Macromolecules **2001,** *34,* 2973−2980

Rheological Behavior and Gel-Point Determination for a Model Lewis Acid-Initiated Chain Growth Epoxy Resin

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Received October 25, 2000; Revised Manuscript Received January 31, 2001

ABSTRACT: The sol−gel transition, or gelation, in a polymer network-forming system is defined as the critical point in the polymerization at which an infinite macromolecule is formed. There are many studies in the literature concerning the exact and accurate determination of the gel point and its interpretation in terms of the critical conversions of reactant functional groups. However, these have mainly involved step-growth polymerizations with few studies of chain-growth polymerizations such as that described in this study. Chemorheological studies on a cationically polymerized epoxy network-forming system are used to determine accurate gel times and critical conversions, which are interpreted in terms of classical branching and chemical bond percolation models for nonlinear polymerizations. Rheological studies during the polymerization of a trifunctional epoxide monomer, using BF_3 as the Lewis acid initiator, yielded a gel conversion of 0.17 ± 0.02 and a power law dependence for the development of shear modulus, with a critical exponent $n = 0.64 \pm 0.03$, which is shown to be independent of temperature and BF_3 concentration. The viscosity at conversions close to the gel point was shown to vary according to a power law with a critical exponent $k = 1.33 \pm 0.03$ in the pregel region. The critical behavior of this complex network-forming system is shown to be closely predicted by percolation theory.

Introduction

In the processing of network-forming polymers, the most important parameters are the development of viscosity and the gel point. The gel point is defined as the point at which the first macromolecule of infinite dimensions is formed and determines the transition from liquid to solid. The chemical and macroscopic mechanical changes that occur during polymerization in both pre- and postgel regions can be monitored continuously by calorimetric, spectroscopic, and rheological experiments. There have been many studies in the literature that clarify how the gel point is determined accurately from rheological measurements and about the nature of the transition from liquid to solid. However, these studies mainly describe step-growth polymerizations, whereas there have been few studies describing the behavior of chain-growth polymerizations, such as that described in this study.

Viscosity is very sensitive to changes in polymer chain length and branching and is therefore related to molar mass and molar mass distribution.[1] In the case of nonnetwork-forming systems producing linear and branched polymers viscosity determined via solution methods can be used for monitoring structural development. For network-forming systems, however, the viscosity diverges as the gel point is approached, and incipient network formation occurs.[2] The simplest method of determining the gel point from rheological measurements is by the extrapolation of the steady-state viscosity to infinite viscosity,[1] although this method suffers from inaccuracies due to shear thinning with increasing viscosity and by the eventual destruction of the sample as gelation occurs. Errors are also introduced in the extrapolation to infinite viscosity. Divergence of viscosity can also occur due to other phenomena, such as vitrification[3] and/or phase separation,[4] and care must be taken not to mistake these phenomena with chemical gelation.

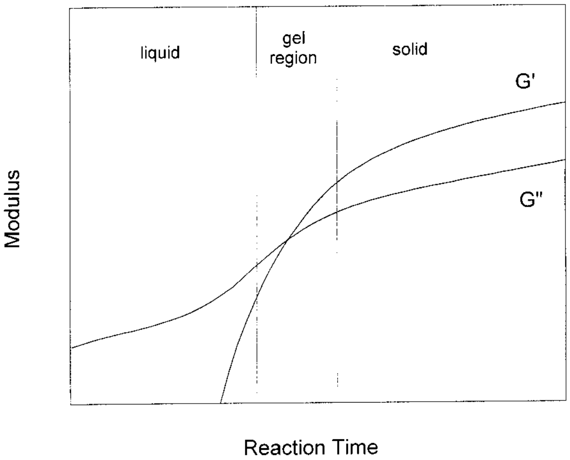

Figure 1. Schematic representation of the dynamic mechanical behavior observed during a cross-linking reaction.

Another method proposed[5] for determining the gel point is the point of crossover of the shear storage (G') and loss (G'') moduli in small-amplitude oscillatory shear experiments. Figure 1 shows the evolution of storage and loss moduli for a typical cross-linking polymerization and the crossover in G' and G'' which is the functional definition of solidification. Initially, in the liquid state, the viscous properties are dominant, and more energy is dissipated than stored and $G'' > G'$. In the solid state and as complete reaction is approached, the elastic properties dominate and more energy is stored than dissipated so that $G' > G''$. Consequently, it was proposed by Tung and Dynes[5] that the point at which $G' = G''$ may be used to define the gel point.

The work of Winter[6−9] has shown that this definition is not universal and only holds true for certain types of

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10.1021/ma001835x CCC: $20.00

Table 1. Values for Critical Exponents Derived from Percolation and Branching Theories[12]

theory	γ	k	n	κ	z
percolation	1.76	1.33	0.67	0.25	2.67
branching	1	0	0.5		

step-growth polymerizations of balanced stoichiometry. Thus, the crossover point of G' and G'' cannot be universally assigned as the gel point. A more general method of detecting gel points from dynamic moduli data is based on the observation[7] that, at the gel point, tan ∂ is independent of frequency and is given by

$$\tan \partial(\omega) = \frac{G''(\omega)}{G'(\omega)} = \tan\left(\frac{n\pi}{2}\right) \qquad (1)$$

Thus, for a cross-linking system subject to a multifrequency, oscillatory shear deformation during formation, the gel point is defined as the reaction time at which tan ∂ becomes independent of frequency. The value of tan ∂ at this point, when substituted into eq 1, then enables the value of the power law exponent n to be determined. Only in the special case where $n = 0.5$ for stoichiometrically balanced network-forming systems can the gel point be determined from G' and G'' plots. To avoid discrepancies due to vitrification effects, the temperature of measurement must be well above the T_g of the finally formed network, that is, $T \geq T_g + 30$ °C.

More recently, it has been shown that the viscoelastic behavior and structure development of network-forming system in the pre- and postgel regions can be predicted by dynamic scaling relationships based on percolation models.[10] Percolation is where bonds randomly connect sites (monomers) on a lattice of arbitrary dimensions and is described in detail elsewhere.[11,12] In the region close to the gel point, critical phenomena occur in properties such as viscosity (η), weight-average molecular weight (M_w), and shear moduli (G', G'', and G^*) and are predicted by power law-dependent expressions with predictable critical exponents. That is

$$M_w = \epsilon^{-\gamma} \qquad \eta = \epsilon^{-k} \qquad G' \propto G'' \propto \omega^{n}$$

$$G' \propto \epsilon^{z} \qquad \frac{\partial(\log G^*)}{\partial t} \propto \omega^{-\kappa} \qquad (2)$$

where ϵ is a dimensionless parameter characterizing the region around the gel point, defined as

$$\epsilon = \frac{|p_c - p|}{p} \qquad (3)$$

where p is the conversion at any time during the reaction and p_c is the conversion at the gel point. Similar relations are also predicted by branching theory,[12] but different values for the exponents γ, k, and n in eq 2 are obtained. Table 1 summarizes values of the respective exponents for percolation and branching theories.

Percolation predictions were tested experimentally by Adolf et al.[13] using a stoichiometrically balanced epoxy network-forming system: molecular weight measurements gave $\gamma = 1.7 \pm 0.1$, and viscosity measurements gave $k = 1.4 \pm 0.2$, which were both in close agreement with percolation predictions. The dynamic moduli at the gel point followed a power law dependence with the critical exponent $n = 0.70 \pm 0.05$, which again is in close agreement with that predicted by percolation. These studies also showed unexpectedly large critical regions over which agreement with the power law relationship was observed, with the values of k and γ constant over a period of the polymerization corresponding to more than one-third of the pregel reaction. Further studies[14,15] have shown the critical region to be extremely broad, extending over the entire postgel region, that is, up to complete reaction for networks formed by step-growth polymerizations.

In a separate study of a step-growth epoxy resin system,[16] where the stoichiometry was varied from $r = 0.67$ to $r = 2$ ($r = [\mathrm{NH}]/[\mathrm{epoxy}]$), the power law exponent, n, was again shown to be 0.71 over the whole range of reactant ratios, r.

Eloundou et al. studied the temperature dependence of the chemorheological behavior of network-forming systems by evaluating epoxy−amine systems which, when fully reacted, formed both low-[17] and high-T_g[18] networks. At reaction temperatures well above the glass transition the reacting mixtures showed classical behavior, and the values determined for the exponents n and k were found to be in good agreement with those obtained from the percolation theory, with chains obeying the Rouse model.

The power law dependence of the dynamic moduli at the gel point has now been investigated by several authors. For epoxy network-forming systems[13−18] it was shown that the critical exponent $n = 0.67$, in agreement with percolation theory, independent of stoichiometry. For polyurethane[19,20] and siloxane[9] systems, however, the critical exponent n is dependent on stoichiometry and varies from $n = 0.5$ for balanced stoichiometry to $n = 0.67$ for imbalanced stoichiometry. None of the above studies have investigated chain growth polymerizations where the reactant systems are clearly highly nonstoichiometric, and the evolution of network structure can be expected to be different from that of step-growth polymerizations.

In the present study a trifunctional epoxide monomer has been used in a cationic chain-growth polymerization with the Lewis acid, boron trifluoride (BF_3), as initiator. Detailed studies[21−24] on the reaction mechanisms of such epoxide polymerizations have proposed that polymerization proceeds via a combination of the activated chain end and the activated monomer mechanisms, as outlined in Figure 2. The activated monomer mechanism, first proposed by Penczek,[25] is considered to be more favored at higher hydroxyl concentrations. The aim of the present study was to determine the effects of BF_3 concentration and reaction temperature on viscosity development and gel points in epoxy network-forming systems based on chain-growth polymerizations and also to determine whether such polymerizations follow classical branching theory or a percolation model of structure development.

Experimental Section

The epoxide monomer used was ELM 100 (Sumi Epoxy), which is a triglycidyl derivative of the mixed isomers of methyl-substituted aminophenol. The epoxide equivalent weight of ELM 100 was 110.4 ± 1.2 g mol^{-1} as determined by the perchloric acid and tetraethylammonium bromide method[26] of end group analysis. The Lewis acid initiator, BF_3, was complexed directly with the nitrogen atom present in ELM 100, via an interchange reaction with a BF_3−butanol complex. The total butanol content of the formulation was 1.3 wt %, which should become incorporated into the final network structure via the activated monomer mechanism. Network formation

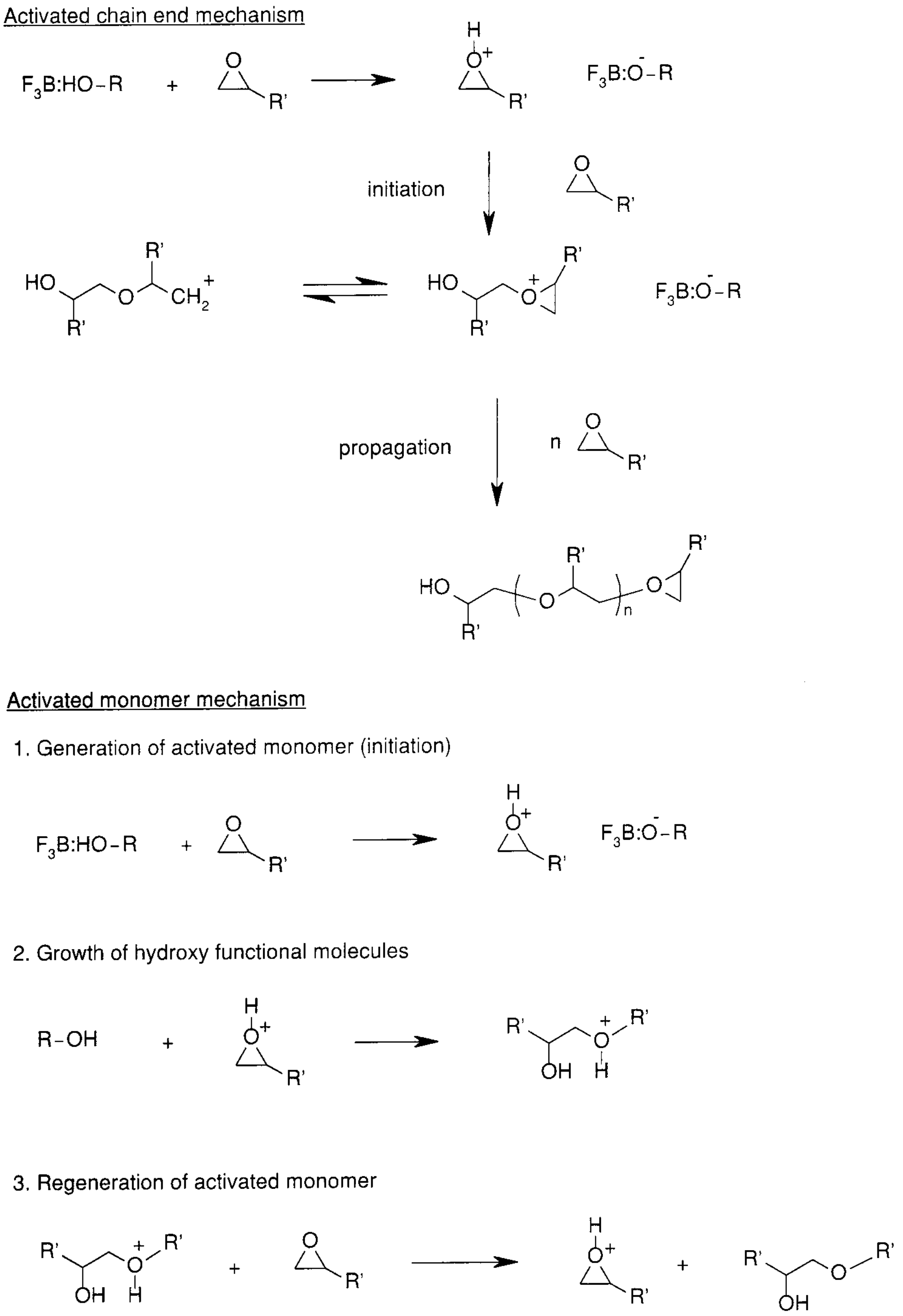
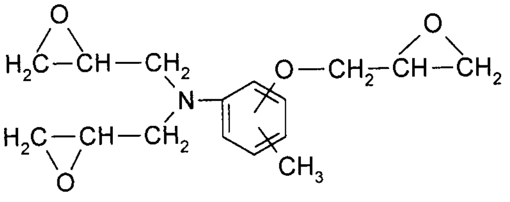


Figure 2. Reaction mechanisms for cationially polymerized epoxy systems.

involved only the homopolymerization of the epoxide monomer, resulting solely from the ring-opening of epoxide groups and chain transfer reactions.



ELM 100

Calorimetry was used to determine extents of reaction of quenched epoxy samples cured isothermally for different times. A Dupont 2000 thermal analyzer equipped with a DSC 990 cell was operated under a nitrogen atmosphere using samples of ~20 mg encapsulated in aluminum pans. Extents of reaction were calculated from residual exotherms, observed in scans over the temperature range 0−250 °C, with heating rates of 10 °C min^{-1}, normalized by the total exotherms for uncured samples. Rheological measurements were made in steady-state and oscillatory shear deformations over a range of isothermal temperatures from 60 to 80 °C, on epoxy network-forming systems with a range of initiator molar concentration ratios of BF_3:epoxy groups of 1:400 to 1:200. All rheological measurements were performed on a Rheometrics RMS 800 rheometer using 50 mm diameter plates with a gap of 1 mm. The viewing port of the oven encasing the test fixture was replaced with a port to allow direct injection of the reactant mixture between the rheometer plates, via a syringe equipped with a 6 in. long needle. Steady-state shear experiments were performed at a shear rate of 1 rad s^{-1} and ranges of different temperatures and initiator concentrations, and the gel points were estimated from divergence of the steady-state shear viscosities. The dynamics of the gel point were determined by oscillatory shear experiments in the multifrequency mode. Measurements were made at six frequencies over the range 1−100 rads s^{-1}. The six frequencies were combined into a single complex oscillation from which the individual frequencies can be resolved by a Fourier transform method using the instrument software. The time taken for a single measurement across the frequency range was 23 s.

Results and Discussion

Reaction Kinetics. Since the only exothermic process occurring in the cationic homopolymerization of the BF_3-ELM 100 system results form the ring-opening of epoxide groups, the theoretical exotherm for full conversion should be directly proportional to the enthalpy of ring-opening of epoxide groups ($\Delta H = 94.5$ kJ mol^{-1}).[27] The enthalpies of reaction for the BF_3-ELM 100 formulations with different molar ratios of BF_3:epoxide groups, determined from the areas under the DSC curves and the extent of reaction, *p*, at any time *t* was calculated from the expression

$$p = \frac{\Delta H_0 - \Delta H_t}{\Delta H_{\text{epoxy}}} \tag{4}$$

where ΔH_t is the residual exotherm after isothermal reaction for time *t*, ΔH_0 is the exotherm for the unreacted material, and ΔH_{epoxy} is the enthalpy for the ring-opening of epoxide groups.

Two series of DSC experiments were carried out. In the first, the conversion of epoxide groups as a function of time was determined at different isothermal reaction temperatures in the range 60−80 °C for network-forming systems with a constant molar ratio of BF_3: epoxide groups = 1:200. In the second, extents of reaction as a function of reaction time were determined for systems in which the molar ratio of BF_3:epoxide groups was varied from 1:400 to 1:200 at a constant temperature of 80 °C. Plots of the extent of reaction of epoxide groups, *p*, as a function of reaction time, at different reaction temperatures and with different catalyst concentrations, are shown in Figure 3. The polymerization reactions do not follow simple integral order kinetics, and previous detailed studies on systems with similar chemistry[22,23] have shown the polymerization to be complex, involving many competing reactions. Studies involving polymerizations of DEGBA, initiated by a BF_3−amine complex dissolved in poly(ethylene glycol), were shown to be first order in epoxy but −0.55 and −0.57 order in BF_3−amine and glycol, respectively.[23] By contrast, polymerizations of a monoepoxide were observed to be first order in epoxy but 0.32 and −0.55 order in BF_3−amine and glycol, respectively.[22] The objective in the present study is to monitor the development of network molecular structure in terms of the rheological changes, obtained as a function of extents of reaction (or conversion) which have been determined from phenomenological correlations of DSC reaction kinetics data according to the expression

$$p = A + Bt^C \tag{5}$$

where *p* is the conversion of epoxide groups, *t* is the isothermal reaction time, and *A*, *B*, and *C* are constants used to fit the DSC data. Conversion−time data obtained at various isothermal cure temperatures and BF_3 concentrations are shown in Figure 3, in which the solid curves through the data were obtained using eq 5. Although the power law relationship employed has no molecular basis, it does provide a semiquantitative basis for transforming the time axes of rheological data into conversion axes.

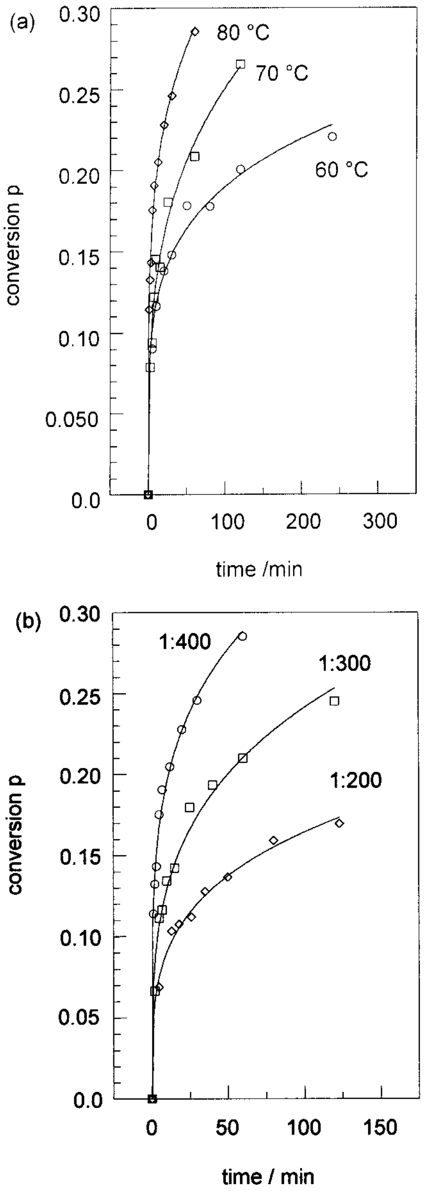


Figure 3. Conversion as a function of reaction time for BF_3-ELM 100 formulations polymerized at (a) different temperatures with BF_3:epoxy = 1:200 and (b) different molar ratios of BF_3:epoxide groups at 80 °C.

Effect of Temperature on the Gel Point. The buildup with time of the steady-state shear viscosity (η) during isothermal reactions, at different temperatures in the range 60 and 80 °C, for the BF_3-ELM 100 model system, with a constant molar ratio of BF_3:epoxy = 1:200, is shown in Figure 4. The time to gelation, t_{gel}, taken as the asymptotic time at which the diverging steady-state viscosity became infinite, varied from approximately 9 min at 80 °C to almost 50 min at 60 °C. Assuming that the gel point occurred at a constant conversion (i.e., the reaction mechanism was independent of temperature), then the dependence at the gel time

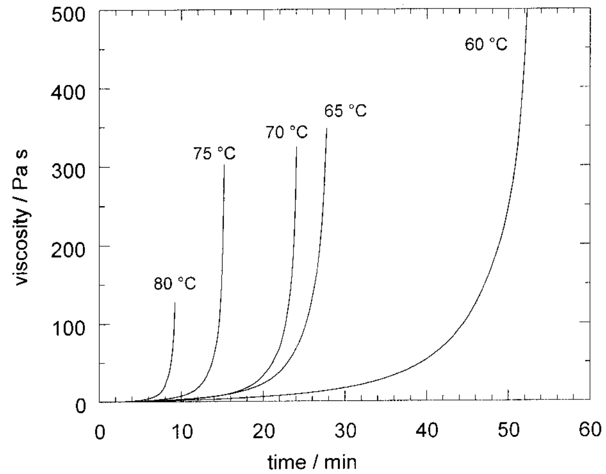


Figure 4. Steady-state shear viscosity (1 Hz) as a function of cure time, at the various temperatures shown by each curve, for a BF_3-ELM 100 formulation with a molar ratio of BF_3:epoxide groups of 1:200.

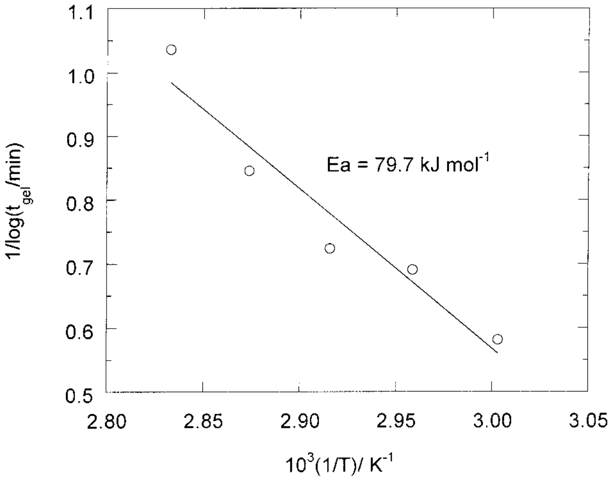


Figure 5. Arrhenius plot of reciprocal gel time as a function of reciprocal reaction temperature, $1/T$, for a BF_3-ELM 100 polymerization with a molar ratio of BF_3:epoxide groups = 1:200.

on temperature may be interpreted using an Arrhenius expression

$$\frac{1}{t_{\text{gel}}} = A\mathrm{e}^{-E_a/RT} \tag{6}$$

Figure 5 shows an Arrhenius plot obtained using eq 6, the slope of which gives an activation energy (E_a) of 79.7 kJ mol^{-1}, a value which is in reasonable agreement with literature data for other cationic epoxy polymerizations.[27] Within the limits of experimental error associated with the DSC and rheological experiments, the gel point for this cationically polymerized triepoxide system is shown to occur at an epoxide group conversion of $p_{\text{gel}} = 0.17 \pm 0.02$ independent of reaction temperature.

Effect of Catalyst Concentration on the Gel Point. The steady-state shear viscosity of the BF_3-ELM 100 model system was measured as a function of reaction time at an isothermal temperature of 80 °C for reactions with molar ratios of BF_3:epoxide groups in the range 1:400 to 1:200. The viscosity as a function of reaction time for these systems is shown in Figure 6. The gel time, taken as the asymptotic time at which the diverging steady-state viscosity became infinite, was shown to exhibit a power law dependence on BF_3 concentration according to the expression

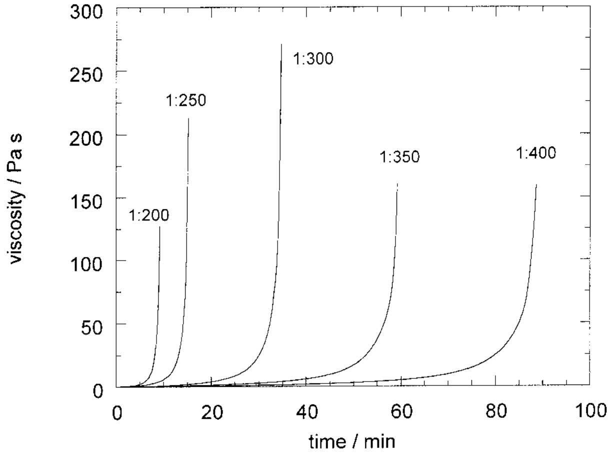


Figure 6. Steady-state shear viscosity (1 Hz), as a function of reaction time for BF_3-ELM 100 polymerizations with different molar ratios of BF_3:epoxide groups, as shown by each curve, reacted isothermally at 80 °C.

$$t_{\text{gel}} = 2.2 \times 10^{-4}[\mathrm{BF_3}]^{-3.4} \tag{7}$$

where the BF_3 concentration is in mol kg^{-1} and the gel time in minutes. As stated previously, the polymerization reactions do not follow simple integral order kinetics,[22,23] and the power law dependence observed in the reaction kinetics gives rise to a power law dependence for the gel time, giving a value of $p_{\text{gel}} = 0.17 \pm 0.02$ independent of initiator concentration. This value is in excellent agreement with the single value of gel conversion obtained as a function of reaction temperature.

Multifrequency Oscillatory Shear Measurements. Multifrequency rheological experiments were performed during BF_3-ELM 100 polymerizations to examine the validity of the $G'-G''$ crossover point as a definition of the gel point and to assess whether percolation theory describes the rheological behavior of the polymerizations close to the gel point. The formulation selected was that with the longest gel time, as determined in previous experiments. That is, the system with a molar ratio of BF_3:epoxide groups = 1:400 reacted isothermally at 80 °C to give $t_{\text{gel}} \sim 90$ min. A relatively slow curing system was required so that any changes due to reaction during the multifrequency sweep would be negligible. Measurements were made over the frequency range 1−100 rads s^{-1}, with six frequencies combined into a single, complex oscillation from which the individual frequencies were resolved by a Fourier transform method using the instrument software. The time taken for a single measurement across the frequency range was 23 s.

The general definition of the gel point is the time at which tan ∂ becomes independent of frequency. Accordingly, rheological data obtained during the reaction period around the $G'-G''$ crossover point were analyzed to give plots of tan ∂ vs frequency. Figure 8 shows that tan ∂ becomes independent of the frequency of the applied oscillation between 81.1 and 83.6 min and that the gel time for this particular formulation is 82.1 ± 0.4 min. The uncertainty in the gel time (±0.4 min) arises from the time (23 s) taken for the frequency sweep in multifrequency rheological experiments.

The critical exponent, n, for the dependence of G' and G'' on the frequency of oscillation is determined from plots of the dynamic moduli at the gel point vs the

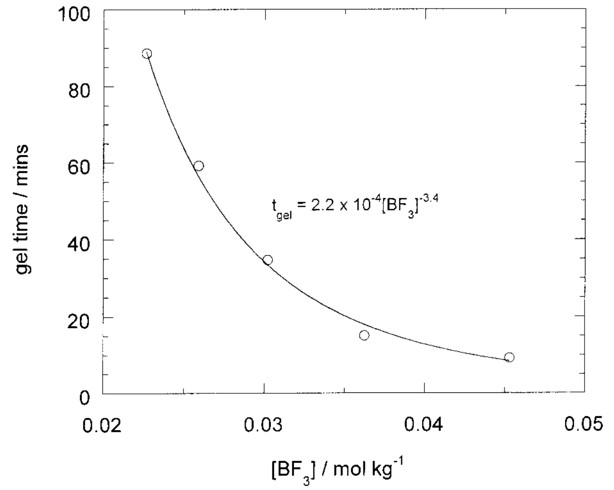


Figure 7. Effect of the molar ratio of BF$_3$:epoxide groups on the gel time of BF$_3$-ELM 100 polymerizations reacted isothermally at 80 °C. Data points (circles) have been fitted by a power law (curve) according to the expression shown alongside the curve.

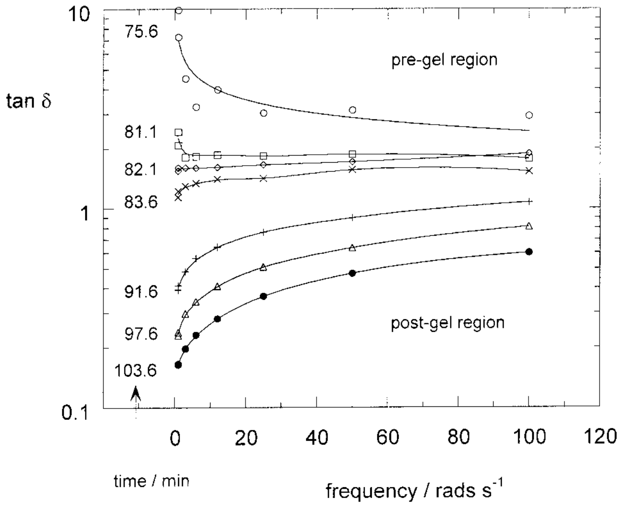


Figure 8. Plots of tan ∂ vs frequency for the determination of the gel point. The gel point is determined as the time at which the tan ∂ vs frequency plot becomes independent of the applied frequency.

applied frequency, as shown in Figure 9. The values of n determined from the G' and G'' data are 0.64 ± 0.04 and 0.61 ± 0.04, respectively. These values are in close agreement with the value of 0.67 predicted by percolation theory[12] and in agreement with observations[6-8,14-18] that, for stoichiometrically imbalanced systems, n is in the range $0.5 \leq n \leq 1$. An alternative method of determining the value of n is from the frequency-independent value of tan ∂ at the gel point given in terms of the expression

$$\tan \partial(\omega) = \frac{G''(\omega)}{G'(\omega)} = \tan\left(\frac{n\pi}{2}\right) \qquad (8)$$

Using eq 8, a value of $n = 0.65 \pm 0.04$ is obtained, which is in good agreement with the values obtained from the frequency relationship of the dynamic moduli. Since the value of n obtained does not equal 0.5, it must be concluded that the crossover of dynamic moduli does not correspond to the gel point. The crossover of dynamic moduli occurs after 85.9 min, which is 3 min after the gel point as determined from the frequency independence of tan ∂. The value of n observed is in good agreement with those observed for epoxy resins cured with amines,[14-18] despite the fact that the reaction mechanisms, that is step growth and cationic chain growth, are significantly different.

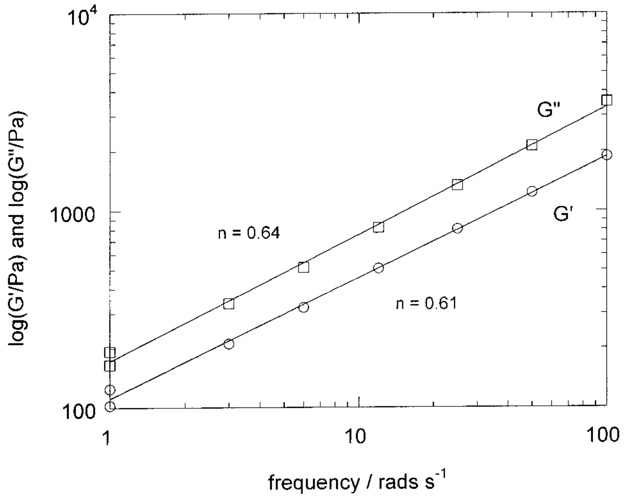


Figure 9. Plots of dynamic moduli (G' and G'') vs frequency at the gel point for the determination of the critical exponent, n, for the power law dependence of the dynamic moduli on frequency. The values of n determined from a linear least-squares analysis are shown by each line.

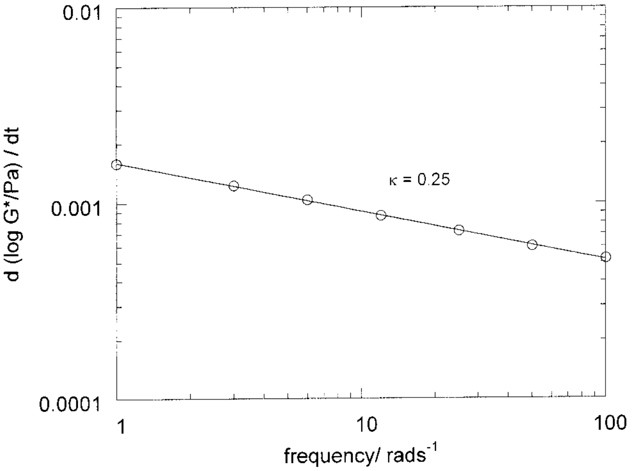


Figure 10. Plot of the derivative of the logarithmic complex modulus vs frequency around the gel point. The value of the critical exponent κ is determined from a linear least-squares analysis of the data shown as a solid line.

In the region of the gel point, plots of d(log G^*)/dt vs frequency enable the critical exponent κ to be determined, as shown in Figure 10 for the system with a molar ratio of BF$_3$:epoxide groups = 1:400 reacted isothermally at 80 °C. The solid line indicates a power law fit to the experimental data and yields a value of $\kappa = 0.25$, which is in agreement with that predicted by percolation theory.

Combined DSC–rheometry data also allow the calculation of the critical exponents that characterize the dependence of dynamic viscosity, η, and storage modulus, G' on ϵ, relative to the extent of reaction around the gel point. The respective equations for the η and G' are

$$\eta = \epsilon^{-k} \qquad G'' = \epsilon^{z} \qquad (9)$$

Equation 7 shows that the quantity $|p_c - p|$ is always

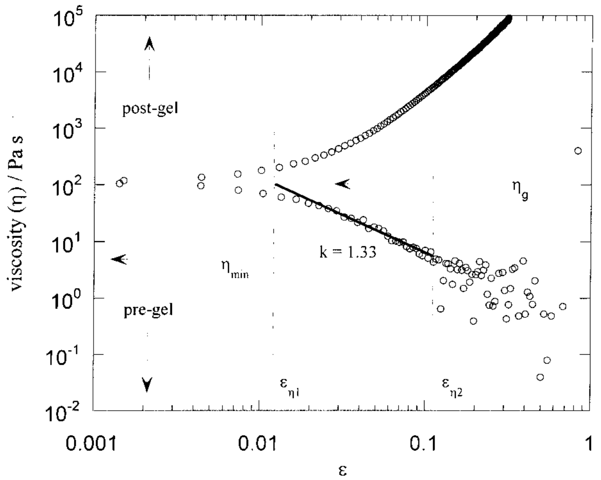


Figure 11. Dynamic viscosity (η) as a function of ϵ, showing the power law dependence of η on ϵ between $\epsilon_{\eta 1}$ and $\epsilon_{\eta 2}$ in the pregel region. The value of viscosity $\eta_{\min}$ signifies the lower limit of accurate rheometer transducer measurements. The viscosity η_g is the point at which the pre- and postgel curves converge and defines the gel point.

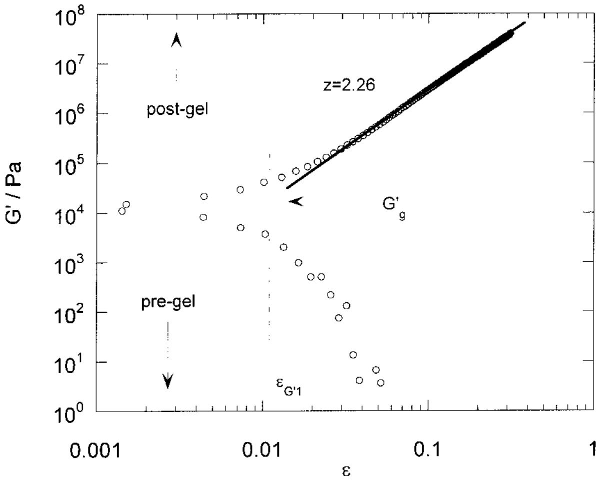


Figure 12. Storage modulus (G') as a function of ϵ, showing G' to exhibit a power law dependence on ϵ in the postgel region for $\epsilon > \epsilon_{G'1}$. The pre- and postgel curves converge at $G' = G'_g$, which defines the gel point.

positive, so that the variation of η and G' with ϵ will give two regions of dependent behavior: one in the pregel region, with a negative slope, and the other in the postgel region with a positive slope. Plots of η and G' as functions of ϵ are shown in Figures 11 and 12, respectively, for a formulation with a molar ratio of BF_3:epoxide groups = 1:400, reacted isothermally at 80 °C. Figure 11 shows that in the pregel region the lower limiting value of η ($=\eta_{\min}$) is governed by the transducer limit, below which the data are very scattered. Where the two curves converge defines the gel point in terms of a critical dynamic viscosity, $\eta_g = 100$ Pa s. In the region between $\epsilon_{\eta 1}$ and $\epsilon_{\eta 2}$, η exhibits a power law dependence on ϵ as indicated by the solid line, and a power law curve fit to the data, in between this pregel region, gives a value of $k = 1.33$ for the power law exponent. This value is in agreement with that ($k = 1.33$) predicted by percolation theory[12] and with the values observed by Eloundou et al.[17,18] and Adolf et al.[14] for epoxy resins formed by step-growth polymerization. Figure 12 shows that in the postgel region there is also a power law dependence of G' on ϵ for values of $\epsilon > \epsilon_{G'1}$, as indicated by the solid line. A power law curve fit to the data in this postgel region gives a value of $z = 2.26$ for the power law exponent. This value is slightly less that the value of 2.67 predicted by percolation theory and can be attributed to the influence of vitrification effects in network-forming systems reacted at temperatures below the glass transition temperature of the fully reacted network.[17] It should be noted that the power law dependence of G' extends almost to the full range of ϵ in the postgel region, an observation that is in agreement with other studies[15−18] on step-growth epoxy polymerizations, and suggests that the critical region extends to high values of ϵ in the postgel region, even up to complete conversion.

Conclusions

The BF_3-ELM 100 polymerization reaction did not follow integral-order kinetics but was fitted with a phenomenological power law. The gel time followed an Arrhenius law with a reasonable activation energy of 79.7 kJ mol^{-1}. The dependence of gel point on temperature was found to occur at $p = 0.17$ and was independent of both the reaction temperature and the initiator concentration. Detailed rheological measurements on the model BF_3-ELM 100 system showed that, for Lewis acid chain-growth polymerizations, the divergence of the steady-state shear viscosity is the best definition of the gel point and that the definition of the $G'-G''$ crossover point as the gel point is not valid. The rheological properties in the region of the gel point have been shown to follow the percolation model, rather than branching theory, for describing theoretically the structure development during the formation of cationically polymerized epoxy networks.

Acknowledgment. This work was kindly funded by Kobe Steel Europe, in the form of a PhD studentship for S. Mortimer in the Materials Science Centre, UMIST.

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MA001835X