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ARTICLES

Broadband Dielectric Study of Dynamics of Poly(vinyl pyrrolidone)−Ethylene Glycol Oligomer Blends

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Broadband dielectric measurements for blends of poly(vinyl pyrrolidone) (PVP) and ethylene glycol oligomer (EGO) from 0 to 40 wt % PVP were carried out at 25 °C in the frequency range from 20 Hz to 20 GHz. The EGOs used in this study were ethylene glycol (EG), diethylene glycol (2EG), and PEG400 (MW = 400). For the PVP−EG, −2EG, and −PEG400 blends, relaxation processes caused by the motion of EGO in the GHz range and the micro-Brownian motion of the PVP chain at 10 kHz−1 MHz were observed. Although the PVP−EGO blend is miscible, relaxation processes caused by the molecular motion of EGO and the local chain motion of PVP were observed individually. The relaxation time of the local chain motion of PVP showed a strong PVP concentration dependence and a solvent viscosity dependence, which are similar to those reported so far for the solutions in nonpolar solvents.

Introduction

Polymer−solvent interactions, the dynamics of solvent molecules, and the micro-Brownian motion of polymer chains in a complex system are the most important subjects in the physics of polymer solution. Poly(vinyl pyrrolidone) (PVP) is an amorphous and nontoxic synthetic polymer, which has a randomly coiled and highly flexible chain behavior in polar solvents. The solubility of PVP in hydroxyl group-containing solvents, such as water, ethanol, ethylene glycol oligomer (EGO), i.e., low molecular weight poly(ethylene glycol) (PEG), and glycerol, is due to the formation of hydrogen bonds between the carbonyl groups of the PVP monomer units and the hydroxyl group/s of the solvents. The dielectric behavior of PVP solvation has been studied extensively in water,[1−11] alcohol,[12,13] and EGO.[14,15] Furthermore, it has also been studied in dimethyl sulfoxide (DMSO),[16] tetramethylurea (TMU),[16,17] *N*-methyl-2-pyrrolidone (NMP),[11] and pyrrolidone,[18] with a concentration variation, by dielectric spectroscopy. Earlier,[19−21] PVP−EGO and PVP−ethanol systems were investigated in dilute solutions of nonpolar solvents to investigate the dynamics of solvent in the polymer solutions. These studies were particularly performed to investigate the relationship between the dynamics and molecular structure of solvent.

Feldstein and co-workers[22−29] studied the PVP−PEG400 blend and they proposed the formation of a complex of PVP and PEG molecules in the blend. The appearance of two glass transitions for the macroscopically homogeneous mixture was interpreted to be due to the microscopic heterogeneous structures. The glass transition phenomena originate from the structural relaxation of local structure; thus, these results forced the authors to investigate the broadband dielectric behavior of this blend, with a concentration variation, to the dynamics of EGOs of different repeat units, and the segmental motion of PVP. Furthermore, it is interesting to investigate the dynamics of solvent molecules of different chain lengths and their effect on the segmental motion of PVP.

In the present paper, to clarify the local chain motion of PVP, we investigated the broadband dielectric behavior in the frequency range of 20 Hz to 20 GHz using different advanced measurement techniques. The dielectric behavior of PVP with different EGO molecules of repeat units 1, 2, and 9 was investigated by using 0−40 wt % PVP at 25 °C.

Experimental Section

The polymer investigated in this work was poly(vinyl pyrrolidone) (PVP; average molecular weight MW = 40 000) obtained from Sigma. Ethylene glycol (EG), diethylene glycol (2EG), and poly(ethylene glycol) (9EG) (PEG400) were used in these experiments. EG was purchased from Wako Pure Chemical Industries and 2EG and PEG400 were purchased from Aldrich. These materials were kept in a drybox with a relative humidity of less than 2% at 25 °C for more than 10 days before the mixing of PVP and EGO. The water contents determined by Karl Fischer for EGO and gravity measurement values before and after heating with an infrared heater at 105 °C for PVP were less than 1% and 3%, respectively. Therefore, the contribution of the dielectric strength of water was approximately less than 1.5. The PVP−EG, PVP−2EG, and PVP−PEG400 blends with a concentration variation were prepared in the range of 0−30, 0−30, and 0−40 wt % of PVP, respectively.

Dielectric measurements were performed in the frequency range of 20 Hz to 20 GHz, using a time domain reflectometry

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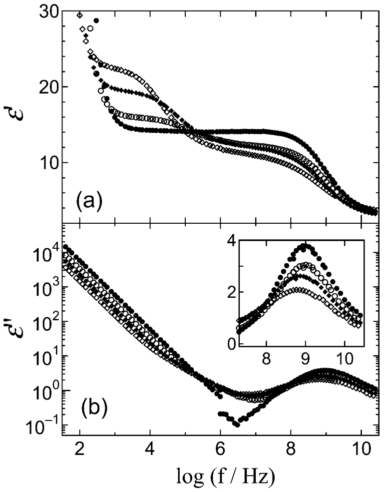

Figure 1. Frequency dependences of dielectric constant (a) and loss (b) of PVP-PEG400 blends prepared with various PVP concentrations at 25 °C: pure PEG400, ●; PVP-PEG blend with 10 wt % PVP, ○, 20 wt % PVP, ◆, and 30 wt % PVP, ◇. The inset shows the dielectric loss around the loss peak.

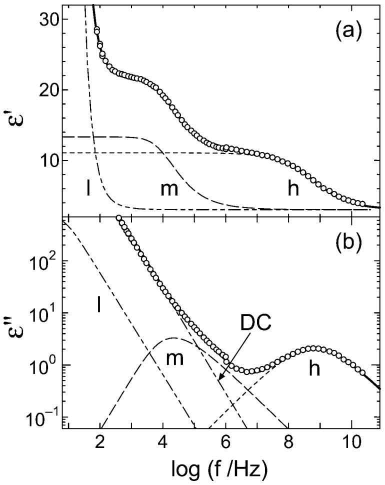

Figure 2. Frequency dependences of dielectric constant (a) and loss (b) of PVP-PEG400 with 30 wt % PVP. The lines were drawn by using eq 1: dashed double dotted line, l-process; dashed line, m-process; dotted line, h-process; solid line, summation of three relaxation processes; dashed dotted line, contribution of dc conductivity.

(TDR) (Hewlett-Packard 54124T) (100 MHz−20 GHz), an impedance/material analyzer (Hewlett-Packard 4291A) (1 MHz−1.8 GHz), and an LCR meter (Hewlett-Packard 4284A) (20 Hz−1 MHz) at 25 °C. The detailed explanations for the apparatus and procedures of the system were previously reported.[30,31]

Results

Figure 1 shows the concentration dependence of the dielectric constant and loss of the PVP−PEG400 blends prepared with 0, 10, 20, and 30 wt % PVP at 25 °C. Similar concentration dependence plots were also obtained in the PVP−EG and PVP−2EG blends in the same frequency range. The dielectric constant and loss for the 30 wt % PVP−PEG400 blend in the frequency range of 20 Hz to 20 GHz at 25 °C are shown in Figure 2.

The dielectric constant and loss for the PVP−EG, −2EG, and −PEG400 mixtures at various concentrations could be described by the simple summation of three relaxation processes and the contribution of dc conductivity by the following equation

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_\mathrm{h}}{\{1 + (j\omega\tau_\mathrm{h})^{\beta_\mathrm{h}}\}^{\alpha_\mathrm{h}}} + \Delta\epsilon_\mathrm{m}\int_0^\infty \left(-\frac{\mathrm{d}\Phi_\mathrm{m}}{\mathrm{d}t}\right)\exp(-j\omega t)\,\mathrm{d}t + \frac{\Delta\epsilon_\mathrm{l}}{1 + (j\omega\tau_\mathrm{l})^{\beta_\mathrm{l}}} - j\frac{\sigma}{\epsilon_0\omega} \quad (1)$$

for

$$\Phi_\mathrm{m} = \exp\left[-\left(\frac{t}{\tau_\mathrm{m}}\right)^{\beta_\mathrm{K}}\right]$$

where ω is the angular frequency, t is the time, ϵ_0 is the dielectric constant in a vacuum, ϵ_∞ is the limiting high-frequency dielectric constant, $\Delta\epsilon$ is the relaxation strength, τ is the relaxation time, α and β are the asymmetric and symmetric broadening parameters ($0 < \alpha, \beta \le 1$), respectively, and σ is the conductivity. The subscripts h, m, and l denote the high-, middle-, and low-frequency processes, respectively. The h-, m-, and l-processes can be described well by the Havriliak−Negami equation,[32] the Kohlrauch−Williams−Watts function,[33] and the Cole−Cole equation,[34] respectively. The relaxation times of the h- and m-processes were not determined with these equations. They were determined from the dielectric loss peak frequency f_p by using $\tau = 1/2\pi f_\mathrm{p}$. The relaxation times in the empirical equations have no physical meaning. Furthermore, the way to estimate the relaxation time is still controversial. Therefore, in this paper, we use the relaxation time derived from the loss peak frequency because it is model free and statistically equivalent to the mode relaxation time. The dielectric loss peak of the h-process was clearly observed for all the mixtures measured. However, the dielectric loss peak of the m-process was covered by the slope of the l-process. In this case, the curve-fitting procedure was carried out mainly for the dielectric dispersion, and the loss peak frequencies of the curve given by eq 1 were employed. The accuracies of the loss peak frequencies, i.e., the relaxation times of the m- and h-processes, were within ±0.2 and ±0.1 digits, respectively.

Figure 2 shows that the frequency at the dielectric loss peaks of the m-process is approximately five decades lower than that of the h-process. The low-frequency side of the dielectric constant could be described by the l-process, but the contribution of dc conductivity was necessary to describe the low-frequency side of the dielectric loss. The low-frequency process with a large relaxation strength is caused by the electrode polarization. When an electric field was applied to the materials, large values of dielectric constant and loss due to the long-range drift of ions and barrier layer formation on the electrode surface were observed, and dielectric spectra were described by using certain model equations.[35−38] It has been proposed that the electrical properties of the sample−electrode interface lead to large low-frequency tails of complex permittivity. The loss peak of the l-process was outside the low-frequency limit of our experiment and only its high-frequency tail was observed. Thus, its relaxation parameters could not be correctly determined. To extract information on the m- and h-processes, we assumed the dielectric loss peak of the l-process far below our low-frequency limit and the appropriate relaxation strength and shape parameters were given. Then the contributions of electrode polarization and dc conductivity were subtracted from the dielectric spectra.

Figure 3 shows the plots of $\Delta\epsilon_\mathrm{h}$ and $\Delta\epsilon_\mathrm{m}$ versus PVP concentrations, C_PVP (wt %), for the PVP−EG, PVP−2EG, and PVP−PEG400 blends. The h-process is observed for pure EGO

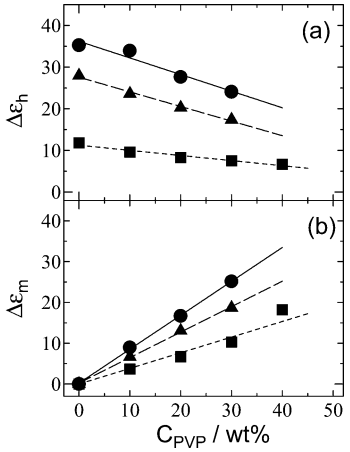

Figure 3. Plots of relaxation strength of the h-process (a) and the m-process (b) against concentration of PVP, C_{PVP}, for PVP-EGO blends with ethylene glycol, ●, diethylene glycol, ▲, and PEG400, ■, at 25 °C. Lines are linear fits through the data points.

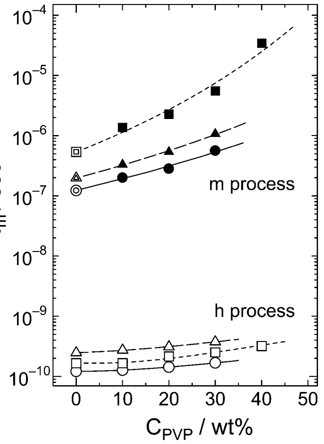

Figure 4. PVP concentration, C_{PVP}, dependences of relaxation times of h- (open symbols) and m- (filled symbols) processes for PVP−EGO blends with ethylene glycol, circle; diethylene glycol, traiangle; and PEG400, square, at 25 °C. Double symbols are the extrapolated values to $C_{PVP} = 0$ wt % from the relaxation time of 10 to 30 or 40 wt % PVP−EGO blend.

and its relaxation strength decreases with increasing PVP concentration. The decrease in $\Delta\epsilon_h$ with an increase in C_{PVP} is due to an increase in the density of EGO molecules. This implies that the molecular motion of EGO induces the h-process.

The relaxation strength of the m-process increases with PVP concentration and it vanishes in pure EGO, as shown in Figure 3b. The relaxation strength of the m-process depends on the EGO molecular size. The relaxation strength of the h-process depends on the EGO molecular size. In this case, the internal electric field due to the dielectric constant of the h-process at a frequency higher than that of the m-process affects the dipole moment contributing to the m-process. Figure 4 shows the PVP concentration dependences of the relaxation times of the h- and m-processes for the PVP−EG, PVP−2EG, and PVP−PEG400 blends. The concentration dependences of the relaxation time of the m-processes are larger than those of the h-processes.

Discussion

The occurrence of two peaks in our earlier dielectric studies on PVP10000−water mixtures[1,2] over the frequency range of 10^6−10^{10} Hz with use of the TDR suggested that the high-frequency process was due to the rotational diffusion of water clusters, whereas the low-frequency process was attributed to the water molecules bound to the PVP chain, i.e., the segmental motion of PVP along with the water molecules bound to it. However, the low-frequency process detected in these studies was incorrect due to the wrong choice of time window in the TDR measurements. The limit in time window produced a truncation error in dielectric constant and loss around the frequency range corresponding to the reciprocal of the time window. The error resembles a relaxation process. We measured the PVP−water mixtures again using the TDR, impedance analyzer, and LCR meter, and the relaxation process of PVP was observed in the frequency range lower than the experimental results in the literature.[1,2] We measured the dielectric complex permittivity down to 20 Hz, and the relaxation process of PVP in the blends was clearly detected in the frequency range of 10 kHz−1 MHz. According to our recent experimental results of PVP−alcohol mixtures with various types of alcohol,[39] the relaxation process of PVP was observed in the frequency range of 10 kHz−10 MHz, in which the relaxation process of PVP for the PVP−EG, −2EG, and −PEG400 blends presented in this paper was observed. The relaxation time of the isolated PVP chain was estimated by extrapolation to the zero PVP concentration of the concentration dependence of the relaxation time of PVP in PVP−alcohol mixtures. The relaxation time of the isolated PVP chain was found to depend on the viscosity of alcohol.

Here, we consider our results for the m-process with a variation in PVP concentration (C_{PVP}) in the blends. Figures 1 and 2 indicate that there are three types of relaxation processes in the studied blends over the frequency range of 20 Hz to 20 GHz. The relaxation time of the m-process shows an extremely large concentration dependence compared with that of the h-process, as shown in Figure 4. This large concentration dependence is due to the larger moving unit of the m-process than that of the EGO molecules contributing to the h-process. The interactions among the PVP chain are the main cause of the increase in the relaxation time of the m-process with increasing PVP concentration. Such a large concentration dependence is also observed for the local chain motion of polymer in nonpolar solvent.[40−42] In a polymer solution, the solvent behaves as the free volume for the local chain motion of polymer. The increase in PVP density reduces the free volume for the rearrangement of the PVP chain provided by the EGO molecules with an increase in the relaxation time of the m-process.

The relaxation time of the m-process increases with PVP concentration for all the blends. In pure EGO, the m-process does not exist, but the plots given by double lines for pure EGO in Figure 4 indicate the values extrapolated from the concentration dependence of the relaxation time of the m-process observed for the blends, $\tau_m(C_{PVP}{=}0)$. The extrapolation was carried out by using an equation that described well the relationship between the dielectric loss peak of the local chain motion of polymer and the concentration of polymer in polymer solution with nonpolar solvent.[41] In such a case, the polymer concentration dependence of relaxation time is described by

$$\log \tau = \log \tau_0 - \frac{BC}{C - C_\infty} \tag{2}$$

where τ is the relaxation time, C is the concentration of polymer, τ_0 is the relaxation time at infinite dilution of polymer, C_∞ is the polymer concentration at which relaxation time becomes infinity, and B is a parameter for the degree of concentration dependence of relaxation time. $\tau_m(C_{PVP} = 0)$ implies the relaxation time of the isolated PVP molecule in the infinite dilution of PVP. $\tau_m(C_{PVP}{=}0)$ is plotted against the dielectric

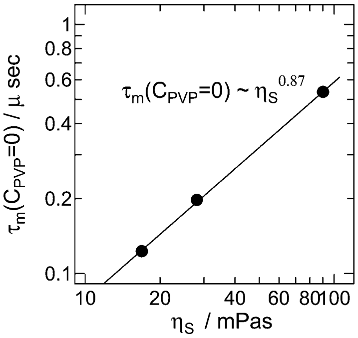

Figure 5. Plot of relaxation time of the m-process extrapolated to infinite dilution of PVP, $\tau_m(C_{PVP}=0)$, for PVP−EGO blends against viscosity of pure EGO, η_s. The line is a linear fit through the data points.

relaxation time and viscosity of the solvent, i.e., pure EGO, as shown in Figure 5. $\tau_m(C_{PVP}=0)$ depends on the viscosity of pure EGO, η_S, and their relation is obtained by using Figure 5 as

$$\tau_m(C_{PVP}=0) \propto \eta_S^{0.87} \tag{3}$$

The relationship between the dielectric relaxation time of the polymer in dilute solution and solvent viscosity was reviewed.[43] The relationship between the dielectric relaxation time of the local chain motion of isolated polymer and the viscosity of solvent has at times been discussed. According to the Debye−Stokes equation,[44] this relationship is given by

$$\tau = \frac{V\eta_S}{k_B T} \tag{4}$$

in which k_B is the Boltzmann constant, V is the effective volume of a moving unit, and T is the absolute temperature. The proportionality between the relaxation time of the local chain motion of isolated polymer and the viscosity of solvent was reported experimentally for the polymer solutions with nonpolar solvents, as determined by dielectric[45] and fluorescence depolarization spectroscopy.[46] On the other hand, Adolf et al. reported $\tau \approx \eta_S^{0.74}$.[47] The exponent obtained for the PVP−EGO mixtures is the same as that for the nonpolar solvent. The local chain motion of polymer is not a simple rotational motion of sphere, because the dipole moments are on the covalently bonded chain structure. In addition, the real motions of dipole moments on PVP chains are correlated with each other, and the carbonyl and imide groups on PVP molecules and the hydroxyl group at the end of EGO molecules are connected by hydrogen bonds. Despite the existence of hydrogen bonds between PVP and EGO molecules, the local chain motion of PVP is treated as the motion in homogeneous viscous media, similarly to the polymer chain motion in a nonpolar solvent. The difference between the exponents of the relationship between the dielectric relaxation time of polymer and the solvent viscosity in our result and those in the literature[45−47] is considered to be due to the difference between the macroscopic η_S and a microscopic viscosity of solvent in the vicinity of the polymer chain. The microscopic viscosity is determined by the polymer−solvent interaction. To clarify the physical meaning of these exponents, more systematic studies of this relationship in polymer solutions with various polymers and solvents are required.

Conclusion

Broadband complex dielectric data of PVP−EGO blends are characterized by three relaxation processes, i.e., the h-, m-, and l-processes, corresponding to the motion of EGO, the local chain motion of PVP, and electrode polarization, at 25 °C. Despite the fact that the PVP−EGO blend is miscible, two distinct time scale motions coexist. The molecular motions of EGOs have a small relaxation time, similar to the hydrogen-bonded molecular liquid with a high mobility. On the other hand, the local chain motion of PVP shows a characteristic behavior, i.e., the solvent−viscosity-dependent relaxation time of the local chain motion of the polymer, that is similar to those reported so far for the solutions of nonpolar solvent.

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