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Photon transmission technique for monitoring free radical crosslinking copolymerization in various crosslinker contents

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Abstract

Photon transmission technique was used to monitor the free radical crosslinking copolymerization (FCC) of acrylamide (AAm) and *N,N′*-methylenebis (acrylamide) (Bis) in time. FCC experiments were performed with various Bis contents. It was observed that transmitted photon intensity, I_{tr} decreased dramatically at a certain gelation time, which is attributed to the increase in scattered light intensity, I_{sc} during macrogel formation from interconnected microgels. Increase in I_{sc} was modeled using Rayleigh's equation where gelation time was found to be proportional to the volume of the microgels. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photon transmission technique; Free radical crosslinking copolymerization; Scattered light intensity

1. Introduction

It has been 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 solution 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 tremendously, given strong opacity to the gel [1].

Extensive work has been reported in the literature for the physical properties of PAAm gels, however very few of them are concerned with the formation mechanism by free-radical crosslinking copolymerization (FCC). FCC of AAm and Bis monomers in water solution was studied extensively [2,3] and inhomogeneous crosslinking in PAAm gel was attributed to the difference in the vinyl group reactivity. Recently AAm and Bis copolymerization was investigated in water at a monomer concentration of 1.8 w/v% [4]. Experiments indicate that 80% of pendant vinyl groups are consumed by cyclization reactions and it was observed that the equilibrium degree of swelling of the PAAm gel is independent of their crosslinker content. These results suggested the formation of microgels prior to the onset of macrogelation, and as the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends. The microgels seem to act as the junction points of the final heterogeneous network.

In situ photon transmission study for aging in acrylamide gels due to multiple swelling was recently reported from our laboratory [5], where it was observed that transmitted light intensity I_{tr}, decreased continuously as PAAm gel is swelled. The decrease in I_{tr} was attributed to the increase in scattered light intensity, which have originated from the contrast between frozen blob clusters and holes in the swollen gel. In this work in situ photon transmission experiments are reported during the copolymerization of AAm with various Bis contents. It was observed that transmitted photon intensity, I_{tr} decreased dramatically, during gelation process, which was attributed to the increase in scattered light intensity, I_{sc} from the gel due to spatial phase separation, which appear during copolymerization of AAm with Bis. The increase in I_{sc} against time was modeled using Rayleigh's equation. It was observed that volume v, of microgel particles grows linear in time and numerical concentration, c of particles are found to be proportional to the Bis content.

2. Light scattering

Light scattering is caused by density and concentration fluctuations, i.e. by deviation of density and concentration

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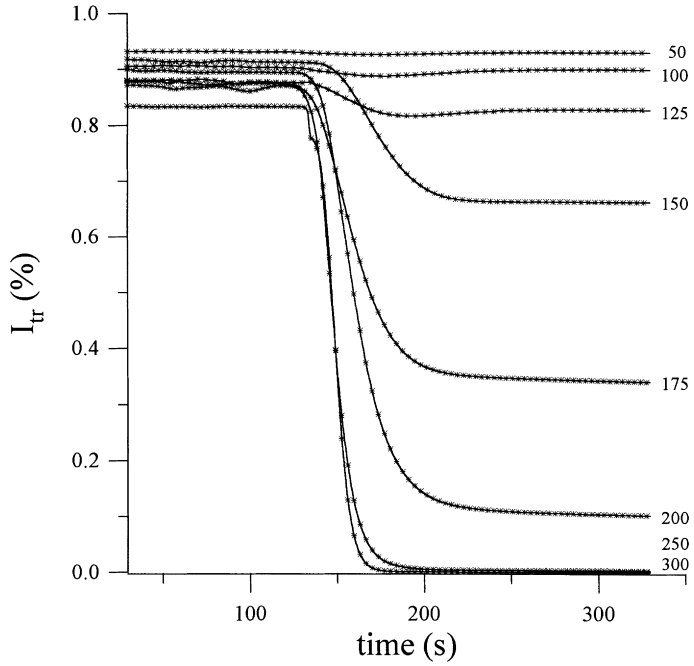

Fig. 1. Variation in transmitted photon intensities, I_{tr} versus gelation time, t during in situ FCC in eight different Bis content at 690 nm wavelength. Numbers on each curve present the Bis content in milligrams.

from their uniform values in a dispersed medium. Light is scattered only when a light wavelength, λ is greater than the size of a particle of the dispersed phase. If λ is much smaller than the particle diameter, light is reflected. If the intensity of incident light is I_0 on passage of the light through a dispersed medium, the incident intensity is reduced to I_{sc} as a result of scattering. Rayleigh derived an equation by excluding the absorption of light by the medium, which connects I_0 with I_{sc}, the intensity of light scattered per unit volume of a dilute system as follows [6]:

$$I_{sc} = av^2 I_0, \tag{1}$$

where $a = kc\lambda^{-\eta}$. This equation is valid for spherical particles which do not conduct electric current and are small in comparison with the wavelength, λ of the incident light. Here k is the coefficient related to the indices of refraction of the dispersed phase and the dispersion medium [6]. (Here polymer phase and aqueous AAm medium corresponds to the above description.) v represents the volume of a single particle and c is the numerical concentration, i.e. the number of particles in 1 cc of the system in Eq. (1). Rayleigh's equation determines the opalescence of the medium and can be used for particles whose size is not more than 0.1 of the wavelength of light, i.e. for particles of diameters from 40 to 70 nm. In this case I_{sc} varies in inverse proportion to the fourth power of λ ($\eta = 4$). In fact it was observed that η changes from 4 to 2.8 depending on the particle size [6].

When the size of particles in the dispersed medium becomes much greater than λ, light is no more scattered but reflected, regardless of the wavelength of the incident light. If the particles are too large in size, reflection of light from them increases which causes the reduction of the intensity of scattered light, however in the mean time the intensity of light scattering decreases as the particle size decreases. Therefore dispersed medium scatters light to the greatest extent.

3. Experimental

Each gel was prepared by using 2.5 g of AAm and 40 mg of ammonium persulfate (APS) as an initiator by dissolving them in 25 cc of water in which 10 μl of tetramethyl ethylenediamin was added as an accelerator. Eight different gels were obtained by adding 50, 100, 125, 150, 175, 200, 250 and 300 mg Bis into the each of the gels prepared by the above procedure. Gelations were performed at room temperature in 1.0×1.0 cm^2 quartz cells in air which are placed in UVV spectrometer. Gelations were monitor in time and in situ photon transmission measurements were performed using a Perkin–Elmer UVV spectrometer. Photon transmission intensities, I_{tr} were measured at 690 nm in time by using the time drive mode of the spectrometer during copolymerization of AAm with Bis.

4. Results and discussion

Typical I_{tr} curves against gelation time are given in Fig. 1 for the FCC in eight different Bis contents. In Fig. 1 it is seen that I_{tr} intensity decreased dramatically above a certain Bis content by indicating that opalescence occurs during

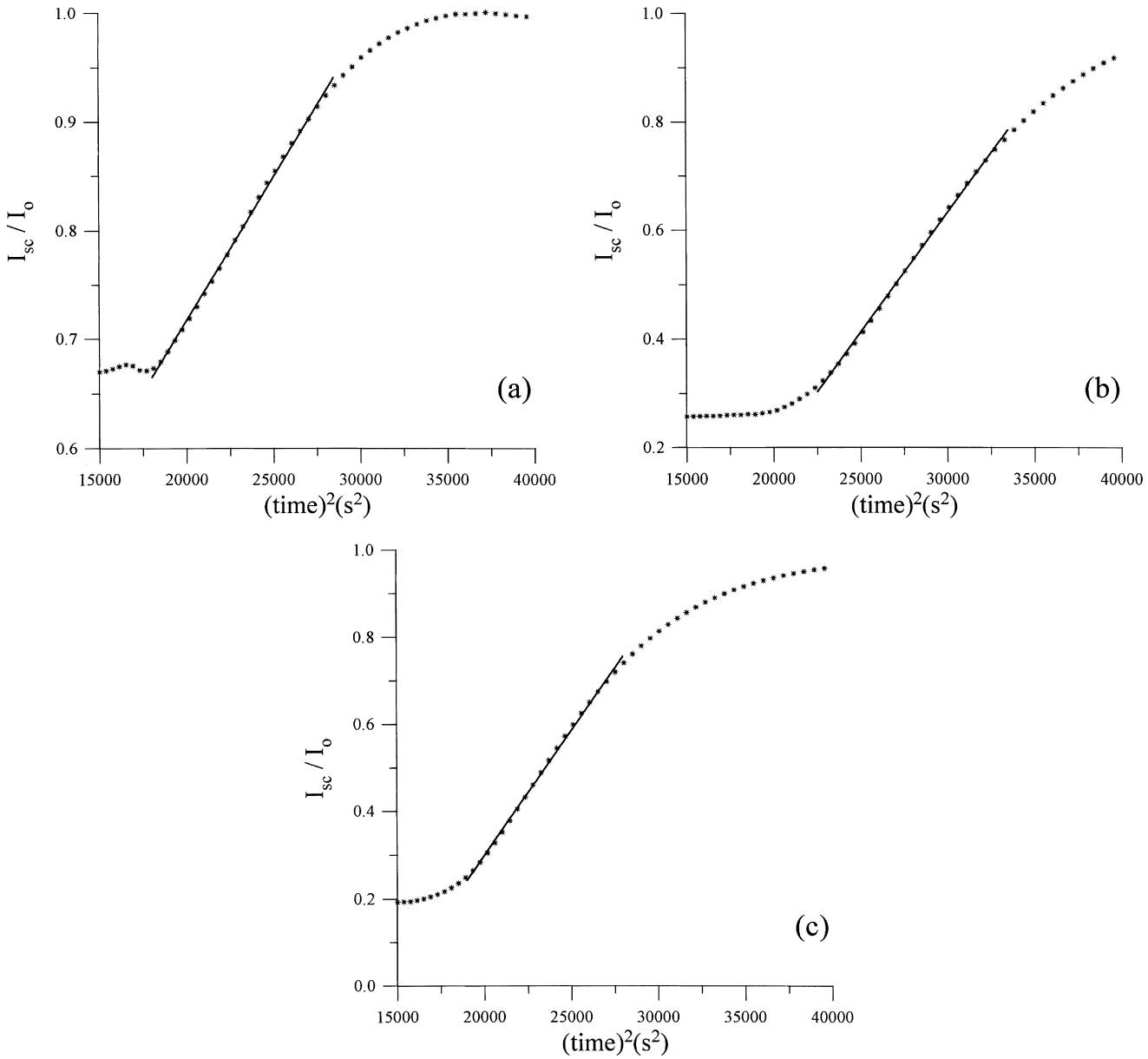

Fig. 2. Variation in the scattered light intensity, I_{sc} at 690 nm versus t^2 during in situ FCC for: (a) 125; (b) 150; (c) 175 mg Bis content samples.

gelation. In order to interpret the results in Fig. 1, Eq. (1) is employed where it can be assumed that the decrease in I_{tr} during gelation solely originates from the increase in scattering intensity, I_{sc}, i.e. $I_{sc} = (1 - I_{tr})$. We try to fit the I_{sc} data to various time dependences such as $t^{1/2}$, t, t^2 and t^3. The best fits are obtained when I_{sc} is taken as proportional to t^2. In Fig. 2(a)–(c) normalized I_{sc} intensities are plotted versus t^2 for the experiments for 125, 150 and 175 mg Bis content samples, respectively. It is seen in Fig. 2 that I_{sc} present an increase above a certain time by indicating that hydrogel system scatters light dramatically by presenting a strong opalescence above this critical time. These results can be modeled by knowing the fact that formation of PAAm microgels occurs prior to the onset of macrogelation [4]. Then as the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends due to the high extent of cyclization reactions. At this stage highly intramolecularly crosslinked microgel particles formed in the pre-gel period act as junction points. The microgels are presented as the junction points of the final inhomogeneous network structure. Increasing the crosslinker content only increases the compactness or the concentration of the junction points without changing the distance between the microgels [4]. Fig. 3(a)–(c) presents the three different network structures formed from microgels by increasing the amount of crosslinker contents. As the crosslinker content increases the number of microgel particles increase which results in high compactness of the network, even the particle sizes decrease due to highly intramolecular crosslinking.

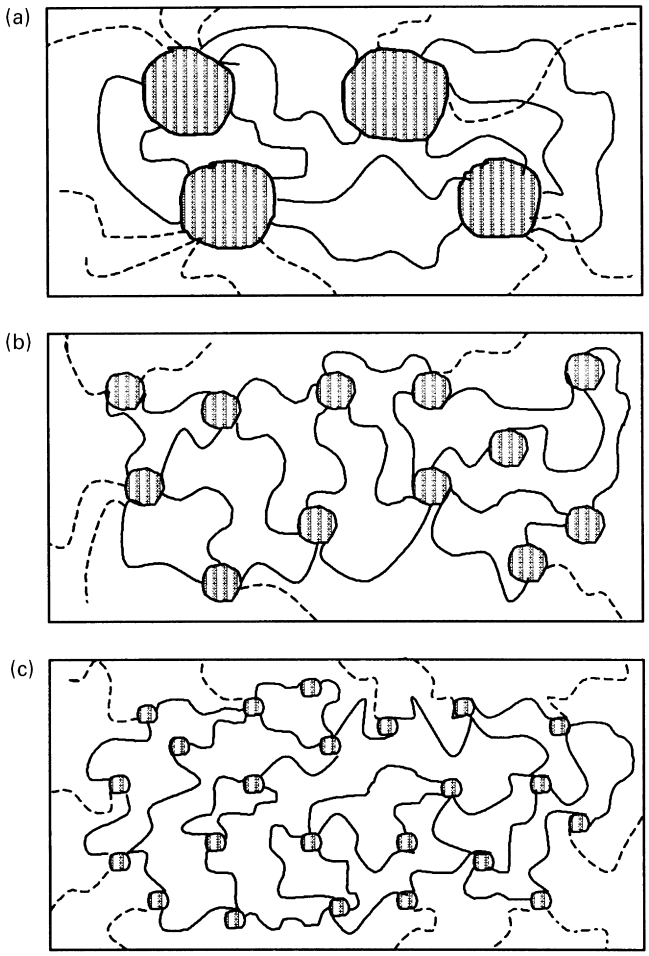

Fig. 3. Cartoon representation of the PAAm macrogels formed from microgels from: (a) low; (b) medium; and (c) high Bis content samples.

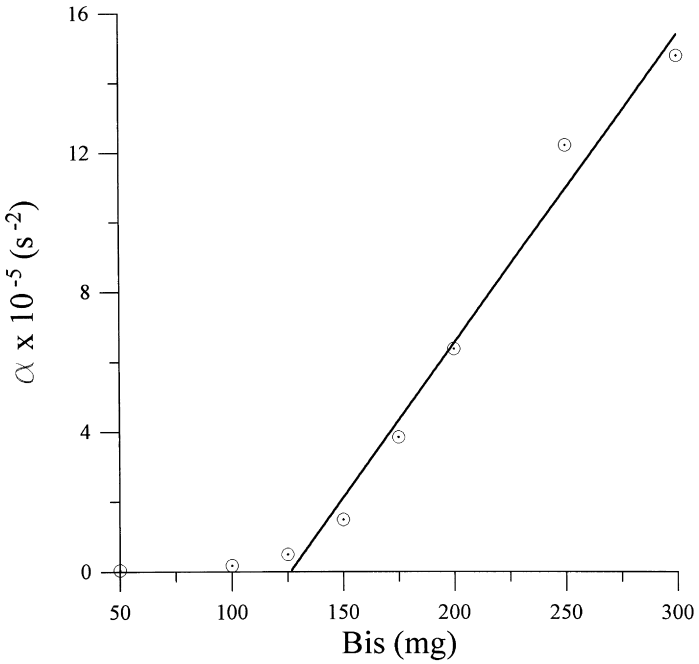

Fig. 4. The plots of α $(= a\beta)$ versus Bis content, at 690 nm wavelength.

Here the gel in Fig. 3(c) scatters more light than the gel in Fig. 3(a) and (b).

If the microgel particles are assumed to be spherical with the volume v which grows linear in time, t during gelation, then the linear portions of I_{sc} data in Fig. 2 are fitted to Eq. (1). I_{sc}–t^2 curves in Fig. 2 produces the slopes which provides the values of α $(= a\beta)$, where β is the proportionality constant. The measured α values in various crosslinker content are plotted versus crosslinker (Bis) content in Fig. 4, where except very low Bis content the relation is quiet linear. This behavior indicates that increasing Bis content increases the number of microgel particles which causes the increase in the compactness of the macrogel structure (see Fig. 3). Here it has to be noted that the volume, v of the microgel particle grows as the gelation time, t is increased which satisfies the requirements in Eq. (1). Here we have to note that the growth of the size of a microgel occurs at a very short time interval (140–170 s) dependent on the Bis content as seen Fig. 1.

In conclusion this manuscript reports the preliminary work for monitoring gelation using photon transmission technique. This work has to be extended for monitoring of gelation at various wavelengths, which may help one to monitor the evolution of the microgel sizes. As in Eq. (1), η is the exponent of the wavelength of scattered light intensity, then log–log plot of I_{sc} versus λ should produce η which can predict the particle size of microgels during the gelation process. Besides that similar experiments can be done in various water content at various wavelengths from which one may understand the phase separation mechanism during gelation.

References

[1] Dusek K. In: Chompff AJ, Newman S, editors. Polymer networks structure and mechanical properties, New York: Plenum Press, 1971.
[2] Nieto JL, Baselga J, Hernandez-Fuentes I, Llorente MA, Pierola IF. Eur Polym J 1987;23:551.
[3] Baselga J, Llorente MA, Hernandez-Fuentes I, Pierola IF. Eur Polym J 1989;25:471.
[4] Naghash HJ, Okay O. Appl Polym Sci 1996;60:971.
[5] Pekcan Ö, Çatalgil-Giz H, Çalışkan M. Polymer 1998;39:4453.
[6] Voyutsky S. Colloid chemistry, Moscow: MIR, 1978.