

State Analysis of Bound Water in Hydrophilic Polymer by High frequency Spectroscopy

Takaya Takei, Yousuke Inoue and Yoshinori Sugitani

Faculty of Science, Department of Chemistry, Kanagawa University

Tsuchiya2946, Hiratsuka, Kanagawa, Japan

Fax: 81-0463-58-9684, e-mail: sugitani@kanagawa-u.ac.jp

Polyethylene oxide (PEO) has high hydrophilicity and high-crystallinity. Moreover, the crystallinity affect on the hydrophilicity of the PEO. In this study, PEO-H₂O systems, which were given cyclic temperature change between 30 °C and 60 °C, were measured by high frequency spectroscopic method, which can detect the change of the solution structure and/or the boundary state of molecules sensitively. From the results, the temperature dependence of the resonance frequency showed deference with the water content and the molecular weight of the PEO. Water rich mixture, which was containing water with the ratio of EO : H₂O=1:10, showed similar temperature dependency with water. On the other hand, low water content sample with the ratio of EO : H₂O = 1 : 1 showed a characteristic behavior suggesting the bound state change of water molecules caused by PEO melting. Same results were obtained from lower molecular weight PEO samples by perform the measurements at lower temperature range (15 °C~40 °C). These results suggest that bound state of water deeply relate on the crystallinity of PEO, and high frequency spectroscopy can detect these changes as resonance frequency shifts in the spectra.

Key words: polyethylene oxide, high frequency spectroscopy, water, state analysis, secondary structure

1. INTRODUCTION

Polyethylene oxides (PEO) are viscous liquid or solid with high hydrophilicity and high-crystallinity, and are widely used as lubricant in the case of metalworking, rubber molding, and dispersing agents of cosmetics and medical supplies. Moreover, it was used in artificial organs for adhesion prevention.¹⁻⁴ In this case, the grafted PEO layer formed hydrated layer at the surface of artificial organs, and it prevent the adhesion of the biological component such as proteins and platelets. Thus, hydrophilicity of PEO was widely used in various fields.

But the property changes completely when PEO crystallizes. It is known that PEO takes the helix structure in which oxygen atoms align to the inside of the helix, and the hydrophilicity of PEO was reduced. The hygroscopicity of PEO was reported as about 5% in the relative humidity of 80%.⁵ This value is very low in comparison with the other hydrophilic polymers. In this way, the hydrophilicity of PEO greatly depends on the secondary or tertiary structure which changes by the water content or the temperatures. Therefore, PEO-H₂O mixture is very interesting system when we study the hydration state of the hydrophilic polymers.⁶⁻⁸

On the other hand, we have reported the study of alcohol-water solution structure change using high frequency spectroscopy that detect the permittivity change of the sample as the shifts of the resonance frequency.⁹⁻¹⁰ As the results, it was found that the stepwise change of the resonance frequency were occurred at certain alcohol concentrations. These results suggest that the solution structure change at those concentrations. These showed good agreement with the results obtained by MS,¹¹ NMR,¹² and Raman scattering.¹³ Further, we applied this high frequency

spectroscopic technique to the PEO-H₂O system, and reported that water molecules in the sample containing hydroquinone (HQ), are strongly bound by HQ, and can be referred to as non-freezable water.¹⁴ Thus, high frequency spectroscopy can detect the change of the bound state of molecules, especially the mixture of nonpolar molecule and polar molecule such as polymer-water system.

In this study, we performed high frequency spectroscopic measurement to PEO-H₂O system, and considered to the change of the bound state of water caused by secondary structural change of PEO.

2. EXPERIMENTAL

2.1 Preparation

The weight-average molecular weights of PEO used in this study were 200, 1000, and 10000. Pure water (18.2MΩ) was added to PEO and samples with molar ratio of EO : H₂O = 1 : 1 to 1 : 10 were prepared. These samples were kept in a thermostatic water bath which was controlled at 60°C until it became transparent solutions. Then, it was preserved for two weeks at measurement start temperature (30 °C or 15 °C) in order to equilibrate the hydration of samples.

2.2 Measurement

Fig. 1 shows a scheme of the setup employed in the present study. As a high frequency source and signal detector, the MH680A type tracking generator (TG) and MS2601B type spectrum analyzer (SA) made by ANRITSU were used respectively. The sample cell comprised a couple of copper plates. In the measurement it was immersed into a sample solution. The temperature of solution was controlled by the water jacket connected to the thermostatic circulator (NCB-3100, TOKYO

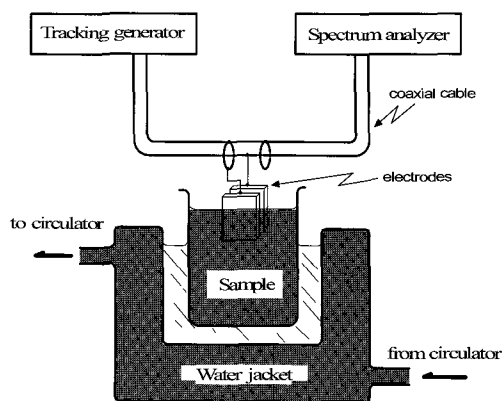


Fig. 1 Schematic figure of the experimental system employed in present study.

RIKAKIKAI). When a cell is filled with solution, an LC series resonance circuit will be formed. The resonance frequency of the circuit changed as a function of the permittivity (ϵ_r) of the solution. Using such setup, high frequency spectroscopic measurements were performed at the temperature between 30 °C and 60 °C. For the samples of $M_w=200$ and 1000, measurements were also performed between 15 °C and 40 °C. DSC measurements were also performed and compared with the results of high frequency measurement.

3. RESULTS AND DISCUSSION

Fig. 2 shows the high frequency spectra at several temperatures ($M_w=10000$, EO : H₂O = 1 : 10). The resonance frequency was observed at around 510MHz at 30°C. When solution temperature rose, resonance frequency was shifted to higher, and it was observed at around 540MHz at 60 °C.

The amount of resonance frequency shift (Δf) caused by such temperature change were shown in Fig. 3. The Δf was calculated by following equation.

$$\Delta f = f_t - f_0$$

Here f_0 is the resonance frequency obtained at measurement start ($t=0$), and f_t is the value observed at t minutes later. The solid line in the figure shows sample temperature. As Shown in Fig. 3, the samples were given cyclic temperature change between 30 °C and 60 °C. In the case of the sample with the molecular weight 10000 and molar ratio 10 of H₂O to EO, the Δf increased when the temperature rose, and decreased when the temperature fell. The sample with the molar ratio 5 of H₂O to EO showed same tendency. On the other hand, the sample with molar ratio 1 of water to EO showed quite different temperature dependency. In the first heating process, the Δf increased steeply at around 40 °C (around 50min. in time) and the temperature dependence of the Δf was opposite to former; the Δf decrease by heating and increase by cooling. Moreover, it turned out that the low water content sample shows larger change of Δf than the high water content sample. Considering that the crystallinity of PEO remains at low water concentration and that the rate of water molecule bound to PEO directly was high, it is thought that the

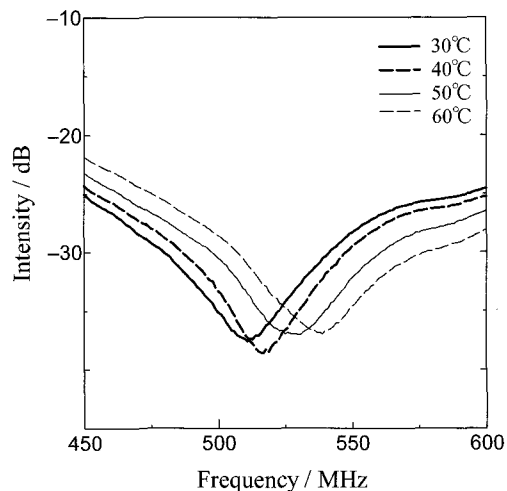


Fig. 2 The spectrum change of the high frequency spectra with the sample temperature.

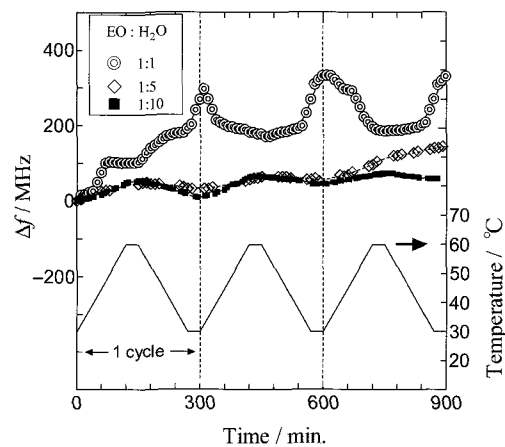


Fig. 3 Plots of the Δf vs. time for the PEO-H₂O system that have different water content, and the molecular weight of PEO is 10000.

large change of Δf observed at low water content sample was caused by crystallinity change of the PEO by temperature.

Crystallinity of PEO also changes by its molecular weight. So, same experiment was performed to PEO-H₂O mixed system of various molecular weights. The results were shown in Fig. 4. In the case of the sample with the molecular weight 1000 and molar ratio 1 of H₂O to EO, the steep increase of Δf was not observed in the first heating process. Other behavior was almost same as the results obtained from the sample of molecular weight 10000. However, in the case of molecular weight 1000 the shift width of Δf was decreased to 180MHz from 330MHz which obtained from the sample of molecular weight 10000. Furthermore, in the case of molecular weight 200 which have almost no crystallinity the change of Δf became very small. From these results, it is strongly suggested that the shifts of resonance frequency observed in the case of low water content samples were caused by the

bound state change of the water related to crystallinity change of the PEO.

The difference of Δf between molecular weight 10000 and 1000 is thought that the molecular weight 1000 has less crystallinity than 10000 at same temperature. So we performed high frequency spectroscopic measurement at lower temperature range for the sample of molecular weight 1000. Measurement was performed between 15 and 40°C lower than the melting point of PEO of the molecular weight 1000. The results were shown in Fig. 5. As shown in figure, about 50MHz of the high frequency shift was observed near 40°C, and after that the temperature dependency of the frequency shift changed to increase by cooling. Moreover, the amount of shift (Δf) increased to 350MHz which is almost equal to the result of a molecular weight 10000. These changes of properties were considered that the crystallinity of PEO having low molecular weight was increased by cooling to a temperature lower than the melting point.

As mentioned above, it is thought that the change of temperature dependency of resonance frequency

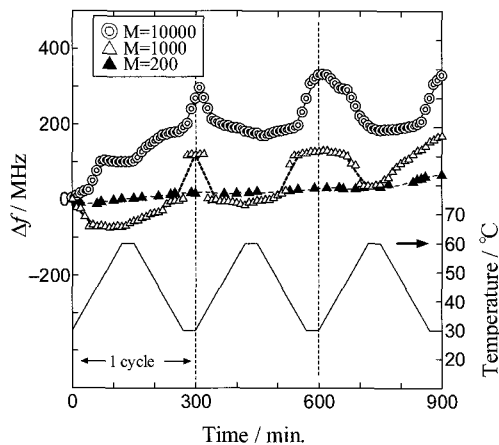


Fig. 4 Plots of Δf vs. time for the PEO-H₂O system that have different molecular weight and constant rate of water content (EO: H₂O=1:1).

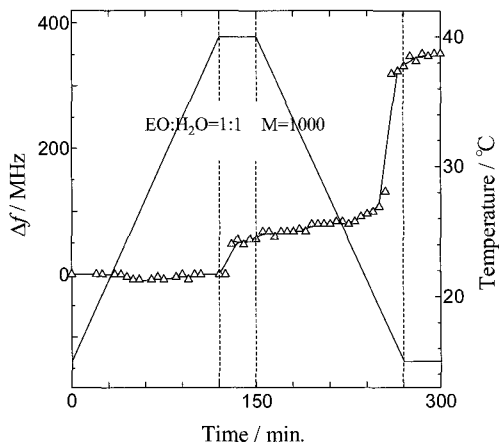


Fig. 5 Results of the measurement for lower molecular weight PEO at lower temperature range (15°C~40°C).

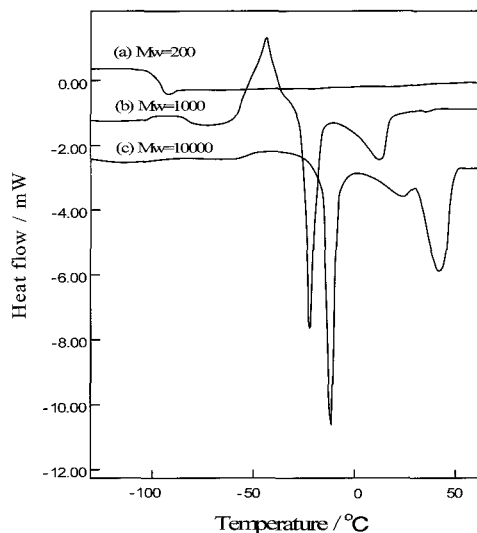


Fig. 6 Result of DSC measurement for the PEO-H₂O system that have different molecular weight and constant rate of water content (EO: H₂O=1:1).

obtained by high frequency measurement was related to the change of crystallinity of PEO and change of the bound state of the water which was accompanied with crystallinity change of PEO. Then, in order to consider the crystallinity of the sample, DSC measurements were performed to PEO-H₂O mixture. Results were shown in Fig. 6. Mixture with molar ratio 1 of water to EO was used as measurement sample. As shown in figure, the sample of molecular weight 10000 showed endothermic peak at 43°C. This result shows that the sample of molecular weight 10000 partially crystallized when the sample is cooled to 30°C. On the other hand, the sample of molecular weight 1000 showed the endothermic peak at 14°C. This result showed that the sample of the molecular weight 1000 had low crystallinity compared with the sample of the molecular weight 10000 at the temperature between 30 °C and 60 °C. Furthermore, the sample of molecular weight 200 showed no melting peak in the measurement temperature range, so it is clear that the crystallinity of PEO was not change during measurement. These crystallinity changes of the sample observed by DSC were shown a good agreement with the amount of Δf obtained by high frequency measurement.

From the above result, bound state change of the water accompanying a crystalline change of a PEO-H₂O mixture system is summarized as follows; in the case of the molecular weight 10000, a part of sample crystallizes during the preservation at 30°C, and this crystallized PEO melt in heating process. As described in introduction, the hydrophilicity of PEO becomes remarkably high by melting, and then the surrounding water is restricted strongly by PEO. Since the orientational polarization of water molecules will be obstructed if the water molecule is bound to PEO, the dielectric constant of the sample becomes low.— In such a case, it is detected as a high frequency shift of resonance frequency from the principle of a high

frequency spectroscopic method. This is the cause of the high frequency shift observed in the first heating process. Since re-crystallization of PEO will progress in hydrated state if it is cooled, many water molecule will be incorporated into the helix structure of PEO. This is considered to be the reason which resonance frequency shifted to the high frequency side at the cooling process. Since the crystallinity of the high water content sample is falling by hydration, the bound state of the water was not changed steeply by heating and cooling. For this reason, it is thought that the above resonance frequency shifts were not observed.

As described so far, we studied PEO-H₂O mixed system by high frequency spectroscopy and DSC, and found that high frequency spectroscopy can detect the change of the bound state of the water in polymer sensitively. Moreover, since the high frequency spectroscopy detects the bound state change of water directly, wide applications are expected for the macromolecule sample containing water such as a living body sample.

REFERENCES

- [1] Y. Mori, S. Nagaoka, H. Takiuchi, T. Kikuchi, N. Noguchi, H. Tanzawa and Y. Noishiki, *Trans. Am. Soc. Artif. Intern. Organs*, **28**, 459(1982).
- [2] A. Kishida, K. Mishima, E. Corretge, H. Konishi and Y. Ikada, *Biomaterials*, **13**, 113(1992).
- [3] Y. C. Tseng and K. Park, *J. Biomed. Mater. Res.*, **26**, 373(1992).
- [4] W. R. Gombotz, W. Guanghai, T. A. Horbett and A. S. Hoffman, *J. Biomed. Mater. Res.*, **25**, 1547(1991)
- [5] K. L. Smith and R. Van Cleve, *Ind. Eng. Chem.*, **50**, 12(1958).
- [6] N. B. Graham, M. Zulfiqar, N. E. Nwachuku and A. Rashid, *Polymer*, **31**, 909(1990).
- [7] N. B. Graham and C. F. Chen, *Eur. Polym. J.*, **29**, 149(1993).
- [8] S. Lusse and K. Arnold, *Macromolecules*, **29**, 4251(1996).
- [9] T. Takei, Y. Sugitani, C. Amano and Y. Nishimoto, *Bunseki Kagaku*, **45**, 903(1996).
- [10] T. Takei, C. Amano, Y. Nishimoto and Y. Sugitani, *Anal. Sci.*, 1997, 13, 1043.
- [11] N. Nishi and K. Yamamoto, *J. Am. Chem. Soc.*, **109**, 7353(1987).
- [12] A. Coccia, P. L. Indovia, F. Podo and V. Viti, *Chem. Phys.*, **7**, 30(1975).
- [13] Y. Amo and Y. Tominaga, *Chem. Phys. Lett.*, **320**, 703(2000).
- [14] T. Takei, K. Kurosaki, Y. Nishimoto and Y. Sugitani, *Anal. Sci.*, 2002, **18**, 681(2002).

(Received January 3, 2008 ; Accepted June 16, 2008)