

Dielectric Study on Dynamics for Volume Phase Transition of PAAm Gel in Acetone-Water System

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We investigated dielectric properties of poly(acrylamide) (PAAm) gels immersed in acetone-water mixtures with various compositions, using a time domain reflectometry (TDR) method. A relaxation due to solvent molecules in the gel was observed for each sample. Relaxation parameters obtained for solvent in the gel were changed accompanying the change in the volume of gel and the composition of solvent. In order to compensate the change in the composition of solvent, the relaxation parameters were normalized by those for respective solvent outside gel. Normalized relaxation parameters thus obtained suggest that the composition of solvent in the gel is different from that surrounding gel in acetone rich region. Normalized relaxation time is explained by a ratio of the average molecular weight of the solvent molecules to the volume of the mesh.

Keywords: dielectric relaxation, volume phase transition, PAAm gel, aqueous polymer system, TDR

Introduction

Though polymer gels exist extensively in our life, we have not completely understood physical properties of gels yet. The gel is a crosslinked polymer network immersed in a solvent. Volume phase transition is one of interesting properties of gel and it has been recently studied as a significant subject. The polymer gel swells and shrinks with changing various conditions: temperature, electric field, composition of the solvent, and so on. Poly(acrylamide) (PAAm) and related polymers are typically used to investigate the volume phase transition. Especially the volume change of the PAAm gel in acetone-water mixtures with various compositions has been well revealed [1-3].

Molecular dynamics accompanying the volume change of the polymer gel have not been studied enough yet. We have recently reported that dielectric relaxation measurements on gel through a time domain reflectometry (TDR) method offer informative data to

understand molecular dynamics of solvent in the gel [4]. In the present paper, we performed dielectric relaxation measurements for acetone-water mixtures in PAAm gels, using TDR method, in order to discuss dynamics of solvent molecules affected by the polymer network.

Experimental

The procedure of the preparation of PAAm gel was referred to Tanaka et. al. [3]. At first, acrylamide (5g), N, N'-methylene-bis-acrylamide (0.133g), ammonium persulfate (40mg), and N, N, N, N-tetra-methylethylene-diamine (TEMED) (240 μ l) were dissolved in distilled and three times deionized water (milli-Q: MILLIPORE Co., Ltd.) at 25°C to the final volume of 100ml. All the chemicals were purchased from Wako Pure Chemicals Industries, Ltd.. The solution was put into a glass tube (length: 50mm, diameter: 6mm) and was kept for 1 day in order to complete the formation of gel. The gel was cut in the 10 mm column and immersed in pure water for 3days in order to wash away residual acrylamide, bis-acrylamide, etc. Then several gels were placed in

TEMED aqueous solution (pH 10.8) for 4 days to hydrolyze a portion of the acrylamide groups into acrylic acid groups ($-\text{CONH}_2 \rightarrow -\text{COOH}$). These procedures were performed at 25°C. Residual components were washed away again after the hydrolysis.

Gels were placed in acetone-water mixtures with various acetone concentrations from 0 to 80 vol% at 10 vol% intervals. For acetone rich composition, the gels were soaked in solvent with 30 vol% acetone concentration at first and the acetone concentration were increased at 5~10 vol% intervals, as gels did not form any patterns with the change in composition. After gels had reached their equilibrium conditions, the microscope measured the diameter and the length of each gel. Furthermore the balance in the air and in the solvent measured the mass of each gel, respectively, and the volume was obtained from Archimedes's law.

Dielectric measurements for gels were performed with TDR system [5-6] over the frequency range from 100 MHz to 20 GHz at 25°C. Aqueous solutions of poly(acrylic acid) (PAA) (POLYSIENGE, INC.) and PAAm (Sigma-Aldrich Co., Ltd.) were also measured by TDR to compare results with the gels.

Results and Discussion

Figure 1 shows acetone concentration dependence of the swelling ratio, V/V_0 , of the gel. Here V is the equilibrium volume of the gel at a certain acetone concentration and V_0 is the initial volume of the gel cut in 10 mm column. The volume decreases with increasing acetone concentration, and shows a distinct decrease between 30 vol% and 40 vol% acetone concentration. The volume of hydrolyzed gel exhibits an abrupt decrease.

Dielectric dispersion and absorption curves for PAAm gels in acetone-water mixtures of various compositions and those for the solvent existing out of gels are shown in Figures 2 and 3, respectively. A relaxation peak is observed at higher frequency for each mixture. The peak frequency for the solvent surrounding the gel is shifted to the lower frequency once and is shifted to the higher frequency side again with increasing acetone concentration. However the peak frequency for the gel was simply shifted to the lower frequency. This relaxation process is due to reorientations of acetone and water molecules. The relaxation process was described by the Cole-Cole equation as

$$\varepsilon^*(\omega) = \frac{\Delta\varepsilon}{1 + (j\omega\tau)^\beta} + \varepsilon_\infty \quad (1)$$

where $\Delta\varepsilon$ is the relaxation strength, τ is the relaxation

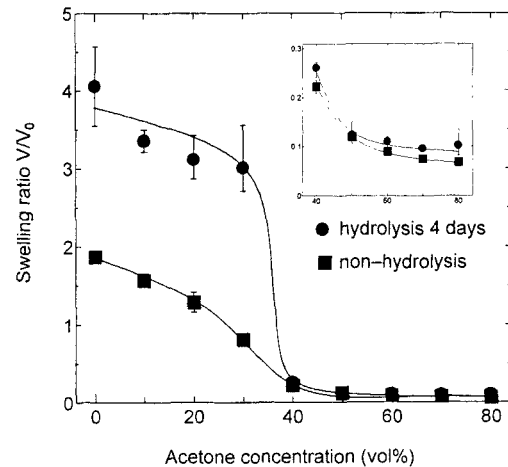


Fig.1 Acetone concentration dependence of the swelling ratio V/V_0 for PAAm gels. The curve was for hydrolyzed gel immersed in TEMED solution (pH 10.8) for 4 days.

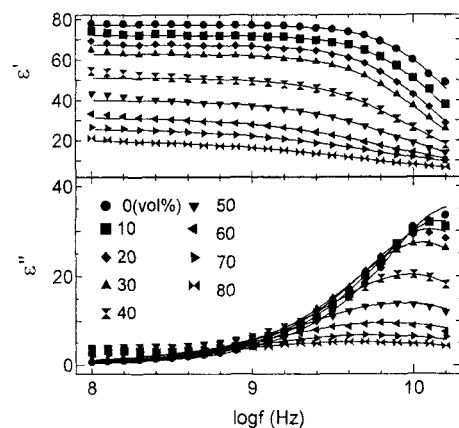


Fig.2 Dielectric dispersion and absorption curves for PAAm gels in acetone-water of various compositions.

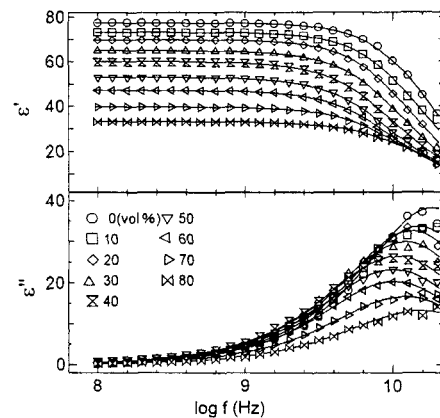


Fig.3 Dielectric dispersion and absorption curves for the solvent out of gel in acetone-water of various compositions.

time, ω is the angular frequency, β ($0 < \beta \leq 1$) is the shape parameter, and ϵ_∞ is the limiting high-frequency permittivity. These relaxation parameters were determined by the fitting procedure.

Plots of τ (s), β and $\Delta\epsilon$ against the acetone concentration are shown in Figure 4. The relaxation time for solvent surrounding gel shows a maximum around 60vol%. The shape parameter, β , for solvent surrounding gel keeps similar value for the whole composition range. The relaxation strength for the outside solvent decreases with increasing acetone concentration. These tendencies for the solvent have already been reported [7]. All of the relaxation parameters for the gel clearly show a difference from the outside solvent above the acetone concentration 40vol%. This concentration coincides with shrinking process of the gel shown in Figure 1. The shrink of the gel means increasing density of polymer network. These changes in relaxation parameters with increasing polymer density have been generally observed for water in aqueous polymer solutions.

Plots of $\Delta\epsilon$ against water content for aqueous polymer solutions are shown in Figure 5. Aqueous solution of PAA corresponds to the PAAm gel completely hydrolyzed. The relaxation strength was decreased with decreasing water content of aqueous polymer solution. A solid line indicates the relaxation strength estimated from the water content. Relaxation strength observed for PAAm aqueous solution is well overlapped on the solid line.

Plots of the relaxation strength for the PAAm gel, $\Delta\epsilon_G$, and its ratio to the relaxation strength for the solvent existing out of the gel, $\Delta\epsilon_G/\Delta\epsilon_S$, against polymer concentration are shown in Figure 6. Relaxation strength, $\Delta\epsilon_G$, decreases with increasing acetone and polymer concentrations. In order to compensate the effect of the change in the composition of solvent, the relaxation strength for the gel was normalized by the each relaxation strength of outside solvent. Normalized relaxation strength, $\Delta\epsilon_G/\Delta\epsilon_S$ thus obtained simply decreased with increasing polymer concentration. Values of $\Delta\epsilon_G/\Delta\epsilon_S$ for PAAm gel are larger than that for PAAm aqueous solution. The $\Delta\epsilon_G/\Delta\epsilon_S$ values for the hydrolyzed PAAm gel are similar to PAAm aqueous solution. Hydrolyzed PAAm gel is substituted from the acrylamide groups to acrylic acid groups, and $\Delta\epsilon_G/\Delta\epsilon_S$ values for the hydrolyzed PAAm aqueous solution are expected to be taken between PAAm and PAA aqueous solutions. Therefore $\Delta\epsilon_G/\Delta\epsilon_S$ values for the hydrolyzed PAAm gel are also larger than those in the aqueous solution. In higher acetone concentration region, $\Delta\epsilon_G/\Delta\epsilon_S$ values for

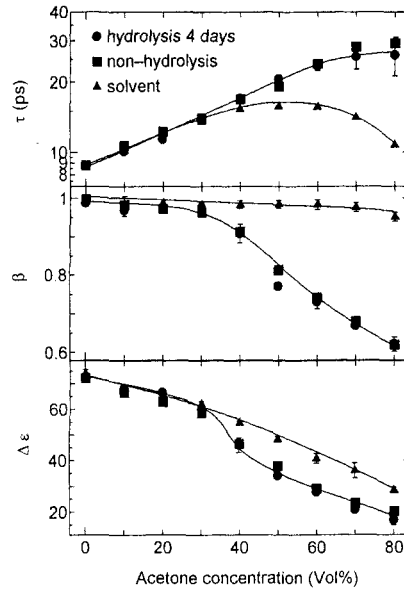


Fig.4 Plots of relaxation time τ (s), shape parameter β and relaxation strength $\Delta\epsilon$ against acetone concentration

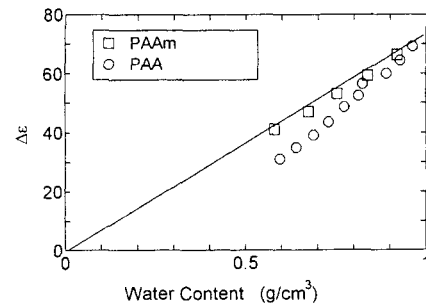


Fig.5 Plots of relaxation strength $\Delta\epsilon$ against water content

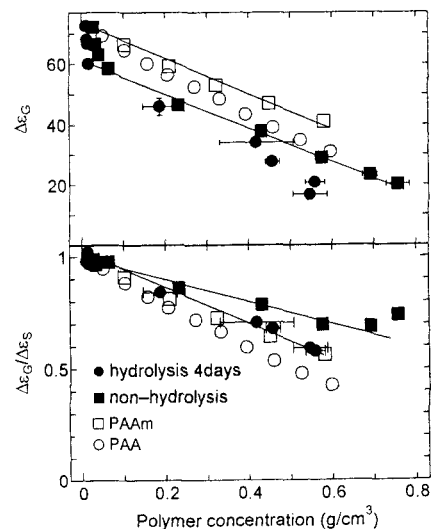


Fig.6 Plots of relaxation strength $\Delta\epsilon_G$, and its ratio to the relaxation strength for outside solvent, $\Delta\epsilon_G/\Delta\epsilon_S$, against polymer concentration

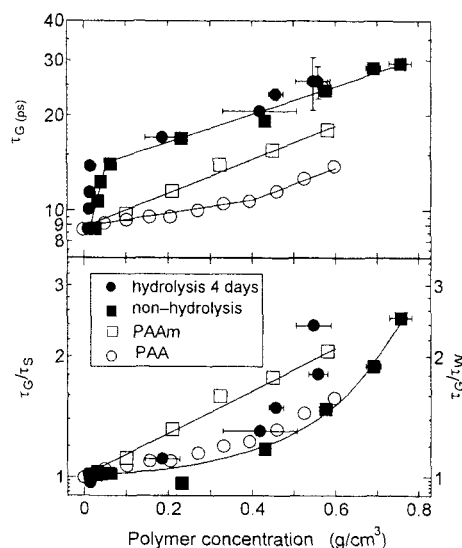


Fig.7 Plots of relaxation time τ_G , and its ratio to the relaxation time for outside solvent, τ_G/τ_S , against polymer concentration

PAAm gel did not decrease with increasing polymer concentration. This result suggests that the composition of solvent existing in the gel is different from that existing out of the gel. Acetone concentration in the gel is considered to be lower than that out of the gel, since PAAm chain is hydrophilic.

Plots of relaxation time τ_G , and its ratio to the relaxation time for outside solvent, τ_G/τ_S , against polymer concentration are shown in Figure 7. The τ_G value increasing with increasing polymer concentration in the lower polymer concentration was compensated for the normalized relaxation time. Normalized relaxation time, τ_G/τ_S simply increased with increasing polymer concentration.

Considering a scaling variable of the form

$$x \propto R/\xi \quad (2)$$

where R and ξ are the size of solvent molecules and the correlation length of polymer network. We examine our experimental results on the polymer concentration dependency of the normalized relaxation time written as

$$\tau_G/\tau_S = f(x^n) \quad (3)$$

Power law relationships generally expressed as [8]

$$R \propto M^{1/3} \quad (4)$$

$$\xi \propto Cp^{-3/4} \quad (5)$$

suggest that the scaling variable is written as

$$x = M^{1/3} Cp^{3/4} \quad (6)$$

where M is the average molecular weight of solvent and Cp is the polymer concentration.

Plots of the normalized relaxation time τ_G/τ_S against

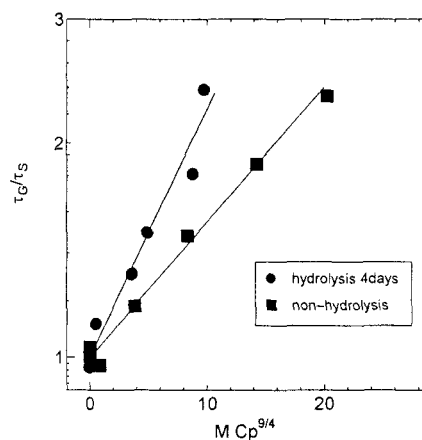


Fig.8 Plots of the normalized relaxation time τ_G/τ_S against the scaling variable $M Cp^{9/4}$. Here M is the average molecular weight of solvent and Cp (g/cm^3) is the polymer concentration.

the scaling variable x^3 are shown in Figure 8. The τ_G/τ_S value increases with increasing x^3 , and well overlaps on the straight solid line. Figure 8 also indicates that the gel hydrolyzed takes another straight line and the difference reflects each molecular structure.

These straight lines suggest that the normalized relaxation time is expressed as

$$\tau_G/\tau_S \propto \exp(x^3) \quad (7)$$

According to a report by Tokita et. al. [9], the diffusion coefficient of the probe molecule in the gel, D , measured by the pulsed field gradient NMR measurements suggests the scaling function of the form

$$D/D_0 \propto \exp(-x) \quad (8)$$

The inconsistent result for n values obtained from eqs. (7) and (8) is supposed to reflect the difference between the principles of each measuring technique. Eq. (7) implies that the relaxation time is determined by the intermolecular interaction that is related to the ratio of volumes for the solvent molecule and the mesh of network. More quantitative treatment of the molecular mechanism is expected in our following study.

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