In situ photon transmission technique for monitoring formation of hydrogels in real-time at various water contents

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Abstract

In situ photon transmission technique was used to monitor the free radical crosslinking copolymerization (FCC) of acrylamide (AAm) and N,N'-methylenebis (acrylamide) (Bis) in real-time. Gelation experiments were performed in various water contents at various wavelengths. 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 FCC. Increase in I_{sc} was modeled using Rayleigh's equation where gelation time was found to be proportional to the volume of the microgels. The change in I_{sc} is found to be inversely proportional to the thirth power of the wavelength, λ, for high water content samples at early times. However, low water content samples produce smaller and constant power of λ during FCC at all times. The sizes of microgel particles and phase-separated domains were estimated. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the last decade considerable attention has been paid to the use of hydrophilic gels called hydrogels as specific sorbents and support carriers in biomedical applications. Investigations of the swelling behavior of acrylamide (AAm) based hydrogels have been reported constantly in the last few decades. It is well known that swelling behavior of hydrogels are dependent on their network hetero-geneities. These structural heterogeneities of hydrogels affect its physical properties such as optical and phase properties. Thus, understanding the formation mechanism of hydrogel is of great interest in predicting their physical properties.

Very few crosslinked polymers are known with uniformly distributed crosslinks, i.e. crosslinked polymers are frequently inhomogeneous both as to their chemical com-position and the distribution of crosslinks within their network [1,2]. Inhomogeneous structures may originate from phase separation during polymerization and crosslink-ing. In some instances heterogeneous networks can be prepared intentionally by copolymerizing reactive spherical particals of submicron size with difunctional monomers [1]. Polymerization of tetrafunctional or multifunctional monomers in emulsion or highly dilute solutions can be used to synthesize these spherical particles which are known as microgels. The reactive microgels are intra-molecularly crosslinked macromolecules of colloidal sizes and can be used as multifunctional crosslinkers to form inhomogeneous networks [1,3]. A drawback of reactive microgels is their instability due to the pendant double bonds at the surface, which may react easily with each other to form insoluble agglomerates.

The first experiments on synthesizing mocromolecules with spherical structure go back to Staudinger [4]. The idea to synthesize reactive microgels has derived from the fact that they are formed as intermediates in copolymeriza-tion reactions. The formation of microgels during the network formation process, long before macrogelation process originates from the existence of unequal reactive groups and cyclization. During copolymerization reaction the growing chains in the pregel stage are rich in crosslinker units due to higher reactivity of them, as a result these chains are highly diluted by the monomer and the solvent. Then cyclization predominates in the early stage of the reaction. As a consequence, the growing chains become internally crosslinked and their structure approaches the microgels. Therefore, the appearance of the microgels during the network formation processes can be compared with the formation of primary molecules as intermediates in the classical gelation theories [5].

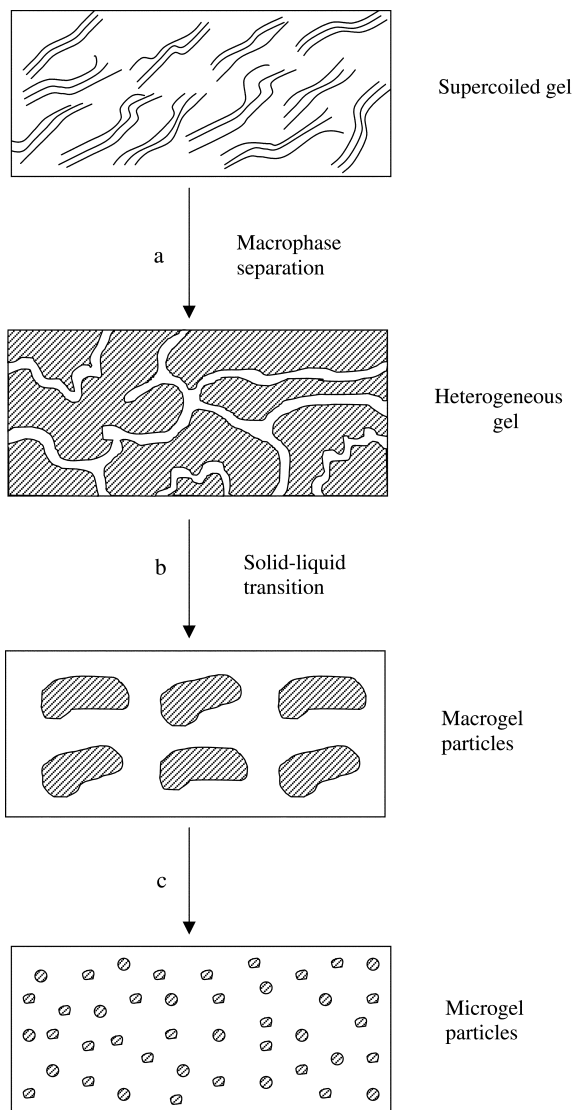* Corresponding author. Tel.: +90-212-285-3213; fax: +90-212-285-6366.

Fig. 1. Formation of various structures in FCC in various water contents.

For spherical, homogeneous, and isotropic particles the scattered-light intensity and particle size can in certain conditions be unambiguously correlated. This does not hold true, however, for irregularly shaped particles or for those possessing an internal structure, since in such cases, the scattered-light intensity depends on orientation of the particle within the measuring medium. A number of authors have used photon correlation spectroscopy to investigate the light-scattering properties of gels [6,7]. The collective diffusion coefficient in polyacrylamide (PAAm)—water gels was measured using light scattering properties of this system. The values of the collective diffusion coefficient was measured from macroscopic swelling experiments in spherical and cylindrical PAAm gels using quasielastic light-scattering technique [8]. In situ photon transmission study for aging in acrylamide gels due to multiple swelling was recently reported from our laboratory [9], 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 real-time photon transmission experiments are reported during the copolymerization of AAm in various water contents. It was observed that transmitted photon intensity, I_{tr}, decreased dramatically above certain critical time, during gelation process. Decrease in I_{tr} was attributed to the increase in scattered light intensity, I_{sc}, from the gel due to microgel formation, which appear during copolymerization of AAm with Bis. The increase in I_{sc} against time was modeled using Rayleigh's equation and it is observed that volume v, of PAAm particles grows linear in time. It is found that numerical concentration, c, of particles are proportional to the water content. The change in I_{sc} is found to be inversely proportional to the third power of the wavelength, λ, of incident light for high water content samples at early times. Lower water content samples, however, produce smaller power of λ during FCC.

2. Light scattering

It has been well known that light scattering causes opalescence when a light beam is passed through a solution. Light scattering is caused by density and concentration fluctuations, i.e. by deviation of density and concentration 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 and 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:

$$I_{sc} = I_0 k c v^2 \lambda^{-\eta} \tag{1}$$

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. In Eq. (1) k contains n_1 and n_0 which are the indices of refraction of the dispersed phase and the dispersion medium, respectively. v represents the volume of a single particle and c is the number of particles in 1 cm^3 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} changes in inverse proportion to the fourth power of λ ($\eta = 4$). However, for larger particles I_{sc} changes in inverse proportion to a smaller power of λ. The dependence of η on particle size was studied in mono-dispersed latex systems of polystyrene [10] and it was observed that η decreased from 4 to 2.8.

Table 1
Recipe for the gel preparations

Sample number	1	2	3	4	5	6
Water (cm^3)	15	20	25	30	35	45
Acrylamide (monomer) (g)	2.5	2.5	2.5	2.5	2.5	2.5
Ammonium persulfate (mg)	25	33	40	47	55	70
Methylenebis (acrylamide) (mg)	95	122	150	177	205	260
Tetramethyl ethylenediamin (μl)	10	10	10	10	10	10

When the size of the particles in the dispersed medium becomes much greater than λ, light is no longer 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 media scatter light to a great extent.

3. Phase separation

In general when a good solvent is used in solution polymerization the formed gel may have a supercoiled (expanded) structure. Naturally supercoiled gel swells in a good solvent more than the gel synthesized with bulk polymerization. If the amount of the solvent is increased, phase separation increases and two continuous phases, a gel and a solvent phase can be formed. This structure is called a heterogeneous gel. Further increase in the solvent above a

critical point, the system becomes discontinuous, because the amount of monomer is not sufficient and growing chains cannot occupy the whole available volume. In this case the macrogel particles are formed. Increasing the amount of solvent then decreases the size of the gel particles that are called microgels. Here it may be expected that at infinite dilution the macromolecules consist of only intra-molecularly crosslinked primary chains, which may be considered as primary particles. In conclusion, during solution polymerization, three main transitions can be distinguished: (a) the transition from supercoiled to hetero-geneous gels (macrophase separation); (b) solid–liquid transition which happens from heterogeneous gel to macro-gel particles; and (c) macrogel–microgel transition. There-fore, increasing water content during FCC results in an increasing number of microgel particles in the system. The structures and transitions between them are presented in Fig. 1.

4. Experimental

Six different gels were produced by using AAm monomer and ammonium persulfate (APS) as an initiator by dissolv-ing them in water in which 10 μl of tetramethyl ethylene-diamin was added as an accelerator. Water, AAm, APS and Bis contents are listed in Table 1 for the six different gel samples. Gelations were performed at room temperature in 1.0×1.0 cm^2 quartz cells which are placed in UVV spectro-meter. 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 copolymeriza-tion of AAm with Bis at five different wavelengths (440, 500, 550, 600 and 690 nm). Typical I_{tr} curves against gela-tion time are given in Fig. 2 for the experiments made at 440 nm wavelength for six different water content samples. In Fig. 3, I_{tr} curves at various wavelengths are compared for 30 cm^3 water content sample. In Figs. 2 and 3 it is seen that I_{tr} intensity decreased dramatically above a certain time and water content by indicating that opalescence occurs during gelation. Here one can predict that below 15 cm^3 water content the formation of a hydrogel seems quite homogeneous.
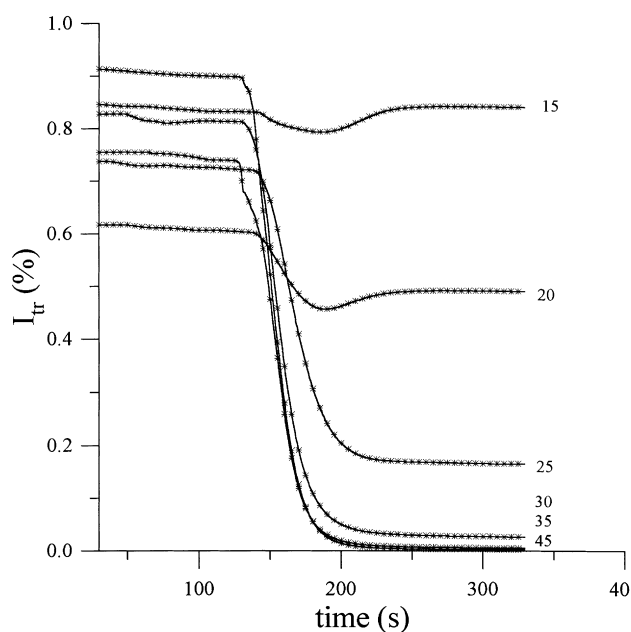

Fig. 2. Variation in transmitted photon intensities I_{tr} versus gelation time t during in situ FCC in six different water contents for 440 nm wavelength. Numbers on each curve represent the water content in cm^3.
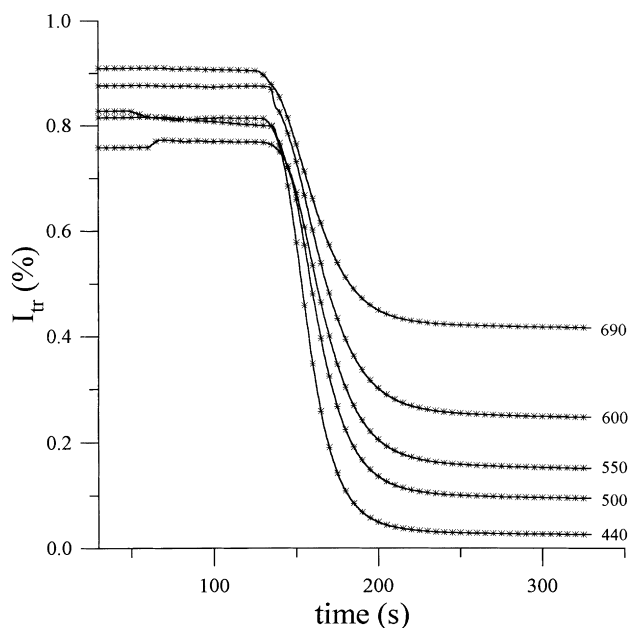
Fig. 3. Variation in transmitted photon intensities I_{tr} versus gelation time t during in situ FCC at different wavelengths for 30 cm³ water content sample. Numbers on each curve indicate the wavelength of the transmitted light.

5. Results and discussion

In order to interpret the results in Figs. 2 and 3, 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}. In Fig. 4 normalized $I_{sc} = (1 - I_{tr})$ intensities are plotted versus t^2 for the 440 nm wavelength experiments for 25, 30 and 35 cm³ water content samples. It
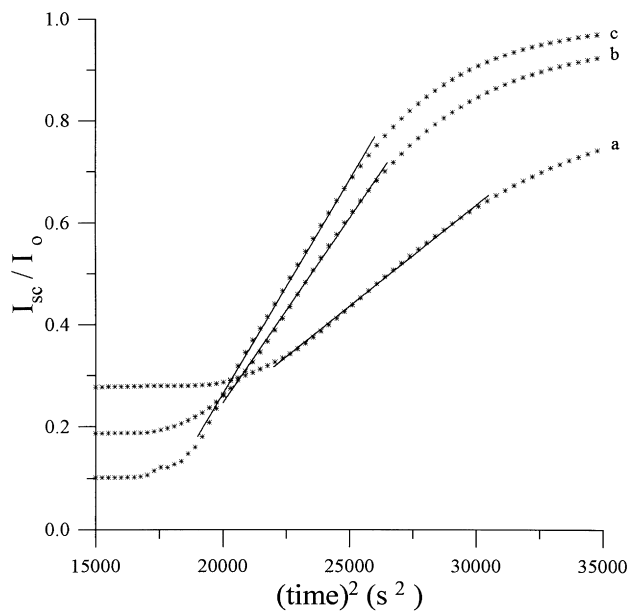
Table 2
a is the slope of I_{sc}–t^2 curves in Fig. 4

| λ (nm) | a values ($\times 10^{-5}$) | | | | | |
	15 (cm³)	20 (cm³)	25 (cm³)	30 (cm³)	35 (cm³)	45 (cm³)
440	0.57	1.37	3.99	7.23	8.38	6.73
500	0.39	1.04	3.09	5.47	7.23	6.62
550	0.24	0.71	2.64	4.27	6.50	5.97
600	0.10	0.60	2.13	3.93	5.57	5.48
690	0.08	0.33	1.48	3.22	4.44	4.31

is seen in Fig. 4 that I_{sc} represents 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 [11,12]. 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 water content increases the phase separation or the concentration of the junction points [12].

If the microgel particles are assumed to be spherical with volume v which grows linear with time t during gelation, then the linear portions of I_{sc} data in Fig. 4 are fitted to Eq. (1). The slopes of $(I_{sc}$–$t^2)$ curves in Fig. 4 produce $a (= kc\lambda^{-\eta})$ values. The measured a values for all the gel samples in various water contents and at different wavelengths are given in Table 2. The plots of a versus water
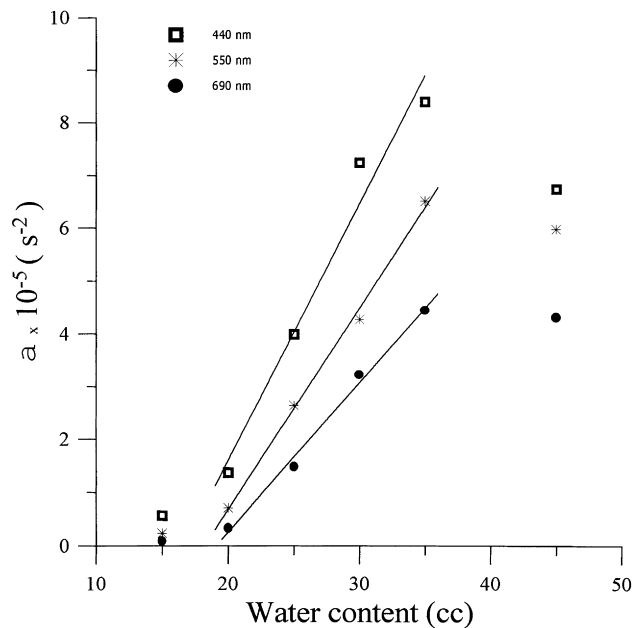

Fig. 4. Variation in the scattered light intensity I_{sc} at 440 nm versus t^2 during in situ FCC for: (a) 25; (b) 30; (c) 35 cm³ water content samples.

Fig. 5. The plots of a ($= kc\lambda^{-\eta}$) versus water content at various wavelengths.

Table 3
η is the slope of the log I_{sc} versus log λ curve

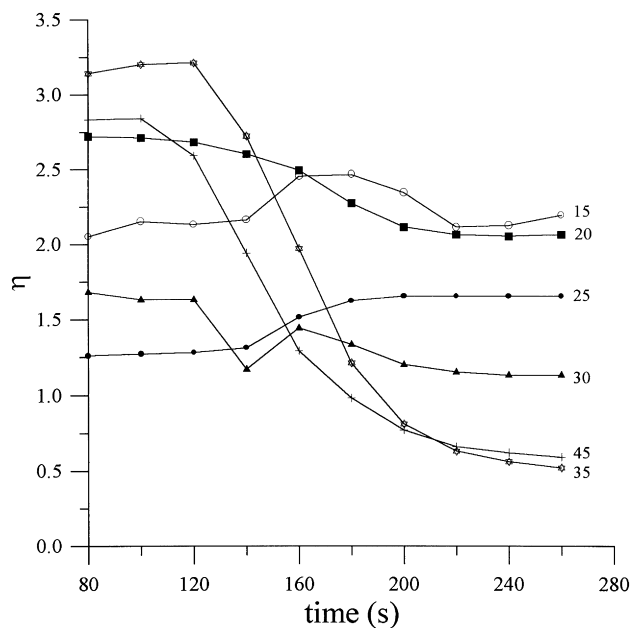| t (s)	η values					
	15 (cm³)	20 (cm³)	25 (cm³)	30 (cm³)	35 (cm³)	45 (cm³)
80	2.05	1.26	2.72	1.68	3.14	2.83
100	2.15	1.27	2.71	1.63	3.20	2.84
120	2.13	1.28	2.68	1.63	3.21	2.59
140	2.16	1.31	2.60	1.17	2.72	1.94
160	2.45	1.51	2.49	1.44	1.97	1.29
180	2.46	1.62	2.27	1.33	1.21	0.98
200	2.34	1.65	2.11	1.20	0.81	0.77
220	2.11	1.65	2.06	1.15	0.63	0.66
240	2.12	1.65	2.05	1.13	0.56	0.62
260	2.19	1.65	2.06	1.13	0.52	0.59

Fig. 6. Plot of η versus gelation time t for the gel samples in various water contents. Numbers on each curve represent the water content in cm³.

content for different wavelengths are shown in Fig. 5, where except very high (45 cm³) and very low (15 cm³) water contents, the relations are quiet linear. This behavior indicates that increasing water content increases the phase separation in the macrogel structure, which causes an increase in the number of microgel particles at the junction points. The larger slope of the curve in Fig. 5 for the smaller wavelength (440 nm) predicts the inverse wavelength dependence on a in Eq. (1).

Eq. (1) can also be used to fit the data in Fig. 3 for a given time (volume) and water content. Slope of log I_{sc} versus log λ plots produce η values. The observed η values for all gel samples are listed in Table 3 and plotted in Fig. 6, where it is seen that microgel particles are formed at early times during gelation of 35 and 45 cm³ water content samples. η values of these samples at early times predict that the size of the microgel particles are around 100 nm, which grows in time and possibly form aggregates at later times. Samples with low water contents (30, 25, 20 and 15 cm³) form either macrogel particles or heterogeneous gel (see Fig. 1) throughout the FCC. These gels produce smaller and constant η values during FCC which predicts that the size of the particles or domains are much larger than 100 nm.

In conclusion, this paper presents a simple method for studying FCC in water. Photon transmission measurements at various wavelengths may help us to understand the mechanism of hydrogelation and can estimate the sizes of primary particles during FCC.

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