

Fluorescence Quenching Method for Measuring Monomer Consumption Rates During Free-Radical Crosslinking Copolymerization

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ABSTRACT: The steady-state fluorescence (SSF) technique was used to study the polymerization rate in free-radical crosslinking copolymerization (FCC) of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM). Pyrene (Py) was used as a fluorescent probe for the *in situ* polymerization experiments. The increase in Py intensity was monitored during FCC. The Stern–Volmer kinetic was employed to determine the MMA consumption rate during gelation process for various EGDM contents and at different temperatures. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1907–1913, 2001

Key words: fluorescence; gelation; monomer consumption; polymerization rates

INTRODUCTION

Free-radical crosslinking copolymerization (FCC) has 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 the sol–gel phase transition.^{1–3} Also considered has been mean-field theory, another type of theory, which includes statistical and kinetic theories based on “tree approximation.” The statistical theories originated from Flory⁴ and Stockmayer⁵ and assume equal reactivity 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 copoly-

merization 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 relation during crosslinking process between the molecular weight of the polymer and the conversion or reaction time. In the classical kinetic theory the rate constant is proportional to the product of the number functional groups in each reactant. Modification of this classical kinetic theory has been done by using a rate constant that also depends on the structural features of the reactants.¹⁰

Organic fluorescent dyes can be used to study local environments basically in two types of experiments.^{11,12} When the dye is simply added to the system as a small molecule, it is referred to as a probe, which is available commercially. As a consequence, such experiments are easy to carry out. If a particular experiment allows the dye to be attached covalently to a specific component of a system such as a polymer chain segment, such a dye is referred to as a label. The question can be raised that the presence of the dye perturbs the system or perturbs its own local environments in

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the system. Perturbations are most common where a high dye concentration leads to aggregation and in crystalline systems where the order in the system can be affected by the dye. Perturbations are much less likely when the fluorescent dye is incorporated into an amorphous fluid or glassy phase.

The steady-state fluorescence (SSF) technique was employed to study isotactic polystyrene in its gel state. Pyrene derivative was used as a fluorescent molecule in order to monitor the polymerization, aging and drying of aluminosilicate gels.¹³ These results were interpreted in terms of the chemical changes occurring during the sol-gel process and of the interactions between the chromophores and the sol-gel matrix. We report here *in situ* observations of the sol-gel phase transition in free-radical crosslinking copolymerization using the SSF technique.¹⁴⁻²⁰

This article details the quenching properties of the excited state of the Py molecule that was used to study monomer consumption in free-radical crosslinking copolymerization of MMA. The rates of polymerization were determined at different temperatures and for various crosslinker contents. Activation energy for the FCC was determined and found to be 15 kcal mol⁻¹.

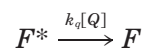
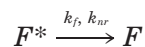
Theoretical Considerations

Fluorescence Quenching

It is known that the fluorescence intensities of aromatic molecules are affected by both radiative and nonradiative processes.²¹ If the possibility of perturbation because of oxygen is excluded, the radiative probabilities are found to be relatively independent of the environment and even of the molecular species. Environmental effects on non-radiative transitions that are primarily intramolecular in nature are believed to arise from a breakdown of the Born-Oppenheimer approximation.²² The role of the solvent in such a picture is to add the quasi-continuum of the states needed to satisfy the energy resonance conditions. The solvent acts as an energy sink for the rapid vibrational relaxation that occurs after the rate-limiting transition from the initial state. Years ago Birks et al. studied the influence of solvent viscosity on the fluorescence characteristics of pyrene solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality.²³ 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.²⁴ A matrix that changes little with temperature enables the study of the molecular properties themselves without changing environmental influence. Poly(methyl methacrylate) (PMMA) has been used as such a matrix in many studies.²⁵

Emission of fluorescence is the radiative transition of an electronically excited molecule from its singlet excited state to its ground state.^{11,12} Fluorescence quenching normally refers to any bimolecular process between the excited singlet state of a fluorescent dye and the second species that enhances the decay rate of the excited state. This process can be schematically represented as



where F and F^* are the fluorescent molecule and its excited form, respectively; Q is the quencher; and k_f , k_{nr} , and k_q are the fluorescence, nonradiative, and quenching rate constants, respectively. Many types of processes lead to quenching. Kinetically, the quenching process can be divided into

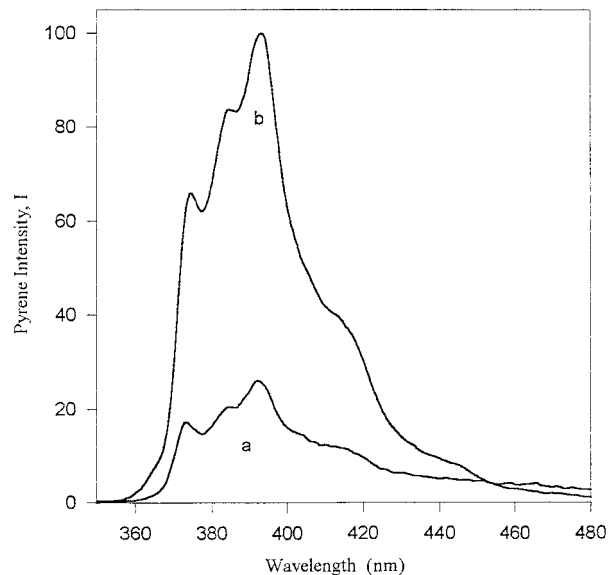


Figure 1 A typical fluorescence emission of Py (a) before and (b) after FCC of MMA in the presence of AIBN (0.26 wt %). Py molecules are excited at 345 nm.

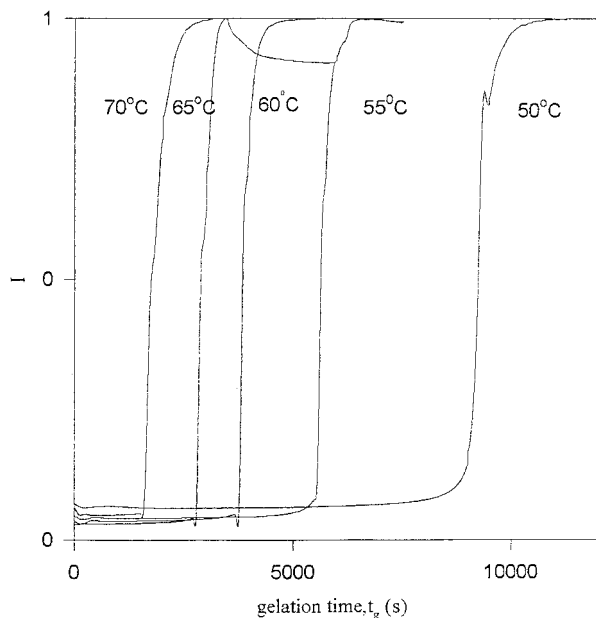


Figure 2 Plots of normalized fluorescence intensity, I , against gelation time, t , during FCC of MMA in bulk at various temperatures. Time drive mode of the spectrometer was employed, and the maximum intensity peak at 395 nm was monitored for data collection. Numbers above the curves indicate the polymerization temperatures in degrees Celsius.

two main categories: dynamic and static. In dynamic quenching, diffusion to form an encounter pair during the excited-state lifetime of the dye leads to quenching. In static quenching diffusion does not occur (an area outside the scope of the current study). Dynamic quenching is most likely to occur in fluid solution, in which the dye or quencher is free to move. If the quenching rate can be characterized in terms of a single rate coefficient (k_q) and the unquenched decay rate of F in terms of a unique lifetime, τ_0 , then the quenching kinetics will follow the Stern–Volmer equation as follows

$$\frac{I_0}{I} = 1 + k_q \tau_0 [Q] \quad (1)$$

where $[Q]$ is the quencher concentration and I and I_0 are the fluorescence intensities in the presence and absence of the quencher, respectively. This equation requires that the collection of fluorescent probe decay occur according to monoexponential decay law and that quenching interactions occur with a unique rate constant, k_q .

Kinetic Model

The first step in free-radical polymerization is decomposition of the initiator molecule with the rate constant k_i 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 with the propagation rate constant, k_p . Finally two radicals react to end each other's growth activity and form one or more polymer molecules.²⁶ This bimolecular process is called termination reaction and is identified with the rate constant k_t . During free-radical crosslinking copolymerization (FCC), the addition of divinyl monomers to the growing chain results in the formation of polymer molecules with reactive sites, called pendant vinyl groups. These reactive sites on polymer chains offer the possibility of forming polymer gels, chemical structures of macroscopic dimensions. The rate of consumption of monomer is usually called the rate of polymerization and is given by the following equation

$$\frac{d[M]}{dt} = - \frac{k_p k_i^{1/2}}{k_t^{1/2}} [M][I]^{1/2} \quad (2)$$

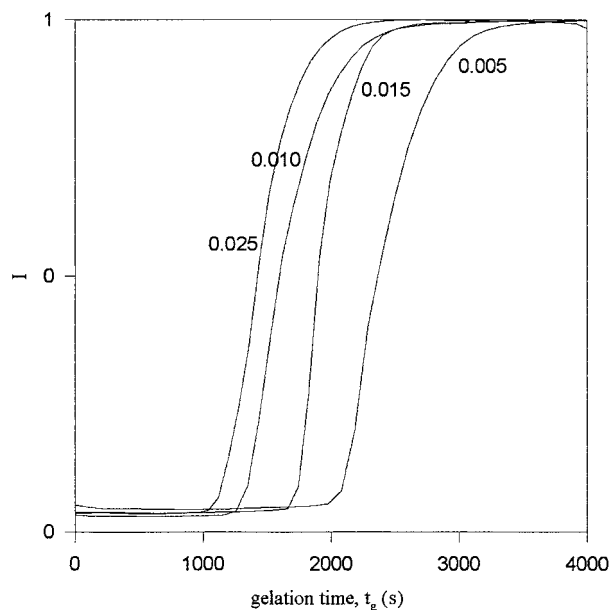


Figure 3 Plots of normalized Py intensity against gelation time during FCC of MMA in bulk at 70°C for various EGDM contents, listed in percent. Numbers above each curve indicate the EGDM content.

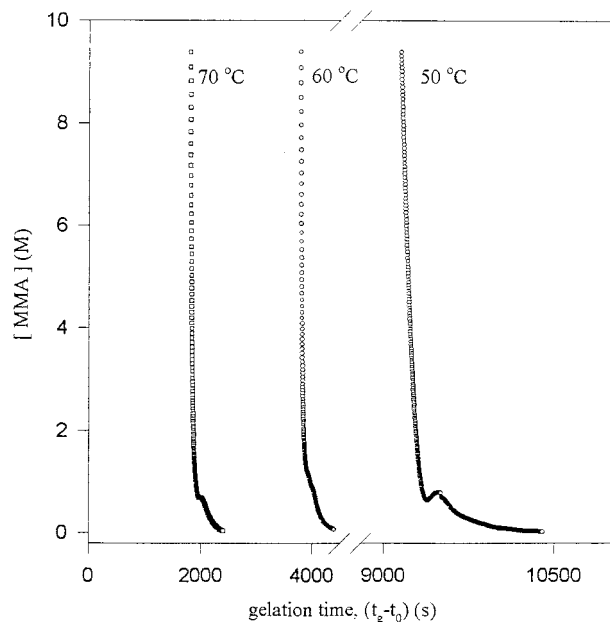


Figure 4 Plots of [MMA] consumption against gelation time at (a) 50°C, (b) 60°C, and (c) 70°C.

which is applied only under steady-state conditions, where $[M]$ and $[I]$ are, respectively, the concentration of monomer and of initiator. Often the rate constant for initiation, k_i , is large, and only a small propagation of the initiator breaks down into radicals, which means $[I]$ stays constant during the polymerization process and eq. (2) can be written as

$$\frac{d[M]}{dt} = -k_r[M] \quad (3)$$

where k_r is the composite rate constant. The solution of the eq. (3) produces the relation for the monomer consumption as follows:

$$[M] = [M_0] \exp(-k_r t) \quad (4)$$

where $[M_0]$ is the concentration of monomer at $t = 0$.

EXPERIMENTAL

In this work we monitored the FCC of methyl methacrylate (MMA) by using an *in situ* steady-state technique in which two types of experiments were performed. In the first the FCC processes were carried out separately at 50°C, 55°C, 60°C,

65°C, and 70°C and monitored against gelation time, t . In the second type of experiment, FCC processes were performed separately at 70°C in EGDM contents of 0.005%, 0.001%, 0.015%, and 0.025%. The radical polymerization of MMA was performed in bulk in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator. The monomer, MMA (Merck), was freed from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water, and drying over sodium sulfate. It was then distilled under reduced pressure over copper chloride. The initiator, AIBN (Merck, Germany), was recrystallized twice from methanol. Pyrene (Py) was used as a fluorescent probe to detect the FCC process, in which MMA acts as a quencher for the excited Py during polymerization. The later formation of bulk

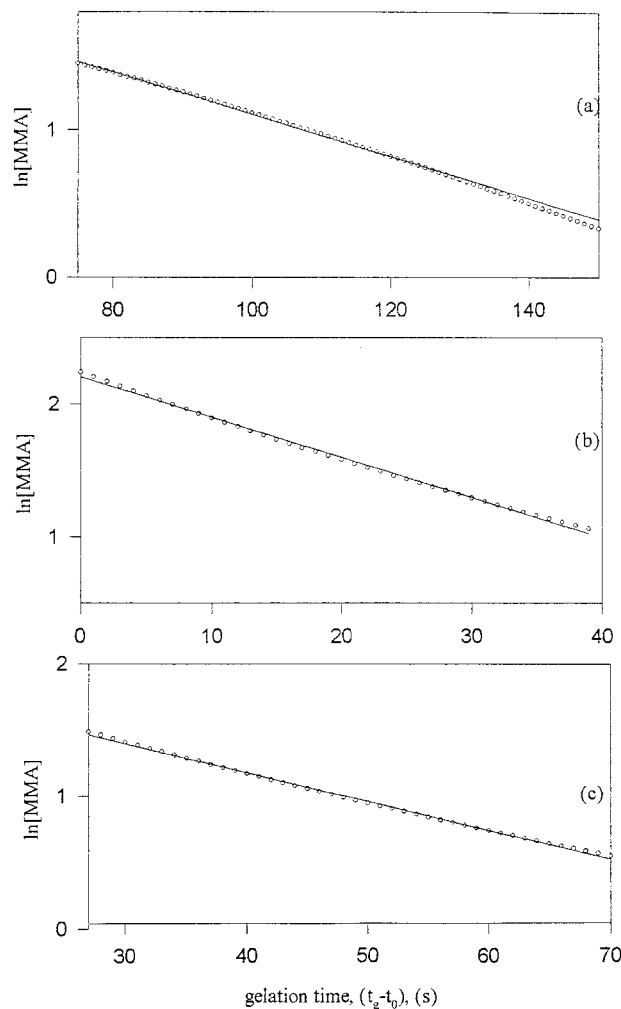


Figure 5 Logarithmic plots of [MMA] versus $(t_g - t_0)$ for the samples polymerized at (a) 50°C, (b) 60°C, and (c) 70°C.

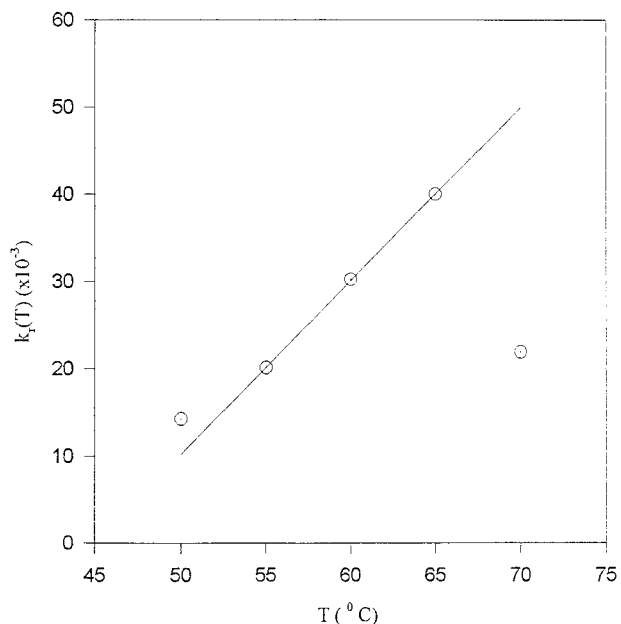


Figure 6 Plots of $k_p(T)$ versus temperature (T) for the samples polymerized at 50°C, 55°C, 60°C, 65°C, and 70°C.

PMMA provided an ideal, unchanged environment for the excited Py molecules. Naturally, from these experiments a substantial increase was expected in the fluorescence intensity, I , of Py at a certain time interval.

AIBN (0.26 wt %) was dissolved in MMA, and this solution was divided and transferred into a round quartz cell with a 10-mm internal diameter in order to make fluorescence measurements. All samples were deoxygenated by bubbling nitrogen for 10 min, and then radical polymerization of MMA was performed in the fluorescence accessory of the spectrometer. The Py molecule was excited at 345 nm during the *in situ* experiments, and variation in fluorescent emission intensity, I , was monitored with the time-drive mode of the spectrometer by staying at the 395 nm peak of the Py spectra. *In situ* steady-state fluorescence measurements were carried out using a Model LS-50 spectrometer (PerkinElmer) equipped with a temperature controller. All measurements were made at a position of 90° with slit widths kept at 4 nm.

RESULTS AND DISCUSSION

Typical Py spectra before and after gelation are shown in 1. No shift was observed in the wave-

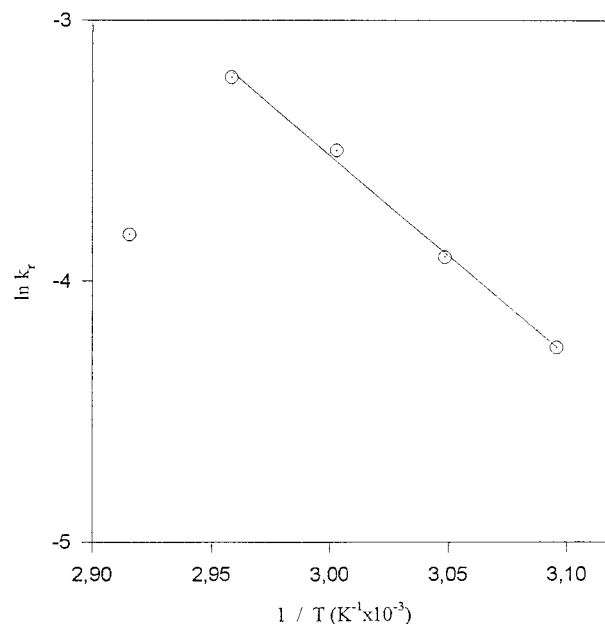


Figure 7 Logarithmic plots of $k_p(T)$ versus T^{-1} for the samples polymerized at 50°C, 55°C, 60°C, 65°C, and 70°C. The activation δE produced from the slope of the best fitting lines is 15 kcal/mol.

length of the maximum intensity of Py, and all samples maintained their transparency during the polymerization process. Normalized Py intensities, I , versus gelation time are plotted in Figure

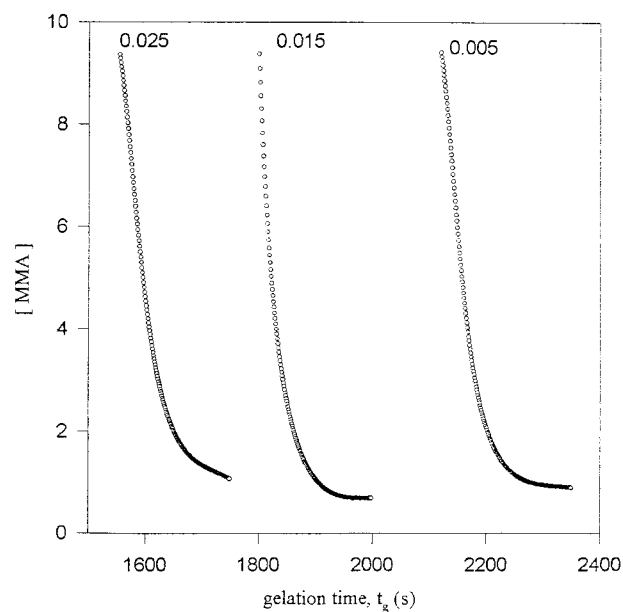


Figure 8 Plots of $[MMA]$ consumption against gelation time at (a) 0.005% EGDM, (b) 0.015% EGDM, and (c) 0.025% EGDM.

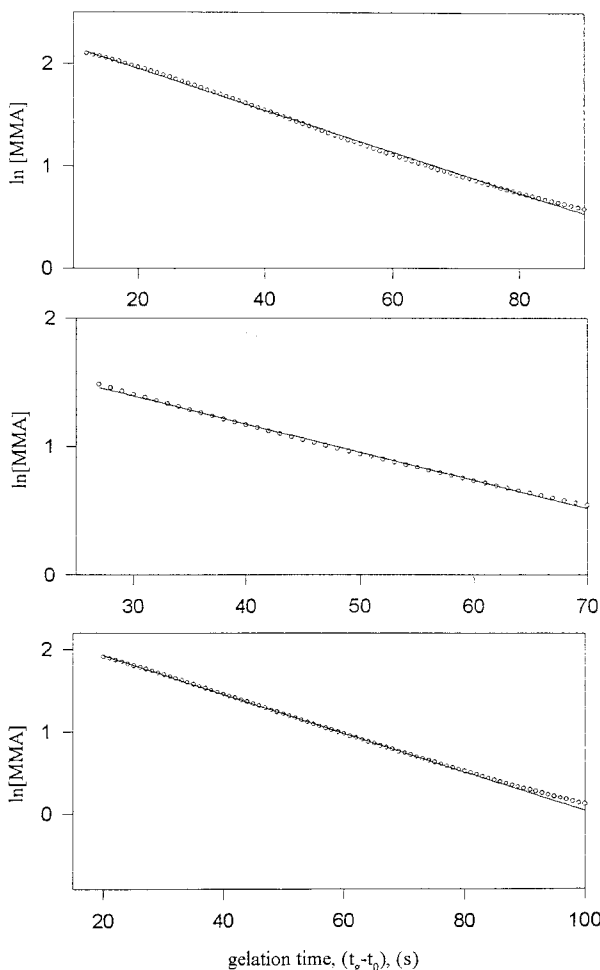


Figure 9 Logarithmic plots of $[MMA]$ versus $(t_g - t_0)$ for the samples polymerized at (a) 0.005% EGDM, (b) 0.015% EGDM, and (c) 0.025% EGDM.

2 for samples polymerized at elevated temperatures. Figure 3 presents the behavior of I against gelation time for various EGDM contents at 70°C . In Figures 2 and 3 it can be seen that all curves present a sudden increase at a given temperature and/or EGDM content, then reach a later equilibrium. These results can be explained by assuming that the Py intensity, I , increases as polymerization propagates. In other words, as monomer consumption increases because polymerization, Py molecules start to be trapped in the rigid PMMA environment; as a result, I increases.

In order to quantify these results, a Stern-Volmer type of quenching mechanism was proposed for the fluorescence intensity of P_y during the gelation process in which eq. (1) can be employed as

$$[MMA] = \frac{\left(\frac{I_0}{I} - 1\right)}{k_q \tau_0} \quad (5)$$

Here it is assumed that MMA is the only quencher for the excited P_y molecules. $\tau_0 = 200$ ns was chosen for the unquenched environment where the gelation has completed and the ideal solid network has been reached. By knowing the $[MMA_0]$ value as 9.4 M, k_q is measured before the polymerization is started and found to be $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Using the k_q value and the I/I_0 values from Figure 2 during the gelation process at various temperatures, $[MMA]$ values are obtained from eq. (5) and plotted versus $(t_g - t_0)$ in Figure 4. Here t_0 is the onset of gelation time, which corresponds to the $[MMA_0]$ value. MMA consumption curves in Figure 4 obeys the relation in eq. (4), which are fitted and plotted in Figure 5(a–c) for the gelation temperatures of 50, 60, and 70°C , where the slope of the linear relation produce the composite rate constant, k_r . The produced k_r values are plotted versus temperature in Figure 6, where it can be seen that as temperature is increased, k_r values increase, which predicts that the following Arrhenius relation has to be satisfied:

$$k_r(T) = k_{r0} e^{-(\Delta E/kT)} \quad (6)$$

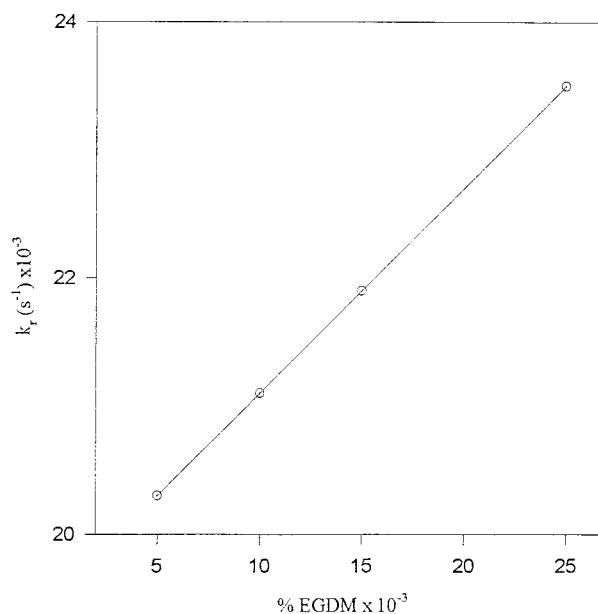


Figure 10 Plots of $k_r(E)$ versus percent EGDM for the samples polymerized at 0.005% EGDM, 0.015% EGDM, and 0.025% EGDM.

where ΔE is the activation energy for monomer consumption and k is the Boltzmann constant. This equation is fitted to the data in Figure 6, and the result is given in Figure 7, where the slope of the curve produces a ΔE value as 15 kcal/mol, which is consistent with the value obtained in the literature.¹⁶

The I/I_0 values in Figure 3 are used to produce MMA values at various EGDM contents by using eq. (5), values that are plotted against gelation time in Figure 8. These curves obey the relationships in eq. (4), which are fitted and plotted in Figure 9(a–c) at various EGDM contents. The slope of the linear relation in Figure 9 produces the $k_r(E)$ values, which are presented in Figure 10, where it can be seen that as EGDM is increased, $k_r(E)$ increases according to following relation:

$$k_r(E) = k_{r,0} + \beta(\text{EGDM}) \quad (7)$$

where $k_{r,0}$ and β are the related rate constants. From this it can be concluded that eq. (7) has to be included in the kinetic modeling for the polymerization of MMA and EGDM.

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