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In situ fluorescence experiments to test the reliability of random bond and site bond percolation models during sol–gel transition in free-radical crosslinking copolymerization

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Sol–gel phase transition during the free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate was studied using the steady-state fluorescence method. Copolymerization was performed both in the absence and presence of toluene at 75°C. Sol–gel phase transitions were monitored by observing the direct intensity of an excited pyrene methyl pivalate during *in situ* fluorescence experiments. Random bond and site bond percolation models were employed to quantify the results of bulk and solution polymerizations, respectively, during the sol–gel phase transition. Gel points were determined and the β exponents were found to be around 0.37 and 0.38 during gelation in bulk and solution polymerizations, respectively. Copyright © 1996 Elsevier Science Ltd.

(Keywords: free-radical copolymerization; sol–gel phase transition; *in situ* fluorescence method)

INTRODUCTION

The sol–gel phase transition occurs during a random linking process of subunits into larger and larger molecules. A critical point called the gel point divides the liquid and solid phases. This critical point always exists if the system is disordered and if all processes are random[1]. At gel point the system behaves neither as a liquid nor as a solid on any time or length scale.

Scaling theory provides a basis for modelling the sol–gel phase transition. Various models for this liquid–solid transition have been proposed; the most well known are percolation theory[2] and an aggregation approach[3]. The percolation model can predict critical exponents for gel fraction, weight-average degree of polymerization, radius of gyration, etc., near the sol–gel phase transition. The critical exponents in percolation theory differ from those found in the classical theories of Flory and Stockmayer[4,5].

In polymeric systems a gel is a crosslinked polymer network swollen in a monomeric liquid medium, where the liquid prevents the polymer network from collapsing into a compact mass. The polymer network of a gel can be formed in various ways[4]. In condensation polymerization, a network is formed by polymerizing bifunctional and polyfunctional units. The bifunctional units form linear chains and the polyfunctional units serve as crosslinkers. A polymer network can also be formed by crosslinking polymers formed from bifunctional monomers by free-radical polymerization.

A polymer at its gel point is in a transition state between liquid and solid, its molecular weight distribution is infinitely broad and molecules range from the smallest unreacted oligomer to the infinite cluster. Polymers around the gel point are of interest for a broad spectrum of applications including gel processing, reactive processing and the development of new polymeric materials such as adhesives, absorbents, porous catalysts, vibration dampers and membranes[6].

The 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 excited states. This energy difference is called the Stokes shift, and depends on the refractive index and dielectric constant of the solvent. Recently, by measuring the Stokes shift of a polarity-sensitive fluorescence species, the gelation during epoxy curing was monitored as a function of cure time[7]. Time-resolved and steady-state fluorescence techniques have been employed to study isotactic polystyrene in its gel state[8]. Excimer spectra were used to monitor the existence of two different conformations in the gel state of polystyrene. A pyrene derivative was used as a fluorescence molecule to monitor the polymerization, ageing and drying of aluminosilicate gels[9]. These results were

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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 sol–gel phase transition in free-radical crosslinking copolymerization, using the fluorescence technique[10]. The bond percolation model was employed to obtain some critical exponents of sol–gel transitions in such a system

In this work we use the quenching properties of the excited state of a fluorescing molecule to study the sol–gel transition in free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate. Pyrene methyl pivalate (PMP) is used as a fluorescence probe for the *in situ* polymerization experiments. A random bond percolation model is employed to measure the gel fraction exponent and toluene is used as a solvent to test the reliability of the sitebond percolation model during sol–gel phase transitions.

THEORETICAL CONSIDERATIONS

The fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes[11]. 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 non-radiative transitions, which are primarily intramolecular in nature, are believed to arise from a breakdown of the Born-Oppenheimer approximation[12]. The role of the solvent 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.

Some 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[13]. Weber and co-workers reported the solvent dependence of energy trapping in phenanthrene block polymers and explained the decrease in fluorescence yield with static quenching, caused by solvent-induced trapping states[14]. As the temperature of the 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 properties themselves, without changing the environmental influence. Poly(methyl methacrylate) (PMMA) has been used as such a matrix in many studies[15]. Recently, we have reported the effect of viscosity on the low frequency, intramolecular vibrational energies of excited napthalene in swollen PMMA latex particles[16].

In this work these properties of aromatic molecules were used to monitor the sol–gel phase transition in free-radical crosslinking copolymerization. We employed the lattice percolation model[17],where monomers are thought to occupy the sites of a periodic lattice. Between two nearest neighbours of this lattice a bond is formed randomly with probability p. Thus, for $p = 0$, no bonds have been formed and all monomers remain in isolated clusters. However, at the other extreme, i.e. for $p = 0$, 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.

Usually, there is a sharp phase transition at some critical point $p = p_c$, where an infinite cluster starts to appear. This point is called the gel point; $p < p_c$ only a sol exists, but for $p > p_c$ both sol and gel coexist together. Thus, gelation is a phase transition from a state without gel to a state with gel[17–19]. The sol–gel transition occurs asymptotically near the sol–gel transition point, and the gel fraction satisfies the following relation[17]:

$$G = B(P - P_C)^{\beta} \qquad (1)$$

with a suitable constant β, called the critical exponent. The asymptotic proportionality factor B is referred to as the critical amplitude. A simulation of the gel fraction dependence on the bond formation probability, p is given in *Figure 1a* for a simple cubic lattice.

During gelation, if solvent molecules are present in the system then one should denote the probability of a site being occupied by a monomer molecule as ϕ (mole fraction of monomer in the solvent) and the probability of site occupation by a solvent molecule as $(1 - \phi)$. Now the two nearest-neighbour monomers may form a bond with probability p; however, no bonds can be formed between solvent–solvent and solvent–monomer molecules. In this case a random site bond percolation model has to be employed instead of the random bond percolation model. In the site bond percolation model, clusters, connected by random bonds, are formed from randomly distributed monomers. The phase diagram of random site bond percolation in a simple cubic lattice is shown in *Figure 1b*.

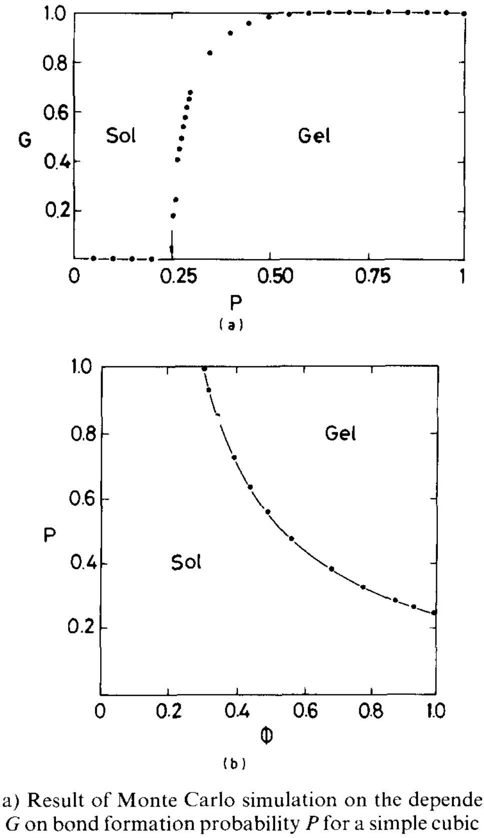

Figure 1 (a) Result of Monte Carlo simulation on the dependence of gel fraction G on bond formation probability P for a simple cubic lattice of size 50^3 (ref. 17). (b) Phase diagram of random sitebond percolation, obtained by Monte Carlo simulation for a simple cubic lattice (ref. 17). ϕ is the probability of site occupation by a monomer

Table 1 Experimentally measured β and t_c values during bulk polymerization (experiment set I) and toluene polymerization (experiment set II). All measurements were performed at 75 ± 2°C, AIBN content was kept at 0.26 wt% for all samples

Experiment		1	2	3	4	5	6
I	EGDM (vol%) $\times 10^{-3}$	2.5	7.5	10	12.5	15	20
	β	0.40	0.47	0.34	0.24	0.43	0.35
	t_c (s)	2095	1432	1401	1315	1242	1205
II	Toluene (vol %)	0.10	0.13	0.15	0.20	0.23	0.30
	β	0.40	0.43	0.27	0.47	0.32	–
	t_c (s)	1715	1772	1855	2035	2950	–

EXPERIMENTAL

In this work we plan to probe the sol–gel transition in free-radical crosslinking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) using a steady-state fluorescence technique. The radical copolymerization of MMA and EGDM was performed in bulk or in toluene solution at 75°C in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Pyrene methyl pivalate (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 the fluorescence intensity I of PMP around the gel point.

EGDM has commonly been used as a crosslinker in the synthesis of polymeric networks[20]. Here, for our use, the monomers MMA (Merck) and EGDM (Merck) were freed from 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. The polymerization solvent, toluene (Merck), was distilled twice over sodium.

In situ steady-state fluorescence measurements were carried out using a Perkin–Elmer Model LS-50 spectrometer, equipped with a temperature controller. All measurements were made at the 90° position at 75°C and slit widths were kept at 2.5 mm.

RESULTS AND DISCUSSION

Two different sets of experiments were carried out. In the first set (set I), 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 with various EGDM contents for bulk polymerization. Details of the samples are listed in *Table 1*. 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 spectrometer fluorescence accessory. The PMP molecule was excited at 345 nm during *in situ* experiments and the variation in fluorescence emission intensity I was monitored at 395 nm with the time-drive mode of the spectrometer. Typical PMP spectra are shown in *Figure 2*. No shift was observed in the wavelength of the maximum intensity of PMP and all samples kept their transparency during the polymerization process. Scattered light from the samples was also monitored during gelation experiments and no serious variation was detected at 345 nm. Normalized PMP intensities *versus* reaction times are plotted in *Figure 3* for samples with various crosslinker (EGDM) contents. Gelation curves in *Figure 3* represent power law-behaviour which typically gives evidence for critical phenomena. Here, we have to note that the curves in *Figure 3* resemble the curve in *Figure 1a*, which may suggest that percolation theory can be employed to interpret the gelation curves in *Figure 3*.

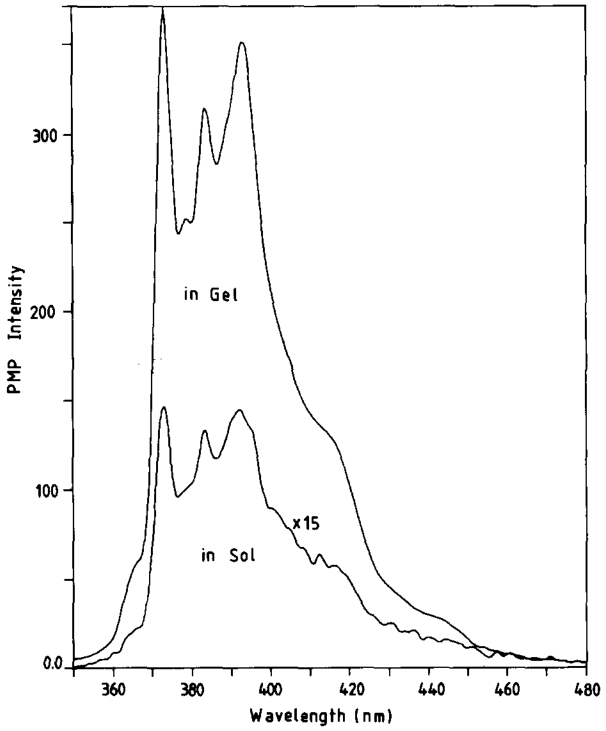

Figure 2 Fluorescence emission spectra of PMP, before and after the gelation process. Molecules are excited at 345 nm

In order to quantify the above results, we assumed that the reaction time t for the polymerization is proportional to the probability p and that the fluorescence intensity I monitors the growing gel fraction G. Then equation (1) can be written as

$$I = A(t - t_c)^{\beta} \qquad (2)$$

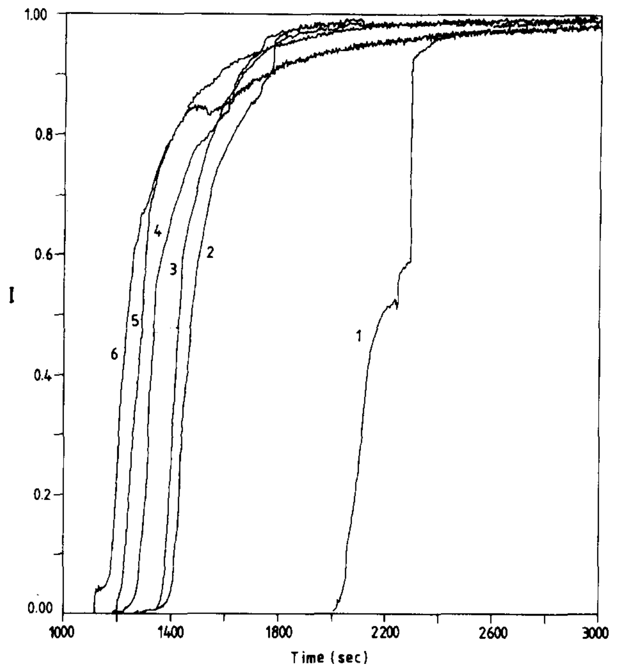

Figure 3 Plots of PMP fluorescence intensity I against reaction time t during bulk polymerization. The time-drive mode of the spectrometer was employed and the maximum intensity peak at 393 nm was monitored for data collection. Numbers 1, 2, 3, 4, 5 and 6 correspond to samples in experimental set I in *Table 1*

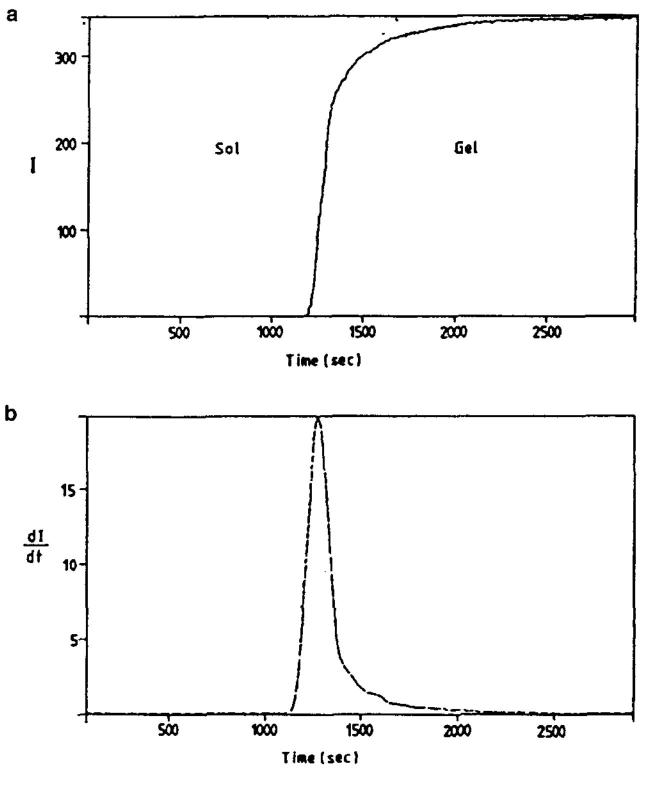

Figure 4 Determination of t_c: plots of (a) PMP fluorescence intensity I and (b) its first derivative dI/dt against reaction time t. The maximum in the t-axis corresponds to t_c

where the critical time t_c corresponds to the gel point, p_c and A is the new critical amplitude. t_c can be determined by taking the first derivative of the experimentally obtained I curve with respect to t. *Figures 4a* and *b* present the I curve and its first derivative (dI/dt) of sample 5 in *Figure 3* against t, respectively. The maximum in the dI/dt curve corresponds to the inflection point in the I curve and gives t_c on the time axis. At $t < t_c$, since PMP molecules are free, they can interact and be quenched by sol molecules; consequently I presents small values. However at $t > t_c$, since most of the PMP molecules are frozen in the EGDM network, I presents very large values. The plot of $\log I = \log A + \beta \log (t - t_c)$ for the data shown in *Figure 3* is presented in *Figure 5*, in the region $10^{-2} < |1 - t/t_c| < 10^{-1}$ above t_c. The critical exponents β were determined and are listed in *Table 1* together with the corresponding t_c values for samples in bulk polymerization. Gelation times t_c are shifted to smaller values as the EGDM content increases.

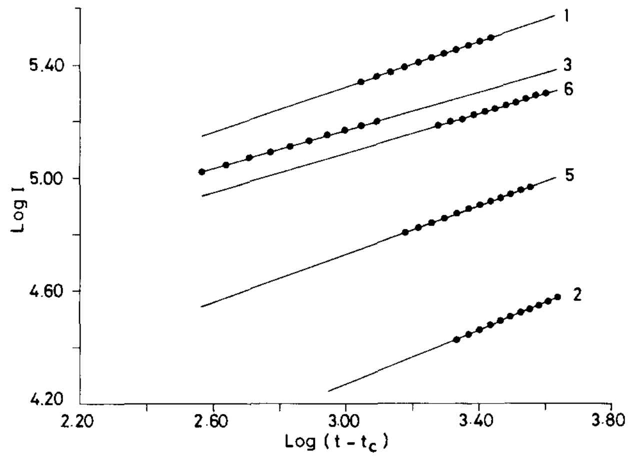

Figure 5 Log–log plot of equation (2) for the data given in *Figure 3*. The $10^{-2} < |1 - t/t_c| < 10^{-1}$ region above t_c was chosen for the best fit to obtain β values

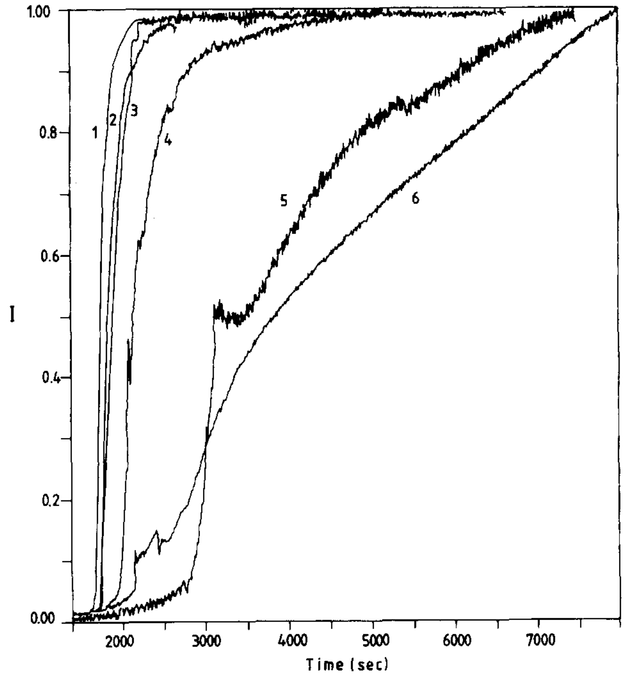

Figure 6 Variation in PMP intensity I *versus* reaction time t during toluene polymerization. Numbers 1, 2, 3, 4, 5 and 6 correspond to samples in experimental set II in *Table 1*

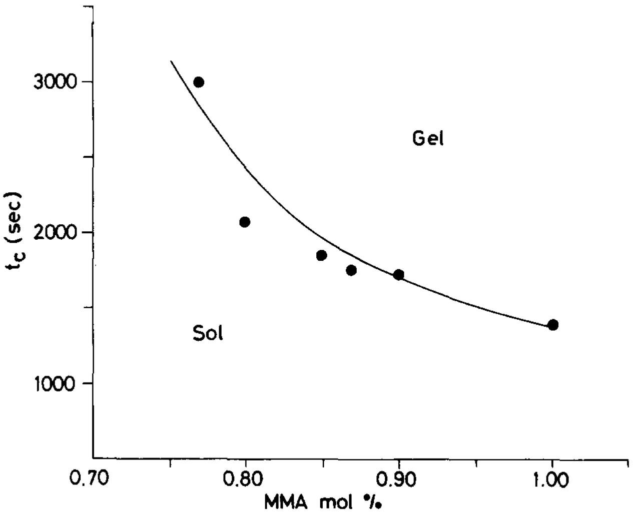

Figure 7 Plot of t_c values against MMA mol% during toluene polymerization

However, the average β value was found to be around 0.37, independent of the EGDM content, which is slightly smaller than the value of the bond percolation as found from computer simulations[17].

In the second set of experiments (set II), six different samples were prepared with various toluene contents using the stock solution of the first experimental set. The amount of toluene in the samples are shown in *Table 1*. Fluorescence measurements were carried out with these samples at 75 ± 2°C during solution polymerizations in toluene, where the EGDM content was constant at 0.01 vol%, the PMP concentration was taken as 4×10^{-4} M and the excitation wavelength was again 345 nm. Fluorescence intensity I *versus* reaction time t was monitored for all samples. Results are shown in *Figure 6*. Asymptotic behaviour was observed only in the samples with lower toluene content (<0.23 vol%). The sample with 0.30 vol% toluene was not able to form a gel, presumable because the high content of toluene molecules prevents the formation of an EGDM network in this sample (6 in *Table 1*). Critical exponents β were obtained by fitting the data to equation (2), and t_c values were found by taking the first derivative of I with respect to t. The results are listed in *Table 1*. The average critical exponent β was found to be 0.38. The t_c values increased in our observation range, however β values were not affected by the increase in toluene content. Since t_c is directly proportional to the bond formation probability (p), in the presence of toluene the behaviour of t_c may be explained by the site bond percolation model. In order to see that, t_c values are plotted against mol% of MMA in *Figure 7*. When the curve in *Figure 7* is compared with the right lower edge of the curve in *Figure 1b*, the similarity between them can be observed. From this we conclude that gel formation is retarded by toluene molecules occupying the sites of the three-dimensional lattice and the gel can be formed only at high MMA content (<0.75 mol%). In other words, the fluorescence technique is able to detect the gel formation process in samples containing 0.75 mol% of MMA during solution polymerization.

The results of these experiments have produced quite reasonable pictures for the random bond and site bond percolation models during sol–gel phase transition in three dimensions. In summary, this paper has introduced a novel technique to study gelation phenomena in which the experiments are quite simple to perform and the fluorescence spectrometer is inexpensive to obtain or already accessible in any laboratory.

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