

Water and chain dynamics in polymer network structure

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We performed dielectric spectroscopy and differential scanning calorimetry measurements for hydroxypropylmethylcellulose (HPMC)/1,4-dioxane solutions and gels in order to investigate dynamical structures of polymer and solvent molecules. A relaxation process was observed for HPMC/1,4-dioxane sol and gel around 100MHz at 298K. The behavior of this process shifting to the lower frequency region with decreasing temperature below the freezing point was similar to those reported so far for the polymer chain motions. We also observed a relaxation process due to unfreezable remnant water.

Key words: dielectric spectroscopy, dynamical structure, polymer network, gel

1. INTRODUCTION

Hydroxypropylmethylcellulose (HPMC) is one of the complex carbohydrate derivatives, which is water soluble and shows a heat reversible sol-gel transition and phase separation [1-4]. Furthermore, HPMC is extensively used as an emulsion stabilizer, a water-holding stabilizer and a protective colloid stabilizer [4].

Recently, irradiation of electron beam to a variety of polymers to yield a hydrogel has been extensively studied in radiation chemistry field. This method yields an additive-free hydrogel, which cannot be obtained from usual polymerization with cross-linkers and/or polymer additives.

A difficulty in dielectric measurements on complex carbohydrates containing water is generally brought from large direct current contributions of ions impurity. Since HPMC has less ions than other complex carbohydrates, we can perform dielectric measurements more easily than other aqueous solutions.

We have studied dynamics of polymer and water in various synthetic and biopolymer solutions by dielectric relaxation measurements [5]. Dynamics of water and polymer observed in gelation process of HPMC aqueous solution by irradiation of electron beam were recently reported [6]. However, the behavior of the chain motions has not been clarified yet in the aqueous solution, because the relaxation process is masked by large contributions of dc conductivity, ion, and water.

In the present work, we studied polymer chain dynamics in the temperature range from 243K to 298K, using HPMC in non-polar solvent, 1,4-dioxane. Additionally, we studied the effect of remnant water dynamics on the dielectric property of HPMC/1,4-dioxane sol.

2. EXPERIMENTAL

HPMC (the weight-averaged molecular weight, $M_w=104,000$, and the nominal degree of substitution of methoxyl group (DS) and the molecular substitution of hydroxypropoxyl groups (MS) per anhydroglucose unit are 1.9 and 0.25, respectively) used in the present work was Metlose 60SH-50 provided from Shinetsu Chemical Co. Metlose was used as HPMC sample without further purification. Distilled and deionized water was added to HPMC to adjust the concentration of a hydrosol, and HPMC gel was made by irradiation of electron beam to the hydrosol at 150kGy. Aerogel was made by lyophilization of the gel for two days, and was swollen in pure 1,4-dioxane during one week. We also prepared HPMC/1,4-dioxane solution from HPMC powder and 1,4-dioxane for a comparison with HPMC/1,4-dioxane gel.

Dielectric measurements of HPMC gel and sol in a frequency range from 40Hz to 110MHz were performed by Precision Impedance Analyzer (IA; Agilent technologies 4294A), Impedance Material Analyzer (IMA; HEWLET PACKARD 4291A), and Time Domain Reflectometry (TDR) method (HEWLET PACKARD 54124T)[7].

Electrodes employed for IA, IMA and TDR measurements are parallel plate type with the plate distance of 0.5mm for IA and IMA, and coaxial cell type with the electric length of 2.0mm for TDR.

Melting point and the transition enthalpy were obtained for HPMC/1,4-dioxane gel and sol by Differential Scanning Calorimetry (DSC) (Perkin Elmer DSC-7) measurements in the temperature range from 203K to 298K.

3. RESULTS AND DISCUSSION

Typical results of dielectric dispersion and absorption observed by IA for 20wt%HPMC/1,4-dioxane gel in heating process from 243K to 298K were shown in Fig.1. HPMC and 1,4-dioxane are hygroscopic materials. Then we examined the existence of remnant water by observing a relaxation process in giga hertz region. Figure 2 shows dielectric dispersion and absorption observed for 20wt% HPMC/1,4-dioxane sol at 298K by TDR (from 300MHz to 1.5GHz), IMA (from 10MHz to 80MHz) and IA (from

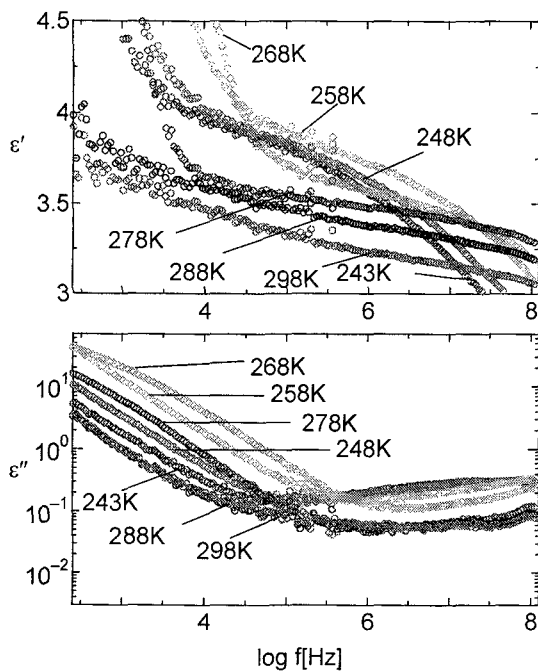


Fig. 1. Dielectric dispersion and absorption curves for 20wt% HPMC/1,4-dioxane gel irradiated at 150kGy in the heating process from 243K to 298K.

40Hz to 80MHz). A relaxation process due to water was usually observed in giga hertz frequency region. The lower frequency tail of the high frequency relaxation process around 1GHz was found as shown in Fig. 2. Therefore, we introduce the relaxation process of water around 10 GHz for the following fitting procedures. As shown in Fig. 3, the relaxation processes at 10 GHz is called h processes. In the frequency range of 10^2 - 10^6 Hz, the other three relaxation processes were found and named m , l_1

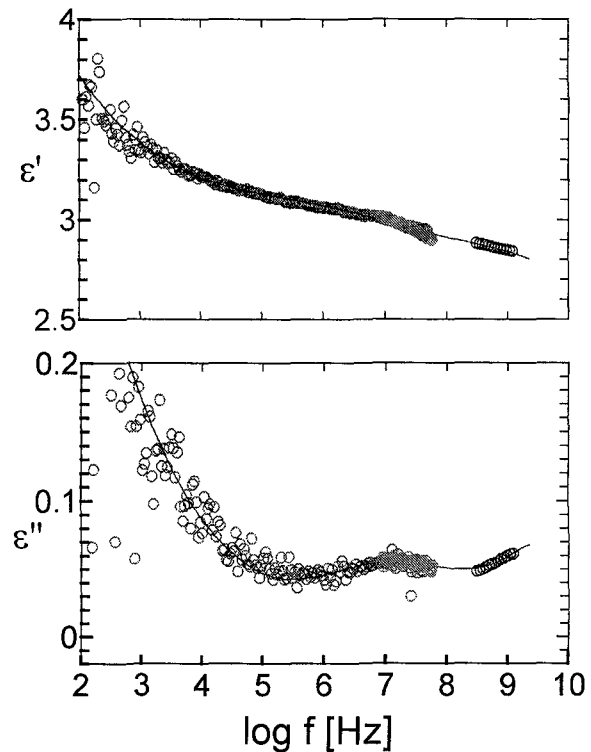


Fig. 2. Dielectric dispersion and absorption curves for 20wt% HPMC/1,4-dioxane sol measured by IMA, IA and TDR at 298K.

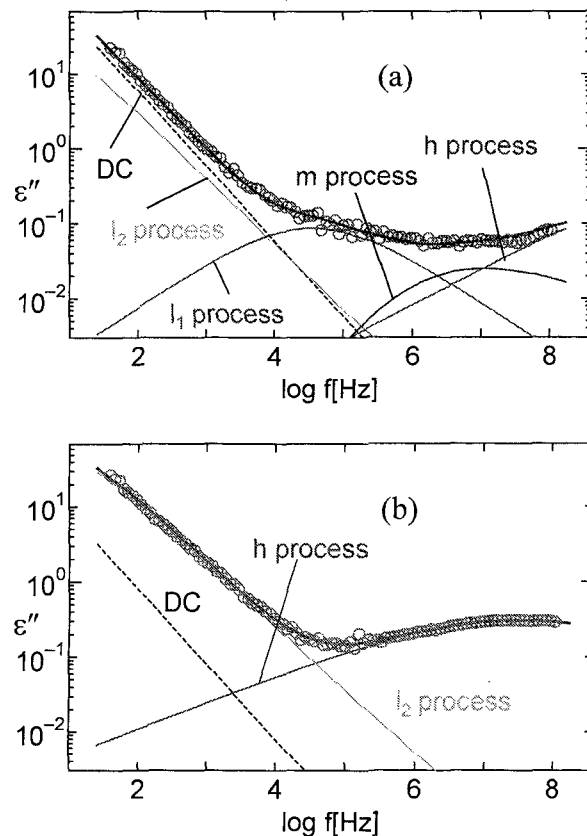


Fig. 3. Dielectric absorption at 298K(a) and 243K(b) for 20wt% HPMC/1,4-dioxane gel. Lines were calculated from equation (1).

and l_2 processes. Takemasa et al. reported that these relaxation mechanisms are related to dynamical behaviors of ions and bonding water [8]. Our interpretations about these processes are described below.

The dielectric dispersion and absorption curves were fitted by eq. (1), which is the summation of relaxation processes expressed by the three Cole-Cole equations, KWW equation and the direct current conductivity as

$$\begin{aligned} \varepsilon^*(\omega) &= (\varepsilon' - j\varepsilon'') \\ &= \varepsilon_\infty + \frac{\Delta\varepsilon_h}{1 + (j\omega\tau_h)^\beta} + \Delta\varepsilon_m \int_0^\infty \left[-\frac{d\Phi(t)}{dt} \right] \exp(-j\omega t) dt \\ &\quad + \frac{\Delta\varepsilon_l}{1 + (j\omega\tau_l)^\beta} + \frac{\Delta\varepsilon_{l_2}}{1 + (j\omega\tau_{l_2})^\beta} + \frac{\sigma}{j\omega\varepsilon_0}, \\ \Phi(t) &= \exp \left[-\left(\frac{t}{\tau_m} \right)^{\beta_{KWW}} \right], \end{aligned} \quad (1)$$

where $\Delta\varepsilon$ is the relaxation strength, τ is the relaxation time, ω is the angular frequency, j is the imaginary unit, ε_0 is the permittivity of vacuum, ε_∞ is the permittivity at limiting high frequency, β is the Cole-Cole's shape parameter to describe the symmetrical broadness, σ is the dc conductivity, and h, m, l_1 and l_2 indicate relaxation processes in the order from the higher frequency side. Examples of fitting results were shown in Fig. 3. Five relaxation processes were fitted well at 298 K (Fig. 3 (a)), while at 243 K, which is below freezing temperature, 3 relaxation processes were found.

The obtained parameters were shown as the plot of the relaxation time, τ_h and τ_m , against the reciprocal of the absolute temperature for 20wt% HPMC/1,4-dioxane gel

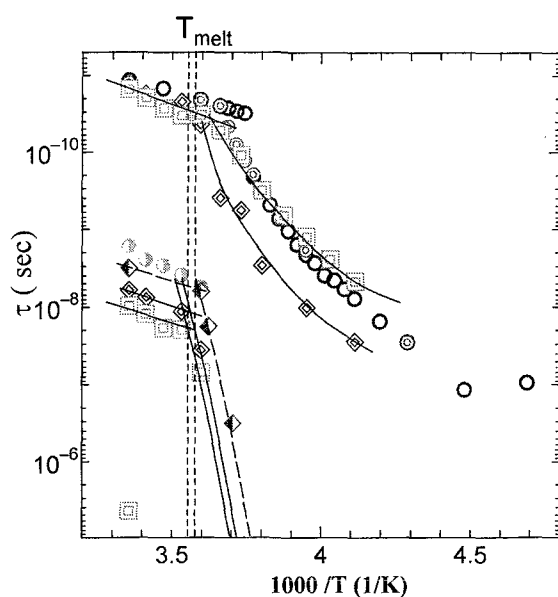


Fig. 4 Arrhenius plot for the h-relaxation and m-relaxation processes.
 □ 20wt%HPMC/1,4-Dioxane gel ◇ 20wt%HPMC/1,4-Dioxane sol
 ● 30wt%PVME aqueous solution ⊙ 10wt%HPMC/water gel
 ◆ 20wt%PVAc-Benzene ○ 10wt%HPMC/water gel (cooling)

and 20wt% HPMC/1,4-dioxane sol in Fig. 4. For comparison, the parameters of 10wt% HPMC aqueous gel irradiated at 10kGy [9], 30wt%PVME aqueous solution [10], and PVAc/Benzene mixture [11] were also shown. 10wt% HPMC aqueous gel froze at around 273K. 20wt% HPMC/1,4-dioxane gel and sol indicate abrupt changes in the relaxation time because of melting between 278K and 283K. Two dotted lines in Fig. 4. show this temperature region of melting temperature, T_{melt} , between 278K and 283K for 20wt% HPMC/1,4-dioxane obtained from the dielectric measurements. In the case of 20wt% HPMC/1,4-dioxane gel and sol, l_1 was also shown as process. DSC measurements suggested that the freezing point for 20wt% HPMC/1,4-dioxane gel was 278K. The freezing point of pure 1,4-dioxane is 285K, and a depression of freezing point was observed for the gel. Freezing temperature for 20wt% HPMC/1,4-dioxane gel obtained from dielectric measurements is corresponding to the value obtained from DSC measurements. The relaxation time of the h-process for 20wt% HPMC/1,4-dioxane gel agrees with that for 10wt% HPMC aqueous gel.

From the DSC measurements for 1,4-dioxane and 20wt% HPMC/1,4-dioxane gel, the amount of unfreezable solvent was calculated from the transition enthalpy. As the results, 9 % of solvent molecules in the HPMC/1,4-dioxane gel are unfrozen at the freezing point of 278K. It is reported for 10wt% HPMC aqueous gel that the h-process relates to the unfreezable water in the frozen matrix [9]. Therefore it is reasonable to consider that the 20wt% HPMC/1,4-dioxane gel and sol also contain a small amount of remnant water, and h-process observed for 20wt%HPMC/1,4-dioxane gel should be also due to the unfreezable water.

Polymer chain motion in non-polar solvent around the freezing temperature was examined for PVAc/Benzene mixture [11]. A large temperature dependence of the relaxation time was reported below the freezing temperature. The similar behavior is also observed for 20wt% HPMC/1,4-dioxane gel. Then the m-process observed around 10kHz is considered to reflect the chain motion. Figure 4 also shows a similar behavior of solution of PVME [10]. Comparing these behaviors for PVAc/Benzene and PVME aqueous solution, the m-process obtained in this study is in similar frequency region. However m-process for the present HPMC/1,4-dioxane sol and gel were observed at slightly lower frequencies. This difference is considered that the polymer chain of HPMC is more rigid than other polymers [12]. HPMC molecules require a large excluded volume. Therefore, the chain motion of HPMC is restricted comparing with the other polymers especially below the freezing point. This leads to a large relaxation time. The similar tendency was also observed for PVP chain motions in PVP/PEG mixture [11]; that is,

the steric hindrance for PVP chain motion is quite large in the polymer mixture.

The polymer chain motion is affected by hydration of HPMC and interacting ions. Relaxation parameters for chain motions usually depend on their circumstances. Then it is considered that the relaxation time of the m-process is associated with interacting polymer chain motions, but the relaxation strength is easily affected by remnant water and ions. For more detailed discussion about polymer chain motions, we need to prepare dehydrated samples in order to eliminate the contributions of water and ions.

4. CONCLUSION

We observed two relaxation processes around 10GHz (h-process) and 100MHz (m-process) at high frequency region and the other two relaxation processes, l_1 and l_2 were found below 1MHz. Comparing with the relaxation time reported for other polymer solutions, the present h-process and m-process are considered to reflect water and polymer chain motions, respectively.

5. ACKNOWLEDGMENTS

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6. REFERENCES

- [1] N. Sarkar, *J. Appl. Polym. Sci.* **24**, 1556 (1979).
- [2] S. Nagura, S. Nakamura, Y. Onda, *Kobunshi Ronbunshu*, **38**, 133 (1981).
- [3] R. Kita, T. Kaku, K. Kubota, T. Dobashi, *Phys. Lett. A* **259**, 302 (1999).
- [4] R. Kita, T. Kaku, H. Ohashi, T. Kurosu, M. Iida, S. Yagihara, T. Dobashi, *Physica A*, **319**, 56 (2003).
- [5] N. Shinyashiki, Y. Matsumura, N. Miura, S. Yagihara, S. Mashimo, *J. Phys. Chem.*, **98**, 13612 (1994).
- [6] K. Furusawa, T. Dobashi, S. Morishita, M. Oyama, T. Hashimoto, N. Shinyashiki, S. Yagihara, N. Nagasawa, *Physica A*, **353**, 9-20 (2005).
- [7] S. Yagihara, et al. *SSTA*, **2**, 15-29 (2001).
- [8] M. Takemasa, T. Sato, A. Chiba, and M. Date, *Trans. Mater. Res. Soc. Japan* **28**, 1001-1004, (2003).
- [9] T. Hashimoto, M. Yamamura, S. Shigemitsu, S. Shioya, M. Oyama, M. Shinomura, N. Miura, N. Shinyashiki, S. Yagihara, Y. Hayashi, M. Tokita, H. Nishida, K. Terao, T. Dobashi and F. Yoshii, *Trans. Mater. Res. Soc. Japan* **28**, 997-1000 (2003).
- [10] N. Shinyashiki, Y. Matsumura, S. Mashimo, S. Yagihara,

J. Chem. Phys. **104**, 6877-6880, (1996).

[11] S. Yagihara, M. Asano, M. Kosuge, S. Tsubotani, D. Imoto, N. Shinyashiki, *Journal of Non-Crystalline Solids* **351**, 2629-2634 (2005).

[12] S. Kondo, K. Kubota, *Report on Progress in polymer Physics in Japan*, **40**, 81-82 (1997).

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