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A Fluorescence Study on Critical Exponents During Sol-Gel Phase Transition in Complex Monomeric Systems

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Summary: Methyl methacrylate (MMA), ethyl methacrylate (EMA) and various combinations of MMA with EMA were used during FCC experiments. Pyrene (P_y) was introduced as a fluorescence probe and fluorescence lifetimes from its decay traces were measured during sol-gel phase transitions. The fast transient fluorescence (FTRF) technique was used to study the critical exponents during sol-gel phase transition in free-radical crosslinking copolymerization (FCC). The results were interpreted in the view of percolation theory. The critical exponents of gel fraction, β and weight average degree of polymerization, γ were measured near the point of gel effect and found to be around 0.37 ± 0.015 and 1.69 ± 0.05 in all systems studied respectively.

Keywords: critical exponents; fluorescence; gelation; lifetimes; percolation

Introduction

A chemical gel appears during a random linking process of monomers to larger and larger molecules. The whole course of the bulk free radikal crosslinking copolymerization (FCC) is divided into three different stages: low concersion stage, gel effect stage and glass effect stage.[1] Monomer conversion first increases very slightly but then it accelerates because of the gel effect. Glass effect state occurs as the last stage of polymerization, if the reaction temperature is lower than the glass transition point of the polymer. Several theories have been developed in the past half century to describe gel formation in FCC, among which Flory-Stockmayer theory and percolation theory provide bases for modeling the sol-gel phase transition.[2-8] Flory-Stockmayer theory based on tree approximation, which are also called mean field or kinetic theory; assume equal reactivities of functional groups and the absence of cyclization reactions. In the language of percolation, one may think of monomers as occupying the vertices of a periodic lattice, and the chemical bonds as corresponding to the edges joining these vertices at any given moment, with some probability p. Then, the gel point can be identified with the percolation threshold p_c, where, in the thermodynamic limit, the incipient infinite cluster starts to form.[5-8] Identifying the weight average degree of polymerization DP_w

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with the average cluster size and the gel fraction G with the probability of an occupied site to belong to the incipient infinite cluster, one can predict the scaling behaviour of these and related quantities near the gel point, as a function of $|p-p_c|$,

$$DP_w = A(p_c - p)^{-\gamma} \quad , \qquad p \to p^- \tag{1}$$

$$G = B(p - p_c)^{\beta} \quad , \qquad p \to p^+ \tag{2}$$

Here, β and γ are the critical exponents and A and B are the proportionality factors. The critical exponents in percolation theory, β=0.41 and γ=1.80, differ from those found in Flory-Stockmayer, β=1 and γ=1.

Gelation is a kinetic phenomenon even if it is irreversible. There are much more developments in sol-gel modeling beyond static percolation. Some realistic features like multiple bonding, reversibility, and effect of solvent are generally not considered in static percolation. In references some kinetics are included to make sol-gel kinetics different from static percolation.[7,9-11] Kinetics, reversibility for physical gels, and the quality of solvent do effect the sol-gel transition.[10] They showed that the exponents γ and β (also, ν of correlation length exponent) change considerably for various solvent conditions for physical gels. Pandey *et al* argued that sol-gel transition for chemical gelation seems also nonuniversal with respect to quality of the solvent, degree of inhomogenity depending on the quality of the solvent and rate of reaction due to interplay between the phase-separation and crosslinking.[11]

The gel effect, accompanied by an increase in both rate and degree of polymerization in the free radical polymerization of vinyl monomers, is a well-known phenomenon both for some of the linear and crosslinked bulk polymers.[12-14]

In this paper we aimed to study the free radical crosslinking copolymerization of methyl methacrylate (MMA) - ethyl methacrylate (EMA), using fast transient fluorescence (FTRF) technique. Extremely short-time response of bulk MMA-EMA crosslinked copolymer is probed by an extrinsic fluoroprobe, pyrene. The lifetime of Py displayed a sharp transition from sol to gel as a function of reaction time, which is a (nonlinear) function of the degree of conversion. Immediately after the transition point, the polymerizing system is found to be glassy. The percolation exponents β and γ near the transition point for complex monomeric systems were measured which are found to be in good agreement with the percolation results.

Fluorescence Technique

When an organic dye absorbs light, it becomes electronically excited, then fluorescence occurs from the lowest excited singlet state and decays over a time scale typically of nanoseconds.[15,16] In addition unimolecular decay pathways for deexcitation of excited state, there are a variety of bimolecular interactions, which can lead to deactivation. These are referred to collectively as quenching processes, which enhance the rate of decay of an excited state intensity. For dilute solutions of dye molecules in isotropic media, exponential decays are common. Because of these features fluorescence dyes can be used to study local environments. For about two decades the transient fluorescence (TRF) technique for measuring fluorescence decay has been routinely applied to study many polymeric systems using organic dyes.[17-20] Fast transient fluorescence (FTRF) technique, which is based on the strobe, or pulse sampling technique[21] was recently used to study gelation of styrene (S)[22] and MMA[23] in FCC. In this technique the photo multiplier tube (PMT) is gated or strobed by a voltage pulse that is synchronized with the pulsed light source. The intensity of fluorescence emission of an organic dye is measured in a very narrow time window on each pulse and saved in a computer. The time window is moved after each pulse. The strobe has the effect of turning of the PMT and measuring the emission intensity over a very short time window. When the data has been sampled over the appropriate range of time, a decay curve of fluorescence intensity versus time can be constructed.

Experimental

In this work we monitored the gelation in FCC of MMA, EMA and their mixtures with ethylene glycol dimethacrylate (EGDM) by using the in situ FTRF technique. EGDM has been commonly used as crosslinker in the synthesis of polymeric networks. The free radical copolymerization of two different monomeric systems, MMA and EMA with EGDM were separately performed in bulk in the presence of AIBN as an initiator. These experiments were carried out at four different temperatures with constant EGDM content and at constant temperature with four different EGDM contents respectively. The reaction temperatures and the EGDM contents for the MMA and EMA samples are given in Table 1. The FCC of MMA–EMA mixtures in various combinations were performed at 70 ^{0}C temperature with a single EGDM content in bulk in the presence of AIBN as an initiator. MMA and EMA contents for the mixtures are presented in Table 2. In all experiments the initiator concentration was held constant at 0.26 wt %, the P_y concentration was taken as $4x10^{-4}$ M and the samples were deoxgenated by bubbling nitrogen for 10 min.

In situ fluorescence decay experiments from which P_y lifetimes were determined were performed using Photon Technology International's (PTI) Strobe Master System (SMS). All lifetime measurements were made at 90° to the incident beam and the slit widths were kept at 10 nm. The gelation experiments were performed in a round quartz cell, which was placed in the SMS, and fluorescence decays were collected over three decades of decay time. The sample was illuminated with 345 nm excitation light and pyrene fluorescence emission was detected at 395 nm. Deconvolution of *I(t)* is performed using iterative linear-least-squared fitting technique. The uniqueness of the fit of the data to the model is determined by χ^2 ($\chi^2 < 1.20$), the distribution of weighted residuals, and the autocorrelation of the residuals.

Results and Discussion

Figure 1 presents the fluorescence decay profiles of P_y in various gelation steps for MMA6 sample. It is observed that as the gelation time, t_g is increased, excited pyrenes decay slower and slower by indicating that quenching of excited pyrenes decrease.

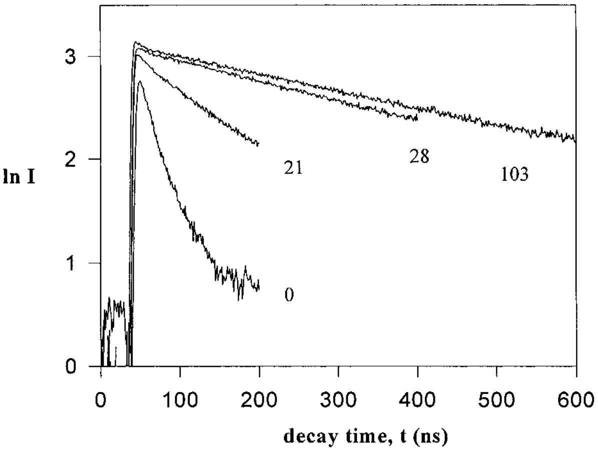

Fig. 1. Fluorescence decay profiles of excited P_y, at various gelation steps for the MMA6 sample. Numbers on each curve present the gelation times, t_g in minute.

In order to monitor gelation processes the fluorescence decay curves are measured and were fitted to the following equation.

$$I = I_0 \exp(-t / \tau) \qquad (3)$$

where I and I_0 are the intensity of P_y at time t and zero and τ is the lifetime of P_y. τ values were produced at each gelation steps using the linear least square analysis. The measured τ values and their best fits during FCC are plotted versus gelation time, t_g in Figure 2a, b and c for the MMA1, MMA2 and MMA3 samples.

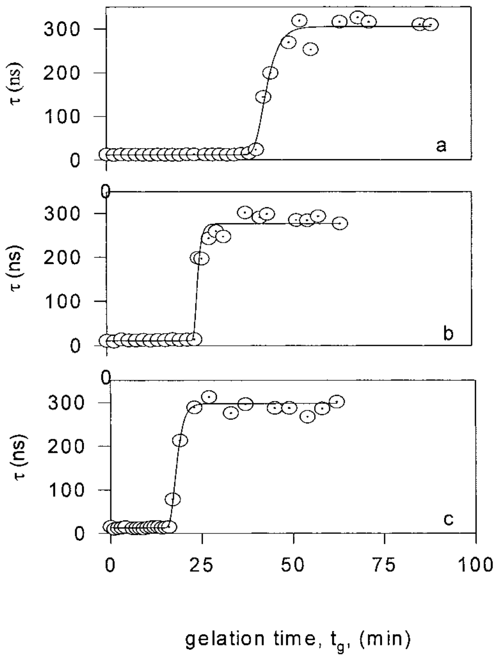

Fig. 2. Plots of the P_y lifetimes, τ , and their best fits during gelation of a) MMA1, b) MMA2 and c) MMA3 samples, respectively.

As seen in Figure 2 P_y lifetimes, τ increased drastically above the certain gelation time called the onset of the gelation time from very low values to their unquenched values during FCC for all samples. The onset of gelation time decreased as the temperature and crosslinker contents are increased, indicating early gelation process takes place at higher temperatures and crosslinker contents for MMA and EMA samples respectively.

The time derivatives of the best fitted curves of the lifetimes are plotted versus gelation time in Figure 3a, b and c for the EMA6, EMA7 and EMA8 samples. These are typical critical peaks, with rounding due to the finite size effects.[17] The maximum of the curves in Figure 3 are evaluated as the gel effect point.

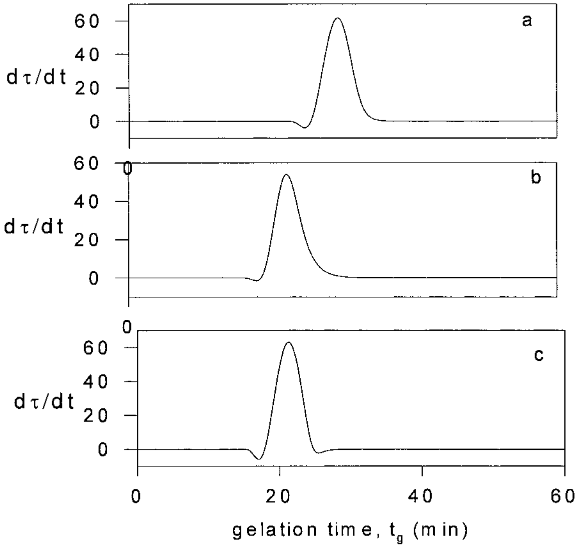

Fig. 3. The time derivatives of the best fitted curves for the lifetimes of a) EMA6, b) EMA7 and c) EMA8 against gelation time, t_g.

The position of the *point of gel effect* on the time axis, called critical time t_c , can be determined with great precision[17], assuming

$$|p - p_c| \propto |t - t_c| \qquad (4)$$

at least in a narrow region about the gel point. We argued that for $t > t_c$, the fluorescence lifetimes, τ monitors the growing gel fraction, G the fraction of the monomers that belong to the macroscopic network, and for $t < t_c$ the weight average degree of polymerization, DP_w is monitored. Before the formation of a macroscopic network, i.e., for $t < t_c$, the pyrene molecules are free to interact with – and be quenched by – the sol molecules. In the sol state, the fluorescence lifetimes becomes appreciable only to the degree that the pyrene molecules find themselves surrounded by the progressively larger clusters that are formed. The number of pyrene molecules trapped in the interior of a cluster, and therefore contributing to τ, increases as the number of monomers belonging to this cluster. Thus, the average normalized fluorescent lifetimes will be proportional to the DP_w. Above the gel point, however i.e., for $t > t_c$, most of the pyrene molecules are trapped in the macroscopic network, and τ then measures the G. In summary, we have, the scaling forms for the quantities DP_w and G near the percolation threshold, p_c together with Eq. (4) yields,

$$\tau \propto DP_w \propto A'(t_c - t)^{-\gamma'}, \quad t \to t_c^- \tag{5}$$

$$\tau \propto G \propto B'(t - t_c)^{\beta}, \quad t \to t_c^+ \tag{6}$$

Here, A' and B' are the new proportionally factors. Notice that we need not subtract the value of τ (t_c) from τ (t) in Eq. (6) since we are assuming that once the threshold has been crossed, the unquenched fluorescence lifetime is being contributed essentially by the monomers trapped in the incipient infinite cluster.

In this work, we fitted the double logarithmic plots of the fluorescence lifetime v.s $|t-t_c|$ for $t > t_c$ and $t < t_c$, to determine the critical exponents β and γ respectively. The critical point for each sample was determined by varying t_c in such a way as to obtain good scaling behaviour for both quantities β and γ over the greatest range in $|t-t_c|$. The results are shown in Figure 4a and b for the MMA1 and MMA2 samples.

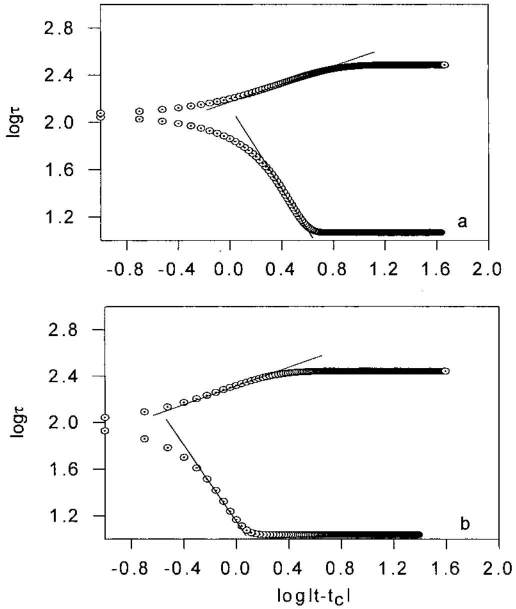

Fig. 4. The double logarithmic plots for a) MMA1 and b) MMA2 data. The β and γ exponents were determined from the slope of the straight lines.

The values of the critical exponents, β and γ which were found from the slope of log-log curves are listed in Table 1, together with the critical times t_c for all MMA and EMA samples.

The agreement with the known values (β=0.41, γ=1.80)[4,5] of the percolation exponents in three dimension is quite good. We find, β=0.37 ± 0.014 and γ=1.70 ± 0.05 as averages over sixteen experiments for two different monomeric systems.

Table 1. Experimentally measured critical exponents β, γ and critical times, t_c for the various MMA and EMA samples in various EGDM content at different temperatures, T.

	EGDM vol %	T °C	t_c min	β	γ
MMA1	2.0	60	42.8	0.38	1.78
MMA2	2.0	65	24.5	0.40	1.63
MMA3	2.0	70	17.5	0.36	1.64
MMA4	2.0	75	20.1	0.37	1.80
MMA5	1.0	70	36.0	0.37	1.70
MMA6	1.5	70	23.5	0.40	1.70
MMA7	2.5	70	16.0	0.36	1.70
MMA8	3.5	70	13.9	0.37	1.80
EMA1	2.0	60	46.8	0.36	1.68
EMA2	2.0	65	42.0	0.37	1.70
EMA3	2.0	70	23.8	0.36	1.70
EMA4	2.0	75	22.1	0.35	1.66
EMA5	1.0	70	32.1	0.38	1.70
EMA6	1.5	70	29.5	0.36	1.66
EMA7	2.5	70	22.0	0.36	1.70
EMA8	3.5	70	20.9	0.37	1.65

P_y lifetimes, τ for MIX2, MIX5 and MIX7 are measured and the double logarithmic plots of the fluorescence lifetime v.s $|t-t_c|$ for $t > t_c$ and $t < t_c$, are fitted to determine the critical exponents, β and γ. The critical point for each sample was determined by varying t_c in such a way as to obtain good scaling behaviour for both quantities β and γ over the greatest range in $|t-t_c|$. The values of the exponents, β and γ which were produce from the slope of log-log curves, are given in Table 2 together with the critical times t_c. We find, β=0.38 ± 0.014 and γ= 1.67 ± 0.04 as averages over eight experiments for mixed polymeric system, which are in good agreement with the literature values (β=0.41, γ=1.80).[4,5] Even though the measured β and γ values are both smaller than (about ~ % 9) their theoretical values given by percolation theory, it should be expectable in real experiments.[4]

Table 2. Experimentally measured critical exponents β, γ and critical times, t_c for the various MMA and EMA samples in various EGDM content at different temperatures, T.

	EMA	MMA	T	EGDM	t_c	β	γ
	vol%	vol%	^{0}C	vol %	min		
MIX1	0.0	98.5	70	1.5	23.5	0.40	1.70
MIX2	5.0	93.5	70	1.5	32.0	0.40	1.70
MIX3	10	88.5	70	1.5	35.4	0.39	1.70
MIX4	30	68.5	70	1.5	42.5	0.38	1.60
MIX5	40	58.5	70	1.5	35.4	0.37	1.70
MIX6	50	48.5	70	1.5	39.3	0.37	1.68
MIX7	70	28.5	70	1.5	36.0	0.37	1.60
MIX8	98.5	0.0	70	1.5	29.5	0.36	1.66

In summary, this paper introduces a novel method which uses the FTRF technique to measure the critical exponents during sol-gel phase transition for different monomeric systems MMA, EMA and their mixtures near the point of gel effect. Here, one has to notice that since we measured lifetimes, no environmental corrections to the data, which are quite problematic when one uses fluorescence intensity from steady state spectrometers, are needed. In this work fluorescence lifetimes are taken proportional to the DP_w below t_c, and to the G above t_c to determine the critical exponents. In conclusion it has been shown that PMMA and PEMA gels produce same β and γ exponents even they own very different glass transition temperature. In other words fluorescence lifetimes here monitores the percolating system rather than microviscosity in the polymeric networks. This work also presents that gels made from MMA-EMA mixtures belong to the same universality class as the PMMA and PEMA systems by producing similar critical exponents.

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