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Preparation of Homogeneous Hydrogels by Controlling the Crosslinker Reactivity and Availability

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Network microstructures of polyacrylamide (PAAm) hydrogels were investigated by static light scattering measurements. The gels were prepared by free-radical crosslinking polymerization of acrylamide (AAm). To suppress the degree of gel inhomogeneity, the crosslinker reactivity during gelation was controlled by decreasing its availability in the reaction system. Our first approach was the addition of the crosslinker N,N′-methylenebis(acrylamide) (BAAm) in one or three portions during the course of the gelation reactions. As a second approach, a slightly water soluble crosslinker, namely ethylene glycol dimethacrylate (EGDM) was used as a crosslinker in AAm polymerization. Due to the low water solubility of EGDM, EGDM phase in the gelation system act as a reservoir of crosslinker so that the crosslinker can be supplied continuously to the aqueous reaction zone during the course of gelation. It was found that the delayed crosslinker addition technique further increases the degree of inhomogeneity of PAAm hydrogels. The results were explained with increasing viscosity of the reaction solution at the time of the crosslinker addition so that the crosslinking reactions are limited to local regions in the reaction system. The second approach, namely use of the slightly water soluble crosslinker EGDM significantly increases the degree of structural homogeneity of PAAm hydrogels.

Keywords: homogeneous hydrogels; inhomogeneity; light scattering; gelation

1. Introduction

Hydrogels are important materials of both fundamental and technological interest. They are mainly prepared by free-radical crosslinking copolymerization (FCC) of acrylamide (AAm) - based monomers with a divinyl monomer (crosslinker) in aqueous solutions. As is well known, gelation during FCC occurs non-randomly due to the existence of various non-idealities such as the unequal reactivities of the functional groups, cyclization and multiple crosslinking reactions (1, 2). These non-idealities during gelation inevitably result in the formation of polymer hydrogels with a large number of network defects, affecting their physical properties such as swelling, elasticity, transparency, and permeability.

One of the network defects is the inhomogeneous distribution of the crosslink points along the gel sample, which is known as the spatial gel inhomogeneity (3, 4). Since the gel inhomogeneity is closely connected to the spatial concentration fluctuations, scattering methods such as light scattering (5–8),

small-angle X-ray scattering (5, 9), and small-angle neutron scattering (10–12) have been employed to investigate the spatial inhomogeneities. The gel inhomogeneities are of considerable interest and importance in attempts to characterize such materials physically. From the practical point of view, spatial inhomogeneity is undesirable because it dramatically reduces the optical clarity and strength of gels, which are properties closely connected with many industrial applications such as contact lenses, super absorbents, etc.

Spatial inhomogeneity in gels mainly originates from the unequal reactivity of the vinyl groups participating in gelation reactions (1, 2). Even assuming equal vinyl group reactivity, the crosslinker reactivity during gelation is at least twice the monomer reactivity due to the existence of two vinyl groups on each crosslinker molecule. Thus, the molecules formed earlier contain more crosslinker units and, therefore, more highly crosslinked than those formed later, which essentially result in the formation of inhomogeneous networks.

The present study focuses on the problem of how to reduce the extent of spatial inhomogeneities in polyacrylamide (PAAm) hydrogels. The effect of the controlled crosslinker addition on the spatial gel inhomogeneity has not been reported previously. Here, a series of PAAm hydrogels was prepared in aqueous solutions by controlling the crosslinker reactivity during gelation. A means to reduce the reactivity

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of the crosslinker is to decrease its availability in the reaction system. Our first approach was the addition of the crosslinker N,N′-methylenebis(acrylamide) (BAAm) in one or in three portions during the course of the gelation reactions. Second, a slightly water soluble crosslinker, namely ethylene glycol dimethacrylate (EGDM) was used as a crosslinker in AAm polymerization. Due to the low water solubility of EGDM (0.1 w/v%), EGDM phase in the gelation system act as a reservoir of crosslinker so that the crosslinker can be supplied continuously to the aqueous reaction zone during the course of gelation. The hydrogels were characterized by static light scattering measurements at a gel state just after their preparation. The gel inhomogeneity was manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration (7, 8). The scattering intensity from gels was always larger than that from the polymer solution. The excess scattering over the scattering from polymer solution was related to the degree of the inhomogeneities in PAAm hydrogels. As will be seen below, use of the slightly water soluble crosslinker EGDM significantly increases the degree of structural homogeneity of PAAm hydrogels.

2. Experimental

2.1 Materials

Acrylamide (AAm), N,N′-methylenebis(acrylamide) (BAAm), ethylene glycol dimethacrylate (EGDM), ammonium persulfate (APS), and N,N,N′,N′-tetramethylethylenediamine (TEMED), all from Merck, Germany, were used as received.

2.2 Crosslinking Polymerization Procedure of AAm/BAAm System

Free-radical crosslinking copolymerization reactions of AAm monomer with BAAm crosslinker were carried out in aqueous solutions at 21°C in the presence of 3.51 mM APS initiator and 0.25 v/v% TEMED accelerator. BAAm stock solution was prepared by dissolving 0.1349 g BAAm in 10 ml of water. APS and TEMED stock solutions were prepared by dissolving 0.080 g APS and 0.25 ml TEMED separately in 10 ml of water.

Several sets of experiments were carried out. Both the initial monomer concentration and the crosslinker ratio denoted by X (the mole ratio of crosslinker to monomer) were set to 5 w/v% and 1/80, respectively. The gel synthesis parameter varied was the time of the addition of BAAm into the reaction solution. The reactions were carried out within a commercial multi-angle light scattering DAWN EOS instrument (Wyatt Technologies Corporation) equipped with a vertically polarized 30 mW Gallium-arsenide laser operating at $\lambda = 690$ nm and 18 simultaneously detected scattering angles. The light scattering system was calibrated against a toluene standard (Rayleigh ratio at 690 nm $= 9.78 \times 10^{-6}$

cm^{-1}, DAWN EOS software). The scattered light intensities were recorded from a scattering angle $\theta = 90°$ as a function of the reaction time. To illustrate the synthetic procedure, we give details for the preparation of a PAAm hydrogel with a delay time of 30 s for the BAAm addition:

AAm (0.5 g), water (7.00 ml), stock solutions of APS (1.00 ml) and TEMED (1.00 ml) were mixed in a 10 ml graduated flask. The solution was filtered through membrane filters (pore size $= 0.2$ µm) directly into the light scattering vial in a dust-free glove box. The vial was then placed in the light scattering instrument. The end of the induction period, at which the scattered light intensity at $\theta = 90°$ abruptly increases, was recorded as time $= 0$. At time $= 30$ s, the vial was taken out of the instrument; after addition of BAAm stock solution (1 ml) and gently shaking, the vial was replaced again in the instrument and the measurement was continued.

After one day of reaction time, the scattered light intensities were recorded from angles $\theta = 14.5°$ to $163.3°$ which correspond to the scattering vector q range 3.1×10^{-4}–2.4×10^{-3} A$^{\circ -1}$, where $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the refractive index of the medium. For the calculation of excess scattering from gels, the crosslinking polymerization was repeated under the same experimental condition except that the crosslinker BAAm was not used.

2.3 Crosslinking Polymerization Procedure of AAm/EGDM System

Under the experimental conditions given above, no gel formation was observed in AAm/EGDM copolymerization reactions. However, PAAm hydrogels using EGDM crosslinker can easily be obtained at 10 w/v% initial monomer concentration in the presence of 4.39 mM APS initiator and 0.025 v/v% TEMED accelerator (13). These synthesis conditions were fixed while the crosslinker concentration was varied over a wide range. Stock solutions of APS and TEMED were prepared by dissolving 0.500 g APS and 0.100 ml TEMED separately in 10 ml of water. EGDM stock solution was prepared by dispersing 0.100 g EGDM in 10 ml of water (13). The gels were prepared as described above except that the crosslinker was added into the reaction solution before the addition of the redox initiator system. The scattered light intensities from the reaction solution were recorded from $\theta = 90°$ as a function of the reaction time. After one day of reaction time, they were recorded from angles $\theta = 14.5°$ to $163.3°$.

3. Results and Discussion

3.1 Late Addition of the Crosslinker BAAm

In this set of experiments, the timing of the addition of BAAm crosslinker into the gelation system was controlled. For this purpose, BAAm was added with various delay times after the addition of the initiator APS. Both the initial monomer

concentration and the crosslinker ratio were fixed at 5 w/v% and 1/80, respectively. We first monitored the gelation reactions by real-time light scattering measurements. Figure 1 shows the scattered light intensity I_s recorded at $\theta = 90°$ plotted as a function of reaction time in free-radical crosslinking copolymerization of AAm/BAAm comonomer system. For comparison, the reaction systems without the crosslinker BAAm were also monitored.

No intensity rise was observed during the induction period of the reactions (not shown in the figure). By repeated measurements, the duration of the induction period was found to be 5 min with a variation of ± 2 min. The scattered intensity profile was however unchanged from these variations. In the following, the reaction time is defined as the total time elapsed minus the time needed for the induction period. Further, the delay time of the crosslinker addition is defined as the reaction time at which the crosslinker BAAm is added into the reaction system. For short delay times, the general trend shown in Figure 1 is that the start of the polymerization is accompanied with a rapid increase in the scattered light intensity I_s, which reaches a maximum after a short reaction time. After passing the maximum intensity, I_s gradually decreases with the reaction time and finally, attains a plateau value after about 10 min. The rapid increase of I_s in short reaction times is due to the very short life time of radicals in the reaction system so that the polymer chains immediately start to form. Since a single polymer coil scatters light intensively, an abrupt intensity rise was observed with the onset of reactions due to the increasing number of coils with time. The number of individual polymer coils attains a maximum value at the overlap concentration c^* so that the scattering curve exhibits a peak at this concentration. Thus, the maximum in the scattering

curve corresponds to the point at which the polymer concentration in the reaction system attains the critical overlap concentration c^* (14). As we demonstrated before, gelation occurs at or beyond the maximum point of the scattering curves (14, 15). Beyond the gel point, only the mesh size of the polymer network is detectable by light scattering and not the size of the individual polymer coils. Since the mesh size is much smaller than the size of molecules, and it decreases further with increasing polymer concentration, I_s decreases with increasing reaction time.

Comparison of the scattering curves in Figure 1 shows several interesting features. First, compared to the linear polymerization system, the addition of the crosslinker into the monomer feed increases the scattered light intensity due to the appearance of the spatial gel inhomogeneities. Moreover, late addition of the crosslinker BAAm further increases the scattered light intensities. This increase is slight up to about a delay time of 30 s. If BAAm is added later than 30 s, scattered light intensity rapidly increases and, the system becomes opaque in a few minutes. This behavior is clearly seen for the experiments with 100 s delay times (Fig. 1). Up to the crosslinker addition, the intensity profile follows that of the uncrosslinked system whereas BAAm addition at time $= 100$ s results in an abrupt intensity increase and the reaction system becomes opaque within one minute. Another point shown in Figure 1 is that the maximum in the scattering curve gradually disappears as the addition of BAAm is shifted towards longer reaction times.

In order to generalize the above findings, we measured the scattered light intensities from PAAm gels at various scattering angles. The reaction time for the hydrogel preparation was set to 24 h. Figure 2A shows the Rayleigh ratio $R(q)$ vs. the scattering vector q plots for the hydrogels ($R_{gel}(q)$) and for the corresponding polymer solution ($R_{sol}(q)$). The delay time for the crosslinker addition is indicated in the figure. The polymer solution was prepared under the same reaction condition as the hydrogels except that the crosslinker BAAm was not used. For both hydrogels and polymer
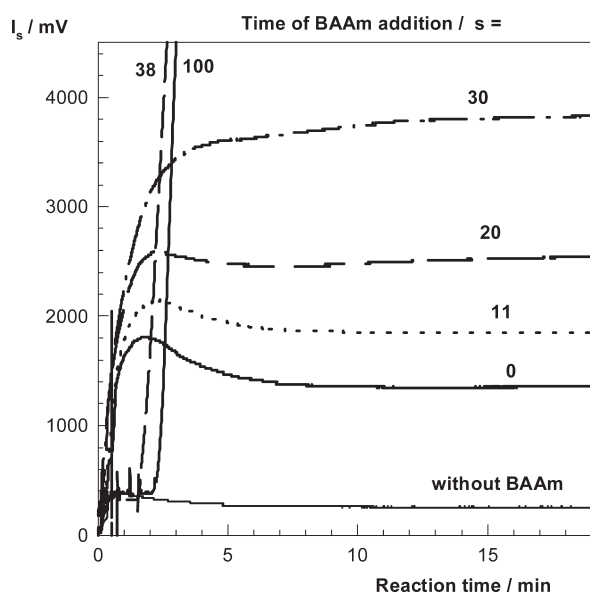

Fig. 1. The scattered light intensity I_s recorded at $\theta = 90°$ shown as a function of the reaction time in AAm/BAAm copolymerizations at various delay times for BAAm addition.
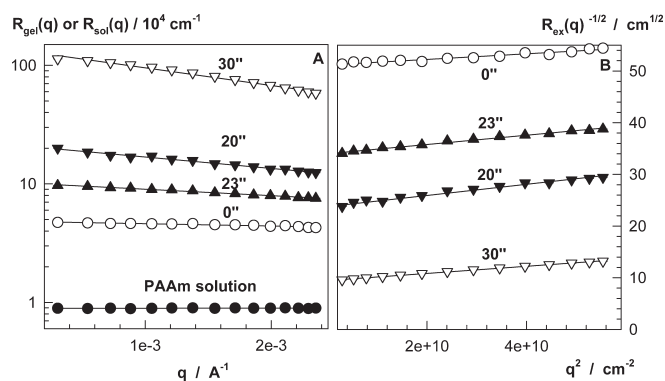

Fig. 2. (A) Rayleigh ratio $R(q)$ versus scattering vector q plots for the PAAm gels ($R_{gel}(q)$) and for the corresponding linear PAAm solution ($R_{sol}(q)$); (B) Debye−Bueche plots for PAAm hydrogels. The time of BAAm addition was indicated.

solution, the light scattering intensity does not change much with the scattering vector q. This is due to the fact that we are in the semidilute regime for polymer solutions and are probing length scales large compared with those typical for polymer hydrogels. It is also seen that the hydrogel scatters much more light than the corresponding polymer solution. Further, increasing delay time of BAAm addition also increases the scattered light intensities from all angles. The results thus demonstrate that the hydrogels become increasingly inhomogeneous with increasing delay time of BAAm addition.

To interpret static light scattering results from gels, several functional forms of excess scattering $R_{ex}(q)$ have been proposed empirically, i.e., Debye-Bueche (16–19), Guinier (20–23), and Ornstein-Zernicke functions (20–24). For example, according to the Debye-Bueche function, $R_{ex}(q)$ is given by:

$$R_{ex}(q) = \frac{4\pi K \xi^3 \langle \eta^2 \rangle}{\left(1 + q^2 \xi^2\right)^2} \qquad (1)$$

where K being the optical constant, $K = 8\pi^2 n^2 \lambda^{-4}$, ξ is the static correlation length of the scatterers, and $\langle \eta^2 \rangle$ is the mean square fluctuation of the refractive index. Excess scattering $R_{ex}(q)$ was calculated from scattered light intensity from gels $R_{gel}(q)$ and from solutions $R_{sol}(q)$ as:

$$R_{ex}(q) = R_{gel}(q) - R_{sol}(q) \qquad (1a)$$

According to Equation (1), the slope and the intercept of $R_{ex}(q)^{-1/2}$ vs. q^2 plot (Debye−Bueche plot) give ξ and $\langle \eta^2 \rangle$ of a gel sample. In Figure 2B, the excess scattering data from hydrogel samples are given in the form of Debye-Bueche plots. Calculated values of ξ and $\langle \eta^2 \rangle$ from the Debye−Bueche analysis are shown in Figure 3 plotted as a function of the delay time for BAAm addition. ξ increases from 10 to 30 nm, while $\langle \eta^2 \rangle$ remains almost constant as the delay time is increased.

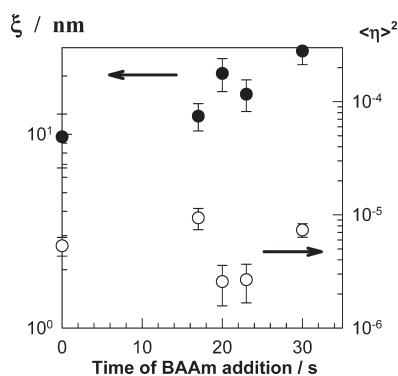The results thus show that, in contrast to the expectation, use of our delayed crosslinker addition technique further increases the excess scattering of gels. The size of the highly crosslinked regions represented by ξ increases, while the concentration difference between the highly and loosely crosslinked domains ($\langle \eta^2 \rangle$) remains unchanged as the crosslinker addition is delayed. A plausible explanation is increasing viscosity of the reaction solution at the time of the crosslinker addition so that the crosslinking reactions are limited to local regions in the reaction system. This would lead to an increase in the size as well as in the number of the highly crosslinked domains. Thus, late addition of the crosslinker produces microgel-like particles in the reaction solution so that the macrogelation occurs by the coagulation of the particles. As a result, a maximum in the scattered intensity profile is not seen for experiments with long delay times of BAAm addition (Fig. 1). The appearance of opacity also reveals that the highly crosslinked domains in the gel forming system have a size order of the wavelength of light.

Experiments were also conducted where the crosslinker BAAm was added into the reaction solution in several portions before the onset of gelation. Addition in three steps and in equal amounts with delay times of 0, 15, and 40 s reduced the scattered light intensities compared to those measured from the usual hydrogels. As seen in Figure 4, both the maximum scattered light intensity and its limiting value decrease with the three step addition of BAAm into the gelation system. However, the improvement in the excess scattering of the resulting hydrogels was not significant.
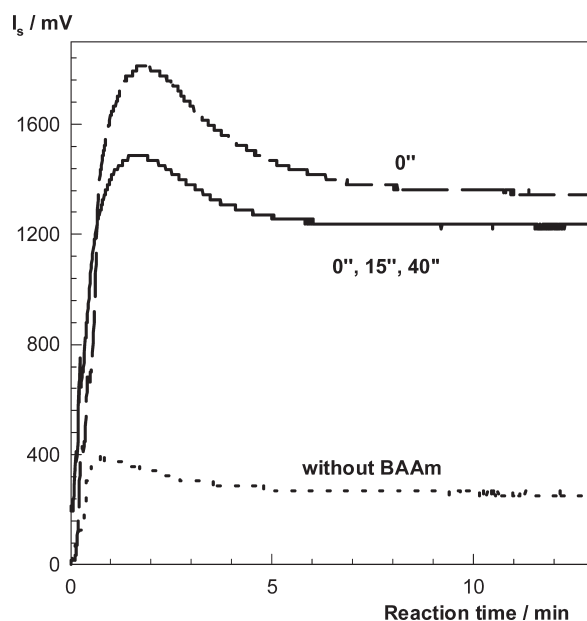

Fig. 3. The correlation length ξ and mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ in PAAm gels shown as a function of timing of BAAm addition.

Fig. 4. The scattered light intensity I_s recorded at $\theta = 90°$ shown as a function of the reaction time in AAm/BAAm copolymerizations at various delay times for BAAm addition. For comparison, the linear AAm polymerization system is also shown by the dotted curve.
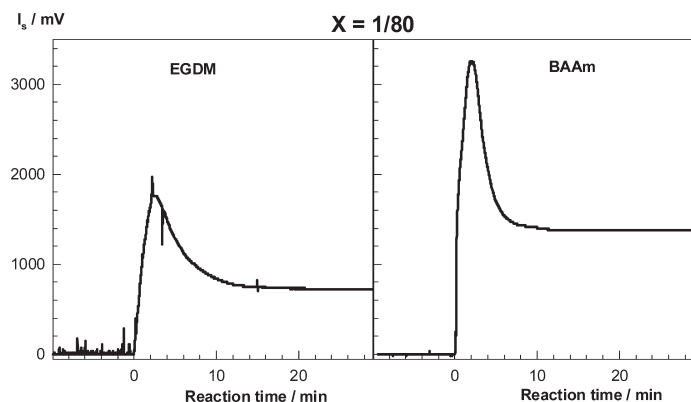
Fig. 5. The scattered light intensity I_s recorded at $\theta = 90°$ shown as a function of the reaction time in AAm/EGDM and AAm/BAAm copolymerizations at X = 1/80.

3.2 Continuous Addition of the Crosslinker EGDM

In this section, the crosslinking polymerization of AAm was carried out in aqueous solutions using EGDM as a crosslinker. Compared to BAAm, EGDM is a slightly water-soluble crosslinker with a solubility of 0.1 g/100 ml of water (25). Thus, even at a high EGDM concentration, the aqueous reaction solution will only contain about 0.1% EGDM, while the remaining insoluble part will act as a reservoir to supply the crosslinker to the reaction phase during gelation. It should be noted that, due to the presence of polymer, some additional amount of EGDM may dissolve in the reaction medium and thus, the EGDM solubility may exceed its water solubility. Therefore, the experiments were conducted over a wide range of EGDM concentration.

The gelation reactions of AAm/EGDM comonomer system were carried out at an initial monomer concentration of 10 w/v% and at various crosslinker ratios. In Figure 5, the scattered light intensity profile of the crosslinking reaction of AAm/EGDM system is compared with that of AAm/BAAm. The crosslinker ratio X in both set of experiments was set to 1/80, which corresponds to an EGDM concentration in the reaction solution of 0.348 w/v%. Since this value is much larger than the water solubility of EGDM, the crosslinker will gradually dissolve in the reaction solution as it reacts with the growing radicals so that a concentration of
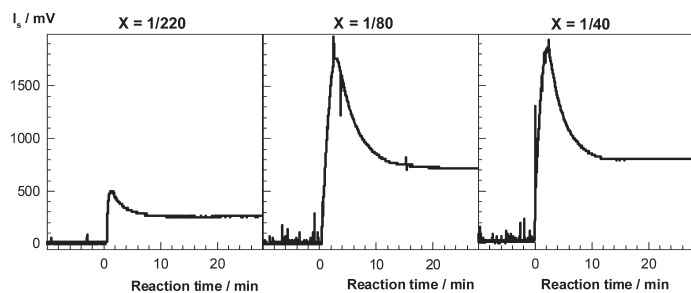

Fig. 6. The scattered light intensity I_s recorded at $\theta = 90°$ shown as a function of the reaction time in AAm/EGDM at various crosslinker ratios X indicated.
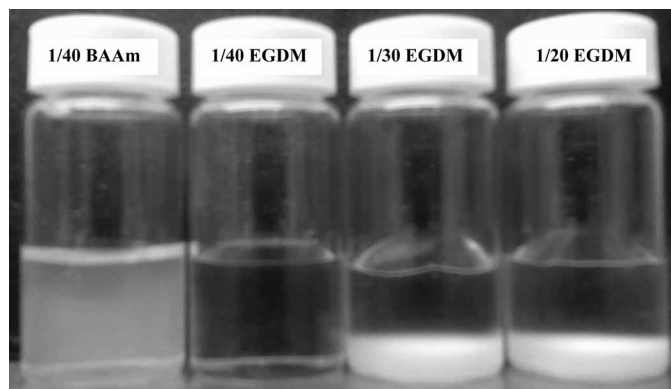

Fig. 7. Pictures of hydrogel samples obtained at various crosslinker ratios. The crosslinker used is indicated.

0.1 w/v% will automatically be adjusted in the aqueous reaction phase. Indeed, as seen from the initial part of the scattering curve of AAm/EGDM system, the scattered light intensity fluctuates due to the existence of the insoluble EGDM droplets in the reaction system. Comparison of the scattering profiles shows that the use of EGDM as a crosslinker significantly reduces the scattered light intensities during the gelation reactions.

Figure 6 shows scattered light intensity I_s vs. time plots in AAm/EGDM copolymerization at three different crosslinker ratios X. As the crosslinker ratio is increased, the amount of insoluble EGDM also increases, which leads to an increase in the extent of fluctuations in I_s during gelation. Further, although increasing amount of EGDM also increases the scattered light intensity from the reaction solution, this increase is smaller compared to the AAm/BAAm system (Fig. 1). Figure 7 shows the appearances of AAm/BAAm hydrogel at $X = 1/40$ and AAm/EGDM hydrogels at various X after a reaction time of one day. At a crosslinker ratio $X = 1/40$, the gel obtained using BAAm is opaque, while that obtained using EGDM is transparent indicating that the spatial gel inhomogeneities can be suppressed using EGDM crosslinker. The transparency of AAm/EGDM hydrogels
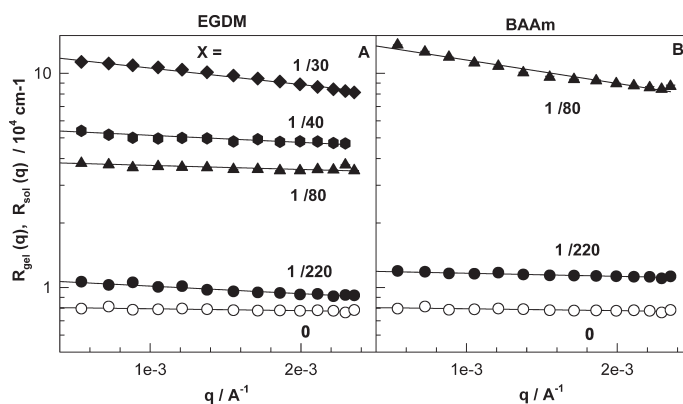

Fig. 8. Rayleigh ratio R(q) versus scattering vector q plots for the PAAm gels obtained using EGDM (A) and BAAm crosslinker (B). The crosslinker ratios are indicated.
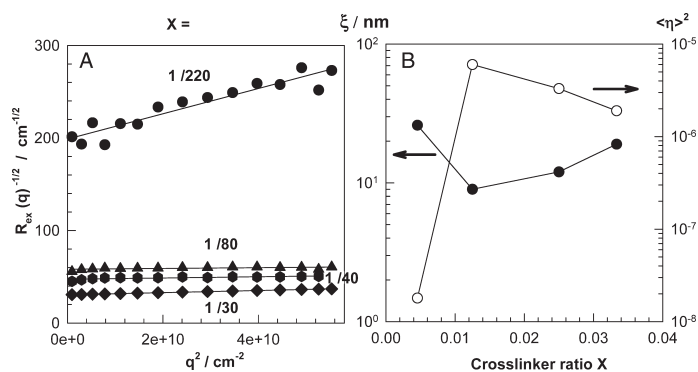
Fig. 9. (A) Debye−Bueche plots for PAAm hydrogels obtained using EGDM crosslinker. The crosslinker ratios X are indicated. (B) The correlation length ξ and mean square fluctuation of the refractive index $\langle \eta^2 \rangle$ in PAAm hydrogels shown as a function of EGDM concentration in terms of the crosslinker ratio X.

also indicates that the insoluble EGDM plays no part in the polymerization and only serves as a crosslinker reservoir. However, at higher crosslinker ratios, opacity in the lower sections of the AAm/EGDM gel samples appear while the upper section remains transparent (Fig. 7). This indicates that if the crosslinker ratio exceeds 1/40, insoluble EGDM polymerizes separately in the lower part of the reaction system to form a highly crosslinked opaque gel zone.

The scattered light intensities from AAm/EGDM hydrogels were also measured at various scattering angles. The reaction time for the hydrogel preparation was set for 24 h. Figure 8 shows the Rayleigh ratio $R(q)$ vs. the scattering vector q plots for the hydrogels prepared at various crosslinker ratios using EGDM (A) and BAAm crosslinker (B), respectively. Comparison of the results shows that hydrogels become more homogeneous if EGDM is used as a crosslinker instead of BAAm. In Figure 9A, the excess scattering data of hydrogel samples obtained using EGDM are given in the form of Debye-Bueche plots. Calculated values of ξ and $\langle \eta^2 \rangle$ from the Debye−Bueche analysis are shown in Figure 9B plotted as a function of the EGDM concentration. Increasing the crosslinker ratio from 1/220 to 1/80 results in a decrease in ξ from 30 to 10 nm while $\langle \eta^2 \rangle$ increases. A further increase in the crosslinker ratio does not change the microscopic properties of the hydrogels much.

4.   Conclusions

Network microstructures of PAAm hydrogels were investigated by light scattering measurements. To suppress the degree of gel inhomogeneity, the crosslinker reactivity during gelation was controlled by decreasing its availability in the reaction system. Our first approach was the addition of the crosslinker BAAm in one or in three portions during the course of the gelation reactions. As a second approach, a slightly water soluble crosslinker, namely EGDM was used as a crosslinker in AAm polymerization. Due to the

low water solubility of EGDM, EGDM phase in the gelation system act as a reservoir of crosslinker so that the crosslinker can be supplied continuously to the aqueous reaction zone during the course of gelation. The gel inhomogeneity was manifested by comparing the scattering intensities from the gel and from a semi-dilute solution of the same polymer at the same concentration. It was found that, in contrast to the expectation, use of our delayed crosslinker addition technique further increases the degree of inhomogeneity of PAAm hydrogels. The size of the highly crosslinked regions represented by ξ increases while the concentration difference between the highly and loosely crosslinked domains ($\langle \eta^2 \rangle$) remains unchanged as the crosslinker addition is delayed. The results were explained with increasing viscosity of the reaction solution at the time of the crosslinker addition so that the crosslinking reactions are limited to local regions in the reaction system. The second approach, namely use of the slightly water soluble crosslinker EGDM significantly increases the degree of structural homogeneity of PAAm hydrogels

5.   Acknowledgments

6.   References

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