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Real-Time Laser Sheet Refraction To Monitor in Situ the Heterogeneity of Polymerization Process on Teflon Surface

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ABSTRACT: Real-time laser sheet refraction (RT-LSR) was used to study the polymerization kinetics of the hydrophilic monomer 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) in aqueous solution and the heterogeneity of the polymerization process on the surface of a Teflon substrate. The spatial distribution of refractive index along the vertical direction in the polymer solution was obtained in real time from the deflection of refracted light during polymerization. It was found that the polymerization of AMPS in the aqueous solution follows the first-order reaction mechanism. Inhomogeneous distribution of refractive index in the interface region near the Teflon surface, which results from the suppression of polymerization in the interface region, is also observed directly.

Introduction

It was reported in our previous papers that obvious heterogeneity occurs in the interface region when hydrophilic vinyl monomers underwent solution polymerization on hydrophobic substrates, such as Teflon, polypropylene, polyethylene, polystyrene, and poly(vinyl chloride).[1−4] This phenomenon is of great importance to the application of hydrogels, because the surface properties of the hydrogels that are synthesized on a hydrophobic substrate are quite different from that of gels synthesized on a hydrophilic surface, such as surface friction coefficient,[1] swelling degree,[2] surface viscoelasticity,[3] interfacial adhesion, and interaction with biological cells.[4]

Interference techniques, which can determine a change in refractive index as small as 10^{-7}, have the highest sensitivity compared with other methods of measuring refractive index and were used to study polymerization kinetics in the early 1960s.[5] The electronic speckle pattern interferometry (ESPI) technique, a novel kind of interference technique, was used in our laboratory to study the substrate effect during hydrogel polymerization. It has been proven that ESPI is a powerful real-time noninvasive monitoring technique for the investigation of polymerization and gelation processes and also the spatial distribution of refractive index in hydrogels.[6,7]

In the ESPI technique, a laser beam is divided into a reference beam and an object beam by a beam splitter. The object beam traverses the sample cell and interferes with the reference beam on the CCD array. The refractive index of the solution in the sample cell increases during polymerization and leads to the phase change of the objective beam. Therefore, the intensity of the interferogram changes during the polymerization. When the polymerization is performed in the presence of a hydrophobic substrate, the intensity of the interface region is different from that of the bulk region during polymerization because of the inhomogeneous concentration distribution of monomer and polymer in the solution. This fact has been proven to result from the monomer migration from the interface region to the bulk region during polymerization.[2,6]

The phase change in the ESPI experiment can be induced either by an increase or decrease in refractive index. The disadvantage of ESPI technique is that it cannot automatically determine whether the phase change is induced by the former or by the latter. This disadvantage is of no problem for the polymerization in the bulk region, because refractive index increases monotonically with the increase of conversion. In the interface region close to the hydrophobic substrate, the refractive index may decrease because of obvious migration of monomer from the interface region to the bulk region. This is the reason why the evolution of the refractive index in the region very close to the hydrophobic substrate was not discussed in our previous papers.[2,6]

Various kinds of light refraction techniques have been extensively used to measure the refractive index of transparent materials.[8] Thanks to the development of optics technology and information technology, it was possible to develop a novel light refraction technique in the present paper to measure in real time the evolution and distribution of refractive index in the aqueous solution of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) during polymerization. Compared with the ESPI method, the real time laser sheet refraction (RT-LSR) method has the advantage of direct determination of the absolute value of refractive index in the interface region. Therefore, the spatial heterogeneity induced by the hydrophobic substrate can be studied. Furthermore, this technique can also be used to the study the diffusion of small molecules in gels.

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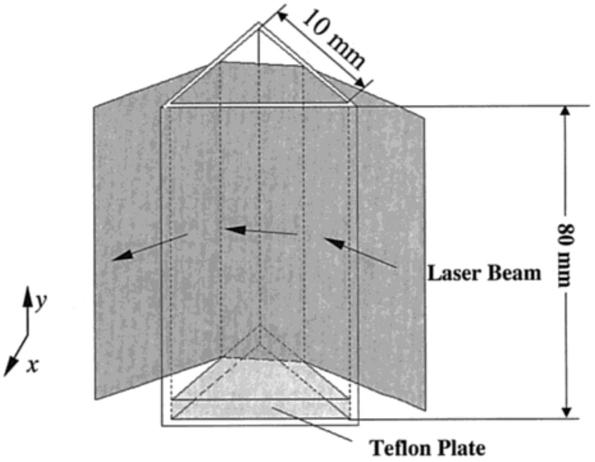

Figure 1. Schematic diagram of the sample cell used in the light refraction experiment.

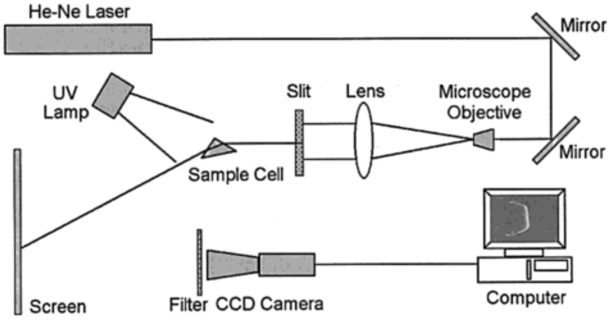

Figure 2. Schematic diagram of the optical and recording system used in the light refraction experiment.

Apparatus and Principle of RT-LSR

Figure 1 presents the schematic diagram of the triangular sample cell used in the refraction experiment. The sample solution is placed in the cell. The Teflon substrate is placed on the bottom of the cell. A laser sheet, with the plane perpendicular to the horizon, enters into the cell from one side of the cell and then comes out from the neighboring side. The direction of the laser sheet is deflected because the sample solution in the cell acts as a prism that refracts the light passing through. The refracted laser sheet then impinges onto a vertical screen placed at the left side of the cell. The screen is perpendicular to the incident laser sheet. With the increase of the refractive index of the solution in the cell during polymerization, the deflection angle between the refracted laser sheet and the incident laser sheet increases. Therefore, we can observe that the light stripe on the screen moves continuously during the polymerization.

When the solution is homogeneous, a straight vertical light stripe on the screen can be observed. On the contrary, when there exists gradient distribution of refractive index in the solution along the vertical direction *y*, the position of the refracted light in the *x*-axis of the screen is different for different *y* position; thus, we can observe a bent light stripe on the screen.

Figure 2 presents the diagram of the full optical and recording system for the laser sheet refraction measuring apparatus. A He−Ne laser (model 127, Spectra-Physics Lasers, Inc.) is used as the light source with the wavelength of 632.8 nm. The laser beam is first focused through a pinhole spatial filter by a 25× microscope objective, it passes through a series of collimating lenses, and it is enlarged into a parallel light column with the diameter of 50 mm. The light column is then filtered by a slit with the width of 1 mm and height of 50 mm. The sheet-shaped laser beam transverses the sample cell and is refracted by the solution. It appears on the screen.

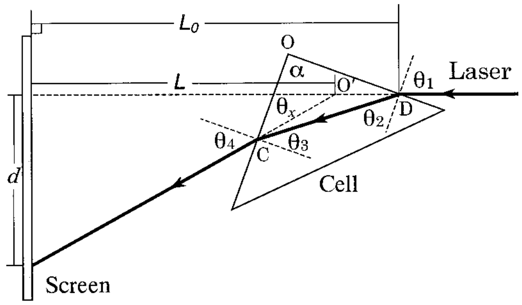

Figure 3. Parameters for the optical path of the solution filled cell in the light refraction experiment.

The position of the refracted laser sheet on the screen is recorded with a cooled CCD camera (C4742-95, Hamamatsu Co., Japan), which is electronically interfaced to a personal computer. The total area of each recorded image contains 1280 × 1024 pixels, and the maximum frame rate is 9 Hz. The maximum resolution of the CCD camera is about 12.5 μm. In the experiment, the images are sequentially taken by the CCD camera with certain time interval and stored on the hard disk. The intensity of the refracted light is much larger than that of the background, so the coordinates of the refracted light on the screen can be determined according to the intensity difference between the refracted light and the background.

Figure 3 shows the detailed light path of the laser sheet passing the sample cell, in which α is the angle of the sample cell, θ_1 and θ_3 are the incident angles at the first and second cell wall, respectively, θ_2 and θ_4 are the angles of refraction at the first and second cell wall, respectively, θ_x is the angle between the incident laser sheet and the refracted laser sheet, namely the deflection angle of the laser sheet passing the cell, d is the position of the refracted light on the screen, and L_0 is the distance between the cell and screen.

According to the definition of refractive index, relationships between θ_1 and θ_2, θ_3, and θ_4 are presented in eq 1

$$\frac{n_{\mathrm{air}}}{n_{\mathrm{s}}} = \frac{\sin\theta_2}{\sin\theta_1} = \frac{\sin\theta_3}{\sin\theta_4} \tag{1}$$

where n_{air} and n_{s} are the refractive index of air and the sample solution in the cell, respectively. n_{air} is 1.00027 at 20 °C.

The relationship between θ_2, θ_3, and α can be related by

$$\theta_3 = \alpha - \theta_2 \tag{2}$$

The relationship between θ_x, θ_1, θ_2, θ_3, and θ_4 can be obtained as

$$\theta_x = \theta_1 - \theta_2 - \theta_3 + \theta_4 \tag{3}$$

Δd, the displacement of refracted light on the screen induced by the refractive index increase of the sample solution during polymerization, can be obtained by subtracting the original position $d(0)$ from the present

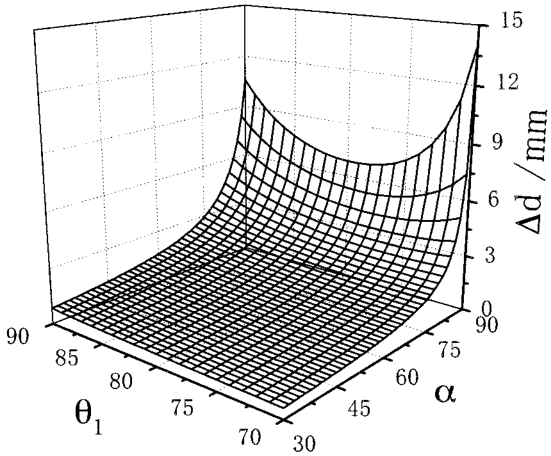

Figure 4. Calculated relationship between displacement Δd of the refracted light on the screen and the incident angle θ_1 and the cell angle α for a change of refractive index from 1.3607 to 1.3649. $L_0 = 100$ mm and $\overline{OD} = 1$ mm were used in the calculation.

position $d(t)$ of the refracted light on the screen.

$$\Delta d = d(t) - d(0) = L(t)\tan(\theta_x(t)) - L(0)\tan(\theta_x(0)) \tag{4}$$

Here $L(t)$ and $L(0)$ are the L values at time t and at the beginning of the experiment, respectively. $\theta_x(t)$ and $\theta_x(0)$ are the deflection angle at time t and at the beginning of the experiment, respectively. It can be proved that $L(t)$ can be obtained as

$$L(t) = L_0 - \overline{OD}\,\frac{\sin(\theta_4 - \theta_3)}{\sin\theta_x(t)}\,\frac{\sin\alpha}{\cos\theta_3} \tag{5}$$

Here, $\overline{OD}$ is the distance between point O and D. Thus, we can obtain the value of displacement Δd of the refracted laser sheet during the whole polymerization process by using eqs 1−5.

It can be found that in Figure 3 four parameters, α, θ_1, $\overline{OD}$, and L_0, are controllable experimentally, and it is important to select proper parameters to optimize the sensitivity of this system. It can be found that the larger L_0, the larger Δd, so we can increase the sensitivity of the system by increasing the distance between the sample cell and the screen. It will be discussed later that $\overline{OD}$ must be as small as possible, and we set $\overline{OD} =$ 1 mm in the experiment. The influence of α and θ_1 is somewhat complicated. According to the published experimental results of ESPI,[5] the refractive index in the bulk region increases from 1.3607 to 1.3647 during the polymerization for the following system: 1 mol L^{-1} monomer AMPS, 5 mol % cross-linking agent N,N'-methylenebisacrylamide (MBAA), and 0.1 mol % initiator 2-oxoglutaric acid. To evaluate the sensitivity of the light refraction experiment, the relationships between Δd, θ_1, and α for $L_0 = 100$ mm, $\overline{OD} = 1$ mm are calculated as is shown in Figure 4. θ_1 ranges from 70° to 90°, and α ranges from 30° to 90°. In case the θ_1 is smaller than 70°, θ_3 is larger than the critical total reflection angle, and the laser sheet is totally reflected at the surface of the second cell wall and thus cannot transmit the sample cell. Therefore, θ_1 should be a value much larger than 70° and much smaller than 90°. We selected $\theta_1 = 80°$. It is found that the value of Δd increases with the increase of α. When α = 90° and $\theta_1 = 80°$, Δd is as large as 6.86 mm when the refractive index increases from 1.3607 to 1.3647. As is mentioned above, the resolution of the CCD camera is about 12.5 μm, which is much more than enough in comparison with the value of Δd. Therefore, we select α = 90° and $\theta_1 = 80°$ in our experiment.

In the above discussion, the thickness of the glass walls of the cell is not taken into consideration. In fact, the thickness of the cell walls used in the experiment is 1 mm. It can be shown that because of the refraction of glasses, d, the position of light stripe on the screen can be horizontally increased for about 2.50 mm when α = 90°, $\theta_1 = 80°$, and refractive index = 1.3606. Fortunately, the error of relative displacement Δd during the whole polymerization process is quite small, because the influence of glass is not sensitive to the refractive index of the solution in the cell. For example, if the refractive index of the solution in the cell is 1.3647, the position of the light stripe is increased for 2.53 mm. So the absolute error of Δd for refractive index increased from 1.3606 to 1.3647 is only about 0.03 mm. On the other hand, the error has no relationship with L_0, the distance between the cell and the screen, because the direction of the light transmitting the plane glass is not changed. As has been mentioned above, Δd is proportional to L_0; thus, we can decrease the relative error by increasing L_0. When α = 90°, $\theta_1 = 80°$, $L_0 = 100$ mm, and the refractive index of the solution increases from 1.3606 to 1.3646, the error of Δd induced by the refraction of the glass is only about 0.3%. In the following discussion, the absolute value of refractive index was corrected during data processing.

Experimental Section

All chemical reagents and monomers used were purified by standard techniques.[9] Monomer AMPS and initiator 2-oxoglutaric acid were dissolved in deionized water at room temperature. The concentration of AMPS in the solution is 1 mol L^{-1} for all the samples in this paper. 5 mol % MBAA is used for the cross-linked sample. Before polymerization, monomer solution was purged by nitrogen with the purity of 99.99% for 20−40 min in a dark room in order to get rid of dissolved oxygen, the inhibitive substance of free-radical polymerization. The cell was also purged by a large amount of nitrogen. Then, with the continuous nitrogen gas flow in the sample cell, the solution is poured into the cell. The sample cell and the solution were further purged by nitrogen gas flow for another 5 min. The polymerization was then conducted under irradiation of UV light with wavelength around 365 nm. The distance between the UV lamp and the sample cell is 12 cm, and the illumination intensity on the cell surface is about 0.45 mW/cm^2. The UV lamp (ENF-260C/J, Spectronics Co., USA) must be perpendicular to one side of the sample cell, as is shown in Figure 2; otherwise, the irradiation of UV light in the cell will be inhomogeneous because of the reflection and refraction of UV light in the sample cell. A Pyrex (Yokota Co. Ltd.) triangle glass cell for spectrophotometer measurement with inner side length of 10 mm and height of 80 mm is used in this experiment. The transmittance of the cell wall measured by using UV spectrophotometer (U-3000, Hitachi, Japan) is 93.2% for the UV light with wavelength of 365 nm. A Teflon plate is placed on the bottom of the cell, and a silicone rubber cap is used to seal the cell. High-vacuum silicone grease was also employed to fill in the possible small gaps between the cap and the cell wall to prevent the permeance of oxygen into the cell during polymerization. The polymerization was carried out at 20 °C.

Results and Discussion

Figure 5 presents the series pattern of refracted light on the screen during polymerization of AMPS, in which

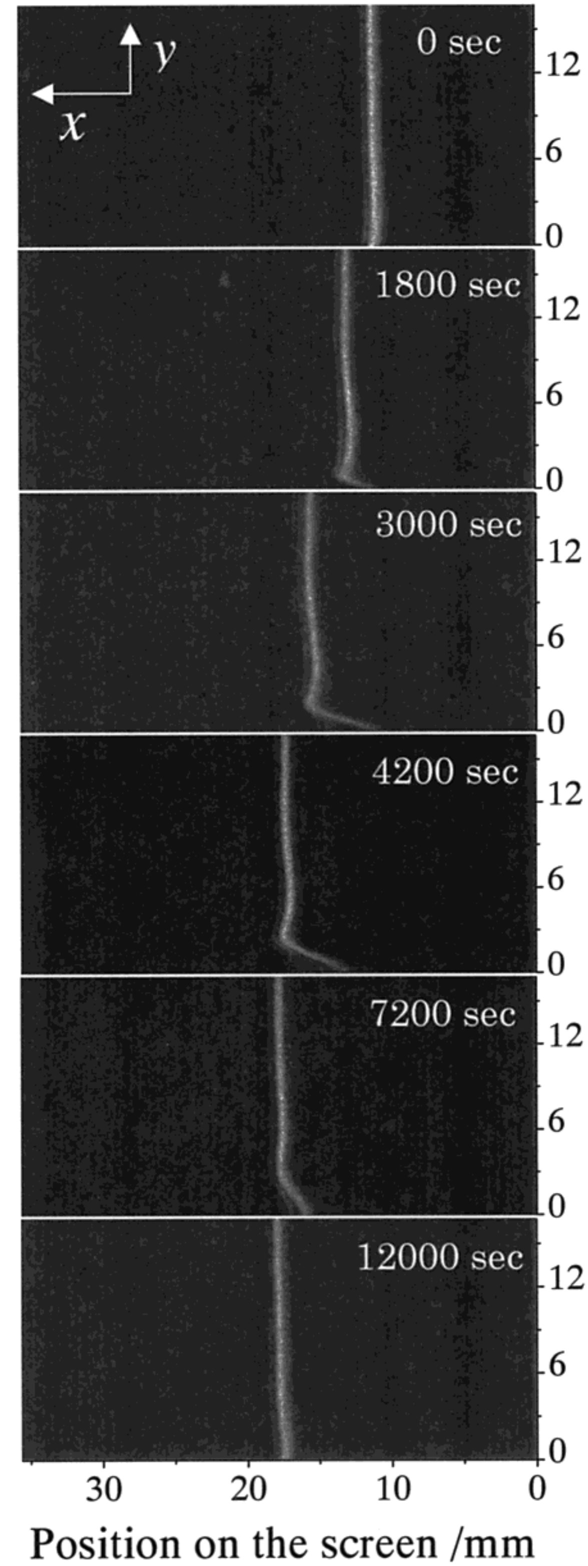

Figure 5. Evolution of the refracted light on the screen during polymerization of 1 mol L^{-1} AMPS aqueous solution. The concentration of initiator is 0.74 mol % of AMPS.

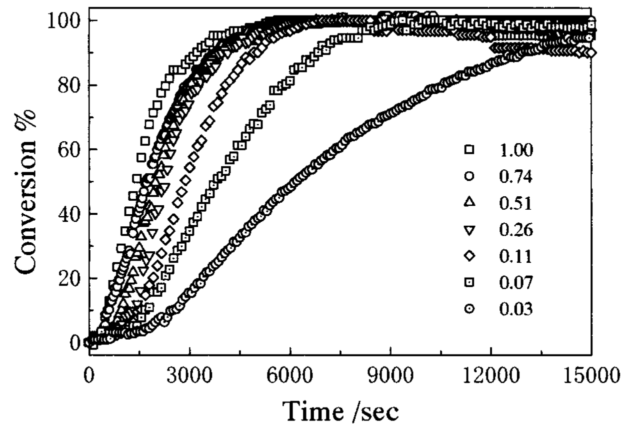

Figure 6. Relationship between conversion of polymerization and time for different concentration of UV initiator. The numbers in the figure are the concentration of initiator in mol % against monomer.

the concentration of UV initiator is 0.74 mol % of AMPS. The *x* and *y* axes in Figure 5 are the coordinate axes of the screen. The zero point of the *y*-axis corresponds to the surface of the Teflon substrate. It can be easily found that the refracted light on the screen moves during polymerization, which is obviously induced by the increase of refractive index of the solution in the sample cell. The maximum displacement of refracted light induced by polymerization is about 6.78 mm, which is only 1.17% lower than the expected value that calculated according to the data obtained from ESPI as is mentioned above. The absolute value of refractive index increases from 1.3612 to 1.3645, which is very close to the value obtained by ESPI.

The refracted light in the region far from the surface of Teflon remains essentially straight during polymerization, which indicates that polymerization in this region is homogeneous and not affected by the Teflon template on the cell bottom. Valuable information about the polymerization kinetics of the sample solution is available from this region. For the 1 mol L^{-1} AMPS aqueous solution, the relationship between refractive index of the sample solution and the concentration of monomer and polymer in the solution follows the linear principle during polymerization.[2,6]

$$n_s = n_w + \frac{dn_m}{dC_m} C_m + \frac{dn_p}{dC_p} \cdot C_p \qquad (6)$$

where n_s and n_w are the refractive index of the sample solution and pure water, respectively, C_m and C_p are the concentration of monomer and polymer in the solution, which follows $C_p(t) = C_m(0) - C_m(t)$ in the homogeneous bulk region, dn_m/dC_m is the refractive index variation with monomer concentration, and dn_p/dC_p is that with polymer concentration. The influence of initiator is neglected because of its very small concentration. Thus, the conversion of the polymerization can be related by the value of refractive index

$$\text{conversion}(t) = \frac{C_m(0) - C_m(t)}{C_m(0)} = \frac{n_s(t) - n_s(0)}{n_s(\infty) - n_s(0)} \qquad (7)$$

where $C_m(0)$ and $C_m(t)$ are the concentration of monomer at the beginning of the experiment and at time *t*, respectively, $n_s(t)$ is the refractive index at time *t*, $n_s(0)$ is the refractive index at the beginning of polymerization, and $n_s(\infty)$ is the resultant refractive index after polymerization is completed. Figure 6 presents the plot of conversion vs time during polymerization for different initiator concentrations. It is shown that the polymerization shows the typical characteristic of free-radical solution polymerization. The polymerization rate is slow at the beginning of polymerization and then becomes faster in the middle stage. At the late stage, polymer-

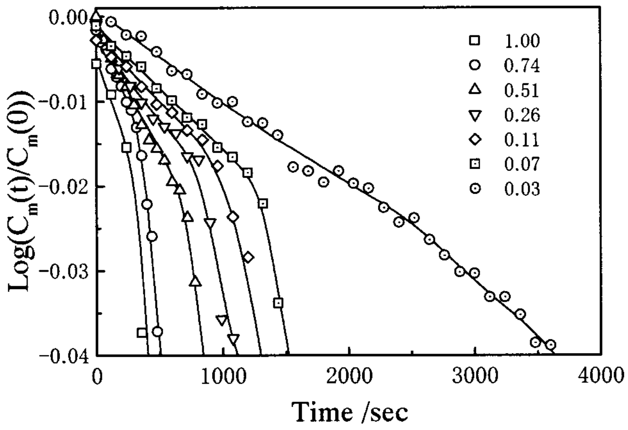

Figure 7. Relationship between $\log(C_m(t))/C_m(0))$ and time for different concentrations of UV initiator. The numbers in the figure are the concentration of initiator in mol % against monomer.

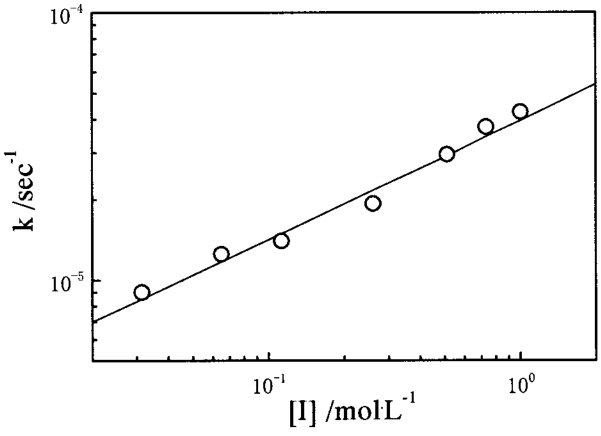

Figure 8. Logarithmic plot of *k*, the velocity constant of the first-order reaction, against concentration of UV initiator, [I].

ization rate is reduced because most of the monomer is consumed. It is also found that the plots of $\log(C_m(t))/C_m(0))$ against time show a satisfactory linearity at the early stage of polymerization, as is shown in Figure 7. Therefore, the polymerization of AMPS in aqueous solution is a first-order reaction. One can obtain $(C_m(t))/C_m(0) = \exp(-kt)$, in which *k* is the velocity constant of the first-order reaction. Figure 8 presents the logarithmic plot of *k* against [I], the concentration of initiator. It is found that log(*k*) almost linearly depends on log[I] with the slope of 0.45, which is approximate to 0.5, meaning that the polymerization rate is proportional to the square root of the concentration of initiator. This is in correspondence with the classic theory for free-radical polymerization.[10] Therefore, on the basis of above discussion, it is reasonable to say that the RT-LSR is effective to the study of polymerization kinetics of AMPS in aqueous solution.

From Figure 5, it is also noted that, in the interface region adjacent to the Teflon surface, the distribution of refracted light is quite different from that of the bulk region. This remarkable bending of refracted light obviously results from the gradient refractive index distribution in the interface region in the sample solution. This phenomenon is in agreement to that reported in our proceeding papers.[2,6,7] By using the present RT-LSR, the distribution of refractive index at the interface region is directly obtained, which indicates that this method is effective not only to the study of polymerization kinetics but also to the study of heterogeneity of polymerization.

The distribution of refractive index for different times during polymerization is given in Figure 9a,b. It can be found that, in the interface region that is adjacent to the Teflon substrate, the refractive index is much smaller than that in the bulk region during polymerization, while in the region neighboring to the interface region, the refractive index is larger than that of the bulk region. The width of the interface region, which is defined as the distance from the point with maximum refractive index to the surface of Teflon, increases with time. The difference between the maximum and minimum of refractive index increases at the early and middle stage of polymerization and then decreases at the late stage. Figure 10 presents the evolution of refractive index with time for various positions with

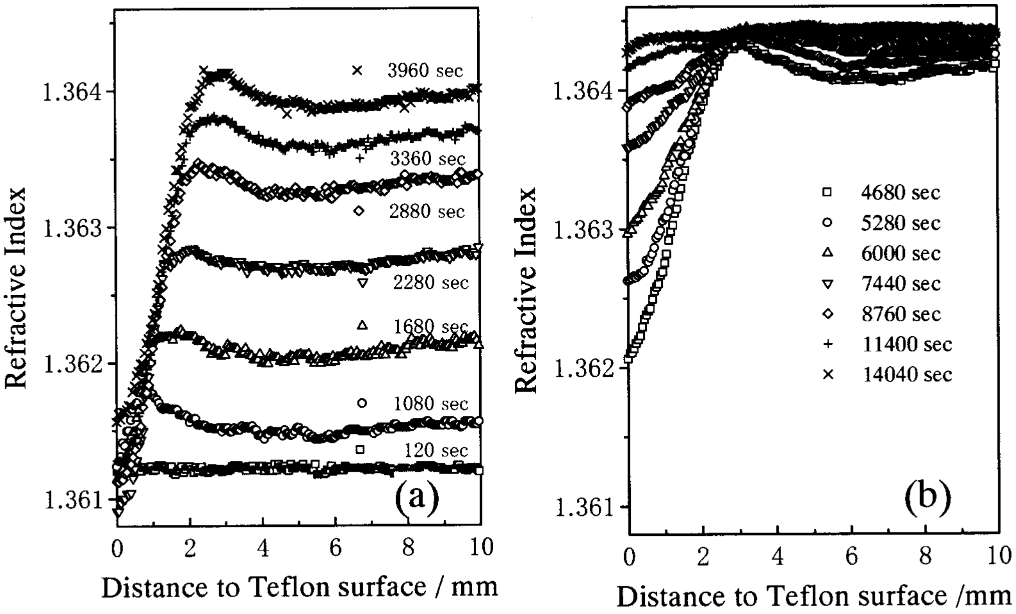

Figure 9. Refractive index distribution during polymerization of PAMPS solution near Teflon surface region (y = 0−10 mm): (a) from 120 to 4680 s; (b) from 4680 to 14 040 s.

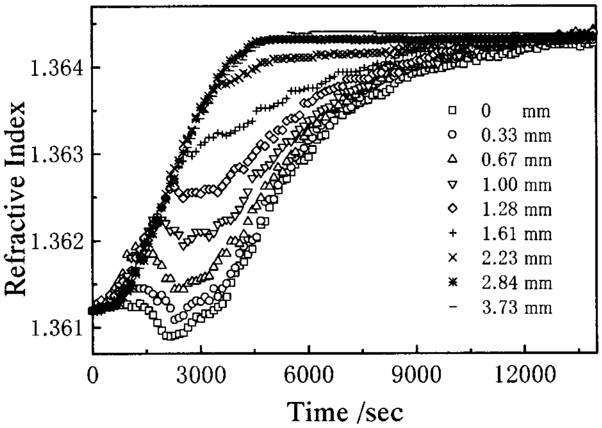

Figure 10. Time dependence of refractive index during polymerization of PAMPS solution for different positions (y = 0–3.73 mm) in the sample solution.

different distances to the Teflon substrate. An obvious decrease of refractive index in the interface region can be observed during polymerization. As mentioned above, in the ESPI experiment, the phase change is supposed to be caused by the increase of the refractive index. Therefore, the refractive index obtained from the phase change in the interface region may be incorrect. In the present light refraction experiment, the refractive index is obtained directly. According to the relationship between refractive index and conversion as is mentioned above, it can be concluded that the polymerization on the hydrophobic surface of Teflon substrate is suppressed to some extent. The reason for the suppression of polymerization is still not clear to date. Because the concentration of polymer in the interface is lower than that in the neighboring region but the concentration of monomer is higher, under the force of osmotic pressure induced by concentration difference, monomer migrates to the neighboring region. This leads to faster polymerization in the neighboring region and thus larger concentration differences, which further hastens the departure of monomer from the Teflon surface to the neighboring region. The polymer migrates in the opposite direction, but the diffusion rate is much slower than that of monomer. At the late stage of polymerization, the refractive index in the interface region increases gradually to almost the same value of the bulk region. One reason is that most monomer is consumed at this stage and polymer in the bulk region migrates to the dilute interface region, which induces the increase of refractive index in the interface region. Another reason is due to the gravity. Because the density of dilute solution in the interface region was much lower than that in the region far from the Teflon surface, the polymer solution should diffuse downward due to its higher density.

Figure 11 and Figure 12 present the refractive index distribution and time dependence of refractive index for the polymerization of PAMPS gel, respectively. Similar to that of PAMPS polymer solution, obvious heterogeneity of polymerization in the interface region can be observed. The difference is that the substrate effect for PAMPS gel is relatively weaker than that for PAMPS polymer solution. For example, in Figure 12, the refractive index in the interface region increases with a slower rate than that in the bulk region but does not decrease during polymerization like that in Figure 10. Furthermore, as is shown in Figure 13a,b, both the width of the interface region and the refractive index difference during polymerization for PAMPS gel are smaller than those for polymer solution. It is interesting that, unlike PAMPS polymer solution, the concentration difference in the interface region of PAMPS gel does not disappear completely at the late stage of polymerization due to the limited diffusion or swelling of cross-linked gel. This supplies a potential way to make hydrogels with gradient structure.

One error source in this experiment is the light refraction along the vertical direction because of gradient distribution of refractive index in the interface region. The refractive index at the position adjacent to the Teflon surface is lower than that in the neighboring bulk region. The passing light will be refracted from the region with lower refractive index to the region with higher refractive index. Therefore, the position of the refracted light on the screen for the interface region may be somewhat larger than the actual value. This effect

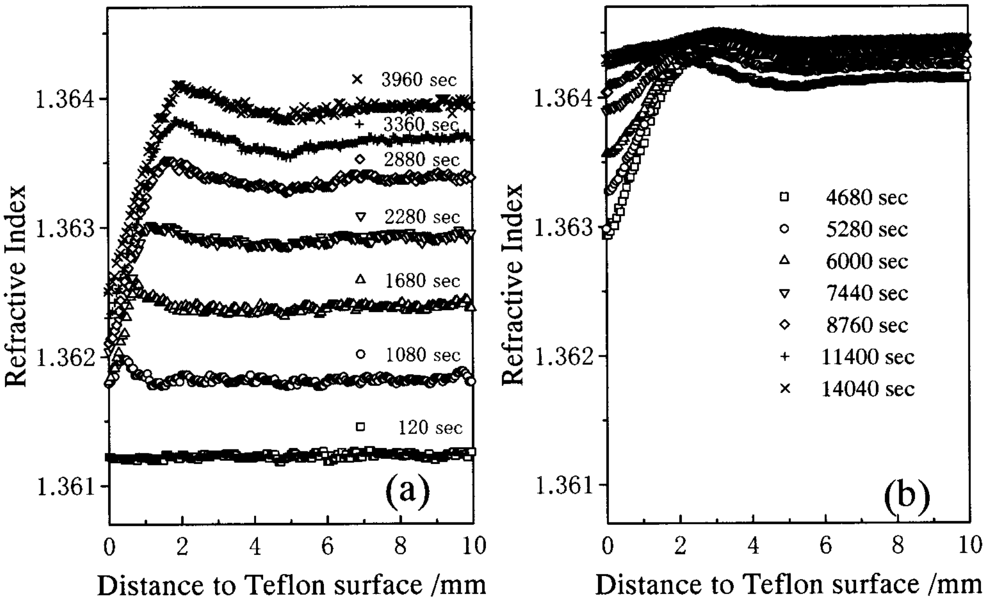

Figure 11. Refractive index distribution during polymerization of PAMPS gel near Teflon surface region (y = 0–5 mm): (a) from 120 to 4680 s; (b) from 4680 to 14 040 s.

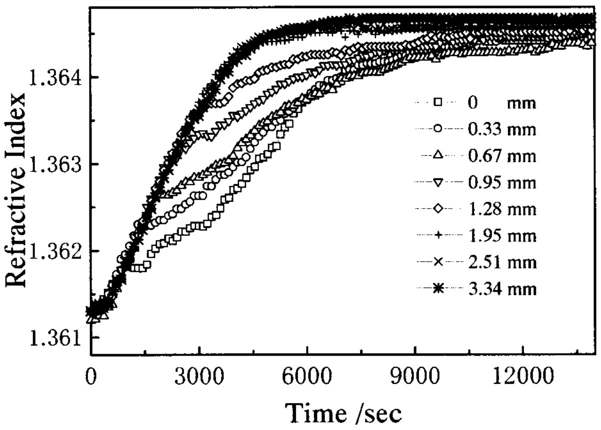

Figure 12. Time dependence of refractive index during polymerization of PAMPS gel for different positions ($y = 0-3.34$ mm) in the sample solution.

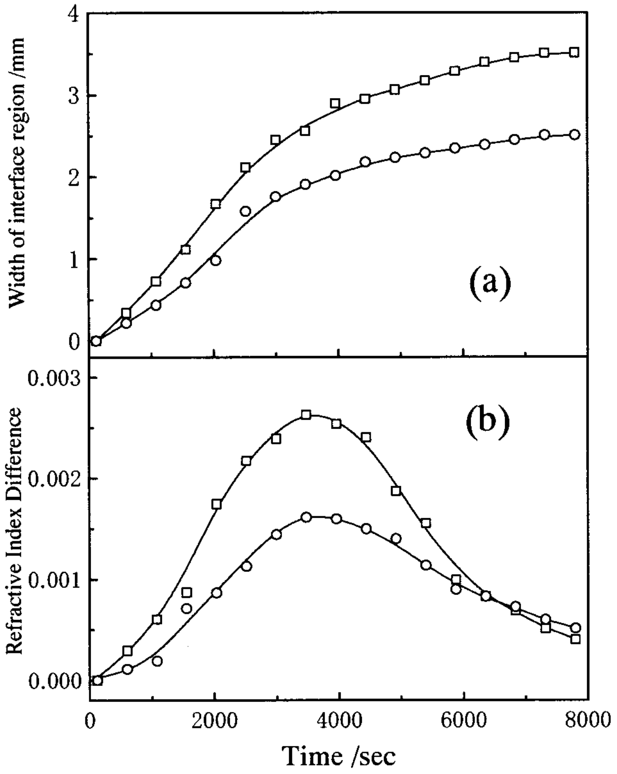

Figure 13. Evolution of the width of interface region during polymerization of AMPS aqueous solution (a) and the final refractive index distribution (b) without (□) and with (○) the cross-linking agent MBAA.

increases with the increase of the light path in the cell $\overline{OD}$. To decrease the light path of laser beam in the cell $\overline{OD}$, as is shown in Figure 3, the position at which the laser beam enters into the cell, namely, point *D*, is selected to be as close as possible to point *O*. This error also increases with the increase of the distance between the cell and the screen. Therefore, it is unwise to use a very large distance between the screen and the sample cell to obtain a larger displacement of refracted light.

Another error of this experiment arises from some parasitic light that appears neighboring the main refracted light during polymerization due to the inhomogeneity of density in the polymerizing solution especially at the early and middle stages when the conversion increases rapidly, because fast polymerization brings about local fluctuations of temperature and concentration and thus fluctuation of density. Light scattering and random refraction will happen in this case. In the present experiments, this obvious inhomogeneity was avoided as far as possible by carrying out the polymerization under a mild condition. Larger light path in the sample solution also results in more parasitic light. So it is necessary to decrease the light path as far as possible, as is mentioned above. In proper conditions, the intensity of the parasitic light is much weaker than that of the main one. Therefore, one can properly determine the position of the main light according to the intensity difference.

Macroscopic convection was not observed in the present system, due to the mild polymerization conditions and the high viscosity of the solution.[11]

Conclusion

RT-LSR for characterization of polymerization of hydrophilic monomer in aqueous solution is proposed in this paper, which allows us to study the polymerization kinetics of AMPS aqueous solution in real time and to determine the spatial distribution of refractive index in the sample solution. The heterogeneous polymerization on the surface of hydrophobic Teflon substrate as reported in previous papers is verified by the present technique. The advantage of RT-LSR is that the refractive index distribution in the interface region can be obtained directly.

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