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## IN SITU INTERFEROMETRIC STUDY ON THE GELATION PROCESS OF POLYACRYLIC ACID GELS\*

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**Abstract** *In situ* interferometry was used to investigate the gelation process of polyacrylic acid (PAA) gels. The basic principle of the *in situ* interferometry technique is illustrated. It can give sufficient information for non-destructive and successful investigation of the whole gelation process. The effect of initiator concentration on the gelation process was studied. The polymerization rate of AA increases with increasing initiator concentration. The error arising from the thermal effect in the gelation process can be neglected.

**Keywords** *In situ* interferometry, Gelation, Polyacrylic acid

Polymer gels are of considerable interest in the field of material science. They are very important in numerous applications<sup>[1-4]</sup>, such as in designing drug delivery system, in formulating cosmetic ingredients, agricultural fertilizers, and in producing storable foods. During the past two decades, both theoretical and experimental aspects of polymer gels have been extensively studied<sup>[5-7]</sup>. Significant advances have been made to understand the gelation process in a variety of systems. Experimental investigation for the gelation processes can be divided into two parts. One deals with the measurements performed on samples, called “quenched samples”, in which the chemical reaction was stopped by freezing or deactivation of the reacting groups and the system was diluted. The other group of measurements, called “*in situ*”, was performed in a reaction bath without any chemical manipulation, such as the real-time infrared spectroscopy<sup>[8]</sup>, light scattering technique<sup>[9]</sup> and holographic grating diffraction<sup>[10]</sup>. However, most measurements cannot give sufficient information to quantitatively describe the whole gelation process *in situ*. The whole gelation process of a given system is often investigated either by light scattering technique before the gel point or by mechanical method after the gel point. The data obtained by these two independent measurements often cannot be compared with each other directly. Hence, an *in situ* investigation, which will not be disturbed by the significant change of reaction system near the gelation point, needs to be established.

Real-time interferometry has become an indispensable technique for mapping the refractive-index field in transparent media<sup>[11]</sup>. During recent years, *in situ* interferometry was used to study the swelling and drying kinetics of thin gel films<sup>[12, 13]</sup>. Due to the existence of microscopic and macroscopic defects in gel structure, the *in situ* interferometry technique has many advantages for non-destructive and *in situ* investigation on the gelation process. There have been few reports concerning the use of this technique in studying the whole gelation process. In this work, an *in situ* interferometric method for investigating the gelation process was established and the

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synthesis process of PAA gels was studied.

As shown in Fig. 1, the laser beam is divided into a reference beam and an object beam by a beam splitter. The object beam traverses the sample cell and the reference beam is reflected in the same way as the object beam. The two beams impinge on the detector, which is electronically interfaced to a computer. The interference intensity  $I$  between the object beam and reference beam at the detector is a function of time<sup>[14]</sup>:

$$I(t) = I_0 \{1 + \gamma \cos[\theta + \phi(t)]\} \quad (1)$$

where  $I_0 = I_1 + I_2$ ,  $I_1$  and  $I_2$  are the intensities of the object beam and the reference beam, respectively,  $\theta$  is the initial phase difference between the two interferometric beams,  $\gamma$  is the visibility factor related to the coherence of the light source and the intensity difference of the two interferometric light beams,  $0 \leq \gamma \leq 1$ , and  $\phi(t)$  is the change in phase difference during the polymerization of gels.

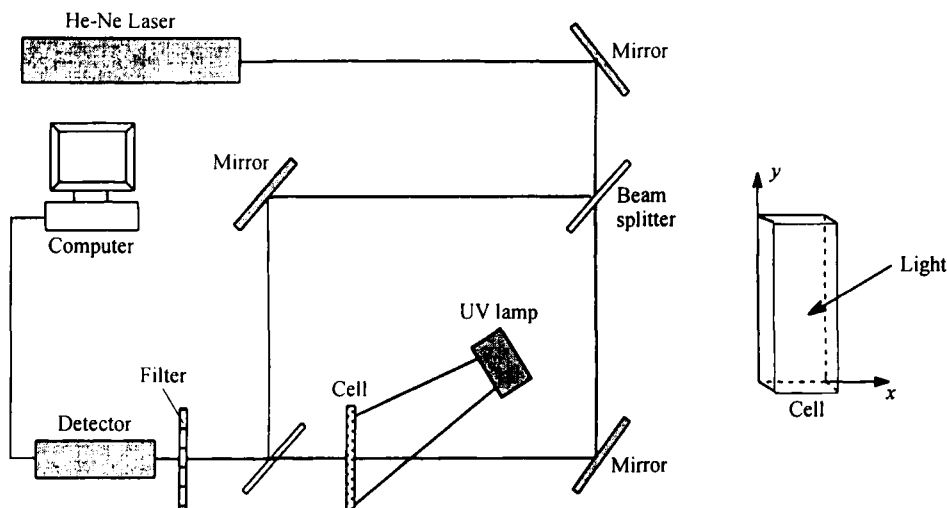


Fig. 1 Schematic diagram of the *in situ* interferometer for measuring the gelation process

In the experiment, the phase difference is related to the refractive-index difference which is caused by the polymerization of monomers:

$$\phi(t) = 2\pi\Delta n(t)l/\lambda \quad (2)$$

where  $\Delta n$  is the refractive-index difference at time  $t$  in the gelation process,  $l$  is the optical path length of the cell, and  $\lambda$  is the wavelength of the laser in vacuum. By using Eqs. (1) and (2), The refractive index difference in gelation process can be evaluated.

All the chemical reagents and monomers used were purified by usual methods. The monomer AA, crosslinker ethylene glycol dimethacrylate (EGDMA) and UV initiator azobisisobutyronitrile (AIBN) were dissolved in dimethyl sulfoxide (DMSO). The monomer concentration was 1.0 mol/L and that of EGDMA was 0.05 mol/L. The concentration of AIBN was chosen as 0.001, 0.0025 and 0.005 mol/L respectively. Before polymerization the sample cell containing monomer solution was bubbled with nitrogen for 30~45 min. The polymerization was conducted at 20°C under UV irradiation (ENF-240 C/J lamp, Spectronics Co., USA) with a wavelength of 365 nm. The distance from the UV lamp to the sample cell is 15 cm and the illumination intensity on the cell surface is about 350 mW/cm<sup>2</sup>. In the control experiment, except that no EGDMA was added and the concentration of AIBN was 0.0025 mol/L, all other experimental steps were the same as above.

Figure 2 shows a typical intensity variation observed in the gelation process. The intensity varies with polymerization time. The decrease of the time interval between the two neighboring minima (or maxima) indicates a rapid process in polymerization. The signal profile shown in Fig. 2 can be converted into the phase and refractive index differences versus time. In the experiment, two assumptions are made. One is that the diffusion of monomer or polymer between two plates of the cell could be neglected during the gelation process.

Hence, the refractive index difference is only caused by the polymerization. The another one is that the polymerization of AA can finish completely when the time is unlimited. So the concentration of monomer is proportional to the variation of the refractive index difference:

$$C_t \propto \Delta n(t) \text{ and } C_0 \propto \Delta n_{\infty} \tag{3}$$

where  $C_t$  is the monomer concentration at time  $t$ ,  $\Delta n_{\infty}$  is the refractive index change when the time is unlimited. From Eq. (3), the gelation process can be traced *in situ* without any destruction.

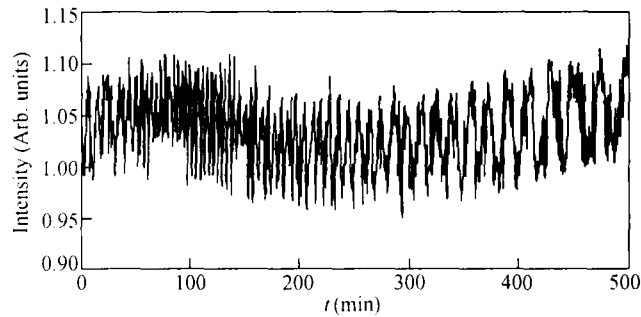


**Fig. 2** Typical intensity signal observed in the gelation process  
[AA]= 1.0 mol/L., [EGDMA] = 0.05 mol/L., [AIBN] = 0.001 mol/L.;  
 $T = 20^{\circ}\text{C}$

Figure 3 shows the effect of the crosslinker concentration on the gelation process of PAA gels. In the control experiment, PAA polymer was synthesized without the addition of crosslinker EGDMA. As shown in a plot of monomer concentration versus time (Fig. 3), the curve for PAA polymer decrease monotonously. But the curve for PAA gels, even if the crosslinker concentration was 0.005 mol/L, showed a point of inflection. After the time corresponding to this point, the monomer concentration decreases rapidly. This fact indicates that this point is the beginning of the gelation process. This point of inflection can be considered as the gel point.

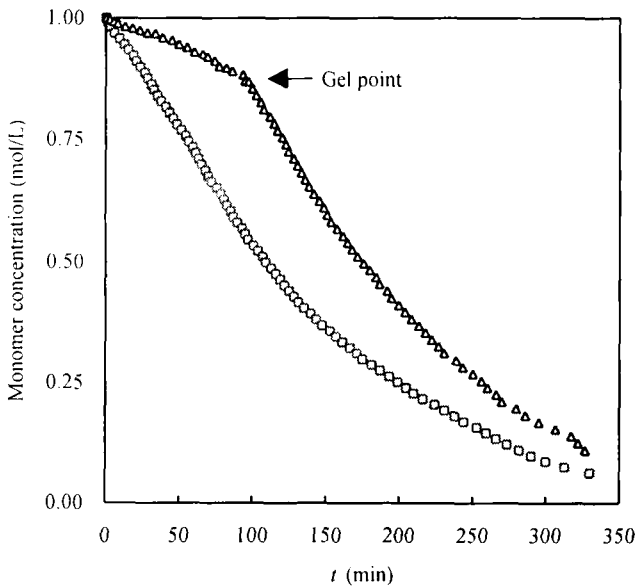


**Fig. 3** Effect of the crosslinker concentration on the gelation process of PAA gels  
□ No crosslinker;  $\Delta$  [EGDMA] = 0.005 mol/L  
○ Ther conditions see Fig. 2.

Figure 4 shows the effect of photoinitiator concentration on the gelation process of PAA gels. At the beginning of the polymerization, a small decrease of monomer concentration was observed. The initial period before the monomer concentration decreases rapidly, reduces from 75 to 25 min with increasing initiator concentration from 0.001 to 0.005 mol/L. After this period, a rapid decrease of monomer concentration happened, and then flattened off with time. The slope of the curve can be regarded as the polymerization rate of monomer ( $-dC_p/dt$ ). The polymerization rate of AA changes during the whole process. It is slow initially. After an induction period, it exhibits a maximum and then drops slowly. The maximum polymerization rates observed are 0.0028, 0.0035 and 0.0054 mol·L<sup>-1</sup>·min<sup>-1</sup> for 0.001, 0.0025 and 0.005 mol/L of initiator concentration, respectively. This shows that the polymerization rate of monomer increases with increasing initiator concentration. These results are in accord with the general law of photoinitiation polymerization<sup>[15]</sup>.

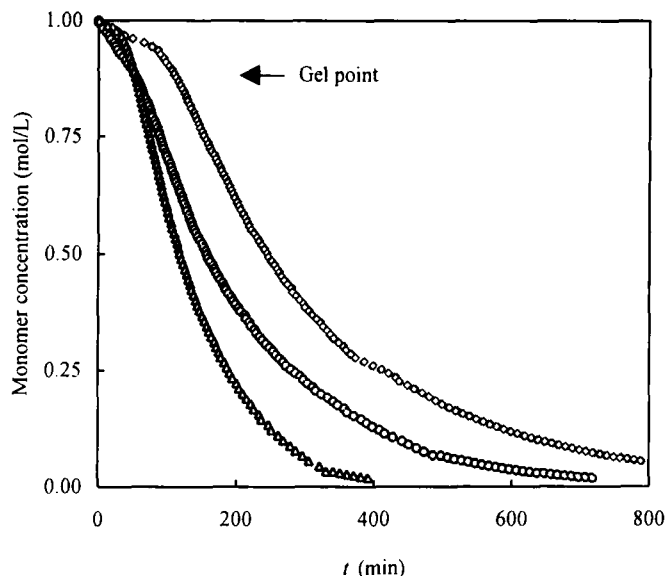


**Fig. 4** Effect of the initiator concentration on the gelation process of PAA gels  
 ◇ 0.001 mol/L; ○ 0.0025 mol/L; △ 0.005 mol/L  
 Other conditions see Fig. 2.

A change of temperature during the polymerization process would change the refractive index difference and introduce error into the final results. The change of refractive index with temperature,  $dn/dT$ , measured by differential refractometry is about  $-1 \times 10^{-5} \text{ K}^{-1}$ . The temperature fluctuation in local areas is less than 5 K, which will not result in significant errors in monomer concentration determinations.

## REFERENCES

- 1 Dusek, K., "Advances in Polymer Science", Springer-Verlag, Berlin Heidelberg, 1982, Vol. 44, p.98
- 2 Russo, P.S., "Reversible Polymeric Gels and Related Systems", American Chemical Society, Washington DC, 1987, ACS Symposium Series 350, p.125
- 3 Domszy, R.C., Alamo, R., Edwards, C.O. and Mandelkern, L., *Macromolecules*, 1986, 19: 130
- 4 Derossi, D., Kajiware, K., Osada, Y. and Yamauchi, A., "Polymer Gels - Fundamentals and Biomedical Applications", Plenum Press, New York, 1991, p.206
- 5 Djabourov, M., *Polymer Int.*, 1991, 25: 135
- 6 Aharoni, S.M., "Synthesis, Characterization and Theory of Polymeric Networks and Gels", Plenum Press, New York, 1992, p.217

- 7 Kremer, F. and Lagaly, G., "Progress in Colloid and Polymer Science", Springer, New York, 1996, Vol. 102, p.65
- 8 Decke, C. and Moussa, K., *Macromolecules*, 1989, 22: 4455
- 9 Nystrom, N., Roots, J., Carlsson, A. and Lindman, B., *Polymer*, 1992, 33: 2875
- 10 Carre, C., Lougnot, D.J. and Fouassier, J.P., *Macromolecules*, 1989, 22: 791
- 11 Vest, C.W., "Holographic Interferometry", Wiley, New York, 1979, p.75
- 12 Wu, C. and Yan, C.Y., *Macromolecules*, 1994, 27: 4516
- 13 Zhou, S. and Wu, C., *Macromolecules*, 1996, 29: 4998
- 14 Zhang, X.M., Xu, J., Okawa, K., Katsuyama, Y., Gong, J.P. and Osada, Y., *J. Phys. Chem. B*, 1999, 103: 2888
- 15 Li, S.T., Ji, C.G., Li, T. and Cheng, J.J., "Mechanism and Applications of Polymer Photochemistry" (in Chinese), Fudan University Press, Shanghai, 1993, p.111