ELSEVIER

4 November 1994

Chemical Physics Letters 229 (1994) 537-540

CHEMICAL
PHYSICS
LETTERS

Fluorescence technique for studying the sol-gel transition in the free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate

Ö. Pekcan [a,*], Y. Yılmaz [a], O. Okay [b]

[a] *Department of Physics, Istanbul Technical University, Maslak, 80626 Istanbul, Turkey*
[b] *TUBITAK Marmara Research Center, Research Institute for Basic Sciences, Department of Chemistry,*
P.O. Box 21, Gebze, Kocaeli, Turkey

Received 30 June 1994; in final form 7 September 1994

Abstract

The steady-state fluorescence technique was used to study the free-radical crosslinking copolymerization of methyl methacrylate and ethylene glycol dimethacrylate in the absence and presence of toluene at 75°C. A sol-gel phase transition was observed and monitored by an excited aromatic molecule during the gelation of the above system. Bond percolation theory was employed to quantify the results. The critical exponent and gel point were found to be around 0.45 and 0.36 both in bulk and solution polymerization.

The fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [1]. 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 [2]. 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.

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 [3]. 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 the solvent induced trapping states [4]. As the temperature of the liquid solution is varied, the environment about the molecule changes and much of the change in the 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 [5]. Recently we reported the viscosity effect on the low frequency, intramolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [6].

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* Corresponding author.

SSDI 0009-2614(94)01112-5

In this Letter we aim to use these properties of aromatic molecules to monitor the sol–gel phase transition in free-radical crosslinking copolymerization. We employed the lattice percolation model [7], where monomers are thought to occupy the sites of a periodic lattice. Between two nearest neighbors of these lattice sites a bond is formed randomly with 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. 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; for p below p_c only a sol exists but for p above p_c both sol and gel coexist together. Thus, gelation is a phase transition from a state without gel to a state with gel [8–10]. The sol–gel transition happens in 'asymptopia' which is in general given by the following relation [7]:

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

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

In this work we plan to probe the sol–gel transition in the free-radical crosslinking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) by using the steady-state fluorescence technique. The radical copolymerization of MMA and EGDM was performed in bulk or in toluene solutions 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 fluorescence intensity, I, of PMP around the gel point.

EGDM has been commonly used as crosslinker in the synthesis of polymeric networks [11]. 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. The polymerization solvent, toluene (Merck), was distilled twice over sodium.

Steady-state fluorescence measurements were carried out using a model LS-50 spectrometer of Perkin-Elmer, equipped with temperature controller. All measurements were made at the 90° position and slit widths were kept at 2.5 nm.

Three different sets of experiments were carried out; in the first set, 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 the fluorescence measurements. Four 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 the 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 and the 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. 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 the gelation experiments and no serious variation was detected at 345 nm intensity. Normalized PMP intensities versus reaction time are plotted in Fig. 1 for samples with various crosslinker (EGDM) contents. The gelation curves in Fig. 1 represent asymptotic behaviours, which give evidence to typical critical phenomena.

In order to quantify the above 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; Eq. (1) can then be written as

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

Here, the critical time t_c corresponds to the gel point p_c and A is the new critical amplitude. Below t_c, since the PMP molecules are free, they can interact and are quenched by sol molecules; as a result I presents small

Table 1
Experimentally obtained β and t_c (or p_c) values using Eq. (2) (or Eq. (1)) during bulk or toluene polymerization

	Experiment [a]											
	I [b]				II [c]				III [d]			
	EGDM (vol%)	β	t_c (s)	p_c	toluene/ MMA(vol%)	β	t_c (s)	p_c	EGDM (vol%)	β	t_c (s)	p_c
1	0.0036	0.42	1629	-	0.25	0.48	1517	0.55	0.0079	0.44	1721	0.33
2	0.010	0.43	1315	0.29	0.5	-	-	-	0.010	0.48	1517	0.55
3	0.020	0.48	1189	0.29	1.0	-	-	-	0.016	0.46	961	0.33
4	0.030	0.43	865	0.33	-	-	-	-	0.024	0.49	890	0.44

[a] I, II and III are the corresponding sets of experiments given in the text.
[b] Polarization in bulk.
[c] Polarization in toluene EGDM 0.0710 vol%.
[d] Polarization in toluene 0.25 vol%.

values. However, above t_c, since most of the PMP molecules are frozen in the EGDM network, the intensity I gives large values. The plot of $\log I = \log A + \beta \log(t - t_c)$ for the data shown in Fig. 1 is presented in Fig. 2, where t_c is chosen for the best linear fit, immediately after gelation has started. The critical exponents β were determined and listed in Table 1 together with the t_c and p_c values for the corresponding samples in bulk polymerization.

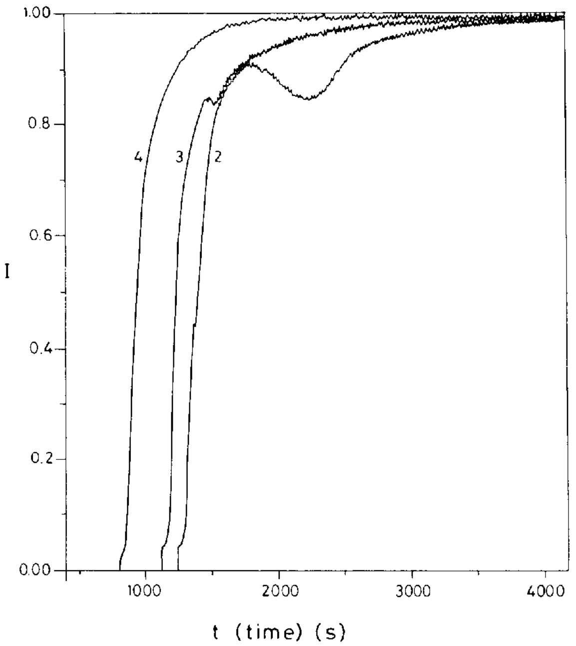

Fig. 1. Variation in PMP fluorescence intensity I against reaction time t during the crosslinking copolymerization of MMA and EGDM in bulk for various EGDM contents. Time drive mode of the spectrometer was employed for the data collection. Nos. 2, 3, and 4 corresponds to samples in experimental set I in Table 1.

The gelation times t_c are shifted to smaller values as the EGDM content is increased. However, the β values varied around 0.45, independent of the EGDM content, as expected from bond percolation theory [7]. However, the p_c values are found to be slightly larger than the predicted value (0.248) in the corresponding theory.

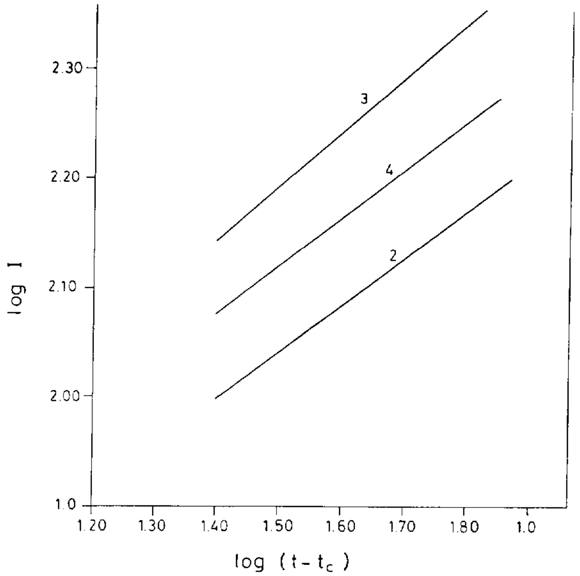

Fig. 2. Log–log plot of Eq. (2) for the data given in Fig. 1. The $0 < |1 - t/t_c| < 10°$ region was chosen for the best fit to obtain β values.

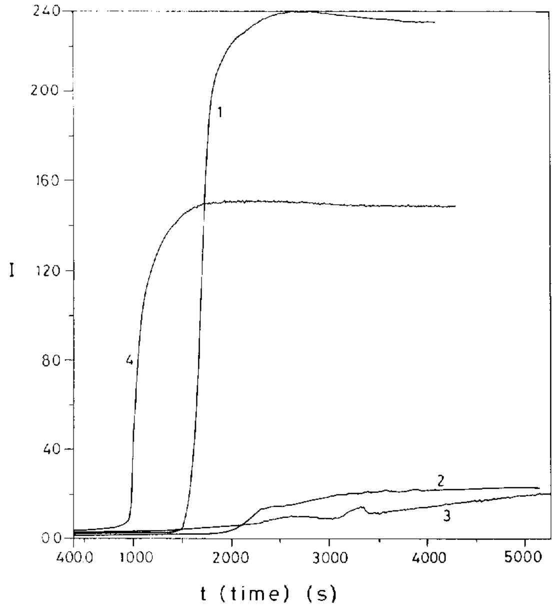

Fig. 3. Variation in PMP intensity I versus reaction time t during the crosslinking copolymerization of MMA and EGDM in toluene. Data were collected with the time drive mode of the spectrometer. Nos. 1, 2 and 3 correspond to samples in experimental set II. Sample 4 of experiment III is given for comparison.

In the second set of experiments, three different samples were prepared with various toluene contents using the stock solution of the first experimental set. The amounts of toluene in the samples are shown in Table 1. Fluorescence measurements were carried out with these samples at 75 ± 2°C during solution polymerization in toluene, where the EGDM content was kept as 0.01 vol%, the PMP concentration was taken as 4×10^{-4} M and the excitation wavelength chosen again as 345 nm. The fluorescence intensity I versus reaction time t was monitored for all samples. The results are shown in Fig. 3. Asymptotic behaviour was observed only in the sample with 0.25 vol% toluene content. The other two samples were not able to form a gel; presumably toluene molecules prevent the formation of the EGDM network in these high solvent content samples (2 and 3 in Table 1 and Fig. 3). Critical values β, t_c and p_c are obtained by fitting the data to Eq. (2) and the results are listed in Table 1.

In the final and third experimental set, the amount of toluene was fixed at 0.25% and the samples were prepared with different EGDM contents. Gelation was monitored in four different samples by detecting the PMP fluorescence intensity versus reaction time at 75°C. As the EGDM content is increased, t_c decreases indicating that gelation occurs earlier at high crosslinker contents. Furthermore, a comparison of the experiments shows that, at a given crosslinker content, the gel formation is retarded with rising dilution. All of these results are in accordance with the theory of gelation [8]. β and t_c values were obtained from Eq. (2) and the results are listed in Table 1 together with EGDM content. Here, the β values are also found to be close to the universal exponent (0.45) in bond percolation theory [7], however, the p_c values were measured to be much larger than theory predicts.

In these experiments, the results produced quite reasonable values for the critical exponent β during the sol–gel phase transition in three dimensions. In summary, this Letter has introduced a novel technique for studying the gelation phenomenon in which experiments are quite simple to perform and the fluorescence spectrometer is inexpensive to obtain or already accessible in any laboratory. These are preliminary results and we found them so provocative as to be reported.

References

[1] L.J. Kropp and R.W. Dawson, Fluorescence and phosphorescence of aromatic hydrocarbons in polymethylmethacrylate, International Conference on Molecular Luminescence, ed. E.C. Lim (Benjamin, New York, 1969).
[2] M. Bixon and J. Jortner, J. Chem. Phys. 48 (1968) 715.
[3] J.B. Birks, M.D. Lumb and I.H. Munro, Proc. Roy. Soc. A 277 (1964) 289.
[4] K. Kamioka, S.E. Weber and Y. Morishima, Macromolecules 21 (1988) 972.
[5] P.F. Jones and Siegel, J. Chem. Phys. 50 (1969) 1134.
[6] Ö. Pekcan, submitted for publication.
[7] D. Stauffer, A. Coniglio and M. Adam, Advan. Polym. Sci. (1982) 44.
[8] P.J. Flory, Principles of polymer chemistry (Cornell Univ. Press, Ithaca, 1953).
[9] P.G. de Gennes, Scaling concepts in polymer physics (Cornell Univ. Press, Ithaca, 1979).
[10] K. Dusek, Makromol. Chem. Suppl. 2 (1979) 35.
[11] O. Okay and Ç. Gürün, J. Appl. Polym. Sci. 46 (1992) 421.