Determination of Reaction Activation Energy During Gelation in Free Radical Crosslinking Copolymerization Using the Steady-State Fluorescence Method

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SYNOPSIS

The steady-state fluorescence technique was used to study the sol–gel transition in free radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate (EGDM). Pyrene methyl pivalate was used as a fluorescence probe for the *in situ* polymerization experiments. The times required for the onset of gelation t_c and the critical exponent β were recorded for various EGDM contents and at different polymerization temperatures. A simple kinetic model was used to interpret the experimental gel point data. The results show that the fluorescence technique can be used to measure the critical exponent β, the gel point t_c, and the activation energy during sol–gel phase transition processes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer networks around the gel point have been of interest for several years. A polymer at its gel point is the critical gel and is in a transition state between liquid and solid. The polymer approaches the gel point at a critical extend of reaction, p_c. The polymer before the gel point, $p < p_c$, is called a sol and beyond the gel point, $p_c < p$, is called a gel.

In chemical gelation, the molecules crosslink into larger clusters by forming covalent bonds in various ways. In condensation polymerization, a network is formed by polymerizing bifunctional units, and polyfunctional units serve as crosslinkers. Free radical crosslinking copolymerization (FCC) has also been widely used to synthesize polymer gels. Several theories have been developed in the past half century to describe gel formation in FCC, among which percolation theory provides a basis for modeling sol–gel phase transition.[1-3] The percolation models based on simulation in n-dimensional space can predict critical exponents for gel fraction, weight-average degree of polymerization, radius of gyration, etc. near

the sol–gel phase transition called the critical region. This theory is, however, unrealistic outside of this region due to the difficulty of introduction of realistic mobilities. Another type of theories are called mean-field theories, such as the statistical and kinetic theories based on a "tree approximation." Statistical theories originate from Flory[4] and Stockmayer[5] and assume equal reactivities of functional groups and the absence of cyclization reactions. The critical exponents in percolation theory differ from those found in Flory–Stockmayer. In FCC, the formation of bonds building the network can be described using differential equations with reaction time or monomer conversion as the independent variable. The kinetic approaches can take into account all the kinetic features of copolymerization and crosslinking reactions, which may suggest a more realistic approach to the mechanism of the gelation process.[6-9] Kinetic models have been extensively used to describe the relations among the molecular weight of polymer and the conversion or reaction time during the crosslinking process. In the classical kinetic theory, the rate constant is proportional to the product of the number of functional groups in each reactant. Modification of the classical kinetic theory by using rate constants that also depend on the structural features of the reactants has been done.[10]

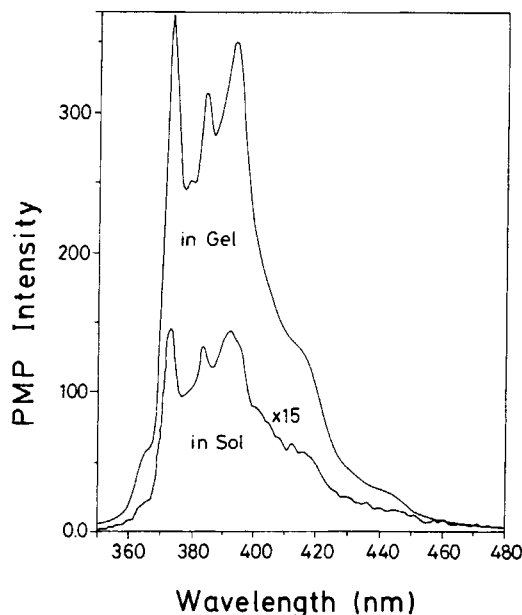* To whom correspondence should be addressed.

Figure 1 Fluorescence emission spectra of PMP, before and after the gelation process. Molecules are excited at 345 nm.

Steady-state fluorescence spectra of many chromophores are sensitive to the polarity of their environment. The interactions between the chromophore and the solvent molecules affect the energy difference between the ground and the excited states. This energy difference is called the Stokes shift, and it depends on the refractive index and dielectric constant of the solvent. Recently, by measuring the Stokes shift of a polarity-sensitive fluorescence molecule, the gelation during epoxy curing was monitored as a function of cure time.[11] Time-resolved and steady-state fluorescence techniques were employed to study isotactic polystyrene in its gel state. Excimer spectra were used to monitor the existence of two different conformations in the gel state of polystyrene. Pyrene derivative was used as a fluorescence molecule to monitor the polymerization, aging, and drying of aluminosilicate gels.[11] These results were interpreted in terms of the chemical changes occurring during the sol–gel process and the interactions between the chromophores and the sol–gel matrix. Recently we reported *in situ* observations of the sol–gel phase transition in free radical crosslinking copolymerization using the fluorescence technique.[12] The bond percolation model was employed to obtain some critical exponents of sol–gel transitions of such a system.

In this article we use quenching properties of the excited state of a fluorescing molecule to study the sol–gel transition in FCC of methyl methacrylate

(MMA) and ethylene glycol dimethacrylate (EGDM). Pyrene methyl pivalate (PMP) is used as a fluorescence probe for the *in situ* polymerization experiments. The times required for the onset of gelation t_c are recorded for various EGDM contents at a constant polymerization temperature. The t_c values at various polymerization temperatures are also detected for a given EGDM content. To interpret the experimental data, a simple kinetic model is employed. A random band percolation model is used to measure the gel fraction exponent at t_c for each gelation experiment.

THEORETICAL CONSIDERATIONS

Fluorescence Method

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and nonradiative processes.[13] If the possibility of perturbation due to oxygen is excluded, the radiative probabilities are found to be relatively independent of environment and even of molecular species. Environmental effects on nonradiative transitions which are primarily intramolecular in nature are believed to arise from a breakdown of the Born–Oppenheimer approximation.[14] The role of the sol-
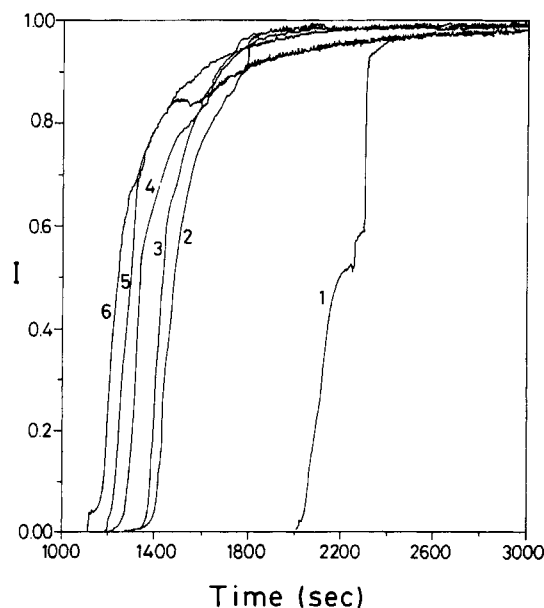

Figure 2 Plots of PMP fluorescence intensity I against reaction time during FCC. The time-driven mode of the spectrometer was employed, and the maximum intensity peak at 395 nm was monitored for data collection. The numbers 1, 2, 3, 4, 5, and 6 correspond to samples of increasing EGDM content.
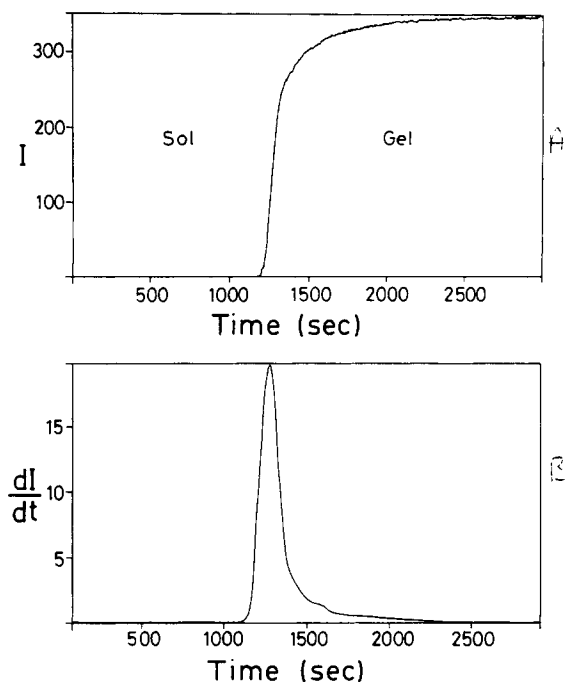
Figure 3 Determination of gel point t_c. Plots of PMP fluorescence intensity I (a) and its first derivative dI/dt (b) against the reaction time t. The maximum corresponds to t_c in the t axis.

Figure 5 Variation in PMP intensity I versus reaction time t during FCC at elevated temperatures. The numbers 1, 2, 3, 4, 5, and 6 correspond to temperatures 65, 70, 75, 80, and 85°C, respectively.

vent in such a picture is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The solvent acts as an energy sink for rapid vibrational relaxation, which occurs after the rate-limiting transition from the initial state.

Years ago, Birks et al. studied the influence of solvent viscosity on fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is af-
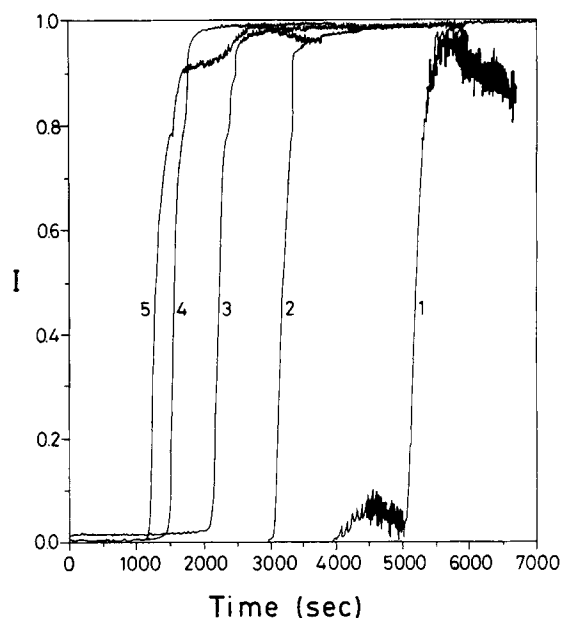
fected by solvent quality.[15] Weber et al. reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence yield with the static quenching, caused by the solvent-induced trapping states.[16] As the temperature of liquid solution is varied, the environment about the molecule changes and much of the change in absorption spectra and fluorescence yields in solution can be related to the changes in solvent viscosity. A matrix that changes little with temperature will enable one to study molecular prop-
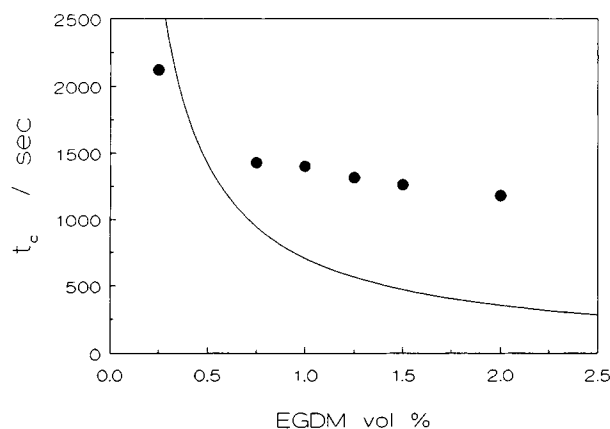

Figure 4 Gelation time t_c shown as a function of the EGDM concentration in FCC of MMA and EGDM at 75°C. The experimental data are shown as symbols. The curve was computed with Eq. (2) by a least-squares curve-fitting method.
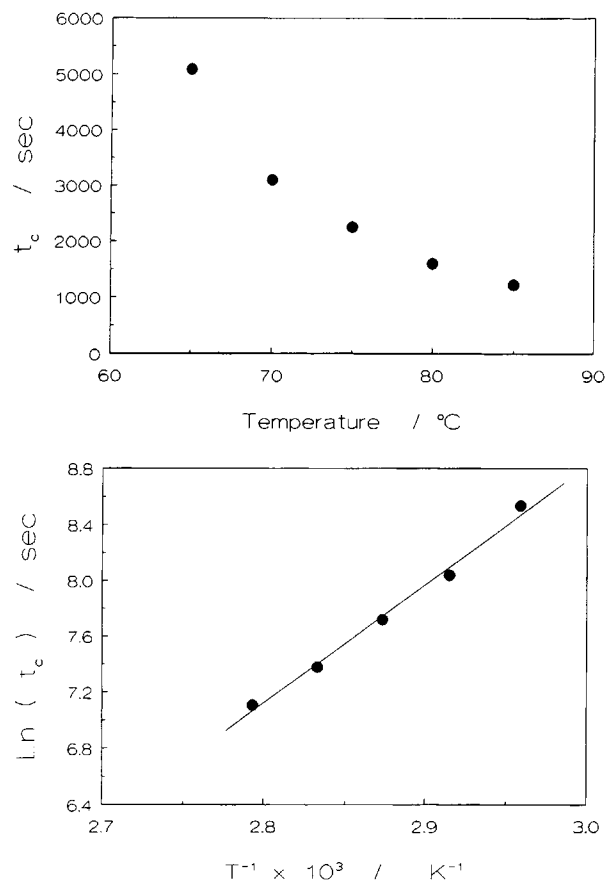
Figure 6 (a) Plot of t_c versus temperature during FCC. (b) Fit of the data in (a) to Eq. (4). The slope of the straight line gives total FCC activation energy ($\Delta E = 17.18$ kcal/mol).

erties themselves without changing environmental influence. Poly(methyl methacrylate) (PMMA) has been used as such a matrix in many studies.[17] Recently we have reported viscosity effects on low-frequency, intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles.[18]

Lattice Bond Percolation Model

In this work these properties of aromatic molecules were used to monitor the sol–gel phase transition in FCC. We employed the lattice percolation model,[2] in which monomers are thought to occupy the sites of a periodic lattice. Between two nearest neighbors of this lattice sites a bond is formed randomly with the probability p. Thus, for $p = 0$, no bonds have been formed and all monomers remain isolated clusters. However, in the other extreme (i.e., for $p = 1$), all monomers in the lattice have clustered into one infinite network. This network is called a gel, and a collection of finite clusters is called a sol. An

infinite cluster starts to appear at $p = p_c$. This point is called the gel point; for p below p_c only a sol exists, but for p above p_c both sol and gel coexist. Thus, gelation is a phase transition from a state without gel to a state with gel.[2] The sol–gel transition happens in "asymptopia," which is in general given by the following relation[2]:

$$G = B(p - p_c)^\beta \tag{1}$$

with a suitable constant β, called the critical exponent.[19] Here G is the gel fraction, which is nonzero for p above p_c. The asymptotic proportionality factor B is referred as the critical amplitude.

Kinetic Model

The first step in free radical polymerization is the decomposition of the initiator molecule into two species carrying unpaired electrons called free radicals. A free radical can then react to open the double bond of a vinyl monomer and add to it, with one electron remaining unpaired. In a very short time, usually a few seconds or less, many more monomers add successively to the growing chain. Finally, two radicals react to end each other's growth activity and form one or more polymer molecules.[20] During the FCC, the addition of divinyl monomers to the growing chain results in the formation of polymer molecules with reactive sites ("pendant vinyl groups"). These reactive sites on polymer chains offer the possibility of forming chemical structures of macroscopic dimensions called polymer gels. On the basis of the kinetic equations given previously,[9] the following equation for the critical time required for the onset of gelation t_c can be written

$$t_c = (kc_0)^{-1} \tag{2}$$

where k is a composite rate constant and c_0 is the initial concentration of the divinyl monomer. Note that Eq. (2) assumes steady-state concentration for the radicals and a "short" pregelation period.

The individual rate constants in FCC, k_i, all depend on temperature and can be given in terms of the Arrhenius relation as

$$k_i = A_i \exp(-E_i/RT) \tag{3}$$

where A_i and E_i are the preexponential factor and activation energy for the corresponding individual reaction, respectively. Combining Eqs. (2) and (3), the following equation is obtained for a fixed concentration of the crosslinker:

$$t_c = \text{cons. } \exp(\Delta E / RT) \qquad (4)$$

where ΔE is the activation energy for gel formation reactions. Equations (2) and (4) will be used in the following sections to interpret the results of experiments carried out at constant temperature and crosslinker concentration, respectively.

EXPERIMENTAL

In this work we monitored the sol–gel transition in FCC of MMA and EGDM by using the *in situ* steady-state fluorescence technique. Here mainly two sets of FCC experiments were performed; in the first set, different EGDM content was used for each FCC experiment at a constant temperature (75°C). In the second experimental set, FCC reactions were performed separately at 65, 70, 75, 80, and 85°C temperatures for constant EGDM content (0.5 vol %). In both sets of experiments, gelation was monitored against reaction time t. The radical copolymerization of MMA and EGDM was performed in bulk in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. PMP was used as a fluorescence probe to detect the gelation process, where below p_c, MMA, linear, and branched PMMA chains act as an energy sink for the excited PMP, but above p_c the PMMA network provides an ideal, unchanged environment for the excited PMP molecules. Naturally, from these experiments one may expect a drastic increase in fluorescence intensity I of PMP around the gel point.

EGDM has been commonly used as a crosslinker in the synthesis of polymeric networks.[21] Here, for our use, the monomers MMA (Merck) and EGDM (Merck) were freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water, and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator, AIBN (Merck), was recrystallized twice from methanol.

In situ steady-state fluorescence measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller. All measurements were made at the 90°C position, and slit widths were kept at 2.5 mm.

RESULTS AND DISCUSSION

AIBN (0.26 wt %) was dissolved in MMA, and this stock solution was divided and transferred into round glass tubes of 15 mm internal diameter for fluorescence measurements. Six different samples were prepared for the first set of experiments with various EGDM contents for bulk polymerization. All samples were deoxygenated by bubbling nitrogen for 10 min, and then radical copolymerization of MMA and EGDM was performed at 75 ± 2°C in the fluorescence accessory of the spectrometer. The PMP molecule was excited at 345 nm during *in situ* experiments, and variation in fluorescence emission intensity I was monitored with the time-drive mode of the spectrometer, by staying at the 395-nm peak of the PMP spectrum. A typical PMP spectrum is shown in Figure 1. No shift was observed in the wavelength of the maximum intensity of PMP, and all samples kept their transparency during the polymerization process. Scattering light from the samples was also monitored during gelation experiments, and no serious variation was detected at 345 nm intensity. Normalized PMP intensities versus reaction times are plotted in Figure 2 for samples with various crosslinker (EGDM) contents. Gelation curves in Figure 2 represent asymptotic behaviors, which give evidence to critical phenomena.

To quantify the aforementioned results, we assumed that the reaction time t for the polymerization is proportional to the probability p and the fluorescence intensity I monitors the growing gel fraction G; then Eq. (1) can be written as

$$I = A(t - t_c)^\beta \qquad (5)$$

Here, the critical time t_c corresponds to the gel point p_c and A is the new critical amplitude. The t_c can be determined by taking the first derivative of the experimentally obtained I curve with respect to t. Figures 3(a) and 3(b) present the curve I and its first derivative (dI/dt) against t, respectively, for sample 5 in Figure 2. The maximum in dI/dt curve corresponds to the inflection point in curve I, which gives the t_c, in the time axis. Below t_c, since PMP molecules are free, they can interact and be quenched by sol molecules; as a result, I presents small values. However, above t_c, since most of the PMP molecules are frozen in the EGDM network, I intensity gives very large values. The critical exponents β were determined from the plot of $\log I = \log A + \beta \log(t - t_c)$ and found to be around 0.40, in accord with our previous observations.[12] Gelation times t_c were shifted to smaller values as EGDM content increased, but β values were found independent of the EGDM content. The average value of β (=0.40 ± 0.03) was found to be slightly smaller than the value that was found from computer simulations.[2]

Figure 4 shows a plot of the critical time for gelation t_c versus EGDM concentration for a fixed polymerization temperature. The experimental data points are shown as symbols. The curve in the figure was computed with Eq. (2) by a least-squares curve-fitting method, which yields the composite rate constant k as $1.4 \times 10^{-3} \text{ s}^{-1}$. It seems that the agreement of the theoretical curve with the experimental data is poor. Gelation occurs much later than calculated by using Eq. (2) and is largely insensitive to the amount of EGDM in the comonomer mixture for EGDM concentrations above 0.5%. This may be due to the variation of the individual rate constants of polymerization and crosslinking reactions with the crosslinker concentration. Such a variation was observed previously due to the conversion-dependent kinetics of FCC.[22] Experimental studies indicate that as the crosslinker content increases, the reactivity of pendant vinyl groups for intermolecular links decreases[23] (i.e., the composite rate constant k decreases with increasing EGDM concentration). Thus, according to the gel point data shown in Figure 4, the increase in the EGDM concentration seems to compare the decrease in the value of k, so that the product kc_0 that is the inverse of t_c becomes insensitive to the EGDM concentration.

PMP intensities versus reaction times are plotted in Figure 5 for samples of constant EGDM content at different temperatures. Gelation curves again present typical critical behavior. The t_c values were determined from the maximum of (dI/dt) curves. Equation (5) was employed to determine β values, and the average value of the critical exponent was found to be around 0.40. In Figure 5 it is seen that as temperature increases, t_c values decrease. The plot of t_c versus temperature is presented in Figure 6(a), and the data are fitted to Eq. (4) in Figure 6(b). The fit looks perfect, and the slope of the straight line in Figure 6(b) gives the total activation energy as $\Delta E = 17.18$ kcal/mol. This value of ΔE seems quite reasonable compared to the result of pure free radical polymerization of MMA monomer, where ΔE was found to be 19.4 kcal/mol for the AIBN initiator.[20]

In summary, this work introduced a novel fluorescence technique to measure the critical exponent β, gel point t_c, and FCC activation energy during the sol–gel phase transition process. The percolation model was used to observe β and t_c values; however, to interpret the temperature dependence of the gel point, a known, simple kinetic model was employed.

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