

Experimental Determination of β and γ Critical Exponents in the Sol-gel Phase Transition by Using Steady-state Fluorescence Technique

Y. YILMAZ and Ö. PEKCAN

*Department of Physics, Istanbul Technical University,
Maslak, 80626, Istanbul-TURKEY*

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Abstract

The gelation of methyl methacrylate and ethylene glycol dimethacrylate was studied using the steady-state fluorescence technique. Samples with various crosslinker densities were prepared and sol-gel phase transitions were observed at various temperatures. Percolation theory was employed to interpret the results. For all samples the gel fraction and the average cluster size exponents, β and γ , were measured and found to be around 0.42 and 1.7 respectively. These values show excellent agreement with theoretical and simulation results.

1. Introduction

Gelation is the phase transition from a state without a gel to a state with a gel, i.e. gelation involves the formation of an infinite network. One particular approach to gelation theory is the percolation model [1]. It can be explained simply as follows: Monomers are thought to occupy the sites of a periodic lattice, and between two nearest neighbours of lattice sites a bond is formed randomly with probability p . The conversion factor p is the ratio of the actual number of bonds which have been formed between monomers at the given moment to the maximally possible number of such bonds. There is in general a sharp phase transition at some intermediate critical point $p = p_c$ where an infinite cluster starts to appear: The gel phase for p above p_c , the sol phase for p below p_c . Such simple gelation theories often make the assumption that the parameter p alone determines the behaviour of the gelation process, though p may in turn depend on temperature, concentration of monomers, and time t [1]. Critical phenomena take place in the region in which p is very close to or same with the gel point p_c . Thus if p is asymptotically close to p_c , critical behaviour is observed. Of course, any real experiment can never reach this purely mathematical limit, but one can try to come as close as possible to asymptopia [1, 14].

Some physical quantities can be described as a power law at the critical point during the sol-gel phase transition. For example, gel fraction, G , and average cluster size, S

(or weight average degree of polymerization DP_w) around $p = p_c$ can be written in the following forms¹:

$$G = A(p - p_c)^\beta, \quad (p \rightarrow p_c^+) \quad (1)$$

$$S = B(p_c - p)^{-\gamma}, \quad (p \rightarrow p_c^-) \quad (2)$$

where β and γ are the critical exponents. A and B are the proportionality factors. At $p = p_c$, the average cluster size, S diverges. Since an infinite macromolecule appears for p above p_c , but not for p below p_c , it is likely that some average molecular size (or weight average degree of polymerization) diverges, if p approaches p_c from below (denoted as $p \rightarrow p_c^-$). One can obtain the exponents and double logarithmic plots of the measured quantities according to Equations 1 and 2 respectively. Such a log-log plot reveals that data should be particularly accurate near the gel point. In particular a small shift in p_c results in a large shift in the critical exponents [1]. To our knowledge so far, no one has yet reached the experimental state of the art to determine the β and γ exponents accurately for the sol-gel transition. However, in this paper we introduced a novel technique, depending on the fluorescence experiments, to determine these exponents quite accurately.

Fluorescence and phosphorescence intensities of aromatic molecules are effected by both radiative and non-radiative processes [2]. 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 [3]. 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. 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 effected by solvent quality [4]. 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 [5]. 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 properties themselves without changing environmental influence. Poly (methyl methacrylate (*PMMA*)) has been used as such a matrix in many studies [6]. Recently we have reported viscosity effect on low frequency, intramolecular vibrational energies of excited naphthalene in swollen *PMMA* latex particles [7].

In this work these properties of an aromatic molecule were used to monitor the sol-gel phase transition in free-radical crosslinking copolymerization using in situ fluorescence technique. Gelation was monitored with the variation of fluorescence intensity against time. The β and γ exponents were determined from these curves.

Experimental

Here we plan to probe the sol-gel transition in free-radical crosslinking copolymerization of methyl methacrylate (*MMA*) and ethylene glycol dimethacrylate (*EGDM*) by using steady-state fluorescence technique. The radical copolymerization of *MMA* and *EGDM* was performed in bulk or in toluene solutions at different temperatures in the presence of 2,2'-azobisisobutyronitrile (*AIBN*) as an initiator. Pyrene (P_y) 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 P_y but above p_c , *PMMA* network provides an ideal, unchanged environment for the excited P_y molecules. Naturally, from these experiments one may expect a drastic increase in fluorescence intensity, I , of P_y around the gel point.

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks [8]. 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.

Steady-state fluorescence measurements were performed using the Model LS-50 spectrometer of Perkin Elmer, equipped with temperature controller. All measurements were made at 90° position and slit widths were kept at $2.5mm$.

Mainly three different sets of experiments were carried out. Details of the samples for all sets are listed in Table 1. Py concentrations were taken as $4 \times 10^{-4}M$ for all samples in these experimental sets. Samples were deoxygenated by bubbling nitrogen for 10 minutes and then radical copolymerization of *MMA* and *EGDM* was performed in the fluorescence accessory of spectrometer. Py molecule was excited at $345nm$ 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 $395nm$ peak of the P_y spectrum. No shift was observed [9] in the wave length of the maximum intensity of P_y , and all samples have kept their transparency during the polymerization process. Scattering light from the samples were also monitored during gelation experiments and no serious variation was detected at $345nm$ intensity. Normalized P_y intensities versus reaction times are plotted in Fig.1 for samples from each set. Gelation curves in Fig.1 represent asymptotic behaviours, which give evidence of typical critical phenomenon [1,9].

Results and Discussions

In order to quantify the above results, we assumed that the reaction time t , for the polymerization about gel point is proportional to the probability p . Since the region in which we calculated the critical exponents is very narrow compared to the total reaction time one may expect that time should be linearly proportional to p in this region. Here we assumed that the fluorescence intensity, I monitors the growing gel fraction, G , and the average cluster size, S above and below t_c , respectively. Below t_c , since the P_y molecules are free they can interact with, and be quenched by sol molecules; as a result I decreases.

Table 1. Experimentally measured β , γ and t_c values during the gelation of the samples prepared with various crosslinker densities at various temperatures. *AIBN* content was kept 0.26wt.% for all samples.

Sets	Gels	EGDM $\times 10^{-3}$ (Vol%)	T ± 2 ($^{\circ}$ C)	t_c (sec)	β	γ
Set 1	1	5	75	2183	0.430	1.403
	2	7.5	75	1435	0.414	1.719
	3	10	75	1396	0.433	1.730
	4	12.5	75	1302	0.423	1.749
	5	15	75	1252	0.445	1.770
	6	20	75	1521	0.426	1.775
	7	30	75	873	0.420	1.704
Set 2	8	2.5	85	1609	0.432	1.582
	9	5	85	1395	0.468	1.713
	10	7.5	85	926	0.430	1.427
	11	25	85	791	0.396	1.789
Set 3	12	5	70	3072	0.408	1.815
	13	5	75	2392	0.420	1.536
	14	5	85	1239	0.427	1.588

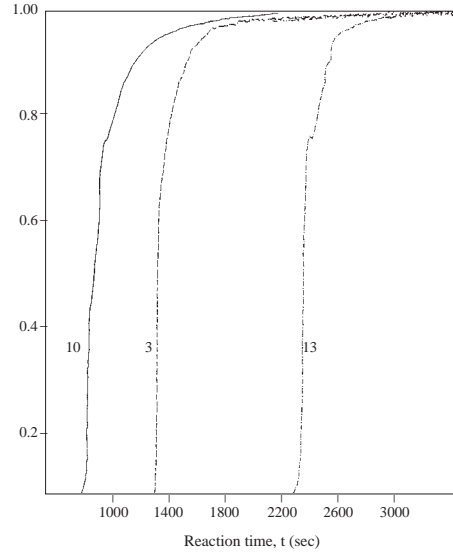


Figure 1. Plots of P_y intensity I versus reaction time t during polymerization. The numbers 3, 10 and 13 correspond to samples in experimental sets 1, 2 and 3 in Table 1.

In this region the fluorescence intensity originates from the clusters embedded in the monomeric medium. Each of these clusters are formed from polymer molecules. The number of P_y molecules trapped in the interior of any cluster increases as the number of

monomer, N belonging to this cluster increases. Since we get the intensity of light from these clusters, I will be proportional to the average cluster size, S . However, above t_c , since most of the P_y molecules are frozen in the *EGDM* network, the intensity, I , yields very large values. Then Eq. 1 and 2 can be written in the following forms:

$$I = A'(t - t_c)^\beta, \quad t \rightarrow t_c^+ \quad (3)$$

$$I = B'(t_c - t)^{-\gamma}, \quad t \rightarrow t_c^- \quad (4)$$

Here, the critical time t_c corresponds to the gel point p_c , and A' and B' are the new proportionality factor. In any computer simulation, the gel point can be found very easily by choosing the point at which the infinite network starts to appear, i.e at the point the spanning cluster has just formed. But, in any real experiment, the determination of the gel point is not so easy. The way of finding the gel point in real experiments is to measure more than one quantity at this point. The critical point is a point at which all the quantities measured will converge their real values which were found theoretically and by computer simulations. We determined the t_c values by this way, measuring the exponents point to point at, above and below the maxima of dI/dt curves. The t_c values which we found experimentally obey the following relation:

$$t_c = t_m - C_y t_{1/2} \quad (5)$$

Here, t_m is the time of the maxima of dI/dt curves and $t_{1/2}$ is the half width at the half high of the left part of the dI/dt curves (the distance between the M and N points in Fig 2.). C_y is a constant which were found as the ratio of the distance KL to the MN of the derivative curves (see Fig 2) and it's value is 0.248 ± 0.005 . The measured t_c values are listed in Table 1. It can be seen that, t_c values decrease as the *EGDM* content is increased at a given temperature (Set 1,2) which indicates that gelation happens faster in high *EGDM* samples. For the samples at constant *EGDM* content, increasing temperature causes faster gelation (Set 3). The plots of $\log I = \log A' + \beta \log(t - t_c)$ and $\log I = \log B' - \gamma \log(t_c - t)$, for the Sample 3 shown in Fig 1 are presented in Fig 3 above and below t_c , respectively. The region in which we calculate the exponents for all samples above and below t_c is $10^{-2} < |1 - t/t_c| < 10^{-1}$. One can find a linear curve only in this region close to p_c . The critical exponents β and γ were determined from the slopes of the curves in Fig 3 and listed in Table 1 together with other β and γ values for the corresponding samples for all experimental sets. Average β and γ values were found to be 0.42 ± 0.03 and 1.7 ± 0.1 respectively, which are independent of the *EGDM* contents, and temperature for sets in Table 1. These values are in good agreement with the values found from the bond percolation theory [1,12].

From Table 1 one can conclude that in the sets labelled 1 and 2, the critical times t_c are shifted to smaller values as the *EGDM* content is increased. Furthermore the experimental set 3 shows that, at a given crosslinker content gel formation is accelerated as the temperature is increased. However in all these sets the β and γ values vary around

0.42 and 1.7 respectively, independently of the *EGDM* and temperature, as it is expected from bond percolation theory¹. All of these results are in accordance with the theory of gelation [13] and measured exponents β and γ are consistent with the universal exponents in bond theory [1]. Another important result of this study is that for *MMA* and *EGDM* system t_c can be calculated by using Eq.5, independent of temperature and concentration of *EGDM*.

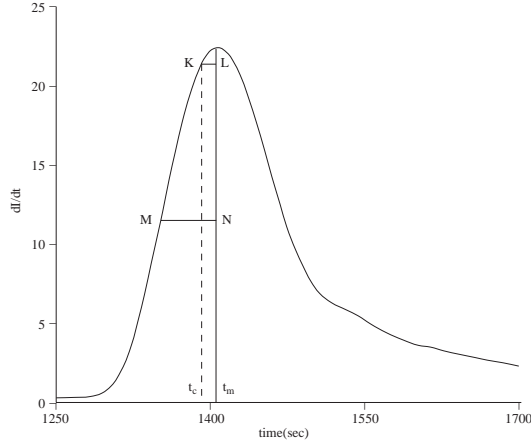


Figure 2. Determination of t_c : the first derivative, dI/dt of Sample 3 against reaction time t . t_c point corresponds to $t_c = t_m - C_y \cdot t_{1/2}$. Here $t_{1/2}$ is the half width at half high (The distance between M and N points) of the dI/dt curve. C_y is a constant explained in the text.

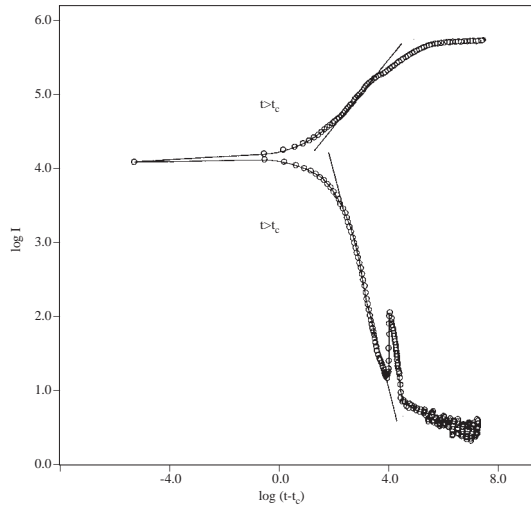


Figure 3. Log-log plots of Equations 4 and 5 for the data given in Fig 1. The $10^{-2} < |1 - t/t_c| < 10^{-1}$ region above and below t_c was chosen for the best fit to obtain β and γ values.

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