Observation of critical opalescence in free radical crosslinking copolymerization of styrene and divinylbenzene by fluorescence method

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Abstract

In situ fluorescence technique was used to study the free-radical crosslinking copolymerization of styrene and divinylbenzene in bulk. Pyrene (Py) was used as a fluorescence probe for the real time gelation experiments. The critical times, t_r required for a dramatic increase in Py intensity, I_p, corresponding to the onset of the gel effect were determined. The spikes in I_p curves were also observed at high crosslinker densities. These spikes were attributed to the existence of "critical opalescence" during the gel formation process where two different gel phases having two different concentrations coexist. t_0 values at which the critical opalescence is occurred are recorded in the close vicinity of the t_r points. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Gelation is a process of random linking of subunits to larger and larger molecules i.e. gelation involves formation of an infinite network. No matter what type of objects are linked, they always exhibit a critical gel point if the system is disordered and if all processes are random. At this critical point the system behaves neither as a liquid nor as a solid on any time and length scale, which means that it forms a critical matter dominated by its fluctuations in structure. Several models have been proposed for gelation [1]. The resulting cluster has one common feature in all these models; its structure has no dominating length scale, there are holes and loops on all scales.

In fluids it is well known that as the temperature is lowered to its critical point, small droplets acquire lateral dimensions on the order of wavelength of light, whereupon the light scatters strongly [2]. This phenomenon is named as "critical opalescence", which states that the density heterogeneities that cause light scattering increase drastically as the critical point is approached. Sufficiently close to the critical point the correlation length becomes as large as the wavelength of light and the density heterogeneities scatter light greatly [2]. In short, density fluctuations cause strong light scattering.

In gels it is known that the turbidity is a direct consequence of light scattered from the spatial heterogeneities of its refractive index. It was proposed that a dispersion of separated pure liquid phase and the remaining gel structure is responsible for the scattering of light [3]. Tanaka et al. examined the effect of gelation temperature on the structural heterogeneities in a polymer gel using quasielastic and elastic light scattering techniques and proposed the existence of three

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types of heterogeneities [4]. First, the dynamic concentration fluctuations in pregel polymer solution are frozen in the final network structure upon the onset of the gelation process. Second, if the polymer solution is in the phase seperation regime there appear to be two gel phases having two different concentrations. The domain sizes of these two phases depend on the condition of the gelation process and can sometimes have a size order of the wavelength of light and scatter light greatly presenting strong opacity to the gel [3]. Third, gel undergoes temporal thermal concentration fluctuations. These heterogeties produce opacity in a gel similar to the critical opalescence of binary fluids. Dynamic concentration fluctuations have been studied by using quasielastic light scattering technique [5,6].

Recently, we have shown that the quenching properties of the excited state of a fluorescing molecule can be used to determine the time for the onset of the gelation during crosslinking copolymerization of methyl methacrylate (MMA) with ethlene glycol dimethacrylate (EGDM) as a crosslinker [7–9]. In the present work, we report that the fluorescence technique can also be used to monitor critical opalescence during free-radical crosslinking copolymerization reactions.

Here, the copolymerization reactions were carried out in bulk using the monomers styrene (S) and commercial divinylbenzene (DVB) with various amounts of DVB as the crosslinker. Commercial DVB consisted of 62% DVB isomers (meta-DVB: para-DVB ratio 2–2.5:1) with the rest being mostly ethylvinyl benzenes (35%). Benzoyl peroxide and pyrene (Py) were used as the initiator and the fluorescence probe for the *in situ* polymerization experiments, respectively. The critical times, t_r required for a drastic increase in the fluorescence intensity I_p of Py were determined by the *in situ* fluorescence experiments, corresponding to the reaction times at which the rate of polymerization becomes maximum due to the gel effect [10]. In this paper we report that a drastic decrease in Py intensity is also observed very close to the t_r point, which creates a spike in intensity, I_p, versus time, t, curve. This spike of I_p at a critical point was interpreted by the concept of "critical opalescence" during the growth of the gel in S-DVB system. It was observed that critical opalescence disappeared at low DVB contents.

2. Fluorescence Technique

Fluorescence and phosphorescence intensities of aromatic molecules are affected by both radiative and non-radiative processes [11]. Whereas the radiative probabilities are relatively independent of the environment and even of molecular species, non-radiative transitions are affected by the enviromental effects [12].

The role of the liquid in such a picture is to add the quasi-continuum of states needed to satisfy energy resonance conditions. The liquid 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 fluorescence charasteristic of Py solutions in various solvents and observed that the rate of monomer internal quenching is affected by solvent quality [13]. 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 liquid 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 [14]. Recently we have reported viscocity effects on low frequency, intermolecular vibrational energies of excited naphthalene in swollen PMMA latex particles [15].

Fluorescence technique for the in situ monitoring of a methacrylate polymerization was first developed by Loutfy [16,17]. A series of fluorescence probes were used to monitor the progress of methacrylate polymerization. The extremely fast deactivation rate of the singlet excited state of these probes was attributed to torsional relaxation [18]. It was shown that environmental factors restricting the internal molecular rotation of these probes lead to a decrease in nonradiative decay rate and consequently an increase in fluorescence yield. Loutfy used these rotor probes to monitor free radical polymerization of MMA, ethyl methacrylate, n-butyl methacrylate and styrene as well as the copolymerization of styrene and n-butyl methacrylate.

In the present work, these properties of fluorescence probes were used to monitor the physical changes occurring during the free radical crosslinking copolymerization of styrene and divinylbenzene.

3. Experimental

Styrene (S, Merck) and commercial DVB (DVB, Merck) were shaken with 10% NaOH, washed with water, dried with anhydrous $CaCl_2$, and finally distilled under reduced pressure. Purity was checked by gas chromatography. Various batches of DVB solution were used. Batch analyses ranged between 50 and 60% DVB isomers (*m*-DVB:p-DVB ratio = 3–3.2:1), the rest being ethylstyrene. Benzoyl peroxide (BP, Merck) was recrystallized from acetone solution. The free-radical crosslinking copolymerization (FCC) of S and DVB was performed in bulk at 70°C in the presence of BP
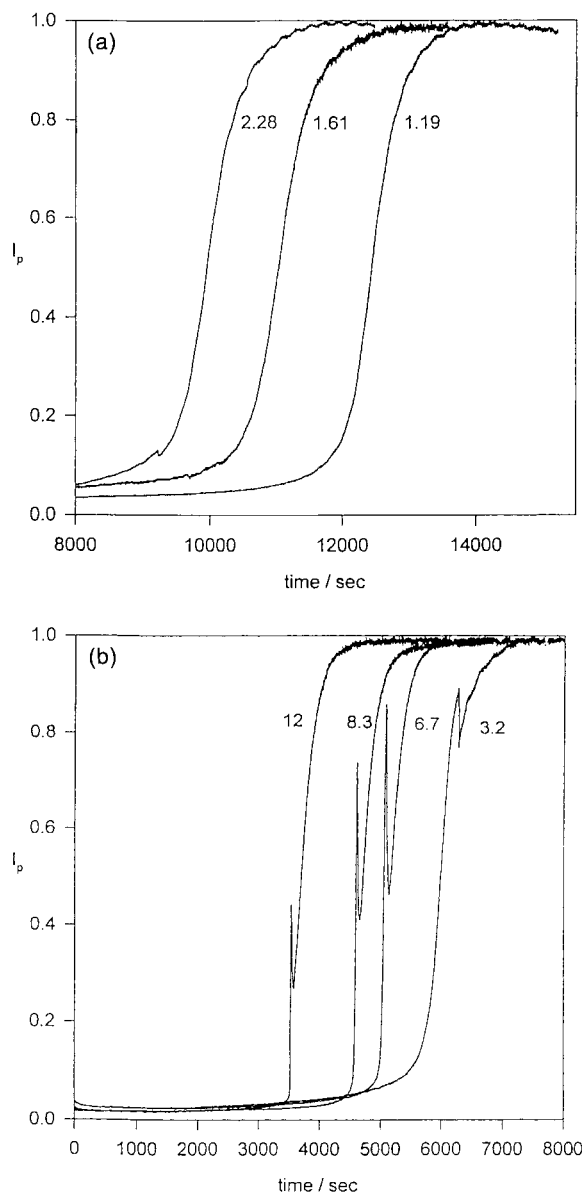
Fig. 1. Plots of Py fluorescence intensity I_p against reaction time t during S-DVB copolymerization in bulk at low (a) and high (b) DVB contents. Time drive mode of the spectrometer was employed and the maximum intensity peak at 395 nm was monitored for data collection. Numbers above the curves indicate the DVB contents in mol%.

as an initiator. The initiator concentration was held constant at 0.100 M. The reaction mixtures were prepared by dissolving BP in the selected S-DVB monomer mixture and flushing with nitrogen 10 min prior to polymerization. DVB concentration is expressed as the mole percent of the DVB isomers in the S-DVB

monomer mixture. In this work, different DVB content in the range from 0.8 to 12 mol% was used for each FCC experiment. Gelation was monitored against the reaction time, t, using in situ fluorescence technique.

Py was used as a fluorescence probe for the in situ steady-state polymerization experiments, where styrene and mobile polymer chains act as an energy sink for the excited Py during polymerization. Later, the formation of bulk polystyrene provides an ideal, unchanged environment for the excited Py molecules. Naturally, from these experiments one may expect a substantial increase in fluorescence intensity, I_p, of Py at a certain time interval. For the fluorescence measurements, reaction mixtures were transferred into round glass tubes of 15 mm internal diameter and they were deoxygenated by bubbling nitrogen for 10 min. The copolymerization of S and DVB was performed in the fluorescence cell of the spectrometer. The Py molecule was excited at 345 nm during the in situ experiments, and the variation in the fluorescence emission intensity, I_p 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 the Model LS-50 spectromer of Perkin-Elmer, equipped with a temperature controller. All measurements were made at 90° position and slit widths were kept at 7 nm.

4. Results and discussion

During the in situ polymerization experiments with Py as a fluorescence probe, no shift was observed in the wavelength of the maximum intensity of Py and all samples kept their transparency except at the point where the critical opalescence occurred during the polymerization process. During in situ fluorescence experiments, drastic increase in the fluorescence intensity of Py was observed at the critical time t_r, which corresponds to the onset of the gel effect, i.e. to the reaction time at which the rate of S-DVB copolymerization reaches a maximum value [10]. Normalized Py intensities, I_p, versus reaction times are plotted in Fig. 1a and b for low and high DVB content, respectively. It is seen that all curves present sudden increase at a given reaction time, and then reach an equilibrium at longer times. Below t_r, where I_p presents small values, Py molecules are relatively free, and they can interact and be quenched by other molecules. However, above t_r, I_p gives large values indicating that the reaction mixture is highly viscous and Py molecules are trapped in a polystyrene network. According to Fig. 1a and b at low DVB content, the increase in I_p takes place at longer times, indicating that trapping of Py molecules in the reaction system is delayed.
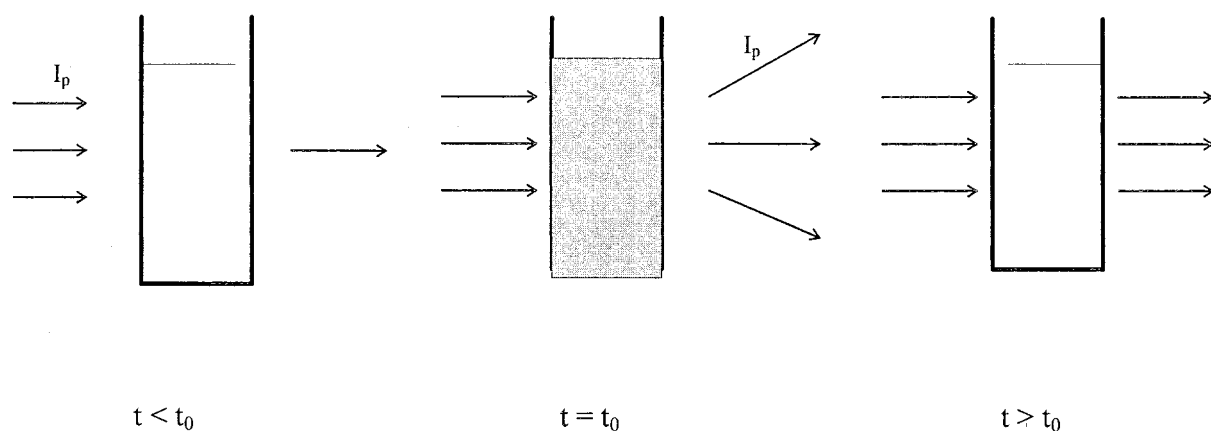
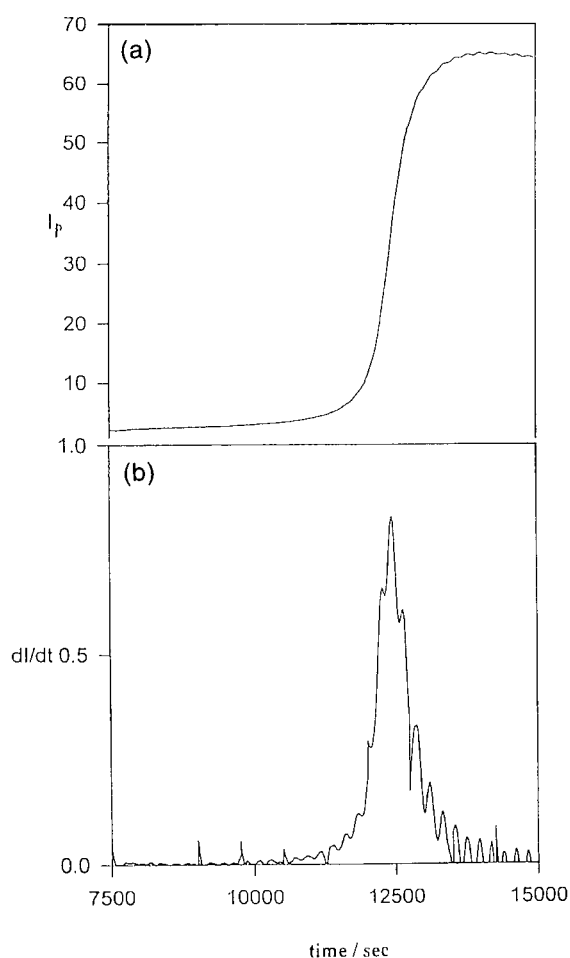Fig. 2. Cartoon representation of critical opalescence phenomenan during gelation below, at, and above t_0.

Fig. 3. Determination of t_r at 70°C for the 1.19 mol% DVB content sample. (a) Plot of Py fluorescence intensity I_p, and (b) its first derivative dI/dt against the reaction time t. The maximum corresponds to t_r in t axis.

Another point shown in Fig. 1b is that the I_p curves exhibit spikes in the close vicinity of t_r, whereas no spikes can be detected at low DVB contents (Fig. 1a). Here we would like to report that the spikes of I_p in Fig. 1b most probably indicate the critical opalescence point, which occurs at the onset of the gel effect, at which the rate of monomer consumption drastically increases. One may expect that, at high DVB concentrations, the gel that grows is highly crosslinked and thus it cannot absorb all the unreached monomers present in the reaction mixture. As a result, it falls in the phase separation regime. Here two gel phases having two different concentrations are formed and the domain sizes of these two phases have a size order of the wavelength of the fluorescence light, which scatter light dramatically producing opacity for the system. By decreasing the DVB content below 3.2 mol% no such spikes in I_p were observed during the gel effect (see Fig. 1b). Morever, the spikes observed at high crosslinker concentrations disappear again due to the conversion of the seperated monomers into the polymer. Cartoon repsesentation of light scattering phenomenon is shown in Fig. 2. Here one may speculate about the existence of the critical crosslinker density above which the critical opalescence occur with two different gel phases having two different concentrations. We have to note that no such critical opalescence was observed during gelation of MMA, which may predict that no such phase separation regime exists during crosslinking copolymerization in MMA system [7,8].

The critical time, t_r, where the onset of gel effect is occured can be determined by taking first derivative of the experimentally obtained I_p curve with respect to time t. Fig. 3a and b present at a typical intensity curve and its derivative (dI_p/dt) against t, respectively. The maximum in the dI/dt curve corresponds to $d^2I_p/dt^2 = 0$, i.e. to the inflection point in curve I_p, which
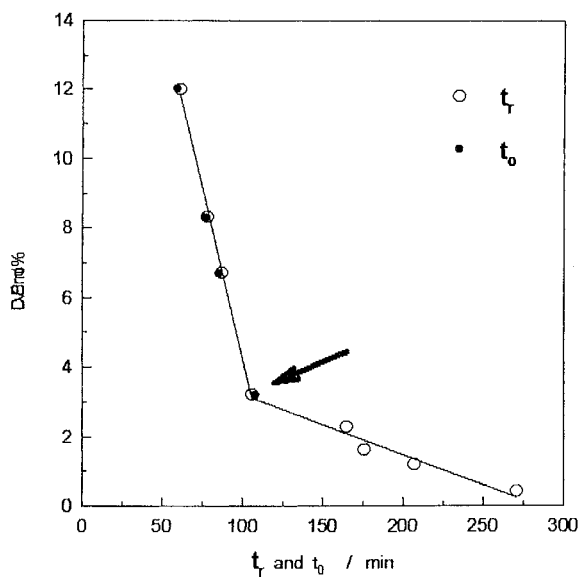
Fig. 4. t_0 and t_r values are shown as a function of the DVB content, the critical crosslinker density is pointed out by an arrow.

gives t_r, on the time axis. On the other hand, the maxima of the spikes shown in I_p versus t curves in Fig. 1b can be taken as the points for the onset of the critical opalescence (t_0). The t_r and t_0 values obtained in this way are plotted versus DVB content in Fig. 4, where the critical crosslinker density is pointed out. Below the critical crosslink density which corresponds to 3.2 mol% DVB, neither phase seperation can occur nor domain sizes of the separated phases are much larger than the wavelength of fluorescence light; as a result, no spikes in I_p were observed during free-radical crosslinking copolymerization in bulk S-DVB system. Interestingly, two different slopes in DVB% versus t_r curves were observed below and above the critical crosslink density.

5. Conclusion

This work presents the existence of "critical opalescence" just below the onset of the gel effect in S-DVB copolymerization where two different phases having two different concentrations coexist. The domain sizes of these two phases have sizes of the order of the wavelength of the fluorescence light and therefore they scatter light dramatically presenting strong opacity to the gel. Here it is shown that in situ fluorescence method can be used to determine the critical opalescence point, t_0 and the critical time t_r for the onset of gel effect as a function of crosslinker density.

References

[1] Family F, Landau DP, editors. Kinetics of Aggregation and Gelation. Amsterdam: North Holland, 1984.
[2] Stanley HE. Introduction to Phase Transitions and Critical Phenomena. New York: Oxford University Press, 1971.
[3] Dusek K. In: Chompff AJ, Newman S, editors. Polymer Networks. New York: Plenum, 1971.
[4] Eriko SM, Michal O, Shao-Tang S, Yong L, Tanaka T. Macromolecules 1994;27:6791.
[5] Tanaka T. Phys Rev 1978;A17:763.
[6] Munch JP, Candau S, Duplessix R, Picot C, Herz J, Benoit J. J Polym Sci, Polym Phys Ed 1976;14:1097.
[7] Pekcan Ö, Yílmaz Y, Okay O. Chem Phys Lett 1994;229:537.
[8] Pekcan Ö, Yílmaz Y, Okay O. Polymer 1996;37:2049.
[9] Pekcan Ö, Yílmaz Y, Okay O. J Appl Polym Sci 1996;61:2279.
[10] Okay O, Kaya D, Pekcan Ö. Polymer (in press).
[11] Kropp LJ, Dawson RW. Fluorescence and phosphorescence of aromatic hydrocarbons in polymethylmethacrylate. In: Lim EC, editor. International Conference on Molecular Luminescence, New York, 1969.
[12] Bixon M, Jortner JJ. Chem Phys 1968;48:715.
[13] Birks JB, Lumb MD, Munro IH. Proc R Soc Lond 1964;A277:289.
[14] Jones PF, Siegel SJ. Chem Phys 1969;50:1134.
[15] Pekcan Ö. J Appl Polym Sci 1995;57:25.
[16] Loutfy RO. Macromolecules 1981;14:270.
[17] Loutfy RO. Pure Appl Chem 1986;58:1239.
[18] Loutfy RO, Law KY. J Phys Chem 1980;84:2803.