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In situ photon transmission technique for monitoring phase separation in real time during gelation

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Summary

In situ, real time photon transmission technique was used to monitor the formation of heterogeneities during the free-radical crosslinking polymerization of acrylamide in the presence of N,N'-methylenebis(acrylamide) (BAAm) as a crosslinker. Two different gelation experiments were performed with various BAAm and water contents separately at room temperature. It was observed that the transmitted photon intensity, I_{tr} decreases dramatically at a certain time, in both type of experiments during the gel formation process from interconnected microgels. Decrease in I_{tr} was interpreted in terms of phase separation during gelation. The extent of phase separation was measured depending on the crosslinker content and on the degree of monomer dilution during the gel formation process.

Introduction

It is well known that the turbidity of a gel is a direct result of light scattered from the spatial inhomogeneities of its refractive index. It was proposed that when a polymer gel is in the phase separation regime, there appear 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 tremendously, given strong opacity to the gel (1,2).

The existence of phase separated domains in polymer gels, i.e., the heterogeneity is a non-ideality affecting directly the physical properties of gels such as swelling, permeability, turbidity, and elasticity (3,4). Heterogeneity appears as a result of phase separation during the gel formation process. Extensive work has been reported in the literature for the physical properties of poly(acrylamide) (PAAm) gels; however very few of them concerned with the formation of heterogeneities in gels (5-11).

In situ photon transmission study for aging in PAAm gels due to multiple swelling was recently reported from our laboratory (12), where it was observed that the transmitted light intensity I_{tr} decreases continuously as PAAm gel is swelled. The decrease in I_{tr} was attributed to increase in scattered light intensity which is originated from the contrast between frozen blob clusters and holes in the swollen gel.

In this work, in situ real time photon transmission experiments are reported for the free-radical crosslinking polymerization of acrylamide (AAm) with N,N'-methylene(bis)acrylamide (BAAm) as a crosslinker at various BAAm and water contents. It was observed that transmitted photon intensity I_{tr} decreased dramatically above certain BAAm or water contents during gelation process. Decrease in I_{tr} due to

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the increase in scattered light intensity indicates spatial phase separation, which appears during the gel formation from AAm and BAAm monomers in aqueous solutions.

Experimental

The free-radical crosslinking polymerization of AAm (Merck) was carried out using BAAm (Merck) as a crosslinker in aqueous solution. Ammonium persulfate (APS, Merck) and N,N,N',N'-tetramethylethylenediamine (TEMED, Merck) were respectively the initiator and the accelerator. The reactions were conducted at room temperature (21±2°C). Two different sets of experiments were carried out. In the first and second sets of experiment only the BAAm and the total monomer concentrations (c in w/v %) were varied separately and all the other parameters are kept constant. The composition of the polymerization solutions is given in Tab. 1 for the first and second experimental sets (FS and SS, respectively).

FS: [AAm] = 1.41 M, total monomer concentration (c) = 10 w/v %,								
Sample Number	1	2	3	4	5	6	7	8
[BAAm] / (mM)	13	26	33	39	45	52	65	78
BAAm mol-%	0.9	1.8	2.3	2.7	3.1	3.6	4.4	5.2

SC: [BAAm] = 38 mM						
Sample Number	1	2	3	4	5	6
[AAm] / M	2.4	1.8	1.4	1.2	1.0	0.8
c / w/v %	17.3	13.1	10.6	8.9	7.7	6.1

Table 1 . Synthesis conditions of PAAm gels at room temperature.
APS concentration = 7 mM. TEMED concentration = 40 μl/100 mL water

Eight and six samples were prepared for FS and SS experiments respectively. After preparing the reaction solutions containing AAm, BAAm, and APS, and after bubbling nitrogen, TEMED was added to the solutions. Gelations were performed at room temperature in 1.0 x 1.0 cm quartz cells which are placed in UVV spectrometer. Gelations were monitored in real time and in situ photon transmission measurements were performed using a Perkin Elmer UVV spectrometer. Photon transmission intensities, I_{tr} were measured in real time by using the time drive mode of the spectrometer during copolymerization of AAm with BAAm at 440 nm wavelength. Typical I_{tr} curves against gelation time for FS and SS are given in Figs. 1a and b respectively. Visual observations indicated that all the FS and SS experiments result in the gel formation after 350 sec of the reaction time.

Results and discussion

Fig.1 shows that the transmitted light intensity I_{tr} decreases dramatically above a certain time by indicating that strong opalescence occurs during gelation for all samples except the first samples of each series. According to Tab. 1, these first samples correspond to the reaction mixtures with the lowest BAAm (0.9 mol-%) and the highest monomer concentrations (17 w/v %). Thus, one can predict that, for this crosslinker or monomer concentrations, homogeneous gels form, or, the heterogeneities appeared can not be captured using this technique.

In Figs. 2a and 2b, the normalized intensities with respect to the intensity at zero polymerization time (I_{tr}/I_0) are shown as a function of the reaction time for the first and second sets of experiments, respectively. It is seen I_{tr} rapidly decreases and attains a limiting value after a given reaction time. The decrease in I_{tr} with time becomes more abrupt as the crosslinker concentration increases (Fig. 2a) or as the monomer concentration decreases (Fig. 2b).

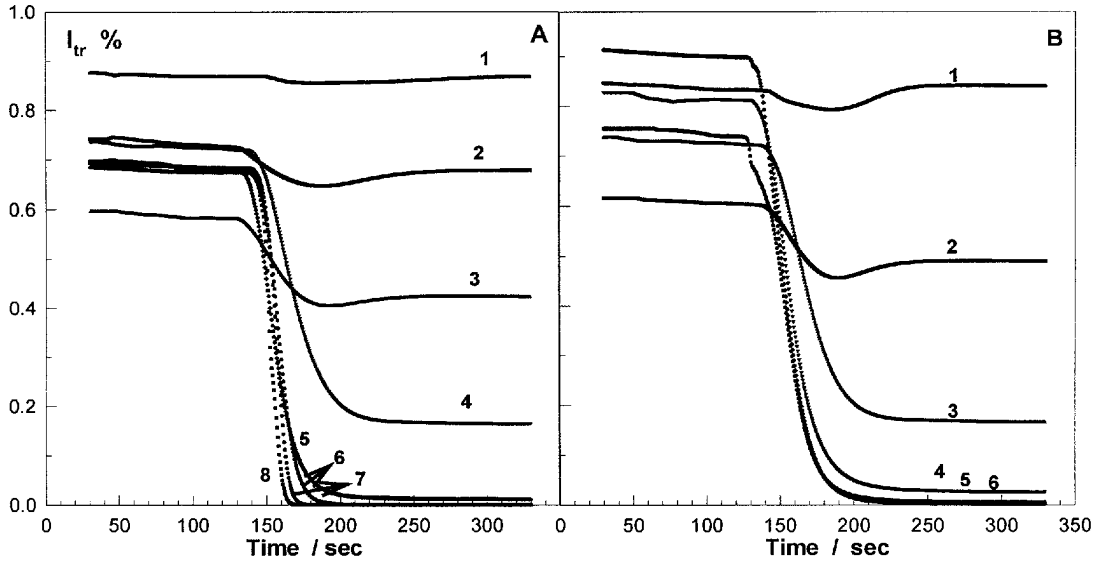


Fig. 1. Transmitted photon intensities from the reaction solutions for the first (A) and second sets of experiments shown as a function of the reaction time of crosslinking polymerization of AAm with BAAm as a crosslinker. The numbers in the figures correspond to the sample numbers in Tab. 1.

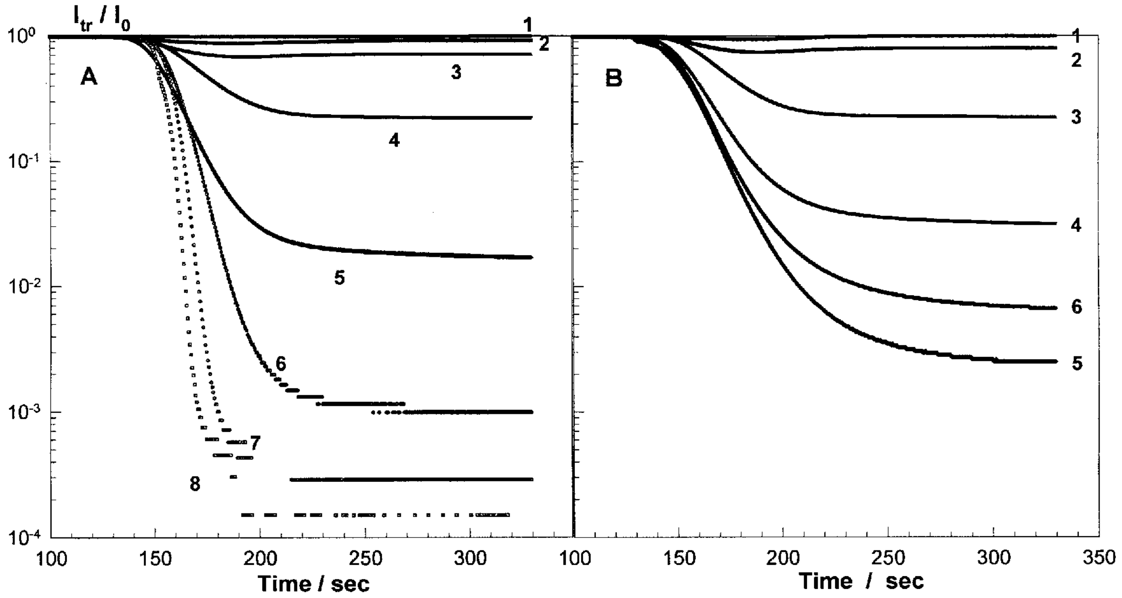


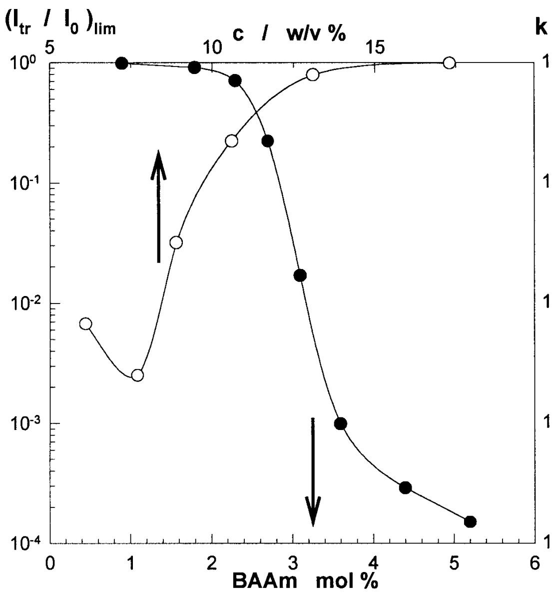
Fig. 2. Normalized transmitted photon intensities from the reaction solutions for the first (A) and second sets of experiments shown as a function of the reaction time of crosslinking polymerization of AAm with BAAm as a crosslinker. The numbers in the figures correspond to the sample numbers in Tab. 1.

In Fig. 3, the limiting values of the normalized I_{tr} intensities are shown as a function of the crosslinker BAAm and monomer concentrations. Increasing concentration of the crosslinker or decreasing monomer concentration (c) shifts the limiting intensities to smaller values. Since the decrease in I_{tr} corresponds to an increase in the scattered light intensity, Figs. 2 and 3 indicate increasing degree of heterogeneity in PAAm gels with increasing crosslinker or water contents in the feed. It was reported that, during the free-radical crosslinking copolymerization of AAm and BAAm, about 80% pendant vinyl groups are consumed in cycle formation reactions (8). Cyclization and multiple crosslinking reactions lead to the formation of microgel particles in the pregel solution and formation of highly crosslinked regions in the final macronetwork (9,10). High crosslinker or high water contents promote formation of compact microgels in the reaction solution, which cannot absorb all the solvent present in the system and lead to a phase separation. Previous works indeed show separation of a liquid phase out of the gel phase and formation of gel particles in the reaction system during the free-radical crosslinking copolymerization of AAm and BAAm (7). Phase separation may occur in the form of microsyneresis (separation of solution droplets from the continuous gel phase) or macrosyneresis (deswelling of the gel phase) (5,6). In both cases, increasing crosslinker concentration or increasing degree of dilution increases the concentration difference between the phases leading to the decrease in the transmitted light intensities at a given reaction time. It should be noted that the samples 5 and 6 of the SS experiments having the lowest initial monomer concentrations (Fig. 2b) do not follow the dependence found for other samples. This may be related to the inhomogeneous distribution of microgels within the reaction system due to the high degree of dilution.

Since the scattered light intensity relates to the number of separated domains, Fig. 3 also indicates formation of increasing number of microgels with increasing crosslinker or with decreasing monomer concentration. Moreover, since light scattering characterizes heterogeneities of a system having dimensions of the order of the wavelength of the incident light, the experimental data also reveal that the microgels in the present system have a size order of about 400 nm.

The rate of change in I_{tr} with time $(-dI_r/dt)$ corresponds to the growth rate of phase separated domains in the reaction system. To compare the growth rates, we calculated the rates *k* at the inflection points in Fig. 2. In Fig. 4, the growth rates *k* are shown as a function of the crosslinker and monomer concentrations. The growth rate of separated domains dramatically increases as the BAAm content increases from 1 and 3 mol-% or as the monomer concentration decreases from 13 to 10 w/v %. These concentrations correspond to the critical concentrations for the formation of macrogels of interconnected compact microgels (10).

In summary, this paper has introduced a novel technique to study the heterogeneities during the gel formation process. It was shown that the appearance of a heterogeneity in crosslinking polymerization is reflected by an abrupt decrease in the transmitted photon intensity in the system. It was also shown that the free-radical crosslinking copolymerization of AAm and BAAm proceeds in a heterogeneous medium.



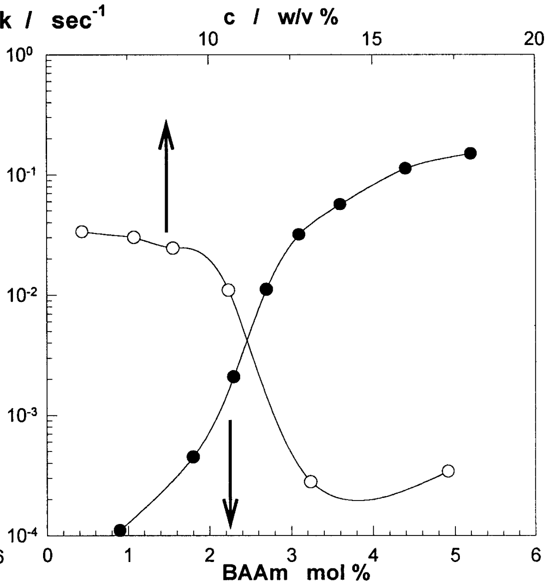


Fig. 3 (left). Limiting values of normalized transmitted light intensity shown as a function of the BAAm (●) and monomer concentration (○).

Fig. 4 (right). Growth rate of phase separated domains *k* shown as a function of the BAAm (●) and monomer concentration (○).

References

1. Dusek K (1971) *In* Polymer Networks, Structure and Mechanical Properties. Chompff AJ, Newman S, Eds, Plenum Press, NY
2. Matsuo ES, Orkisz M, Sun ST, Li Y, Tanaka T (1994) Macromolecules 27: 6791
3. Richards EG, Temple C (1971) J Nat Phys Sci 230:92
4. Bansil R, Gupta MK(1980) Ferroelectrics 30:64
5. Dusek K (1965) J Polym Sci Polym Letters 3:209
6. Dusek K, Prins W (1969) Adv Polym Sci 6:1
7. Durmaz S, Okay O (2000) Polymer 41:5729
8. Naghash HJ, Okay O (1996) J Appl Polym Sci 60: 971
9. Okay O, Kurz M, Lutz K, Funke W (1995) Macromolecules 28: 2728
10. Funke W, Joos-Muller B, Okay O (1998), Adv Polym Sci 136:139
11. Weiss N, van Vliet T, Silberberg A (1974) J Polym Sci Polym Phys Ed 17: 2229
12. Pekcan O, Catalgil-Giz H, Caliskan M (1998) Polymer 39: 4453