A type-K thermocouple allowed temperatures to be observed. The apparatus was heated in a temperature-regulated liquid bath.

Thermoset Resins

ZGluOH/diepoxy/PTS polyesters were prepared by melt-mixing the molar ratios of 1.0/1.0/0.02. To limit the extent of crosslinking, the acid group was selected as the limiting reactive site. The polymer mix was initially placed into a 50-mL

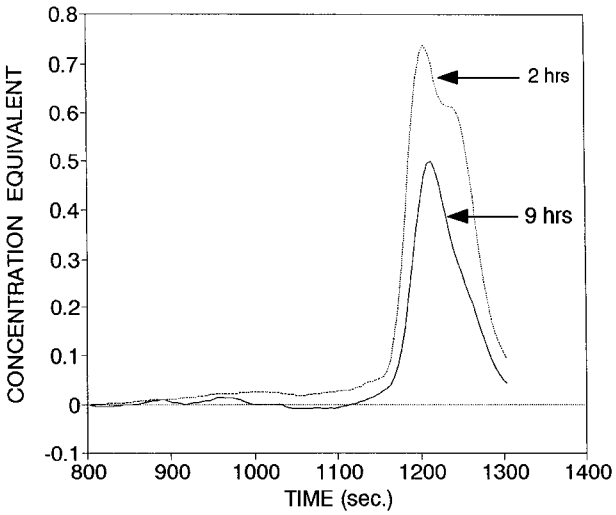

Figure 3 Ethylene glycol–glutamic acid cyclization.

glass beaker and warmed in a preheated, forced-air, electric oven. The chosen, set-point temperatures ranged between 110 and 130°C, ±0.5°C. After 15 min of preheating, approximately 5 mL of the molten mixture was poured into each 10-mL glass tube. The tubes were placed in the oven at the same initial temperature. At different time intervals, a polymerization sample was withdrawn and thermally quenched. The oven was blanketed with nitrogen.

Characterization

Gel Permeation Chromatography

A Waters GPC was equipped with five Ultrastyragel columns of 2 × 100, 500, and 2 × 1000 Å and a differential refractometer. The mobil THF phase was at 0.5 mL/min. Fractionations were at ambient temperature. For miscible materials, 75 mg was dissolved in 50 mL of THF and 0.5 mL of this solution was injected. For thermosets, between 0.2 and 0.3 g was placed with 20 mL of THF in a cylindrical, thick-walled brass container and extracted at a temperature in excess of the specimen's glass transition temperature (T_g). The insoluble gel fraction was dried at 70°C under a vacuum and weighed. The soluble sol fraction was diluted to approximately 75 mg in 50 mL of THF for analysis. The average molecular weight of the oligomeric fraction was compared to a polystyrene semilogarithmic correlation of the standard's molecular weight as a function of its peak elution volume.

End-Group Analysis

On average, a linear polymeric chain has a single carboxylic group. The carboxylic groups in the resin were titrated against KOH using phenolphthalein as an indicator. The polymer samples were dissolved in 50 mL of chloroform. The KOH was dissolved in methyl alcohol to form a 0.01*N* KOH solution. A clear, sharp, color change occurred at the end point. To measure conversion, a similar procedure was followed for the thermosets. Samples were initially finely ground and allowed to swell in the solvent before titration. Titrations were conducted over an interval of time under nitrogen until the end point became stable for at least 24 h.

DATA ANALYSES

Linear Resins

Reaction Dynamics

For the HGluOH/EG/PTS resin, samples collected at different times were screened by GPC. Samples cured for 2 and 9 h indicated a minimal change in molecular weight (see Fig. 3). Molecular weights were close to that for the monomers. Cyclic structures likely formed.[9,10] ZGluOH/EG/PTS was polymerized under the same conditions. With the protected amine group, molecular weight advanced. A quality resin formed. In Figure 4, shifts in chromatograms reveal the development of polymeric materials with advancing cure time.

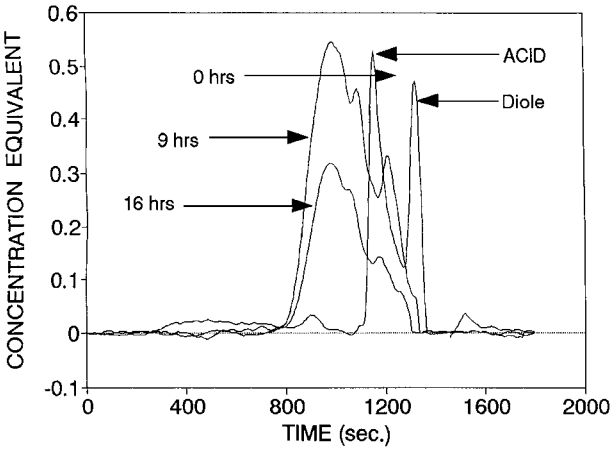

Figure 4 Development of polymers using *Z*-protected glutamic acid.

Table I Conversion and Number-Average Molecular Weight Dynamics, ZGluOH/BDE/PTS Cured at 110°C

Time (h)	Carboxylic Group (mol/g polymer)	Extent of Reaction	Average Molecular Weight
0	0.0079		
0.5	0.0063	0.208	440
1	0.0060	0.236	455
1.5	0.0058	0.271	480
2	0.0055	0.299	495
3	0.0053	0.326	515
6	0.0051	0.356	540
9	0.0047	0.408	585
12	0.0043	0.461	640
15	0.0042	0.467	650
18	0.0035	0.557	780
24	0.0033	0.582	830

Table II Conversion and Number-Average Molecular Weight Dynamics, ZGluOH/DGEBA/PTS Cured at 170°C

Time (h)	Carboxylic Group (mol/g polymer)	Extent of Reaction	Average Molecular Weight
0	0.0079		
2	0.0019	0.760	1450
4	0.0013	0.835	2100
6	0.0009	0.886	3000
8	0.0006	0.928	4800
10.25	0.0002	0.975	14,000
16	0.0001	0.984	22,000

End-Group Analysis

The conversion of acid sites ρ may be expressed in terms of the cumulative molar concentration of molecules within the resin:

$$\rho = \frac{P_1(0) - \sum P_i}{P_1(0)} \quad (1)$$

The molar concentration of all molecules that contain i monomeric links is P_i. If i is even, the molecule contains one unreacted carboxylic group and one unreacted alcohol group. When i is odd, half of these molecules contain two acid sites or two alcohol moieties. Subject to a balanced stoichiometry, their molar concentrations are equal. On average, each molecule of degree of polymerization i contains one acid group.

The number-average molecular weight is

$$MW_n = MW/(1 - \rho) \quad (2)$$

where the average molecular weight of the chain link is MW.

The data tabulated in Tables I and II summarize the end-group dynamics, the calculated extents of reaction [eq. (1)], and the resins' number-average molecular weights [eq. (2)] for cures at 110 and 170°C as functions of time. After 16 h at 170°C, a quality polymer with a molecular weight of 22,000 had formed.

Polymerization dynamics did not yield expected second-order responses.[17] Conversion data correlate as a semilogarithmic function of time (see Fig. 5), with correlation coefficients of 0.97 at 110°C and 0.94 at 170°C. Several factors could contribute to a pseudo-, first-order reaction. Initially, reaction rate constants were considered. Flory[17] observed that rate constants for esterification reactions are dependent on the number of atoms separating carboxyl groups when these atoms are few in number. For the current resin, only three carbon atoms separate the functional groups. Due to electron shielding and steric factors, the first reacting chemical moiety could experience a distinct rate constant.[18] A second consideration is attributed to rate constants becoming conversion-dependent. At higher conversions,

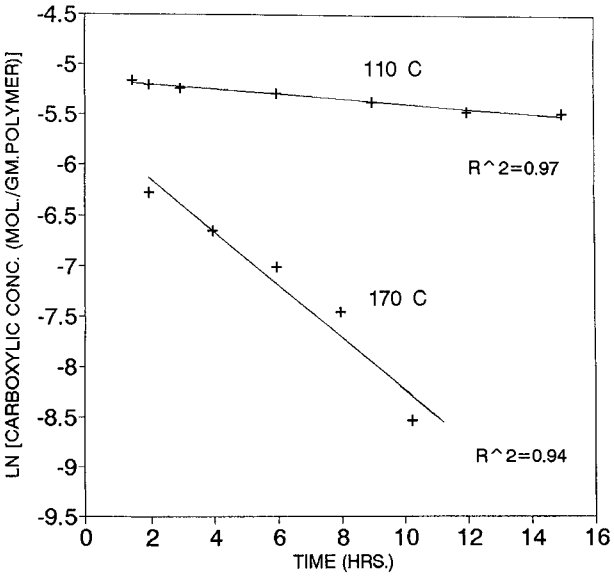

Figure 5 Carboxylic acid conversion as a function of time and reaction temperature.

reaction rates, change for example, due to vitrification[19] and to changing dielectric constants.[20] Finally, chemical equilibrium was addressed. Physical operating conditions can affect observations. In our research, the concentration of the condensation product C was not controlled or observed. But with increasing reaction times and diminishing rates of formation, its concentration could have varied.

To illustrate the consequences of a variable concentration C, equilibrium reactions $P_i + P_j \rightleftharpoons P_{i+j} + C$ are addressed. Stockmayer[21] and Blatz and Tobolsky[22] showed that the most probable distribution is appropriate for both equilibrium and for kinetically controlled, irreversible reactions. The equilibrium population of molecules may be expressed as a function of monomer concentration P_1, the ratio of the equilibrium constant and the by-product concentration K/C, and conversion ρ_{eq}:

$$P_i/P_1 = (KP_1/C)^{i-1} = \rho_{eq}^{i-1}$$

If equilibrium reactions between oligomers are initially considered, the resulting relationship also fits the above, arbitrary bimolecular reaction. The relationships $MW_n/MW = \Sigma\, iP_i/\Sigma\, P_i = 1/(1 - KP_1/C)$ and eq. (2) were utilized in deriving the second result above. One can see that if the ratio K/C varied during an experiment experimental observations will deviate from the most probable distribution. We believe this could be a major contributor to our observations.

Network Resins

With epoxy monomers, the two oxiranes are separated by a sufficient number of atoms so that their reactivities are independent of oxirane reaction states. This has been confirmed with DGEBA.[18] For mathematical simplicity[23–25] and due to limited data, the chemical reactivities of the two acid groups on ZGluOH were also assumed to be independent of their reaction states. Flory's data indicate that rate constants gradually change with the number of carbon atoms separating the functional groups. As will be discussed, our results indicate substantial changes. Our analysis was constrained to distinct reactivities for oxiranes and alcohols only. Derivations implicitly incorporate vitrification constraints on kinetic constants as reported by Cole[19]:

$$K(\rho) = \frac{K_0}{1 + \exp[\alpha(\rho - \rho_c)]}$$

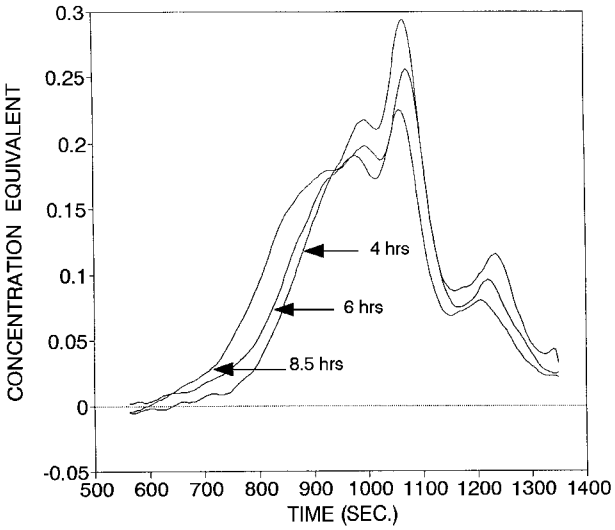

Figure 6 ZGluOH/BDE/PTS polymerization dynamics prior to gelation, 110°C.

This function of conversion indicates that the reaction constant $K(\rho)$ is nearly constant at K_0 for $\rho < \rho_c$, but rapidly decreases at high conversions. The constant α is a data-fitting parameter. Cole assumed reactions to be second-order and irreversible.

Crosslinked Polyesters

ZGluOH/BDE/PTS produced a ductile resin at room temperature with soluble sol and insoluble gel fractions. The chromatograms appearing in Figure 6 show an increasing molecular weight with time of cure at 110°C for a resin before its gel point. Resins cured at 130°C for 5 h resulted in a 12% gel fraction, and for 11.5 h, in a 20% gel fraction. The crosslinked aromatic polyester, ZGluOH/DGEBA/PTS, was cured at 110, 120, and 130°C. Chromatograms appearing in Figure 7 show a gradual increase in the molecular weight of the sol with time of cure at 110°C. Lower molecular weight materials in the elution time interval 1000–1300 s diminish in concentration; higher molecular weight materials appear prior to 1000 s. The resin cured at 130°C for 5 h 40 m yielded a 50% gel fraction. At ambient conditions, the material is hard and brittle.

Reaction Kinetics

A combined kinetic and statistical model was used in the analyses of the thermosetting resins. Distinct rate constants k_{OX} and k_{OH} were assigned to reactions between an epoxy or oxirane

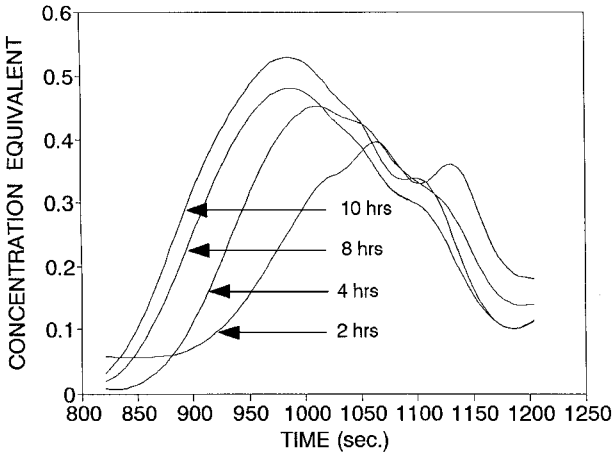

Figure 7 ZGluOH/DGEBA/PTS polymerization dynamics prior to gelation, 110°C.

and a carboxylic acid and between an alcohol and an acid. These rate constants were assumed to be independent of the degree of polymerization. In addition, the isothermal reactions were assumed to be void of intermolecular cyclization reactions. Previous work by Bokar and Gandhi,[23] Gupta and Macosko,[24] and Sarmoria and Miller[25] addressed an amine-cured epoxy when rate constants for primary and secondary amines are distinct with a competing etherification of epoxy groups. Our description[26] is a simplification, in that this minor competing reaction is neglected. Dušek et al.[27] also considered these reactions and formulated a solution using probability-generating functions.

Hydroxyl groups originate from the initial reaction between the carboxylic acid and oxirane moieties. Their reactions produce branch nodes and, ultimately, chain networks. The concentrations of the reactive groups (oxiranes, hydroxyls, and carboxylic acids) are represented by $[OX]$, $[OH]$, and $[A]$. The differential equation describing the molar concentration of oxiranes is

$$d[OX]/dt = -k_{OX}[A][OX]$$

The time t was transformed to the dimensionless time τ by

$$d\tau = k_{OX}[A]dt$$

The solution, subject to the initial condition $[OX]_0$, is

$$[OX] = [OX]_0\exp(-\tau)$$

Therefore, the conversion of oxiranes equals

$$\rho_{OX} = \frac{[OX]_0 - [OX]}{[OX]_0} = 1 - \exp(-\tau)$$

Differentiation plus algebra yield a time-conversion transformation:

$$k_{OX}[A]dt = d\tau = d\rho_{OX}/(1 - \rho_{OX}) \quad (3)$$

The concentration of hydroxyl moieties was expressed in terms of a relative rate constant C, formulation parameter α, and conversion:

$$C = \frac{k_{OH}}{k_{OX}} \quad \text{and} \quad \alpha = \frac{[OX]_0}{[A]_0}$$

For a balanced stoichiometry, $\alpha = \frac{1}{2}$. In our polymerizations, carboxylic acid sites were limiting, $\alpha = 1$. The differential equation describing the molar concentration of hydroxyl sites is

$$d[OH]/dt = -k_{OH}[A][OH] + k_{OX}[A][OX]$$

In the first rate term, the consumption of the hydroxyl groups by reactions with carboxylic groups is addressed. The second rate expression describes the formation of hydroxyls by reactions between carboxylic acids and oxiranes. The total number of hydroxyl sites formed at any time equals the number of oxiranes reacted $[OX]_0\rho_{OX}$. The solution incorporated an integration factor and is expressed in terms of the hydroxyl conversion ρ_{OH}:

$$\rho_{OH} = \frac{1 - C\rho_{OX} - (1 - \rho_{OX})^C}{(1 - C)\rho_{OX}} \quad (4)$$

The differential equation describing the molar concentration of carboxylic acids is

$$d[A]/dt = -k_{OH}[A][OH] - k_{OX}[A][OX]$$

The rate expressions describe the consumption of carboxylic groups by reactions with hydroxyl groups and oxiranes, respectively. The solution expressed in conversion ρ_A is

$$\rho_A = \frac{\alpha}{(1 - C)}[1 + \rho_{OX} - 2C\rho_{OX} - (1 - \rho_{OX})^C] \quad (5)$$

Expectation Theory

Probability functions express the expectation that a reactive site is attached to chain segments of finite dimension, given all possible events. The sketch of a chain segment appearing in Figure 2 is referenced in the following derivation: Chain functionality is emphasized. The epoxy monomer is described as the tetrafunctional link and the bifunctional ZGluOH is described as the linear connector. An oxirane site on a branch node at a is considered. The probability that it is attached to chains of finite dimension looking out of the branch node is represented by $P(F_{OX}^{\text{out}})$. If the oxirane originally at a is unreacted (probability of $1 - \rho_{OX}$), the chain terminates. Alternately, the oxirane is reacted (probability of ρ_{OX}). The probability function looking into the ester bond formed (labeled 1st in Fig. 2) is indicated as $P(F_A^{\text{in}})$. The likelihood that the formed hydroxyl is also part of a finite chain extension $P(F_{OH}^{\text{out}})$ must also be addressed. Therefore, the expectation that a randomly selected oxirane leads to two finite chain segments at this branch point is

$$P(F_{OX}^{\text{out}}) = 1 - \rho_{OX} + \rho_{OX}P(F_A^{\text{in}})P(F_{OH}^{\text{out}}) \quad (6)$$

The expectation that a hydroxyl site is connected to a finite chain extension $P(F_{OH}^{\text{out}})$ at b depends on its reaction state. The probability that this group is unreacted equals $1 - \rho_{OH}$. If it is reacted, the probability is ρ_{OH}. In Figure 2, this site is labeled b. Therefore,

$$P(F_{OH}^{\text{out}}) = 1 - \rho_{OH} + \rho_{OH}P(F_A^{\text{in}}) \quad (7)$$

When looking into a bifunctional connecting link, the likelihood that this reacted site is part of a finite chain segment $P(F_A^{\text{in}})$ equals the probability $P(F_A^{\text{out}})$ that its second acid site is attached to finite structures:

$$P(F_A^{\text{in}}) = P(F_A^{\text{out}}) \quad (8)$$

The reaction state of this second acid site is a function of three independent events: (1) The carboxylic acid may be unreacted (probability of $1 - \rho_a$). (2) The acid group may have reacted with an oxirane. This event is labeled 1st at location c in Figure 2. The quantity $\alpha\rho_{OX}$ equals the number of reacted oxiranes per carboxylic acids initially present. The fraction of reacted acid sites is ρ_A. This yields the second term in eq. (9). (3) The acid site reacted with a hydroxyl group. This event is represented by point c, 2nd. The quantity $\alpha\rho_{OX}$ also equals the number of hydroxyl sites that have formed at the time of observation, relative to the initial concentration of acid groups. The fraction of hydroxyl sites reacted is ρ_{OH}. This event contributes the last expression in the conditional probability function $P(F_A^{\text{out}})$:

$$P(F_A^{\text{out}}) = 1 - \rho_A + \rho_A\left\{\frac{\alpha\rho_{OX}}{\rho_A}P(F_{OX}^{\text{in}}) + \frac{\alpha\rho_{OX}\rho_{OH}}{\rho_A}P(F_{OH}^{\text{in}})\right\} \quad (9)$$

When a branch node is entered from a reacted hydroxyl as at point c, 2nd, the likelihood that the exiting two chain segments are finite is labeled $P(F_{OH}^{\text{in}})$. The probability that finite structures are attached at the second oxirane of the tetrafunctional link is $P(F_{OX}^{\text{out}})$. The probability of a finite chain extension at the reacted oxirane branch point is $P(F_A^{\text{in}}) = P(F_A^{\text{out}})$:

$$P(F_{OH}^{\text{in}}) = P(F_{OX}^{\text{out}})P(F_A^{\text{out}}) \quad (10)$$

Alternately, a branch node is entered from a reacted acid site through the bond that formed when the oxirane reacted (see point c, 1st). The resulting branch point leads to conditional probability functions $P(F_{OX}^{\text{out}})$ at the second oxirane and $P(F_{OH}^{\text{out}})$ at the formed hydroxyl. Point e may be referenced. For these independent events,

$$P(F_{OX}^{\text{in}}) = P(F_{OX}^{\text{out}})P(F_{OH}^{\text{out}}) \quad (11)$$

Equations (6)–(11) yield a cubic equation with roots $P(F_A^{\text{out}}) = 1$ and

$$P(F_A^{\text{out}}) = -\frac{\alpha\rho_{OX}^2\rho_{OH}(3 - \rho_{OH})}{4\alpha\rho_{OX}^2\rho_{OX}^2} + \frac{\sqrt{\begin{array}{l}(\alpha\rho_{OX}^2\rho_{OH}(3 - \rho_{OH}))^2 - 4(2\alpha\rho_{OX}^2\rho_{OH}^2) \\ \quad \times (\alpha\rho_{OX}^2(1 - \rho_{OH})^2 + 2\alpha\rho_{OX}\rho_{OH} - 1)\end{array}}}{4\alpha\rho_{OX}^2\rho_{OH}^2} \quad (12)$$

when $\rho > \rho_c$, $P(F_A^{\text{out}}) < 1$, and when $\rho \leq \rho_c$, $P(F_A^{\text{out}}) = 1$, since all chains are finite. Therefore, eq. (12) may be evaluated for the critical conversion ρ_c for gelation. For example, if $C = 2.0$ and $P(F_A^{\text{out}}) = 1$, $\rho_A = 0.75 = \rho_c$. Recall that eqs. (4)

and (5) correlate the conversion of hydroxyl and acid moieties as functions of oxirane conversion.

Sol Fraction

Relationships partitioning a monomeric link between the sol and gel are now derived. The mol fraction of branch nodes in the sol is labeled ω_{OX}. The fraction of branch nodes in the gel equals $1 - \omega_{OX}$. For a chain link to be in the sol, each of its reactive sites must be part of finite chains. Therefore, the fraction of epoxy units including the monomer in the sol equals

$$\omega_{OX} = [P(F_{OX}^{\text{out}})]^2 \tag{13}$$

The mol fraction of connecting links in the sol equals

$$\omega_A = [P(F_A)^{\text{out}}]^2 \tag{14}$$

The mass fraction of the resin that is soluble is

$$\text{mass}_{\text{sol}} = \frac{MW_{OX}\alpha\omega_{OX} + MW_A\omega_A}{MW_{OX}\alpha + MW_A} \tag{15}$$

where the molecular weights of the epoxy monomer and ZGluOH are MW_{OX} and MW_A.

Branch Node Distributions

In the theory of rubber elasticity, the modulus of elasticity is a function of the number of elastically active junctions that contain three or more chain extensions to the gel.[28,29] Thermoset resins become elastomeric at temperatures exceeding their glass transition temperature T_g. For our resin systems, branch nodes evolve from the diepoxy monomers and are labeled $n_{ROX,ROH}$. The initial index $0 \leq ROX \leq 2$ indicates the number of oxiranes reacted and the second index $0 \leq ROH \leq ROX$ indicates the number of hydroxyls formed that have reacted. In conversion space, a series of first-order reactions associated with the formation and consumption of nodes yields their mol fractions:

$$n_{ROX,ROH} = C_{ROX,ROH}\rho_{OX}^{ROX}(1 - \rho_{OX})^{2-ROX}\rho_{OH}^{ROH} \times (1 - \rho_{OH})^{ROX-ROH} \tag{16}$$

where the coefficient $C_{ROX,ROH} = 1$ unless ROX and/or $ROH = 1$, then $C_{ROX,ROH} = 2$. Kernels address the reaction states of the two functional groups, and, as appropriate, their powers equal the number of these sites reacted or unreacted. Subject to reaction constraints and normalization, the coefficient correlates permutations.

Crosslinks $X_{m,0}$ that contribute to the modulus are nodes that contain a minimum of three chain extensions to the gel or network. Such chains are considered to be infinite.[28,29] The initial subscript is the number of reacted sites, and looking out of the node, the second subscript is the number of these sites attached to the network. Since each reacted site is attached to a bifunctional link, the probability that it extends to the gel is $1 - P(F_A^{\text{out}})$. The normalized molar concentration of elastically active nodes equals[26]:

$$X_{3,3} = n_{2,1}[1 - P(F_A^{\text{out}})]^3$$

$$X_{4,3} = n_{2,2}4P(F_A^{\text{out}})[1 - P(F_A^{\text{out}})]^3$$

$$X_{4,4} = n_{2,2}[1 - P(F_A^{\text{out}})]^4 \tag{17}$$

Analysis of Relative Rate Constant

The conversion of carboxylic acid and the sol fraction for the crosslinked ZGluOH/BDE/PTS sample cured for $11\frac{1}{2}$ h at 130°C was 76 and 80%, respectively. Subject to model constraints and assumptions, eqs. (6)–(15) were solved with eqs. (4) and (5) to determine the value for the relative rate constant C. When $C = 3.0$, the calculated sol mass fraction is 81%, and conversions ρ_{OX} and ρ_{OH} equal 0.47 and 0.60 when ρ_A is 0.76. The rate constant for carboxylic acid reactions with oxiranes is smaller than that with hydroxyl moieties; tetrafunctional chain segments have a preference for branching. The molecular theory of rubber elasticity[28,29] predicts that a resin with more elastically active junctions will have a higher modulus at temperatures above T_g. The resin produced was rubbery, indicating a relatively low level of crosslinking.

For the crosslinked ZGluOH/DGEBA/PTS polymer sample cured for 5 h 40 min at 130°C, the average value for the acid's conversion was 68% and the sol fraction was 0.50. For a solution with $C = 200$, a sol fraction of 0.51 subject to conversions $\rho_A = 0.68$, $\rho_{OH} = 0.99$, and $\rho_{OX} = 0.36$ was calculated. Not only did this resin contain a chain-stiffening, aromatic component within its chain links, but the conversion of hydroxyls to esters also was nearly complete. A high degree of branching and crosslinking occurred. The resin was brittle at ambient temperature.

Crosslink Distributions

To further characterize the network structure, the relative distribution of nodes that contribute to the modulus and other physical properties was calculated. Subject to experimental measurements of conversion and regression estimates of C, the fraction of tetrafunctional branch nodes with three or four extensions to the gel for the resin ZGluOH/BDE/PTS is $X_{3,3} = 7.1 \times 10^{-5}$, $X_{4,3} = 9.3 \times 10^{-5}$, and $X_{4,4} = 1.1 \times 10^{-5}$, and for the resin ZGluOH/DGEBA/PTS, $X_{3,3} = 4.1 \times 10^{-5}$, $X_{4,3} = 3.1 \times 10^{-3}$, and $X_{4,4} = 1.5 \times 10^{-3}$. Although both resins contain a relatively large sol fraction due to an imbalanced stoichiometry and low extent of conversion, the results clearly demonstrate the increased level of network branching in the latter resin. The large value for the relative rate constant C results in a ratio of $X_{4,4}/X_{4,3} = 0.5$ in the resin composed of aromatic chain links (compared to 0.1 for the first thermoset). These numbers show that when an oxirane reacts the formed hydroxyl group is converted to an ester bond at once, forming a branch point in the chain. This chemistry leads to network configurations.

DISCUSSION

A major research objective was to produce quality thermoplastic and thermoset resins from an amino acid. The results of our studies indicate that the thermoplastic resin formulated from ZGluOH/EG/PTS had an average molecular weight of 22,000. Many commercial step-growth resins have similar average molecular weights. Analysis of the thermosetting resins identified their respective gel fractions at a final conversion. These data were incorporated into gelation theory to calculate the relative rate constants for reactions involving oxiranes and alcohols with carboxylic acids. Results indicate that the two rate constants are not equal and that their relative magnitudes are influenced by the chain structure. These observations are consistent with observations for amine-cured epoxies. Aliphatic or aromatic segments significantly alter the reactivities of primary and secondary amines.[18] Furthermore, chemical analysis of chemical intermediates in a curing anhydride/epoxy resin[20] revealed that the alcohol moiety is many times more reactive than is the acid group. Our results are also consistent with their observations. For resin systems described by Cole's model for diminishing reaction rates at higher conversions, the relative rate constant C incorporates these effects when the constants α for the oxirane and alcohol reactions are equal.

The network chemical structure that contributes to the rubbery modulus of elasticity was estimated through branch-node distributions. The results reveal the effects of the conversion and the relative magnitudes for the distinct rate constants. In the ZGluOH/EG/PTS resin, branch points tend to be farther apart. The crosslink average molecular weight of elastically active strands is greater than that for the ZGluOH/DGEBA/PTS resin. Increased chain flexibility caused by the chemical structure within the chains and the higher crosslink average molecular weight yield a ductile resin at room temperature. The increased chain stiffness caused by aromatic components within the chain links and the lower crosslink average molecular weight contributed to a brittle resin in the second case.

In companion articles, the biodegradability of these three resins is reported. In summary, lipase hydrolized all three resins to the monomers, but in the presence of a mixed microbial culture, only the resins ZGluOH/EG/PTS and ZGluOH/BDE/PTS were reduced to biomass and respiratory gases.

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