

In Situ Real-Time Photon Transmission Technique for Monitoring Formation of Polyacrylamide Gels at Various Crosslinker Contents

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ABSTRACT: The *in situ*, real-time, photon transmission technique was used to monitor the free-radical crosslinking copolymerization (FCC) of acrylamide (AAM) and *N,N'*-methylenebisacrylamide (Bis). Gelation experiments were performed with various Bis contents at various wavelengths. It was observed that the transmitted photon intensity, I_{tr} , decreased dramatically at a certain reaction time, which is attributed to the increase in scattered light intensity, I_{sc} , during the formation of microgels in the system. The increase in I_{sc} was modeled using Rayleigh's equation where the reaction time was found to be proportional to the volume of the microgels. In most cases, the change in I_{sc} was found to be inversely proportional to the 2.5 power of the wavelength, λ , from which the size of the microgel particles were estimated during the FCC. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 823–830, 2001

INTRODUCTION

It has been known that polyacrylamide (PAAm) gels are obtained by free-radical crosslinking copolymerization of acrylamide (AAM) and *N,N'*-methylenebisacrylamide (Bis) monomers. Since AAM is solid at the room temperature, where the polymerization is usually performed, it is necessary to carry out the reaction in an aqueous environment. PAAm gels are hydrophilic gels which are called "hydrogels." Several studies showed that the hydrogel structure, and, thus, the hydrogel properties, strongly depends on the initial degree of dilution of AAM.^{1–4} As the amount of water increases during polymerization, the network structure becomes increasingly loose and it is unable to form a continuous network above a critical amount of water.⁵ The same critical be-

havior can be expected when one decreases the Bis concentration in AAM polymerization, that is, no continuous network can be formed below a critical amount of Bis content. It was also reported that acrylamide-based hydrogels have a heterogeneous crosslinked distribution.^{6–9} The formation of the heterogeneities of crosslinked polymer gels has been the subject of great interest for many years. These structural inhomogeneities of a gel affect its physical properties such as its optical and phase properties. The effect of heterogeneities of the network on the swelling equilibrium of PAAm gel during water absorption were studied by Hsu et al.⁶

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 solution is in the phase-separation regime two gel phases appear, having two different concentrations. The domain sizes of these two phases depend on the condition of the gelation process and can sometimes have a

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size in the order of the wavelength of light and scatter tremendously, given the strong opacity to the gel.²

Extensive work has been reported in the literature for the physical properties of PAAm gels; however, very little was concerned with the formation mechanism by free-radical crosslinking copolymerization (FCC). FCC of AAm and Bis monomers in a water solution was studied extensively^{8,9} 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 %.¹⁰ Experiments indicate that 80% of the pendant vinyl groups are consumed by cyclization reactions and it was observed that the equilibrium degree of swelling of the PAAm gel was independent of their crosslinker content. These results suggested the formation of microgels prior to the onset of macrogelation and, as the reaction proceeds, that 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. An *in situ* photon transmission study for aging in acrylamide gels due to multiple swelling was recently reported by our laboratory,¹¹ where it was observed that the transmitted light intensity, I_{tr} , decreased continuously as the PAAm gel swelled. The decrease in I_{tr} was attributed to the increase in the scattered light intensity which originated from the contrast between the frozen blob clusters and the holes in the swollen gel.

In this work, *in situ* real-time photon transmission experiments are reported during the copolymerization of AAm with various Bis contents. It was observed that the transmitted photon intensity, I_{tr} , decreased dramatically above a certain Bis content during the gelation process. A decrease in I_{tr} was attributed to an increase in the scattered light intensity, I_{sc} , from the gel due to spatial phase separation, which appears during copolymerization of AAm with Bis. The increase in I_{sc} against time was modeled using Rayleigh's equation and it was observed that the volume, ν , of the PAAm particles grew linearly with time. It was found that the numerical concentration, c , of the particles was proportional to the Bis content. The change in I_{sc} was found to be inversely proportional to the 2.5 power of the wavelength, λ , of the incident light.

OPALESCENCE DUE TO LIGHT SCATTERING

It is well known that light scattering causes opalescence when a light beam is passed through a solution. Light scattering is caused by the density and concentration fluctuations, that is, by deviation of the 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 the light is through a dispersed medium, the incident intensity is reduced to I_{sc} as a result of the 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:

$$I_{sc} = I_0 k c \nu^2 \lambda^{-\eta} \quad (1)$$

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 is given by

$$k = 24 \pi^3 \left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right) \quad (2)$$

where n_1 and n_0 are the indices of refraction of the dispersed phase and the dispersion medium, respectively. ν is the volume of a single particle and c is the numerical concentration, that is, 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, that is, 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 the particle size was studied in monodispersed latex systems of polystyrene¹² and it was observed that η decreased from 4 to 2.8.

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 in-

tensity of the scattered light. However, in the meantime, the intensity of light scattering decreases as the particle size decreases. Therefore, a dispersed medium scatters light to the greatest extent. In conclusion, Rayleigh's equation provides the following important information to be used: For particles of a given size, the intensity of scattered light is directly proportional to the numerical concentration. This principle can be used to determine the concentration of the dispersed phase by measuring I_{sc} in the system. However, since multiple scattering occurs at very high concentrations, precautions have to be taken. At a given concentration and particle size, from the variation in λ against I_{sc} , one can derive the exponent η , which can be used to determine the particle size.

MICROGELS

A microgel is an intramolecularly crosslinked macromolecule which is dispersed in normal or colloidal solutions, in which, depending on the degree of crosslinking and on the nature of the solvent, it is more or less swollen.¹⁰ Besides linear and branched macromolecules and crosslinked polymers, intramolecularly crosslinked macromolecules may be considered as a fourth class of macromolecules.

Although the term microgel has long been used and is well established, it is not totally satisfactory because it is only appropriate for the swollen state, that is, if crosslinked macromolecules are dissolved.^{13,14} Moreover, "micro" refers to dimensions of more than 1 μm , whereas the dimensions of microgels are usually in the range of nanometers.¹⁵ However, in colloquial language, "micro" is also used for something very small. Another term which has been proposed for microgels is nanoparticles. But this name generally designates particles with dimensions in the nanometer range, irrespective of their chemical or structural nature. Other names which have been used are microglobules, microspheres, microparticles, microlatex, colloidal particles, and even polymer network colloids.

Because the term microgel has the longest tradition and is most commonly used in polymer science and technology, it is reasonable to accept it as the generic term for intramolecularly crosslinked macromolecules in solution, a state in which these species of macromolecules are usually handled and characterized.¹⁶

Microgels are molecular species on the border between normal molecules and particles. Contrary to linear and branched macromolecules, the surface of microgels is rather fixed, thus approaching the characteristics of solid particles. As to their size, it is somewhat difficult to define a limit because the transition from a microgel to a larger polymer particle, for example, in coarser polymer dispersions, is gradual. Nonetheless, optical criteria related to solubility may be applied to distinguish microgels from larger polymer particles as, contrary to normal polymer dispersions, microgels form colloidal, opalescent, or even clear solutions. For a long time, microgels were rather a nuisance to the science and technology of polymers because they interfered with the characterization of macromolecules by light scattering.

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 tetramethylethylenediamine 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 $1.0 \times 1.0\text{-cm}$ quartz cells which were placed in a UV-visible (UVV) spectrometer. Gelations were monitored in real-time and *in situ* photon transmission measurements, which were performed using a Perkin-Elmer UVV spectrometer. Photon transmission intensities, I_{tr} , were measured in real-time using the time drive mode of the spectrometer during copolymerization of AAm with Bis at five different wavelengths (440, 500, 550, 600, and 690 nm). Typical I_{tr} curves against the reaction time for eight different Bis contents are given in Figure 1(a-c) for the experiments made at 440, 550, and 690 nm wavelengths, respectively. In Figure 2(a-c), I_{tr} curves at various wavelengths are compared for 125, 150, and 175 mg Bis content samples, respectively. In Figures 1 and 2, it is seen that the I_{tr} intensity decreased dramatically above a certain time, indicating that strong opalescence occurs during gelation for all samples except the 50 mg Bis content sample. Here, one can predict that, below 100 mg Bis content, the formation of a hydrogel seems impossible or cannot be observed with this technique.

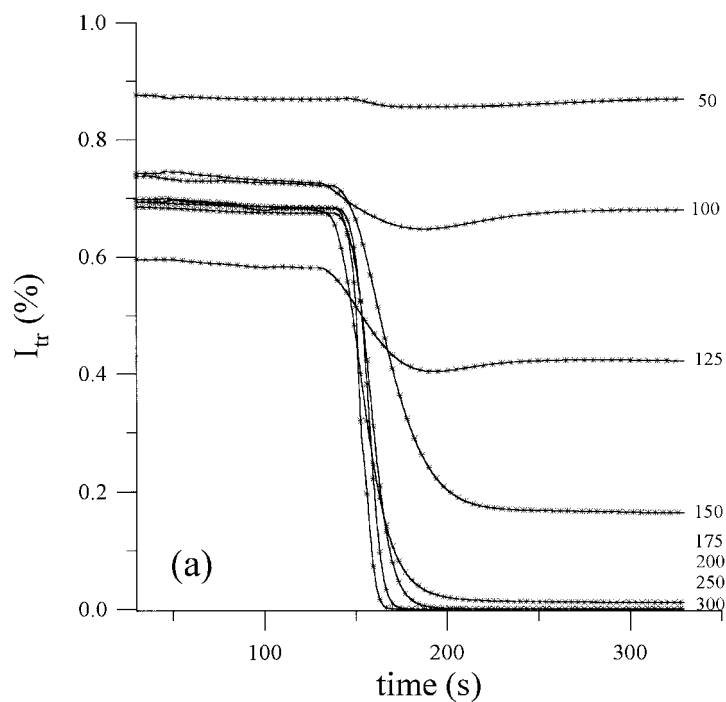


Figure 1 Variation in transmitted photon intensities, I_{tr} , versus reaction time, t , during *in situ* FCC for eight different Bis contents for (a) 440, (b) 550, and (c) 690-nm wavelengths. Numbers on each curve present the Bis content in mg.

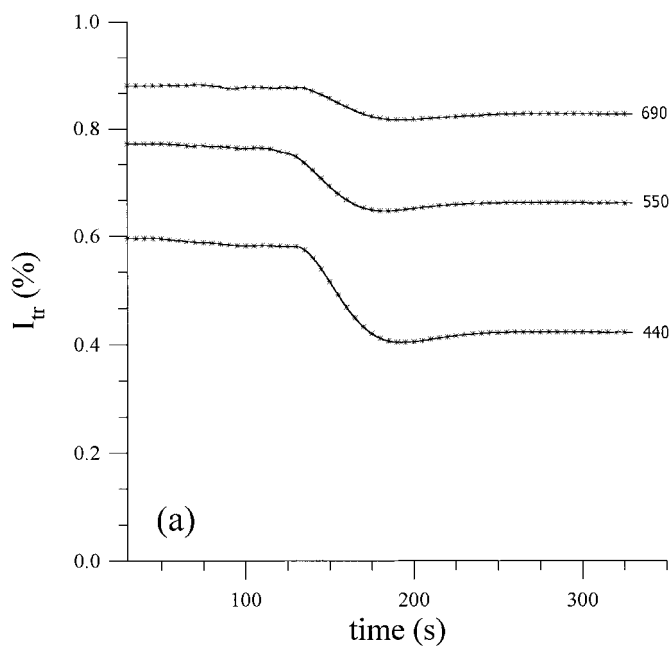


Figure 2 Variation in transmitted photon intensities, I_{tr} , versus reaction time, t , during *in situ* FCC at different wavelengths for (a) 125, (b) 150, and (c) 175 mg Bis content samples. Numbers on each curve indicate the wavelength of the transmitted light.

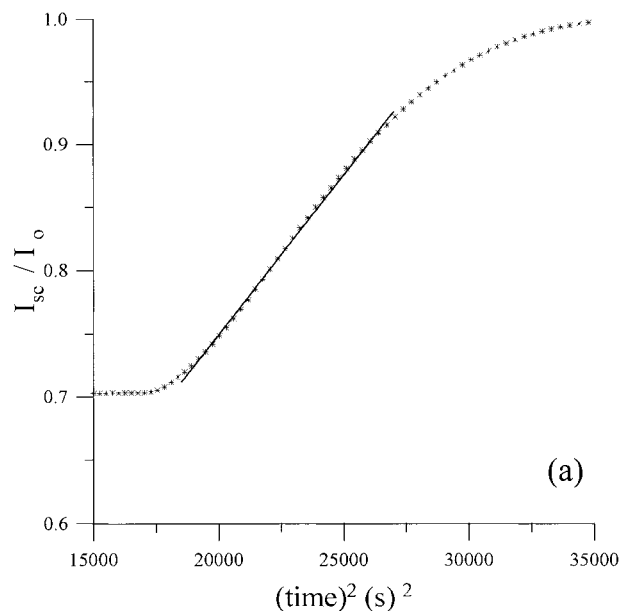


Figure 3 Variation in the scattered light intensity, I_{sc} , at 440 nm versus t^2 during *in situ* FCC for (a) 125, (b) 150, and (c) 175 mg Bis content samples. Fit of the data to eq. (1) produces $a (= kc\lambda^{-n})$ values.

RESULTS AND DISCUSSION

To interpret the results in Figures 1 and 2, 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 Figure 3(a–c), normalized $I_{sc} = 1 - I_{tr}$ intensities are plotted versus t^2 for the 440-nm wavelength experiments for 125, 150, and 175 mg Bis content samples, respectively. It is seen that I_{sc} increases above a certain time, indicating that this hydrogel system scatters light dramatically, presenting a strong opalescence above this critical time during its formation. These results can be modeled by knowing the fact that formation of PAAm microgels occurs prior to the onset of macrogelation.¹⁰

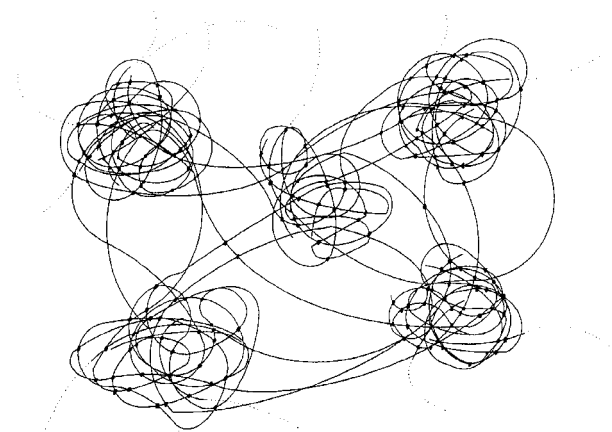


Figure 4 Figure cartoon representation of the PAAm macrogel formed from intermolecularly crosslinked microgel particles (from ref. 10).

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 pregel period act as junction points. Cartoon representation of this picture is presented in Figure 4.¹⁰ 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.

If the microgel particles are assumed to be spherical, with volume v , which grow linearly in time t during gelation, then the linear portions of the I_{sc} data in Figure 3 are fitted to eq. (1). The $I_{sc} - t^2$ curve in Figure 3 has a slope which provides the values of $a = kc\lambda^{-n}$. The measured a values for all gel samples in various crosslinker contents at different wavelengths are given in Table I. The plots of a versus crosslinker (Bis) content for different wavelengths are shown in Figure 5, where,

Table I a is the Slope of the $I_{sc} - t^2$ Curves in Figure 3(a–c)

| λ (nm) | $a \times 10^{-5} (\text{s}^{-2})$ | | | | | | | |
|----------------|------------------------------------|--------|--------|--------|--------|--------|--------|--------|
| | 50 mg | 100 mg | 125 mg | 150 mg | 175 mg | 200 mg | 250 mg | 300 mg |
| 440 | 0.20 | 0.76 | 1.48 | 3.99 | 7.14 | 9.08 | 12.4 | 15.89 |
| 500 | 0.13 | 0.65 | 1.64 | 3.09 | 6.40 | 8.83 | 13.8 | 15.54 |
| 550 | 0.06 | 0.34 | 0.98 | 2.64 | 5.54 | 7.38 | 13.1 | 15.30 |
| 600 | 0.05 | 0.31 | 0.95 | 2.13 | 5.44 | 8.05 | 10.8 | 17.87 |
| 690 | 0.04 | 0.17 | 0.49 | 1.48 | 3.84 | 6.37 | 12.2 | 14.76 |

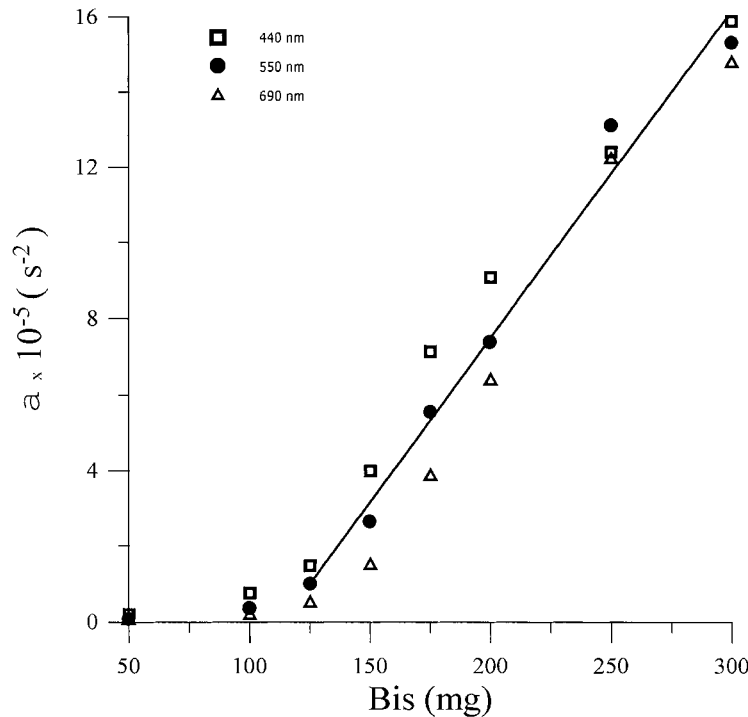


Figure 5 Plots of α ($= kc\lambda^{-n}$) versus Bis content for various wavelengths.

except at very low Bis content, the relations are quite linear. This behavior indicates that increasing the Bis content increases the number of microgel particles at the junction points, which causes the increase in the compactness of the macrogel structure. Here, it has to be noted that the volume, ν , of the microgel particles grows as the reaction time, t , is increased, which satisfies the requirements in eq. (1).

Equation (1) can also be used to fit the data in Figure 2(a–c) for a given time (volume) and concentration (Bis content). In Figure 6(a–c), $\log I_{sc}$ versus $\log \lambda$ plots are shown for 125, 150, and 175 mg Bis contents at a reaction time of 160 s. Slopes of these plots produce η values. Similar plots were obtained at other reaction times and in various crosslinker contents. The observed η values for all gel samples are listed in Table II for increasing reaction times. Plots of η versus reaction time for the samples with various Bis contents are presented in Figure 7, where it is seen that η varies around 2.5 for the gel samples of 100, 125, and 150 mg Bis content. η presents a decrease for the other gel samples above the reaction time of 140 s. Here, one can argue that microgel particles are formed immediately at the very early stage of FCC, most probably with sizes of 70 nm and grow in time up to 100-nm sizes for 100, 125, and 150

mg Bis content samples. Figure 1 predicts that the growth of the volume of microgels occurs at a very short time interval (140–170 s) depending on

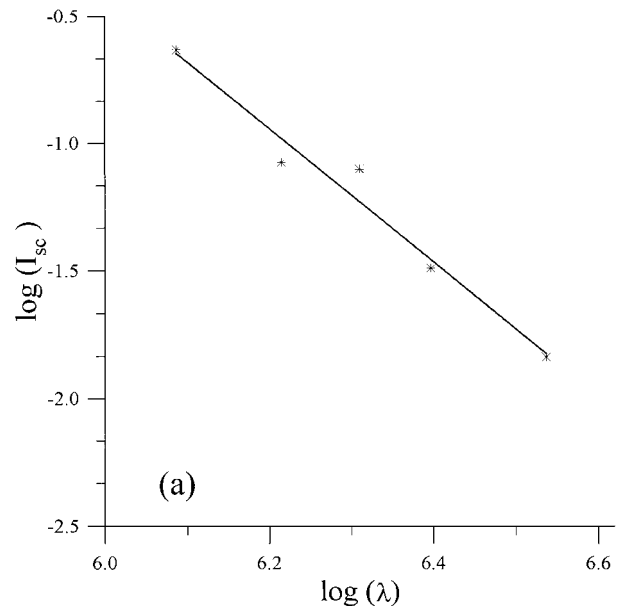


Figure 6 Log–log plots of I_{sc} versus λ for (a) 125, (b) 150, and (c) 175 mg Bis content samples at the reaction time of 160 s. Slopes of the curves produces η values, which are listed in Table II.

Table II η is the Slope of the Curves in Figure 6(a-c)

| t (s) | η Values | | | | | |
|---------|---------------|--------|--------|--------|--------|--------|
| | 100 mg | 125 mg | 150 mg | 175 mg | 200 mg | 250 mg |
| 80 | 2.35 | 2.56 | 2.72 | 2.26 | 2.61 | 1.58 |
| 100 | 2.36 | 2.55 | 2.71 | 2.36 | 2.68 | 1.52 |
| 120 | 2.36 | 2.53 | 2.68 | 2.30 | 2.67 | 1.68 |
| 140 | 2.41 | 2.61 | 2.60 | 1.59 | 2.05 | 0.46 |
| 160 | 2.51 | 2.61 | 2.49 | 1.35 | 0.77 | 0.13 |
| 180 | 2.57 | 2.56 | 2.27 | 1.11 | 0.52 | 0.03 |
| 200 | 2.61 | 2.55 | 2.11 | 0.97 | 0.32 | 0.01 |
| 220 | 2.62 | 2.56 | 2.06 | 0.91 | 0.26 | 0.007 |
| 240 | 2.62 | 2.58 | 2.05 | 0.91 | 0.25 | 0.006 |
| 260 | 2.61 | 2.60 | 2.06 | 0.91 | 0.24 | 0.005 |

the Bis content. Above 170 s, intermolecularly crosslinked macrogels are formed for all gel samples. For gel samples with Bis contents of 175 and 200 mg, microgel particles larger than 100 nm are formed above 140 s, which produces very small η values. For the gel sample of 250 mg Bis content, however, very large (<130 nm) microgels are formed immediately, which then form large aggregates. In this case, the resulting η values are

very small, indicating that the size of the scattered centers out of the range of eq. (1) holds.

From the results of this study, we conclude that the photon transmission technique is quite useful for studying the gelation mechanism during hydrogel formation. Using various wavelengths may help one to understand the mechanism of microgelation and the formation of interconnected microgels during hydrogelation.

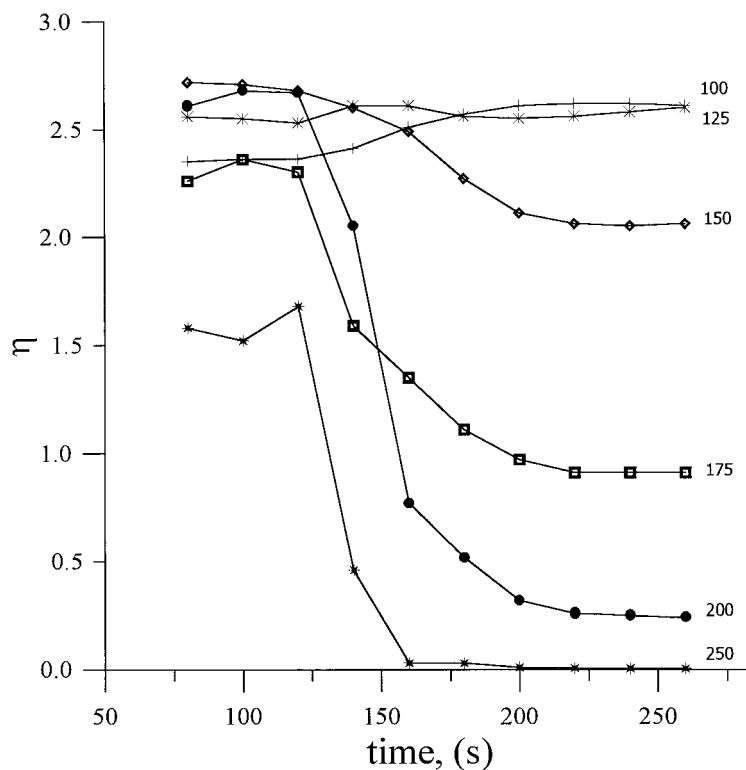


Figure 7 Plot of η versus reaction time, t , for the gel samples of various Bis contents. Numbers on each curve present the Bis content in milligrams.

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