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Heterogeneities during the formation of poly(sodium acrylate) hydrogels

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Summary

In situ fluorescence and light scattering techniques were used to study the formation of heterogeneities during the free-radical crosslinking polymerization of sodium acrylate (NaAc) in the presence of N,N'-methylene(bisacrylamide) (BAAm) as a crosslinker. Pyranine was used as a fluorescence probe in the experiments. The reactions were carried out at room temperature and at a monomer concentration of 20.6 w/v% in water. It was found that the gel forming system became turbid at the start of the reaction; continuing polymerization and crosslinking reactions turned the opaque gels into slightly opaque and finally transparent gels. Two peaks were observed both in the scattered and emitted light intensities versus the reaction time plots. The first peak corresponds to the formation and growth of the phase separated domains whereas the second peak reflects the macrogelation point in the reaction system.

Introduction

Polymer gels are important materials of both fundamental and technological interest. Investigations of the properties of polymer gels have been reported repeatedly in the last four decades. However, theories are still unable to predict their physical properties from the synthesis conditions. This is due to the several non-idealities of the gel forming systems such as the different and conversion dependent reactivities of the functional groups (1,2), cyclization (2-5), inhomogeneities (5-7), and heterogeneities (5). Note that, although there has been some diversity in defining the inhomogeneity and heterogeneity in gels, inhomogeneity usually means the fluctuation of the crosslink density in space whereas heterogeneity indicates the existence of phase separated domains in polymer gels (2-7).

Heterogeneity in polymer gels is a non-ideality affecting directly their physical properties such as swelling, permeability, turbidity, and elasticity (8,9). Heterogeneity appears as a result of a phase separation during the gel formation process. Dusek pointed out that a phase separation during the crosslinking polymerization may occur in the form of microsyneresis or macrosyneresis (10,11). In the first case, a solution phase in the form of droplets separates out of the gel phase, whereas in the latter, the separated solution droplets combine each other to a bulky liquid phase. In both cases, after complete monomer conversion, a two phase system consisting of gel and solution phases is obtained. Depending on the reaction conditions, a phase separation may also occur prior to the onset of macrogelation. In this case, the polymer chains precipitate from the solution and they agglomerate to clusters of various sizes. If the size of the interconnected clusters approaches to that of the reactor, a heterogeneous gel forms in the reaction system. Examples to the heterogeneous gels are those derived from acrylamide (12), N-isopropylacrylamide (13), 2-hydroxyethyl methacrylate (14,15), styrene (16), or methyl methacrylate monomers (17).

Recently, we have shown that the quenching properties of the excited state of a fluorescing molecule can be used to follow the gel point and the gel effect during the free-radical crosslinking copolymerization of vinyl-divinyl monomers (18,19). During the crosslinking process, if a fluorescing molecule such as pyrene is in a mobile micro-environment, the mobile molecules (e.g., the monomers, solvent and free polymer chains) act as an energy sink for the excited pyrene; thus, no change in the fluorescence intensity of pyrene is observed. However, the formation of a gel or, a bulky polymer around pyrene provides an unchanged environment for the excited pyrene molecule. As a consequence, an abrupt increase in the fluorescence intensity of pyrene is observed at a critical point. The peak in the fluorescence intensity versus reaction time plot thus indicates a critical change in the gelation system (18).

Although the understanding of the heterogeneities in gels is important for the prediction of their properties, there are not so many works in the literature relating to this subject (3,8,9). In this work, we use the quenching properties of the excited state of a fluorescing molecule to study the formation of the heterogeneities during the free-radical crosslinking copolymerization reactions. The polymerization of sodium acrylate (NaAc) in the presence of N,N'-methylene(bisacrylamide) (BAAm) as a crosslinker was selected for this purpose. Pyranine was used as a water-soluble fluoresce probe in our experiments. The preliminary experiments showed that, at an initial monomer (NaAc) concentration of 20 w/v% in water and at room temperature, this gel forming system became turbid at the start of the reaction; continuing polymerization and crosslinking reactions turned the opaque gels into slightly opaque and finally transparent gels. The appearance of turbidity during the formation of NaAc based hydrogels has, to our knowledge, not been reported previously. Here, the crosslinking polymerization of NaAc was monitored by the in-situ fluorescence and light scattering techniques as well as by the gravimety.

Experimental

Materials

Acrylic acid (AAc, Fluka) was distilled under a vacuum. N,N'-methylenebis(acrylamide) (BAAm, Merck), ammonium persulfate (APS, Merck), N,N,N',N'-tetramethylethylenediamine (TEMED, Merck), and pyranine (Merck) were used as received. A stock solution of sodium acrylate (NaAc) was prepared by dissolving 15 mL of AAc in 10 mL of distilled water and adding to this solution 20 mL of a 42.5 % NaOH solution under cooling. Then, the solution was titrated with 2 M NaOH to pH = 7.00 and finally, the volume of the solution was completed to 100 mL with distilled water. 1 mL of NaAc stock solution thus prepared contained 2.19 mmol NaAc.

Methods

The free-radical crosslinking polymerization of NaAc was carried out with a small amount of BAAm as a crosslinker in aqueous solution. APS and TEMED were respectively the initiator and the accelerator. The crosslinker ratio (mole ratio of the crosslinker BAAm to the monomer NaAc), the total monomer concentration and the initiator concentration were 1/81, 2.2 M (20.6 w/v %) and 1.75 mM, respectively. The reactions were conducted at room temperature (21±2°C) according to the following scheme:

BAAm (41.6 mg) and APS (4.0 mg) were dissolved in 10.0 mL of NaAc stock solution. For the in-situ fluorescence measurements, 10^{-4}M of pyranine was also included in the above solution. After bubbling nitrogen for 20 min, TEMED (24 µl) was added to the solution just before the start the reaction. The crosslinking polymerization process was examined by light scattering and fluorescence techniques as well as by gravimetry.

By the in-situ steady-state fluorescence technique, the crosslinking polymerization of NaAc was performed in the fluorescence accessory of the Model LS-50 spectrometer of Perkin Elmer, equipped with a temperature controller. The pyranine molecule was excited at 390 nm during in situ experiments and the variation in the fluorescence emission intensity, I, was monitored with the time-drive mode of the spectrometer, by staying at the 510 nm peak of the pyranine emission spectrum. No shift was observed in the wavelength of the maximum intensity peak during the crosslinking process. We also monitored the scattered light intensity in arbitrary units from the samples during the course of the crosslinking process by staying at wavelengths 350 nm up to 700 nm. All measurements were made at 90°C position; i.e., the emitted and scattered lights were monitored in a direction perpendicular to the excited light beam. Both the excitation and emission slit widths were kept at 2.5 nm.

By the gravimetric technique, the reaction solution was poured into several glass tubes of 5.5 mm internal diameters and about 250 mm long. The polymerization was conducted for predetermined reaction times after which the reaction mixture was transferred into a large excess of methanol containing hydroquinone as an inhibitor. The precipitated polymer was dried in vacuo at 50°C and weighed. The gel point was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in water. Dilatometers containing a teflon-covered steel sphere of 5 mm diameter was also used for the gel point measurements. The midpoint between the last time at which the sphere moves magnetically and that at which it stops moving is taken as the gel point ("falling ball technique").

Linear poly(NaAc) was prepared under the same reaction condition as the pol(NaAc) gels except that the crosslinker BAAm was not used. After polymerization, the reaction mixture was diluted with water and poured into a large excess of methanol. The unreacted NaAc or NaAc in the initial monomer mixture was soluble in methanol. The precipitated linear pol(NaAc) was dried in vacuo at room temperature.

Results and discussion

Solubility of poly(NaAc) chains in the reaction solution

Examination of the solubility of linear poly(NaAc) was performed at room temperature using aqueous NaAc solutions. It was found that poly(NaAc) is insoluble in its own monomer solution, if the monomer concentration exceeds 11 w/v%. This means that the crosslinking polymerization of NaAc at 20.6 w/v% initial monomer concentration should proceed in a heterogeneous manner up to about 50 % monomer conversion. Indeed, visual observation showed the appearance of a turbidity in the system at the start of the reaction; opaque poly(NaAc) gels thus formed turned to transparent gels as the reaction proceeds. On the other hand, linear poly(NaAc) was found to be soluble in NaAc solutions at 60°C or above; thus, as expected, the gelation processes conducted at or above 60°C remained homogeneous throughout the crosslinking process.

Gel point

No gel point in its classical meaning was observed in the crosslinking polymerization of NaAc at room temperature. By the gravimetric technique, we found that the first insoluble material in the reaction system forms after a reaction time of 5 min. This reaction time is a critical point at which an infinite cluster starts to appear in the system. However, by use of the dilatometry, we observed that the gel formed does not extend throughout the solution; it starts to form from the bottom part of the reactor and it grows upwards. This is due to the fact that the reaction solution is a poor solvent for the first formed gel so that the swelling capacity of the gel is much less than its degree of dilution; as a consequence, the growing gel cannot occupy the whole available reaction volume.

In-situ fluorescence and light scattering measurements

In Figure 1, the intensities of the scattered (1A) and emitted lights (1B) from the reaction solution are plotted as a function of the reaction time of the crosslinking NaAc polymerization. The wavelength of the incident light in the light scattering experiments was 390 nm. During the crosslinking process at room temperature, we always observed two peaks both in the scattered and emitted light intensities (solid curves in Fig. 1). The peaks in the scattered light intensity versus time plot (1A) indicate formation of heterogeneities in the reaction system whereas those in the emitted light intensity versus time plot (1B) indicate that the pyranine molecules become trapped inside the polymer-rich domains. It is important to observe that the reaction times at which the peaks appear are almost the same in both plots (4 min versus 6 min for the first peak and, 23 min versus 27 min for the second peak in Fig. 1A and 1B, respectively). This reveals that the increase in the scattered light intensity due to the spatial heterogeneities of the system refractive index is reflected in the in situ fluorescence measurements. Note that, at or above 60°C, since the polymer is soluble in the aqueous solution of its monomer, no peaks were detected in the intensity versus time plots (dotted curve in Fig. 1).

When the polymerization is initiated by the reaction between APS and TEMED molecules, the primary radicals formed start to grow by adding the monomer NaAc and the crosslinker BAAm. Considering the insolubility of poly(NaAc) in the initial reaction solution, the growing chains separate out of the solution phase after reaching a critical size. The time needed to convert a primary radical to a polymer molecule is known to be less than one second (20); this means that the onset of a turbidity in the reaction system corresponds to the onset of polymerization and crosslinking reactions. This point is indicated by (A) in Fig. 1A. Indeed, by the gravimetric technique, no polymer formation was detected in the reaction system until the point (A) is reached. This period of time up to (A) is the induction period whose length was found to depend inversely on the bubbling time of nitrogen prior to polymerization, i.e., on the ratio of nitrogen to oxygen in the reaction system.

As the time goes on, more and more primary particles and thus, polymer molecules are generated. As a result, the number of separated polymer chains will increase, which is reflected in the increase of the scattered light intensity between the points (A) and (B) in Fig.1A. Since the reaction solution is a poor solvent for poly(NaAc), the segments of the same and different polymer molecules attract each other to form polymer clusters. Moreover, chemical bonds, i.e., crosslinks between the clusters also form due to the reaction between pendant vinyl groups and the radical centers locating on the clusters. As more and larger clusters are formed during the reaction, pyranine molecules start to trap inside the clusters. This is confirmed by the simultaneous increase of the emitted light intensity shown in Fig. 1B.

The crosslinking reactions taking place in the system increase both the size and the density of the clusters. When a cluster reaches to a density which overcomes the density of the solution it falls down to the sample cell. This point corresponds to the top of the first peak in Fig. 1 represented by (B). The reaction time at this point is 4 min. The decrease of both the scattered and emitted light intensities from the point (B) to (C) is a consequence of the sedimentation of the polymer clusters. Thus, the concentration of the clusters in the path of the incident light, corresponding to the middle of the sample cell containing the reaction solution, decreases as the density of the clusters increases. Note that if the light passes through the upper part of the sample cell, the resulting spectrum (dashed curve in Fig. 1) exhibits no peaks. This reveals that the gel forming system is also heterogeneous depending on the position within the system. This has a consequence that the final gel will swell heterogeneously, i.e., the upper part of the gel will swell more than the lower part.

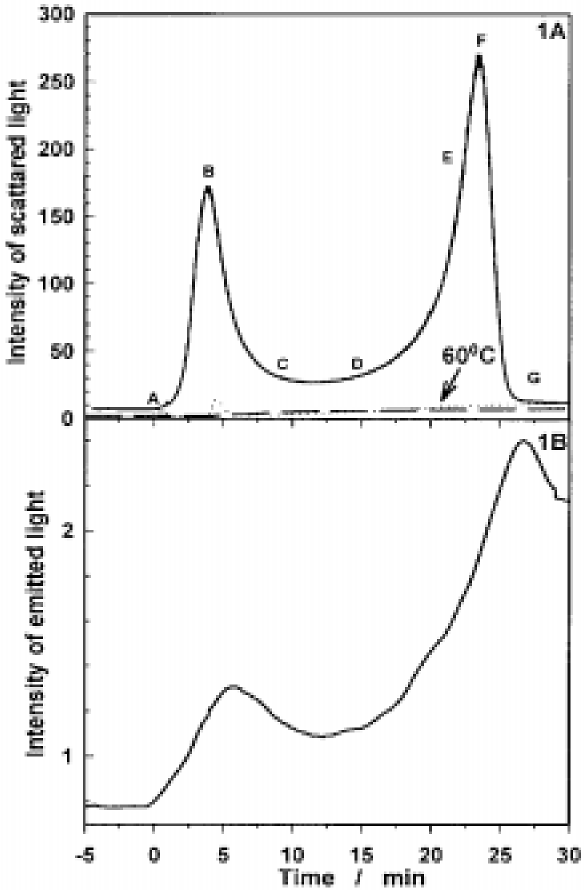
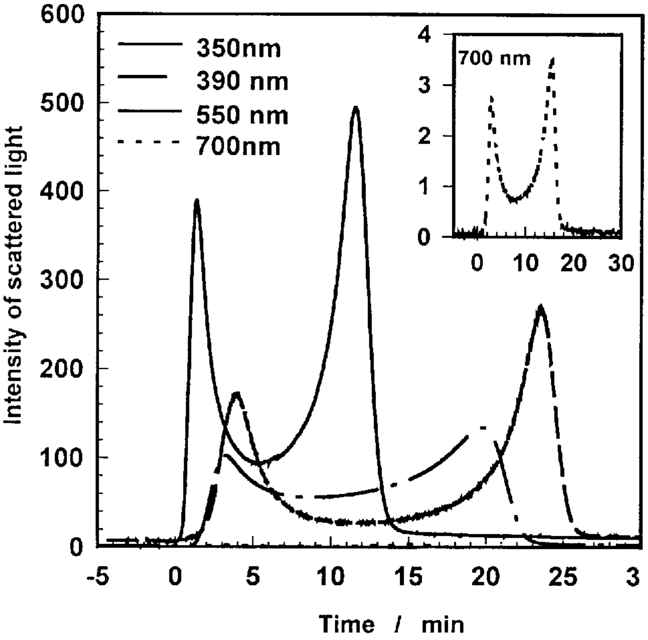


Fig. 1. Intensities of scattered and emitted lights from the reaction solution shown as a function of the reaction time of crosslinking polymerization of NaAc with BAAm as a crosslinker. The wavelength of the incident light in the light scattering experiments was 390 nm. Polymerization temperature: 21±2°C (solid curves), 60°C (dotted curve). Path of the incident light: middle (solid and dotted curves), upper part of the sample cell (dashed curve).

By both gravimetric and dilatometric techniques we observed that the first water-insoluble polymer in the reaction system forms after a reaction time of 5 min. However, as mentioned above, the gel thus formed does not extend throughout the reaction solution; it started to form from the bottom part of the sample cell. Starting from the point (C) in Fig. 1, we observed that the gel grows upwards. This is a consequence of two events: First, as more and more monomers are converted into the polymer, the amount of NaAc in the solution phase decreases so that the solvating power of the monomer solution for the gel increases and the gel swells, i.e., its volume increases. Second, new clusters form continuously as the polymerization proceeds and they are connected to the gel which results in an increase of its volume.

As the reactions proceed, we observed that the interface between the gel and the solution phase goes upward position and finally reaches to the path of the incident light. As a result, the scattered light intensity increases again starting from the point (D) due to the heterogeneity of the gel. The point (E) corresponds to the reaction time at which the system is totally occupied by the gel. This was detected by "falling ball technique" applied in the fluorescence cell. When this point is crossed, the fluorescence intensity suddenly increases because of the transition of the system from liquid to solid-like state which favors the radiative transition of pyranine molecules trapped in the dense regions (clusters) of the gel.

By the gravimetric technique we observed a complete conversion of monomers after 25 - 30 min. This time is indicated by (G) in Fig. 1 at which a homogeneous poly(NaAc) gel forms. As a result of re-homogenization of the reaction system, both the scattered and emitted light intensities decrease at the end of the copolymerization and crosslinking reactions.



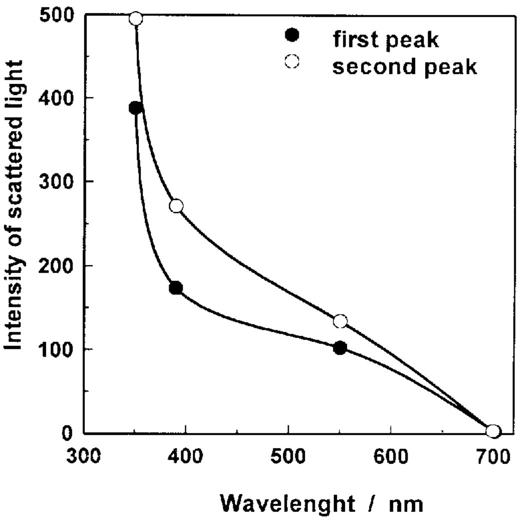


Fig. 2 (left). Scattered light intensities at various incident wavelength of light shown as a function of the reaction time of crosslinking polymerization of NaAc with BAAm as a crosslinker.

Fig. 3 (right). Scattered light intensities at the peaks shown as a function of the incident wavelength of light.

Figure 2 shows the intensity of scattered light versus reaction time plots for various wavelength of the incident light between 350 and 700 nm. Figure 3 illustrates how the scattered light intensities at the first and second peaks vary with the wavelength of the incident light. It is seen that the intensity of scattered light increases as the wavelength of the light decreases from 700 to 350 nm. Since light scattering characterizes heterogeneities of a system having dimensions of the order of the wavelength of the incident light, Figures 2 and 3 reveals that the average size of the phase separated domains in the gel forming system is smaller than 350 nm.

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 increase in the fluorescence intensity of a fluorescence probe in the system. It was also shown that the free-radical crosslinking copolymerization of NaAc and BAAm proceeds in a heterogeneous medium. Although the poly(NaAc) hydrogels isolated after complete monomer conversion were transparent in apperance, it is expected that their formation history will have significant effect on their network structure and physical properties.

References

1. Baselga J, Llorente MA, Hernandez-Fuentes I, Pierola IF (1989) Eur Polym J 25: 471
2. Naghash HJ, Okay O (1996) J Appl Polym Sci 60: 971
3. Tobita H, Hamielec AE (1990) Polymer 31: 1546
4. Okay O, Kurz M, Lutz K, Funke W (1995) Macromolecules 28: 2728
5. Funke W, Joos-Muller B, Okay O (1998), Adv Polym Sci 136:139
6. Weiss N, van Vliet T, Silberberg A (1974) J Polym Sci Polym Phys Ed 17: 2229
7. Matsuo ES, Orkisz M, Sun ST, Li Y, Tanaka T (1994) Macromolecules 27: 6791
8. Richards EG, Temple C (1971) J Nat Phys Sci 230:92
9. Bansil R, Gupta MK(1980) Ferroelectrics 30:64
10. Dusek K (1965) J Polym Sci Polym Letters 3:209
11. Dusek K, Prins W (1969) Adv Polym Sci 6:1
12. Xie S, Svec F, Frechet JMJ (1997) J Polym Sci Polym Chem Ed 35:1013
13. Wu XS, Hoffman AS, Yager P (1992) J Polym Sci Polym Chem Ed 30:2121
14. Coupek J, Krivakova M, Pokorny S (1973) J Polym Sci C42:185
15. Huglin MB, Yip DCF (1992) Macromolecules 25:1333
16. Okay O (1986) J Appl Polym Sci 32:5533
17. Kucuk I, Kuyulu A, Okay O (1995) Polym Bull 35:511
18. Pekcan O, Yilmaz Y, Okay O (1994) Chem Phys Lett 229:537
19. Pekcan O, Yilmaz Y, Okay O (1997) Polymer 38:1693
20. Odian G (1981) Principles of polymerization. John Wiley, NY, pp 251-259.