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In situ monitoring gelation process of *N*,*N*-dimethylacrylamide by refractive index technique

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Abstract

In situ refractive index technique was used to study the gelation process in the free-radical cross-linking copolymerization (RCC) of *N*,*N*-dimethylacrylamide with *N*,*N*′-methylenebisacrylamide as the cross-linker. The change of refractive index was measured and used to monitor the gelation process. The influence of different polymerization conditions on the gelation process, such as monomer, cross-linker and initiator concentrations was investigated and discussed in detail. The kinetic model under steady-state conditions was employed to determine the monomer consumption rate during the gelation process. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogel; In situ refractive index; Gelation

1. Introduction

Hydrogels, consisting of three-dimensional hydrophilic polymer networks containing a substantial amount of water, have been attracting great interest for their unique properties. It has been reported that hydrogels can respond to solvent composition [1], pH [2], temperature [3], electric fields [4] and saccharides [5], which enabled hydrogels to be used as novel types of materials, particularly intelligent materials. Meanwhile, being biocompatible, hydrogels have found numerous important applications in the medical and pharmaceutical fields [6,7], such as biosensors, artificial skin, contact lenses, and drug delivery devices, etc. *N*-Substituted polyalkylacrylamide is a kind of such typical smart materials that have received great attention due to its interesting physical behavior. For example, poly(*N*-isopropylacrylamide) (PIPAAM) is soluble in aqueous media at solution temperatures below 32 °C, its critical solution temperature. Above this point, it undergoes a discontinuous phase transition, precipitating from solution suddenly and reversibly over a narrow temperature range [8,9].

As well known, the understanding of the formation mechanism of polymer gels is of great interest to predict their physical properties. The past few decades have seen significant advances in the research concerning the gel formation process. On the one hand, several theories have been developed to describe the gel formation process, among which percolation theory provides a basis for modeling sol–gel phase transition [10,11]. On the other hand, many experimental methods for studying the gel formation process have been established. These methods can mainly be grouped into two categories. One is called 'quenching method', in which the measurements were performed on quenched samples from the stopped reaction system by freezing or diluting the system. Zuo et al. [12] have studied the gel formation process of styrene–divinylbenzene copolymerization by light scattering technique through timing sampling, and suggested that the tracking can effectively contribute the information for controlling the structure of the polymer networks. Jie et al. [13] measured the viscosity of partially hydrolyzed polyacrylamide (HPAM)/aluminum citrate colloidal dispersion gel, and the concentration range, where the cross-linking system changed from concentrated colloidal dispersion gel to bulk gel. The other is called 'in situ method', which never needs to terminate the reaction, such

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as in situ electroconductivity method [14], in situ photo transmission technique [15,16], in situ fast transient fluorescence technique [17], etc. Electroconductivity method could only monitor the whole process of the system whose conductivity changed during the gelation process. Fast transient fluorescence technique, reported by Kara, can be used to study the sol–gel phase transition in free-radical cross-linking copolymerization reaction of methyl methacrylate and ethylene glycol dimethacrylate with pyrene (Py) as the fluorescence probe. The monomer consumption rate during the gelation process can be obtained using Stern–Volmer model [17]. However, this method requires high resolving power of the apparatus. Therefore, in the previous work, we have developed two kinds of novel methods to study the whole process of gel formation. One is called 'in situ interferometry' [18–20]. This method has advantages in non-destructive and successive study overall process. However, the apparatus is complex and expensive since the measurement is based on the interference of light beams. The other is called 'in situ refractive index technique' [21,22], which is established according to the refraction of light. Aside from the major advantage of achieving the information of the whole gelation process without disturbing the reaction system, this technique has high veracity for measurements and it is easy for manipulation and data processing.

In this paper, we use readily available *N*-substituted acrylamide, *N*,*N*-dimethylacrylamide (DMAAm), as monomer to study the gelation process. Although extensive work has been reported in the literature for the physical properties of PDMAAm hydrogels, few are concerned with the formation process of the PDMAAm hydrogel in the RCC. Therefore, we use in situ refractive index technique to study the gel formation process in the RCC of DMAAm and *N*,*N*′-methylenebisacrylamide (MBAAm). The influence of the different monomer and cross-linker as well as initiator concentrations on the gelation process were investigated. Under steady-state conditions, the monomer consumption rate was determined. We hope this work may be helpful for understanding the mechanism of the gelation process intensively, and contribute basic information for predicting the physical properties of the gels.

2. Theoretical considerations

2.1. Theoretical background

It is known to all that the light will be refracted through triangular prism. The change of the refractive angle is related to the medium within triangular prism. According to this phenomenon, our laboratory designed a suit of in situ refractive index recording technique [22]. As the refractive index of the polymer is larger than that of monomer, the refractive index of the reaction system increases gradually during the polymerization reaction. The refractive index change (Δn) as function of polymerization time (t) can be expressed as:

$$\Delta n(t) = \frac{\Delta l \cos \alpha}{L \sin \theta} = \frac{\sqrt{1 - n^2 \sin^2 \theta}}{L \sin \theta} \Delta l(t) \tag{1}$$

where Δl is the change of the distance from the facula on the screen to the intersection point of the emergence normal, L the distance from the emergence point to the screen, θ and α the incidence angle and refractive angel, respectively, and n the refractive index of the medium in the prism. Each stage of the gelation process in the free-radical cross-linking polymerization exhibits different refractive index change, so this technique can successfully monitor the whole gelation process without disturbing the reaction system.

In the experiment, two assumptions must be concerned in order to convert the refractive index change to monomer consumption ratio: (1) the diffusion of monomer or polymer in cell could be neglected during the gelation process; (2) the monomer can be polymerized completely when the time is long enough. Under these conditions, the monomer concentration change is proportional to the refractive index change:

$$\frac{[M]_0 - [M]_t}{[M]_0} = \frac{[M]_0 - [M]_t}{[M]_0 - [M]_\infty} = \frac{n_t - n_0}{n_\infty - n_0} = \frac{\Delta n_t}{\Delta n_\infty} \tag{2}$$

where $[M]_0$, $[M]_t$ and $[M]_\infty$ are the monomer concentration at time zero, time (t) and time long enough, respectively. Accordingly, n_0, n_t and n_∞ are the refractive index of the medium in the prism at time zero, time (t) and time long enough, respectively. Δn_t and Δn_∞ are the refractive index change at time (t) and time long enough, respectively. Therefore, with the aid of Eq. (1), the relation between monomer concentration $[M]$ and reaction time t can be obtained.

2.2. Kinetic model

As well established, the reaction of photo-initiating free-radical polymerization is composed of three steps. The first step is called 'initiation step', including two reactions: the speed-control reaction in which the photosensitive initiator molecule was activated by light and decomposes into two primary radicals with the initial efficiency Φ, and the secondary reaction in which the primary radicals add to the double bond of the monomer to form monomeric radicals. The second step is 'chain propagating step', where a successive additive reactions, with the rate constant K_p, occurred between the monomer molecules and the active chain containing end radicals so that the chain propagated continuously. Finally, two active chains react each other or one reactive chain reacts with impurity to lose their activity, yielding macromolecules [17,23], which is called 'termination step' whose rate constant is K_t. During the free-radical cross-linking copolymerization, in the presence of multifunctional substances, the cross-linker, the propagating chain with end radicals might form intra- and intermolecular cross-linking structure. Intramolecular cross-linking occurs between pendant vinyls and radical centers located on the same macromolecule and resulting in the formation of cyclic chain and multiple cross-links, which have no influence on the onset of macrogelation [24]. According to Funke and Okay, the aggregation of intramolecularly cross-linked primary particles formed by multiple cross-linking results in the formation of microgels [25]. And the reactions of the functional groups of the microgels in the presence of cross-linker, proposed by Dusek et al. [26] lead to macrogelation. Furthermore, it is known that in free-radical polymerization, cross-linking enhances the gel effect significantly and the auto-acceleration in polymerization rate starts shortly after the start of the polymerization [27]. Therefore, macrogelation occurs instantly after the start of the auto-acceleration effect, resulting in the significant change of the refractive index of the reaction system. Thus, the position of the inflection point, i.e. position of the maxima of the first derivatives of the refractive index change curve of the whole gelation process, is considered as the gel point in this paper. Under steady-state conditions, the consumption rate of the monomer, namely the rate of polymerization, can be expressed as:

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = -\frac{K_\mathrm{p}(\Phi\varepsilon I_0[S])^{1/2}}{K_\mathrm{t}^{1/2}}[M] \tag{3}$$

where $[M]$ and $[S]$ are the concentrations of the monomer and photoinitiator, respectively. The ε is the mole extinction coefficient of the initiator, and I_0 is the incident light intensity. Generally, the amount of the initiator is low and the producing rate constant of initiator radicals is very large [17], so $[S]$ can be considered to stay constant during the polymerization process. Thus, Eq. (1) can be converted to:

$$\frac{\mathrm{d}[M]}{\mathrm{d}t} = -\frac{K_\mathrm{p}K_\mathrm{i}^{1/2}}{K_\mathrm{t}^{1/2}}[M] = -K_\mathrm{r}[M], \quad K_\mathrm{i} = \Phi\varepsilon I_0[S] \tag{4}$$

where K_r is called the composite rate constant. Undergoing logarithmic handling, Eq. (2) can also be written as:

$$K_\mathrm{r} = -\frac{\ln[M]_t - \ln[M]_0}{t - t_0} = -\frac{1}{t}\ln\frac{[M]_t}{[M]_0} \tag{5}$$

where $[M]_0$ is the monomer concentration at $t = 0$.

3. Experimental

3.1. Materials

DMAAm was provided by Johnson Matthey Company (Ward Hill, MA), and was purified by redistilling. MBAAm was recrystallized from alcohol. α-Ketoglutaric acid (KGA), reagent from Wakolure Chem. Inst. Ltd, was used without further treatment. The deionized water was redistilled for use as solvents.

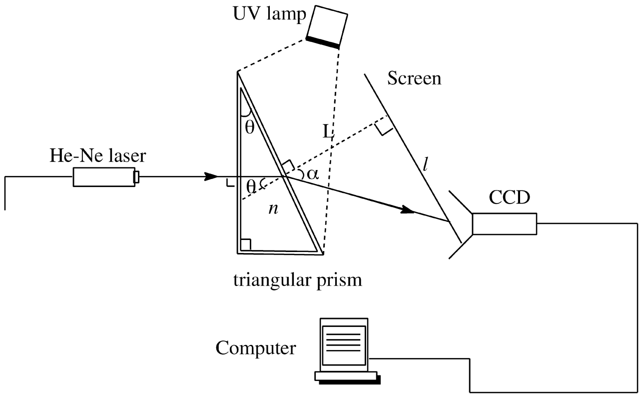

Fig. 1. The in situ refractive index recording system.

3.2. Preparation of PDMAAm gels

PDMAAm gels were prepared by photoinitiation polymerization using KGA as the photoinitiator and MBAAm as the cross-linker. All gelation reaction was conducted at 25 °C and the sample was deoxygenated by bubbling nitrogen through it for 1 h before the polymerization. The polymerization reaction was carried out in a triangular prism under UV irradiation (ENF 260C, Spectronics Co., USA) at the wavelength of 365 nm.

3.3. In situ refractive index recording system

As shown in Fig. 1, a He–Ne laser (Model 127, Spectra-physics Lasers, Inc., $\lambda = 632.8$ nm) was used as the light source. The triangular prism was self-made with spectralite with one angle of the base surface being 30°. The incident light was refracted by the reaction system. The CCD camera recorded the facula position of the emergence light. The position data was reserved and treated by a specific program via the computer.

4. Results and discussion

The influence of the monomer, the cross-linker and the initiator on the gelation process was considered first for the gelation process in free-radical cross-linking polymerization. Dependence of the refractive index change on gelation time under different monomer concentration was shown in Fig. 2. Usually, an increase in the monomer concentration will speed up the polymerization. As shown in Fig. 2, with an increase of DMAAm content, the initiation stage caused by trace oxygen and slow formation of polymer, shortened (12, 10 and 8 min for 0.5, 1.0 and 1.5 mol/l monomer concentration, respectively) and the reaction rate after gel point increased evidently (0.0067, 0.0088 and 0.0147 mol l^{-1} min^{-1} for the 0.5, 1.0 and

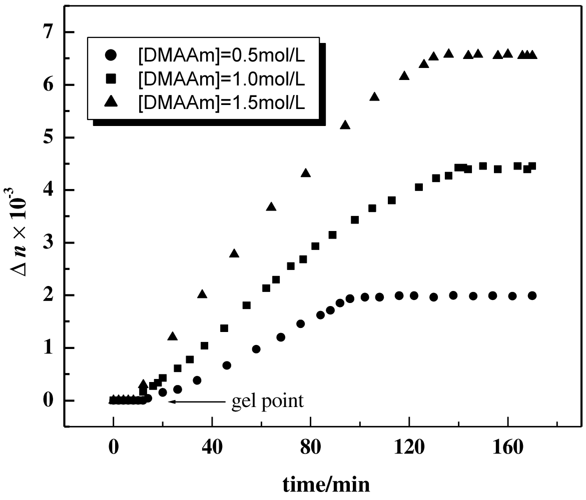

Fig. 2. Dependence of refractive index change on reaction time at various monomer concentrations during the gelation process ([MBAAm] = 0.003 mol/l, [KGA] = 0.003 mol/l).

1.5 mol/l monomer concentration, respectively), owing to the fact that the free radical and monomer molecules have more chances to encounter. Furthermore, it can also be seen that the ultimate refractive indexes were 0.0022, 0.0045 and 0.0065 for 0.5, 1.0 and 1.5 mol/l monomer concentration, respectively. This means that the ultimate refractive index increases proportional to the initial monomer concentration, in good agreement with the deduction proposed previously in the theoretical background part.

The cross-linker played an important role in the formation of polymer networks. The more the cross-linker, the shorter the beginning time of the polymer network formation. Fig. 3 gives the refractive index change under three different cross-linker levels: 0.003, 0.005 and 0.01 mol/l. It is shown that the increase in cross-linker enhanced the rate of polymerization after gel point, implying that higher cross-linker level made the formation of polymer networks more easily due to the more cross-linking sites provided by the cross-linker. Furthermore, the refractive index change of the reaction system without the cross-linker was also investigated for comparing. It can be seen that the auto-acceleration effect begins much later than that of the reaction system with cross-linker. In addition, owing to its small amount comparing with the monomer, the cross-linker used here does not obviously influence the ultimate refractive index change (about 0.0045).

As a trigger for the polymerization, the initiator also has effect on the reaction process. Fig. 4 presents the refractive index change with different initiator concentration. The initial stages for the system containing 0.003, 0.005 and 0.01 mol/l initiator concentration were 10, 8 and 6 min, respectively. And the rate of the polymerization after gel point increased with the increase of initiator content (0.0088, 0.0152 and 0.0259 mol l^{-1} min^{-1} for the reaction system of 0.003, 0.005 and 0.01 mol/l, respectively). These results can be explained that higher initiator content curtails the initial stage. Meanwhile, more the initiator, more the primary radicals, that means, the monomer molecules have more chances to encounter the primary radicals to produce more monomeric radicals in the limited space, which consequently leads to auto-acceleration effect. Similar to the cross-linker, the initiator does not influence the ultimate refractive index change value due to its small amount.

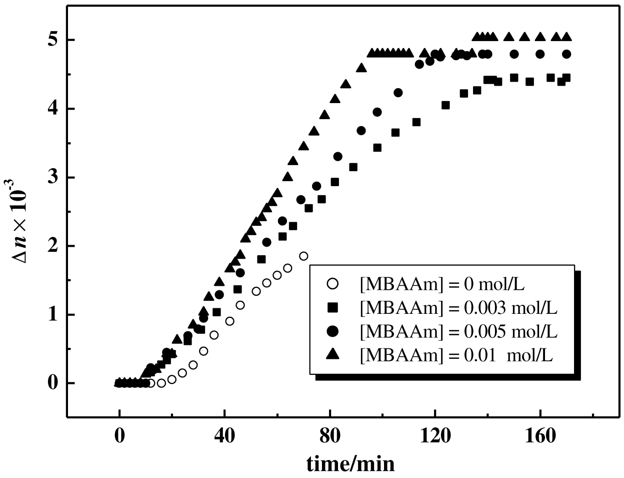

Fig. 3. Dependence of refractive index change on reaction time at various cross-linker concentrations during the gelation process ([DMAAm] = 1.0 mol/l, [KGA] = 0.003 mol/l).

Generally, in terms of monitoring gelation process, it is always expected to achieve the kinetic curve of composition rate, i.e. to get the composition rate constant K_r. Therefore, the reaction system comprising 1.0 mol/l DMAAm, 0.003 mol/l MBAAm and 0.003 mol/l KGA was selected as example to illustrate the relation between monomer concentration and gelation time. As confirmed above, the change of the refractive index is proportional to the change of monomer concentration, which was presented in Eq. (2). Fitting the results from the refractive index change shown in Fig. 2 to Eq. (2), the value of

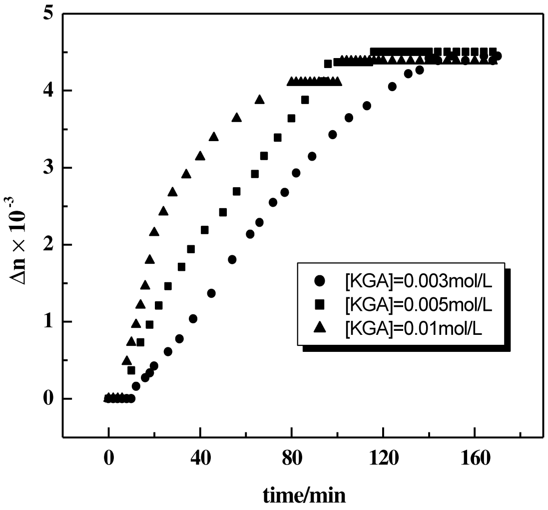

Fig. 4. Dependence of refractive index change on reaction time at various initiator concentrations during the gelation process ([DMAAm] = 1.0 mol/l, [MBAAm] = 0.003 mol/l).

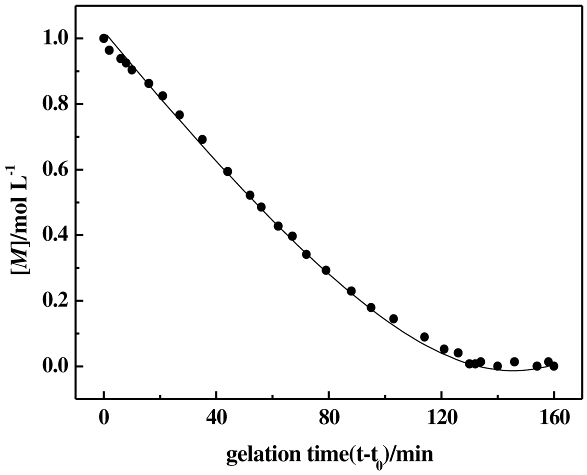

Fig. 5. Change of monomer concentration versus gelation time during the gelation process, where $t_0 = 10$ min is the time for onset of gelation.

$[M]$ at various gelation times was obtained and presented in Fig. 5. It can be seen that the curve of $[M]$ versus t roughly obeys the exponential relation in Eq. (5), implying that the assumption of steady state was practicable. Employing the data of Fig. 5 in Eq. (5), the relation between $\ln[M]$ and gelation time was obtained, as shown in Fig. 6. It can be seen that only the data of the beginning fit the linear relation quite well, which can be attributed to the fact that the steady-state conditions are suitable only when the conversion ratio is low in free-radical polymerization [28]. From the slope of the linear relation, the composite rate constant, K_r, was determined as $2.1 \times 10^{-4}\ s^{-1}$.

5. Conclusions

The gelation process in the free-radical cross-linking copolymerization of DMAAm and MBAAm was successfully monitored with a novel refractive index method. It is observed that the concentration of monomer, cross-linker and initiator has significant effect on the refractive index change. The increase of monomer and cross-linker as well as initiator concentration all contributed to the reaction rate after the gel point. However, the ultimate refractive index change was solely dependent on the original monomer concentration. Employing the steady-state kinetic model into the reaction system containing 1.0 mol/l DMAAm, 0.003 mol/l MBAAm and 0.003 mol/l KGA, we obtained the relation curve between $[M]$ and gelation time, and the linear relation between $\ln[M]$ and gelation time. From the slope of the linear relation between $\ln[M]$ and gelation time, the composite rate constant K_r was calculated as $2.1 \times 10^{-4}\ s^{-1}$. This work might be helpful to understand the mechanism of the gelation process deeply.

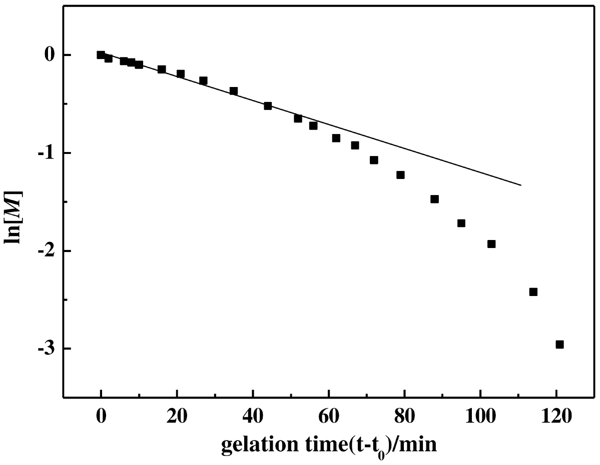

Fig. 6. The dependence of $\ln[M]$ on gelation time.

Acknowledgements

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