Transient refractive index change behavior of poly(\(N\)-isopropylacrylamide) gels 

\textit{via} laser induced photo-thermal conversion process

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Transient refractive index change of poly(\(N\)-isopropylacrylamide) gels (PNIPA gels) by the photo-thermal conversion were measured in water-ethanol mixture solvent. The magnitude of the refractive index change was as large as \(10^3\), and the response time was as small as 10 msec. The transient refractive index change is induced by the thermal expansion of the gels, while the magnitude of the refractive index change is not only affected by the thermal expansion of solvent, but also by the mobility of the solvent, which is restricted by the existence of polymer chain.

Keywords: poly(\(N\)-isopropylacrylamide) gel, volume phase transition, transient refractive index change, photo-thermal conversion

1. Introduction

Recently, information processing technology has been developed remarkably with the expansion and increase in the amount of information. To realize the faster data processing, novel photonics technology is required to realize those information exchange and storage. Especially, reversible optical switching technology is one of the essential techniques which play an important role in optical computing.

Various techniques to control light with the refractive index change of materials has been developed, e.g. organic nonlinear optical materials [1-4], photorefractive materials [5-7] and photo-optical materials which changes the refractive indices by the photochemical reaction [8]. Very fast refractive index modulation is achieved with nonlinear optics, but the magnitude of the refractive index change is small. On the other hand, large refractive index change is obtained with photorefractive materials, while the switching time is usually as slow as several seconds. With photo-optical effects, refractive index modulation in p sec and as large as \(10^2\).

The refractive index change \textit{via} photo-thermal conversion process is expected to be large enough to control the phase of optical signals because the induced refractive index is related to the density change, which is described by eq (1),

\[
\frac{n^2-1}{n^2+2} = \frac{\rho \cdot R}{M}
\]

(1)

where \(R\), \(\rho\) and \(M\) are refraction of molecules \([\text{cm}^3/\text{g}]\), density \([\text{g/cm}^3]\) and molecular weight, respectively [9]. Among various materials, liquids have relatively larger thermal expansion coefficients and they have also fast response time due to their easiness in molecular relaxation. However liquid is not suitable for practical application to devices. On the other hand, solid state polymers are not expected to have fast response because of their slow relaxation though they are applicable to manufacturing devices. Polymer gels have the both feature of solution and of polymer solid, and so, their laser-induced
transient refractive index change via photo-thermal conversion process is important.

Polymer gels have peculiar volume phase transition behavior, whose mechanism has been well understood by the works of Tanaka, but their dynamics of transition is still not developed. Polymer gels are composed of three dimensional polymer network, which involve a large amount of solvent and swelled [10]. Their volume change by the change of outer environment such as temperature [11, 12], composition of solvent [13], pH [14], counter ion concentration [15], light [16] and electric field. Volume phase transition phenomenon is explained by changing the osmotic pressure of polymer gels. This osmotic pressure is described as sum of four pressures described by Flory-Huggins equation, i.e. the rubber elasticity, interaction between polymer and solvent, counter ion, and entropy of mixing. Therefore, a polymer gel shows various phase transition behavior by the difference in the material and the solvents. For example, volume phase transition curve in water-methanol mixtures of various compositions show two critical points.

In own study the dynamics of phase transition of poly(N-isopropylacrylamide) gel is measured.

N-isopropylacrylamide (NIPA) and Eosin Y was purchased from Wako Pure Chemical Industries. N,N'-methylenebisacrylamide (BIS) and 2,2'azo-isobutyronitryl (AIBN) was purchased from Tokyo Kasei Kogyo Co.

PNIPA gels were prepared by the free radical copolymerization of 12 mM N-isopropylacrylamide (NIPA) and 0.8 mM N,N'-methylenebisacrylamide (BIS) in DMSO solution, for 24 h at 70 °C. The NIPA monomer was purified by recrystallization from the mixed solvent of hexane and benzene (6 : 1), and N,N'-methylenebisacrylamide (BIS) as close linker were recrystallized from MeOH. The polymerization was initiated by 0.2 mM 2,2'azo-isobutyronitryl (AIBN). The gels synthesized in glass tubes (i.d. =8 mm), were taken out of the tube, and cut in 5 mm length. These gels were dipped into water-EtOH mixtures of various compositions (EtOH=0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 v%), containing 1mM Eosin Y.

The volumes of these gels were determined by measuring their length and diameter on a Petri dish. The degree of swelling, \( \log (V/V_0) \), whose \( V \) and \( V_0 \) are final and initial volumes of the gel, respectively, were determined based on the equation (2),

\[
\frac{V}{V_0} = \frac{l}{l_0} \left( \frac{d}{d_0} \right)^2
\]

2. Experiment

2.1 PNIPA gel preparation

Figure 1. Experimental arrangement of laser induced transient refractive index change. M1, M2, M3: mirror, PD1, PD: photo diode.
where $d$, $l$ are the diameter and length of the gels, and the subscript 0 stands for the size in the initial stage.

2.2 Experimental set-up

Experimental set-up for the transient refractive index change measurement is shown in Figure 1. The third harmonics of Nd:YAG laser (HOYA Continuum, Minilite I) light was used for the excitation beam, and CW He-Ne laser (JDS Uniphase, 10mW, 633nm) was used for the probe beam. The time dependence of the signal intensity by the probe beam was monitored with a silicon photo-diode (Electro-Optics Technology Inc. ET-2030), collected with a digital oscilloscope (SONY Tektronix TDS620A). The sample cell, which was made of glass plate and silicon sheet, was stuck with bottom surface of a triangular prism.

In this study, two types of measurement were performed. First experiment is shown in Figure 1, where optics is arranged such that. The probe beam is irradiated at total reflection angle and their intensities are monitored by PD1, while samples were excited by pump beam irradiation. When the samples were excited, the probe beam were diffracted by thermal-lens effect. Second measurements were taken place by arranging such that the reflected beam is collected by PD2.

When the sample is excited by the pump beam, the refractive index of sample is changed. To estimate the refractive index change between before and after excitation, we measured the refraction angle of probe beam by which they are monitored by shifting PD2 by x-axis stage.

3. Result and discussion

Figure 2 shows the degree of swelling of PNIPA gels as a function of EtOH concentration at room temperature (25 °C). Tanaka et al. observed that doping ionizable groups in the gel induces the reentrant volume phase transitions twice [17]. In our case, the volume phase

![Figure 3](image3.png)

**Figure 3.** Change in the probe light intensity upon excitation by the Nd:YAG laser pulse for the PNIPA gel in H$_2$O : EtOH (10 : 0) solution.

![Figure 4](image4.png)

**Figure 4.** The lifetime of the thermal diffusion of PNIPA gels as the function of the solvent composition.
change occurred twice, even though the gels do not have ionic groups. We suppose that is due to the difference in the measurement temperature.

Figure 3 shows the change in the probe light intensity upon excitation by the Nd:YAG laser pulse for the PNIPA gel in H$_2$O : EtOH solution. The probe light was detected by PD1, which collect the probe reflected at the interface between the prism base and the gel.

The position of PD1 is adjusted so that the intensity of the probe beam is initially maximum before pumping. The decrease in the signal intensity corresponds to migration of reflected probe beam, which is induced by the refractive index change of PNIPA gel via thermal expansion, and the decay of the signal corresponds to the thermal diffusion of the gel.

The lifetime of the thermal diffusion of PNIPA gels were plotted in Figure 4 as the function of the solvent composition. The open circles in Figure 4 show the signal lifetime of H$_2$O-EtOH mixed solution without PNIPA gel. The thermal expansion of the sample is thought based on the thermal motion of the solvent, and so the difference in the relaxation time between with and without PNIPA gels are thought as corresponding to the change in the mobility of the solvent molecules due to the existence of polymer gel network. The decays of migrated probe beam for the gels in shrinking area are the longer compared to those for swollen gels showing that the mobility of the solvent in gel network decrease in shrinking state.

Next, we measured the refractive angle change of the probe beam by the impulsive thermal stimulation. Figure 5 (a) shows the signal intensity of the decaying probe beam, which is shown in Figure 4, as the function of the detection position of PD1. The probe beam intensity was small at the initial beam position and a point where signal intensity increases was appeared near the position ~5mm from the original point. From these changes, the refractive index change, $\Delta n$, before and after excitation was calculated based on the following equation

$$n_2 = \frac{n_1 \sin \theta_1}{\sin \theta_2}$$  

(3)

$$\Delta n = n_1 - n_2$$  

(4)

where $n_1$ and $n_2$ is the refractive index of gels before and after excitation, and $\theta_1$ and $\theta_2$ is the refraction angle of gels before and after excitation, respectively. $n_1$ was calculated from the refraction angle of probe beam through between prism and samples. $\theta_1$ and $\theta_2$ was calculated by measuring for the distance between the points that the signal intensity is minimum and maximum when the pump beam irradiated. The result was summarized in Table 1. This results indicates that sufficient refractive index change $\sim 10^3$ are induced by even the only one shot excitation, and with response time of $\sim 60$ms.
Table 1. The refractive index change ($\Delta n$) of samples with and without PNIPA gels before and after the excitation beam irradiated

<table>
<thead>
<tr>
<th>EtOH (%)</th>
<th>$\Delta n \times 10^3$ in PNIPA gel</th>
<th>$\Delta n \times 10^3$ in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.24</td>
<td>2.11</td>
</tr>
<tr>
<td>70</td>
<td>4.06</td>
<td>2.13</td>
</tr>
<tr>
<td>80</td>
<td>3.79</td>
<td>2.07</td>
</tr>
<tr>
<td>90</td>
<td>3.09</td>
<td>2.05</td>
</tr>
<tr>
<td>100</td>
<td>3.63</td>
<td>3.16</td>
</tr>
</tbody>
</table>

Moreover, the value of $\Delta n$ are independent on solvent composition from which one can expect the $\Delta n$ is proportional to the average of thermal expansion coefficient of water and ethanol, 1.1x$10^{-3}$ and 0.21x$10^{-3}$ K$^{-1}$ respectively. Thus we conclude that refractive index change of polymer gels depends not only on solvent composition but also on the mobility of polymer which restricts the solvent molecule by the long-range interaction, e.g. hydrogen bonding and hydrophobic interaction. Figure 5 (b) shows the results of the measurement using the sample without PNIPA gel. In this result, the refractive index change increased with the ethanol composition. These data reflects the relation of the thermal expansion coefficient between water and ethanol. We suppose that the different behavior originate from the change in the mobility of the solvent molecules due to the existence of polymer network.

4. Conclusion

We observed transient refractive index change of poly(N-isopropylacrylamide) gels (PNIPA gels) by the photo-thermal conversion in water-ethanol mixed solvent. The magnitude of the refractive index change was as large as 10$^{-3}$, and the response time was as small as 10 msec. We conclude that refractive index change of polymer gels depend not only on solvent composition but also on the mobility of polymer, which restrict the solvent molecule by long range interaction, e.g. hydrogen bond and hydrophobic interaction. And the change in the mobility of the solvent molecules due to the existence of polymer network.

References

15. S. Hiritsu, Y. Hirokawa, T. Tanaka, *J.