

Rapid Communication

A NOVEL METHOD FOR CHARACTERIZING THE WHOLE PROCESS OF POLYMER GELATION*

Qiang Chen^a, Xian-min Zhang^b, Guo-wei Wang^{a***} and Jian Xu^{a**}

^a State Key Laboratory of Polymer Physics & Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

^b Department of Information & Electronic Engineering, Zhejiang University, Hangzhou 310027, China

Abstract A novel method was established to investigate the gelation process of polymers. The change of refractive index of a polymer system during gelation was determined *in situ* in a prismatic cell. It can give reliable information on the whole gelation process. The apparatus and the execution of this technique are illustrated and the error is also discussed.

Keywords Gelation process, *In situ* technique, Refractive index

INTRODUCTION

The gelation of a polymer and its polymerization kinetics have attracted theoretical and experimental efforts to understand these processes. Experimentally the methods for investigating these processes fall into two groups. One group is to perform measurements of the system after terminating the reaction at different stages. On using these methods it is usually difficult to characterize a whole gelation process due to the insolubility of polymer systems after their gel point. Another group of methods, known as "*in situ*" methods, involves measurements on the reaction system without interrupting the process of the reaction. In past two decades many *in situ* techniques, such as real-time infrared spectroscopy^[1], light scattering techniques^[2, 3] and holographic grating diffraction^[4-6] have been used in studying the gelation of different systems. In our previous work, an *in situ* interferometry method was developed to study the gelation and polymerization kinetics of acrylic acid with two- or multi-armed cross-linkers^[7-9]. This paper deals with a novel *in situ* method that records the refractive index change during the gelation of a polymer system. This *in situ* technique is simple and easy to use.

THEORETICAL BACKGROUND

It is well known that the refractive index of a system during polymerization or gelation will change due to the different refraction indices of the monomer and the polymer. It is common knowledge that light beams can be deflected through a prism. If a monomer is put in a prismatic cell, the laser light beam through this cell will move during polymerization or gelation. The whole gelation process and its polymerization kinetics can be characterized *in situ* by determination of the change in position of a light spot on a screen during the process. The new technique is non-destructive and proceeds in real time for monitoring the process of gel formation.

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** Corresponding author: Jian Xu (徐坚), E-mail: jxu@pplas.icas.ac.cn

*** On leave from College of Material Science & Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, China

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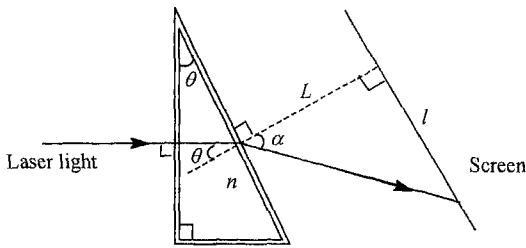


Fig. 1 Deflection of a light beam passed through a triangular prismatic cell

According to the geometry of the cell given in Fig. 1 we can derive Eq. (1).

$$l = L \tan \alpha = L \frac{\sin \alpha}{\cos \alpha} \tag{1}$$

where L is the perpendicular distance from the point of refraction to the screen, l is the distance from the light spot on the screen to its center point and α is the refraction angle. Snell's law gives the relationship between the incident angle θ and the refraction angle, that is:

$$n \sin \theta = \sin \alpha \tag{2}$$

where n is the refractive index of the medium in the measuring cell.

When there is a small change of the refractive index of the medium Δn , Snell's law can be expressed as:

$$(n + \Delta n) \sin \theta = \sin(\alpha + \Delta \alpha) \tag{3}$$

The light spot on the screen will move a small distance, Δl , which can be related to Δn and $\Delta \alpha$. in terms of Eq. (4).

$$l + \Delta l = L \tan(\alpha + \Delta \alpha) = L \frac{\sin(\alpha + \Delta \alpha)}{\cos(\alpha + \Delta \alpha)} = L \frac{(n + \Delta n) \sin \theta}{\cos(\alpha + \Delta \alpha)} \tag{4}$$

When Δn is very close to 0 ($\Delta n \rightarrow 0$), $\Delta \alpha$ is also approaching zero ($\Delta \alpha \rightarrow 0$), so we can replace $\cos(\alpha + \Delta \alpha)$ with $\cos \alpha$. This approximation yields:

$$l + \Delta l = L \frac{(n + \Delta n) \sin \theta}{\cos \alpha} = L \frac{(n + \Delta n) \sin \theta}{\sqrt{1 - n^2 \sin^2 \theta}} = L \frac{n \sin \theta}{\sqrt{1 - n^2 \sin^2 \theta}} + L \frac{\Delta n \sin \theta}{\sqrt{1 - n^2 \sin^2 \theta}} \tag{5}$$

As $l = L n \sin \theta / (1 - n^2 \sin^2 \theta)^{1/2}$, we can obtain:

$$\Delta l = L \frac{\Delta n \sin \theta}{\cos \alpha} = L \frac{\Delta n \sin \theta}{\sqrt{1 - n^2 \sin^2 \theta}} \tag{6}$$

This equation can also be rearranged as follows:

$$\Delta n = \frac{\Delta l \cos \alpha}{L \sin \theta} = \frac{\sqrt{1 - n^2 \sin^2 \theta}}{L \sin \theta} \Delta l \tag{7}$$

In fact Δn and Δl are a function of polymerization time t , so:

$$\Delta n(t) = \frac{\Delta l \cos \alpha}{L \sin \theta} = \frac{\sqrt{1 - n^2 \sin^2 \theta}}{L \sin \theta} \Delta l(t) \tag{8}$$

Since the thickness of the cell wall is small, we therefore neglect its refraction effect on the distance l in the above deduction. By using this *in situ* measuring technique we can detect the reactive index change of this

reaction system. On converting $\Delta n(t)$ to $\Delta C(t)$, the monomer consumption, two common assumptions should be admitted: the refractive index of a mixture is the sum of those of its components and is proportional to the concentration of the mass. Here we also neglect the refractive index difference induced by different molecular weight of the oligomers and also the hydrogels with different cross-linking density. Studying the function $\Delta n(t)$, the whole gelation process and the polymerization kinetics of polymers can be monitored very simply and easily.

EXPERIMENTAL

The polyacrylamide hydrogel was prepared by free-radical solution polymerization initiated by a photoinitiator. Quantified acrylamide (AAM, AR reagent from Xingyi Chemical Cooperation, Beijing, China) was recrystallized from solution in a mixed solvent of benzene and chloroform. The cross-linker, *N,N'*-methylene bisacrylamide (MBAAM), was recrystallized from its alcohol solution. The photoinitiator, α -ketoglutaric acid (KGA, reagent from Wakolure Chem. Inst. Ltd) was used without further treatment. The above components were fed into a right-angle triangle prism cell with redistilled water as solvent, which had been deoxygenated by bubbling nitrogen for about an hour. The mixture solution was polymerized under UV irradiation with a UV lamp (Spectroline® Model ENF 240 C/J, Spectronics Cooperation, New York) at $\lambda = 365$ nm.

Figure 2 illustrates the system used in the experiments. A He-Ne laser (Model JGQ-250, Optical Instrument Co. Zhejiang University, $\lambda = 632.8$ nm) was used as the light source. The prism cell was made of optical glass with one angle being 30 degree. The facula position of the refracted light beam was recorded by using a CCD camera. The data were stored and treated by a computer system.

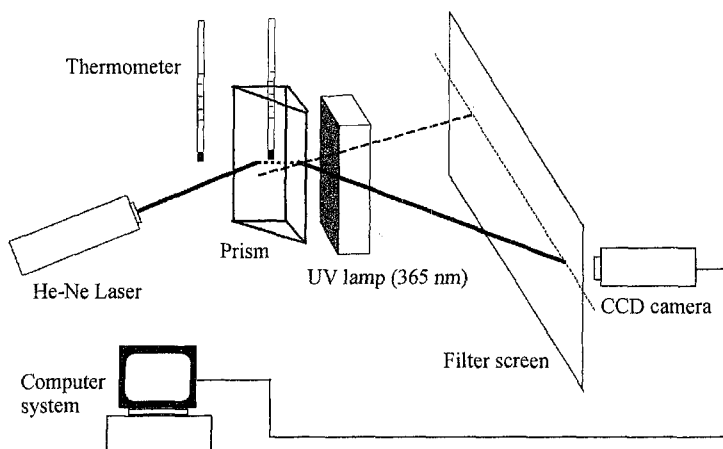


Fig. 2 The *in situ* gelation recording system

The temperature of the reaction system at the point of the incident laser and the laboratory was recorded by two thermometers with the scale of 0.1°C . In the system the distance of the UV lamp from the cell was about 15 cm and the illumination intensity at the cell surface was about $350 \mu\text{W}/\text{cm}^2$.

RESULTS AND DISCUSSION

In general, polymers have higher refractive indices than their monomer. So, under ideal condition the refractive index of the gelation system will increase monotonously along with the polymerization process. Figure 3 shows typical data obtained by this method.

This relation of $\Delta n(t)$ with t obtained by our method is in accordance with theory. At the beginning of polymerization, there is an initiation period due to the presence of trace oxygen. After this initiation period the polymerization speeds up. As we know, the network formed in the free radical polymerization system can cause an auto-acceleration effect due to the increase of the viscosity of the reaction system, which in turn suppresses the

termination probability between two propagating chains and thus increases the polymerization rate. At the last stage of polymerization there is little change of the system, so the refractive index changes only slightly.

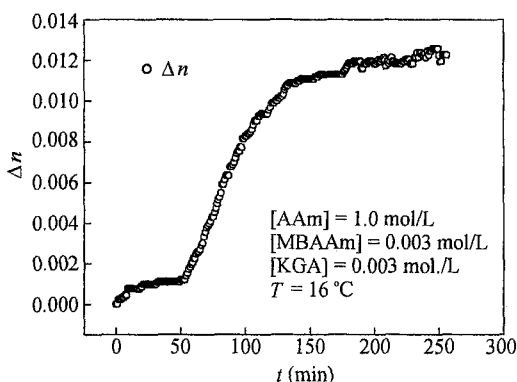


Fig. 3 Typical illustration of the change of refractive index during polymerization

There exist several factors leading to deviations from the theoretical condition. It is well known that polymerization is an exothermal and volume contraction reaction. The heat generated during polymerization or gelation will decrease the refractive index of the system. Also the incident laser beam and the UV radiation will also raise the temperature of the reaction system. The temperature change during polymerization and the Δn change of the polymerized gel with temperature were measured.

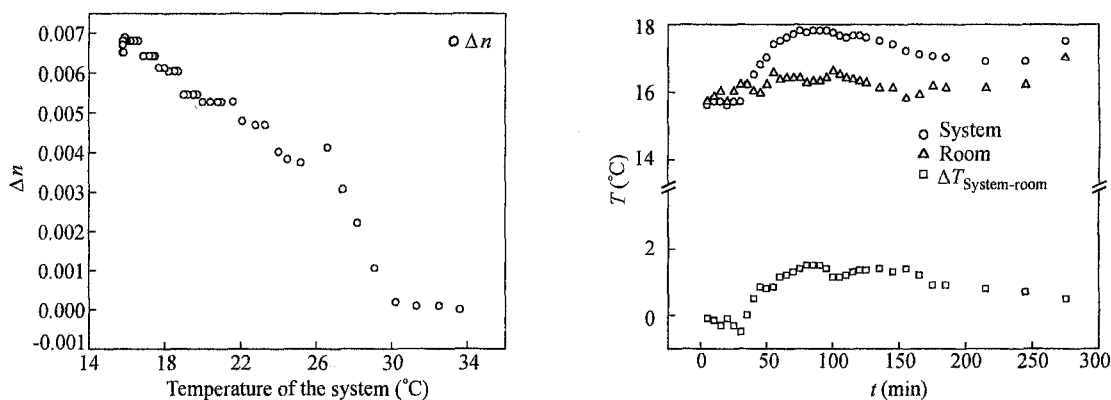


Fig. 4 Temperature change of the system and Δn change of polymerized gel with temperature

As shown in Fig. 4, the maximum temperature change during polymerization is about 2 °C. The corresponding change of refractive index of the polymerized gel is just about 0.0005, while the total change of refractive index during the gelation process is 0.012. It means that the relative error due to temperature fluctuation is about 4%.

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