

Broadband Dielectric Study of Dynamics of Polymer and Solvent in Poly(vinyl pyrrolidone)/Normal Alcohol Mixtures

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Broadband dielectric measurements of poly(vinyl pyrrolidone) (PVP)–monohydroxyl alcohol mixtures of various normal alcohols with the number of carbon atoms per molecule ranging from 1 to 9 were made in the frequency range of 20 Hz to 20 GHz at 25 °C. Two relaxation processes due to the reorientation of dipoles on the PVP and alcohol molecules were observed. The relaxation process at frequencies higher than 100 MHz is the primary process of alcohols, and that at frequencies lower than 10 MHz is attributed to the local chain motion of PVP. For mixtures of alcohol molecules that are smaller than propanol, the relaxation time of the alcohol increases with increasing PVP concentration, whereas for mixtures of alcohol molecules larger than butanol, the relaxation time of the alcohol decreases with increasing PVP concentration. The increase in the density of hydrogen-bonding sites upon the addition of PVP reduces the relaxation time of alcohol in the mixture, and vice versa. The relaxation time of the local chain motion of PVP increases with PVP concentration and solvent viscosity. Different time scales of the molecular motions of polymer and solvent coexist in homogeneous mixtures with hydrogen-bonded polar solvent and polymer.

Introduction

The dynamics of solvent molecules and the micro-Brownian motion of polymer chains govern various physical and chemical properties of polymer solutions. In addition, the dynamics of polymer solutions can be effectively treated as a simple and fundamental model system for molecular motions directly related to the functions of biopolymers.

Poly(vinyl pyrrolidone) (PVP) is a semicrystalline and nontoxic synthetic polymer that exists as a randomly coiled and highly flexible chain in polar solvents. Molecular interactions between PVP and solvent molecules change the dynamics of neat components. The dynamics of polymer solutions has been investigated by dielectric relaxation spectroscopy. Dielectric studies of PVP solutions have provided various important pieces of information on molecular dynamics, the degree of intermolecular interaction, and cooperativity between guest and host molecules. Furthermore, the solvent molecular structure dependences of the dielectric properties of PVP solutions show various characteristic properties. The dielectric behavior of PVP solutions has been extensively studied in water,^{1–12} alcohol,¹³ and ethylene glycol oligomer (EGO).^{14,15}

Despite the fact that the dielectric relaxation process of polymers in solutions of a nonpolar solvent has been studied extensively, only a few results have been reported on the observation of the dynamics of polymers in solutions of a polar solvent in a solvent-rich region.^{11,12,14,15} The difficulty in the observation is caused by the existence of the large contributions of conductivity and electrode polarization. Even if the local chain motion of a polymer existed at frequencies lower than those of the polar solvent, the dc conductivity and electrode polarization would mask the relaxation process of the chain motion. In this case, the local chain motion of the polymer should be detected with a large error^{11,12} or not detected at all.¹⁶ In addition, the

observation of the dielectric relaxation processes of both solvent and solute polymers requires an extremely wide frequency range. Therefore, the systematic experimental study of a polymer chain in a polar solvent has not yet been carried out.

Alcohols are well-known hydrogen-bonding molecular liquids. Various types of alcohol are available, from which we can obtain information on the alcohol structure dependences of physical and chemical properties systematically. The hydroxyl groups of alcohol can form hydrogen bonds, which cause various unique properties. The dielectric properties of alcohols and their water mixtures have been studied extensively.^{17–31} The large dipole moment of the hydroxyl group results in a large primary process and small secondary processes.^{17–23} The large primary relaxation process is considered to be due to the cooperative reorientational motion of alcohol molecules accompanying the formation and deformation of intermolecular hydrogen bonds. On the other hand, the secondary processes are thought to be due to a local reorientation of the hydroxyl groups.

We reported the dielectric relaxation process of PVP in water mixtures with various PVP concentrations at 25 °C.² However, the relaxation processes observed in the frequency range from 300 kHz to 100 MHz reported in our previous papers^{1,2,13} were incorrect owing to the wrong choice of time window for the time domain reflectometry (TDR) measurements. The limited time window produced a truncation error in the dielectric constant and loss in the frequency range corresponding to the reciprocal of the time window. The truncation error resembles a relaxation process. In addition, to subtract the contribution of the dc conductivity of the PVP–water mixtures, we used NaCl aqueous solution as a reference sample for the time domain measurements. The difference in the high-frequency tail of the electrode polarization between the reference sample and the PVP–water mixture affected the dielectric spectrum observed below 100 MHz. Therefore, experimental results below 100 MHz in the previous papers^{1,2,13} were not reliable.

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In this work, broadband dielectric measurements of PVP/alcohol mixtures with various normal alcohol structures and PVP concentrations were made in the frequency range of 20 Hz to 20 GHz at 25 °C. To carry out a reliable observation of the relaxation process caused by the polymer chain dynamics, we introduced the frequency-domain apparatus of an impedance analyzer and an LCR meter for measurement in the frequency range from 1.8 GHz to 20 Hz. According to the experimental results, the relaxation processes caused by the primary relaxation process of alcohol and the local chain motion of PVP were observed. The relaxation process of PVP can be detected in a frequency range lower than those in the previous reports.^{1,2,13} The observation of the dynamics of both the solvent and the polymer can provide important information on the interactions between polar solvents and polymers.

Experimental Section

Monohydroxyl alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-nonanol) were used as the solvents of the mixtures. The nonanol was purchased from Aldrich, and the other alcohols were purchased from Waco Pure Chemical Industry. Alcohols were used without further purification. PVP with an average molecular weight of 40 000, purchased from SIGMA, was used for all the PVP/alcohol mixtures. Distilled and deionized water with an electrical conductivity lower than 18.3 $\mu\text{S/m}$ was obtained from an ultrapure water product (Millipore, MILLI-Q Lab.). The PVP was kept in a drybox with a relative humidity of less than 2% at 25 °C for more than 10 days before mixing with alcohol. The water contents of the alcohols were less than 2 wt %. The water content of the PVP, determined from the weights before and after heating with an infrared heater at 105 °C, was 4%. Therefore, the contribution of water to dielectric strength was less than approximately 1.5. Alcohols and water were mixed with dry PVP at PVP concentrations of 10–50 wt %. These mixtures were kept at ambient temperature for at least one week until they were completely mixed.

Dielectric measurements were performed in the frequency range from 20 Hz to 20 GHz by time domain reflectometry (TDR) (Hewlett-Packard 54124T, 100 MHz–20 GHz), an impedance/material analyzer (Hewlett-Packard 4291A, 1 MHz–1.8 GHz), a precision impedance analyzer (Agilent Technologies 4294A, 40 Hz–110 MHz), and an LCR meter (Hewlett-Packard 4284A, 20 Hz–1 MHz) at 25 °C. A flat-end coaxial probe with a geometrical capacitance of 1.35×10^{-2} pF (electric length of 0.16 mm) was used for the dielectric measurements by TDR in the frequency range above 1 GHz. Details of the apparatus and the procedures of TDR were reported previously.^{30,31} A coaxial cylindrical cell with a geometrical capacitance of 0.20 pF was used for the measurements with the impedance/material analyzer and that with 0.24 pF for the measurements with the impedance analyzer and LCR meter. The viscosities of the pure alcohols were measured with capillary viscometers at 25 °C.

Results

Figure 1 shows the dielectric constants and losses for PVP–1-hexanol mixtures with various PVP concentrations at 25 °C. Similar plots were obtained for other PVP–alcohol mixtures in the same frequency range. The dielectric loss peak for the high-frequency process is observed in the frequency range from 100 MHz to 1 GHz. Its strength decreases and the shape of the loss peak becomes broader with increasing PVP concentration. In the frequency range of 10 kHz to 1 MHz, a process at

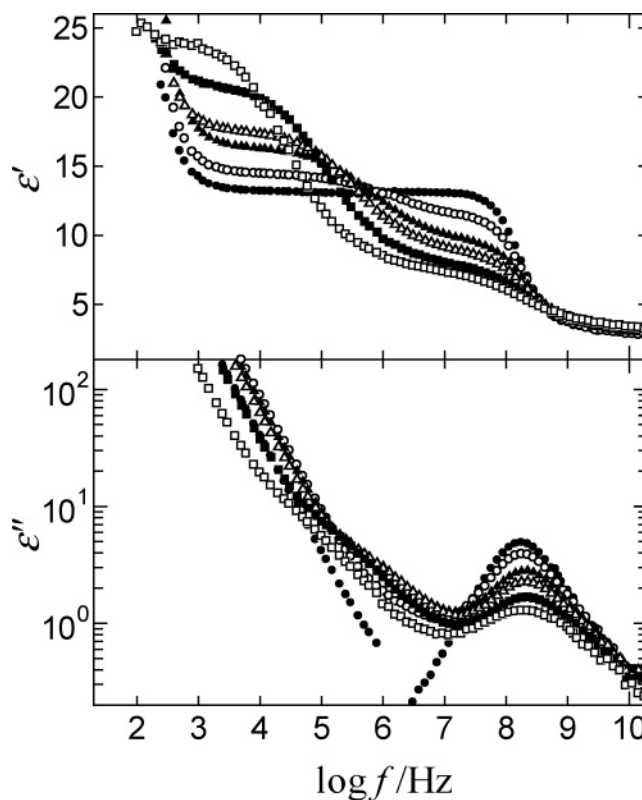


Figure 1. Dielectric constants and losses for PVP/1-hexanol mixtures with various PVP concentrations at 25 °C. The symbols in the figure indicate the PVP concentrations of the PVP–hexanol mixtures: ●, 0 wt % (pure hexanol); ○, 10 wt %; ▲, 20 wt %; △, 30 wt %; ■, 40 wt %; and □, 50 wt %.

intermediate frequencies is observed. In the frequency range below 1 kHz for the dielectric constant and below 10 or 100 kHz for the dielectric loss, these values increase with decreasing frequency. To characterize these processes, curve fitting procedures were carried out. The dielectric constant and loss for the PVP–alcohol and –water mixtures with various concentrations can be described as a simple summation of three relaxation processes and a contribution of dc conductivity as

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_h}{\{1 + (j\omega\tau_h^{\text{HN}})^{\beta_h}\}^{\alpha_h}} + \Delta\epsilon_m \int_0^\infty \left(-\frac{d\Phi_m}{dt}\right) \exp(-j\omega t) dt + \frac{\Delta\epsilon_l}{1 + (j\omega\tau_l)^{\beta_l}} - j\frac{\sigma}{\epsilon_0\omega} \quad (1)$$

for $\Phi_m = \exp[-(t/\tau_m^K)^{\beta_K}]$. Here, ω is the angular frequency, t is the time, j is the imaginary unit given by $j^2 = -1$, ϵ_0 is the dielectric constant in 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 ($0 < \alpha, \beta \leq 1$), respectively, β_K is the asymmetric broadening parameter ($0 < \beta_K \leq 1$) of the Kohlrausch–Williams–Watts (KWW) function,³² and σ is the conductivity. The subscripts h, m, and l denote the high-, middle-, and low-frequency processes, respectively. The superscripts HN and K denote the Havriliak–Negami equation³³ and the KWW function,³² respectively. The h-, m-, and l-processes can be described well by the Havriliak–Negami equation, the KWW function, and the Cole–Cole equation,³⁴ respectively. Figure 2 shows the dielectric constants and losses for a 30 wt % PVP–hexanol mixture with lines obtained from eq 1. The

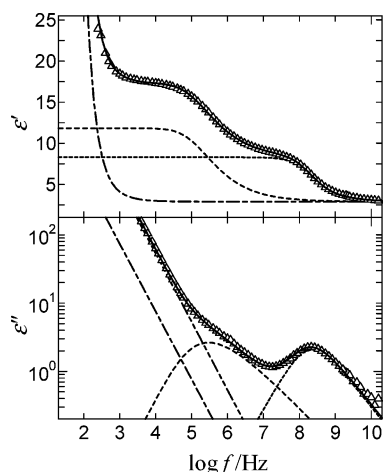


Figure 2. Dielectric constants and losses for 30 wt % PVP/1-hexanol mixtures at 25 °C. The lines were drawn using eq 1: dotted line, h-process; dashed line, m-process; dot-dash line, l-process; and double-dot-dash line, dc conductivity.

relaxation times of the h- and m-processes were not simply determined by using τ_h^{HN} and τ_m^K in eq 1. The relaxation times were determined from the dielectric loss peak frequency of the h- and m-processes, f_{ph} and f_{pm} , using $\tau_h = 1/2\pi f_{\text{ph}}$ and $\tau_m = 1/2\pi f_{\text{pm}}$, respectively. The relaxation times in the empirical equations have no physical meaning. Furthermore, the method of estimating the relaxation time is still controversial. Therefore, in this study, we use the relaxation time derived from the loss peak frequency, because it is model-free and the most probable relaxation time. The dielectric loss peak of the l-process was outside the low-frequency limit of our measurement, and only its high-frequency tail was observed. Thus, the relaxation parameters of the l-process could not be correctly determined. To extract information on the m- and h-processes, we assumed the dielectric loss peak frequency of the l-process as being below our low-frequency limit, and appropriate relaxation strength and shape parameters were given. 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. Then, the contributions of the l-process and dc conductivity were subtracted from the dielectric spectra. The l-process is caused by electrode polarization. Upon applying an electric field to the material, large dielectric constants and losses due to long-range drift of ions and barrier layer formation at the electrode surfaces have been observed, and attempts have been made to describe such dielectric spectra by using some model equations.^{35–38} It has been proposed that the electrical properties of sample-electrode interfaces lead to the large low-frequency tails of the complex permittivity. The relaxation parameters for the h- and m-processes thus obtained are listed in Table 1.

From the experimental results of dielectric complex permittivity at frequencies up to the THz range for methanol, ethanol, and propanol, two relaxation processes were observed at the higher-frequency side of the primary process.^{17–23} In the vicinity of the high-frequency limit of our dielectric measurement, their small contributions can be recognized in the dielectric constant and loss. However, we neglected the contributions for the curve-fitting procedure, since the evaluations of the relaxation time and strength of the primary process of the alcohols (h-process) and the conclusion of this study are not affected.

Figure 3 shows plots of the dielectric relaxation strengths, $\Delta\epsilon_h$ and $\Delta\epsilon_m$, of the h- and m-processes, respectively, against PVP concentration, $C_{\text{PVP}}(\text{wt}\%)$. The h-process is observed for

pure alcohols and $\Delta\epsilon_h$ decreases with increasing PVP concentration. This decrease is due mainly to a decrease in the density of alcohol molecules. This implies that the h-process is the primary relaxation process of alcohol. The m-process is not observed for any of the pure alcohols and $\Delta\epsilon_m$ increases with increasing PVP concentration. $\Delta\epsilon_m$ depends on alcohol structure, and a mixture with larger $\Delta\epsilon_h$ shows larger $\Delta\epsilon_m$. 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 plots of the relaxation times, τ_h and τ_m , of the h- and m-processes, respectively, observed for various PVP–alcohol mixtures. τ_h depends on alcohol structure and is in the range of 10 ps to 1.5 ns. τ_m is at least several hundred times larger than τ_h . The τ_h value of the smaller alcohol at $C_{\text{PVP}} = 0$ has a smaller relaxation time and their PVP concentration dependence is large. However, the larger alcohol shows a larger τ_h value at $C_{\text{PVP}} = 0$ and a smaller PVP concentration dependence. τ_m increases with increasing PVP concentration for all the mixtures, and its concentration dependence is stronger than that of τ_h .

Discussion

A. Relaxation Process of Polymer. The local chain motion of polymers has been studied in a nonpolar solvent,^{39–45} PVP–EGO blends,¹⁵ and PVP–water and PVP–methanol mixtures.^{11,12} In the experimental results obtained at around room temperature,^{15,39–45} the local chain motions of polymers were usually observed in the same frequency range as that of the m-process, and the asymmetric shape of dielectric loss was observed to be the same as that for the m-process. The values extrapolated from the relaxation time of PVP observed at lower temperatures^{11,12} agree with those of the m-process. The concentration dependences of the relaxation time and relaxation strength also support the fact that the m-process originates from the local chain motion of PVP. Therefore, the PVP–alcohol mixture is a highly suitable system for the systematic investigation of the dynamics of a polymer chain in a polar solvent.

The relaxation time of the m-process, τ_m , shows an extremely strong concentration dependence compared with that of the h-process, as shown in Figure 4. This strong concentration dependence is due to the larger moving unit of the m-process than that of the alcohol 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. Such a strong concentration dependence is also observed for the local chain motion of polymers in a nonpolar solvent.^{39–45} In this case, the solvent provides a free volume for the local chain motion of polymers. The increase in PVP density reduces the free volume for the rearrangement of PVP chains with an increase in the relaxation time of the m-process.

The relaxation time of the m-process increases with PVP concentration in all the mixtures. In pure alcohols, the m-process does not exist, but the plots denoted by crosses for pure alcohols in Figure 4 indicate the values extrapolated from the concentration dependence of the relaxation time of the m-process observed for the mixtures, τ_{m0} . The extrapolation was carried out by using an equation applied to the polymer solution with a nonpolar solvent.⁴⁰ In such a case, the polymer concentration dependence of τ_m is described by

$$\log \tau_m = \log \tau_{m0} + \frac{BC}{C_\infty - C} \quad (2)$$

TABLE 1: Dielectric Relaxation Parameters for PVP–Alcohol and Water Mixtures at 25 °C

mixtures	C_{PVP} (wt %)	ϵ_∞	h-process				C_{PVP} (wt %)	m-process		
			$\Delta\epsilon_h$	τ_h (s)	α_h	β_h		$\Delta\epsilon_m$	τ_m^a (s)	β_K
PVP–methanol	0	2.8	30.1	4.98×10^{-11}	1.000	1.000			7.40×10^{-9}	
	10	3.4	26.5	5.09×10^{-11}	1.000	1.000		7.4	1.00×10^{-8}	0.60
	20	3.2	22.8	5.27×10^{-11}	1.000	1.000		15.3	1.26×10^{-8}	0.57
	30	2.6	20.4	5.27×10^{-11}	1.000	0.950		21.8	2.04×10^{-8}	0.55
	40	3.7	16.7	5.71×10^{-11}	1.000	0.940		27.4	3.80×10^{-8}	0.55
	50	3.2	15.3	6.62×10^{-11}	1.000	0.840		31.3	1.00×10^{-7}	0.60
PVP–ethanol	0	4.2	20.2	1.60×10^{-10}	1.000	1.000			1.52×10^{-8}	
	10	4.1	18.9	1.62×10^{-10}	1.000	0.980		5.4	2.01×10^{-8}	0.584
	20	4.5	16.4	1.62×10^{-10}	1.000	0.965		10.9	2.53×10^{-8}	0.584
	30	4.2	14.1	1.70×10^{-10}	1.000	0.940		15.5	4.77×10^{-8}	0.584
	40	4.4	11.5	1.78×10^{-10}	1.000	0.925		20.3	1.11×10^{-7}	0.574
	50	4.1	9.1	1.86×10^{-10}	1.000	0.900		25.4	3.19×10^{-7}	0.574
PVP–propanol	0	3.7	17.0	3.12×10^{-10}	1.000	1.000			3.09×10^{-8}	
	10	3.6	14.7	3.12×10^{-10}	1.000	0.980		4.2	4.22×10^{-8}	0.605
	20	3.6	12.6	3.08×10^{-10}	1.000	0.955		8.6	5.69×10^{-8}	0.600
	30	3.8	10.5	3.05×10^{-10}	1.000	0.935		15.0	1.46×10^{-7}	0.547
	40	3.9	8.5	3.08×10^{-10}	1.000	0.901		21.1	4.21×10^{-7}	0.494
	50	3.8	6.7	3.23×10^{-10}	1.000	0.855		24.5	1.13×10^{-6}	0.534
PVP–butanol	0	3.2	14.5	4.62×10^{-10}	1.000	1.000			4.69×10^{-8}	
	10	3.3	12.1	4.62×10^{-10}	1.000	1.000		3.9	6.53×10^{-8}	0.560
	20	3.3	9.9	4.44×10^{-10}	0.915	0.990		8.1	8.04×10^{-8}	0.530
	30	3.3	8.3	4.31×10^{-10}	0.820	0.960		12.0	1.60×10^{-7}	0.530
	40	3.3	6.8	4.31×10^{-10}	0.860	0.898		14.5	3.10×10^{-7}	0.528
	50	3.2	5.6	4.58×10^{-10}	0.814	0.804		17.5	9.86×10^{-7}	0.570
PVP–pentanol	0	3.0	11.8	6.78×10^{-10}	0.850	1.000			6.06×10^{-8}	
	10	2.9	9.6	6.47×10^{-10}	0.910	0.968		3.2	8.91×10^{-8}	0.620
	20	2.9	7.7	6.17×10^{-10}	0.770	0.958		6.2	1.27×10^{-7}	0.620
	30	2.9	6.2	5.95×10^{-10}	0.680	0.938		9.6	2.75×10^{-7}	0.592
	40	2.8	4.7	5.86×10^{-10}	0.664	0.889		12.9	6.53×10^{-7}	0.592
	50	2.8	3.9	6.03×10^{-10}	0.599	0.819		16.0	2.82×10^{-6}	0.557
PVP–hexanol	0	2.0	10.6	8.95×10^{-10}	0.892	1.000			8.24×10^{-8}	
	10	2.6	8.0	8.55×10^{-10}	0.870	0.990		3.2	1.25×10^{-7}	0.528
	20	2.2	6.6	7.98×10^{-10}	0.720	0.985		7.1	1.97×10^{-7}	0.520
	30	2.6	5.5	7.80×10^{-10}	0.720	0.927		8.9	4.02×10^{-7}	0.544
	40	2.7	4.4	7.80×10^{-10}	0.642	0.887		13.1	1.28×10^{-6}	0.528
	50	2.9	3.8	8.16×10^{-10}	0.750	0.730		16.2	4.87×10^{-6}	0.559
PVP–heptanol	0	2.9	8.7	1.08×10^{-9}	0.892	1.000			1.16×10^{-7}	
	10	2.8	7.0	1.06×10^{-9}	0.894	0.975		3.1	1.76×10^{-7}	0.525
	20	2.9	5.6	9.98×10^{-10}	0.824	0.940		5.8	3.06×10^{-7}	0.510
	30	2.7	4.6	9.53×10^{-10}	0.654	0.926		8.6	6.55×10^{-7}	0.525
	40	2.6	4.0	9.75×10^{-10}	0.614	0.806		11.5	2.20×10^{-6}	0.565
	50	2.6	3.5	1.07×10^{-9}	0.614	0.686		15.2	1.68×10^{-5}	0.564
PVP–octanol	0	2.9	7.0	1.15×10^{-9}	0.830	1.000			2.00×10^{-7}	
	10	2.9	5.9	1.10×10^{-9}	0.830	0.940		3.0	2.79×10^{-7}	0.470
	20	2.8	5.2	1.03×10^{-9}	0.745	0.928		5.4	3.85×10^{-7}	0.482
	30	2.8	4.7	1.05×10^{-9}	0.666	0.861		8.0	7.76×10^{-7}	0.537
	40	2.7	4.2	1.10×10^{-9}	0.666	0.771		11.4	2.72×10^{-6}	0.562
	50	2.8	3.5	1.35×10^{-9}	0.686	0.651		15.1	1.36×10^{-5}	0.557
PVP–nonanol	0	2.7	6.2	1.54×10^{-9}	0.861	1.000			2.76×10^{-7}	
	10	2.7	5.1	1.40×10^{-9}	0.701	0.990		2.4	3.76×10^{-7}	0.510
	20	2.6	4.5	1.31×10^{-9}	0.621	0.930		4.8	5.56×10^{-7}	0.540
	30	2.5	4.1	1.28×10^{-9}	0.561	0.840		7.5	1.57×10^{-6}	0.540
	40	2.6	3.7	1.37×10^{-9}	0.561	0.725		10.6	4.95×10^{-6}	0.570
	50	2.6	3.2	1.37×10^{-9}	0.561	0.725		10.6	4.95×10^{-6}	0.570
PVP–water	0	5.2	73.0	8.71×10^{-12}	1.000	1.000 ^b	0		8.62×10^{-9}	
	4.98	5.2	68.2	8.91×10^{-12}	1.000	0.970 ^b	10	9.9	1.00×10^{-8}	0.64
	8.08	5.2	65.8	9.55×10^{-12}	1.000	0.962 ^b	20	18.2	1.31×10^{-8}	0.65
	13.2	5.2	61.6	1.05×10^{-11}	1.000	0.955 ^b	30	30.3	2.43×10^{-8}	0.55
	20.0	3.1	59.5	1.29×10^{-11}	1.000	0.911 ^b	40	39.7	5.87×10^{-8}	0.53
	20.6	5.2	56.4	1.26×10^{-11}	1.000	0.932 ^b	50	48.5	2.16×10^{-7}	0.53
	40.0	4.0	46.1	2.14×10^{-11}	1.000	0.846 ^b				
	40.2	3.2	46.5	2.29×10^{-11}	1.000	0.845 ^b				
	48.0	3.2	39.8	3.39×10^{-11}	1.000	0.805 ^b				

^a τ_m at $C_{\text{PVP}} = 0\%$ are the τ_{m0} obtained by eq 2. ^b The relaxation parameters of the h-process and ϵ_∞ of the PVP–water mixtures were taken from refs 1 and 2.

where τ is the relaxation time, C is the concentration of polymer, τ_{m0} is the relaxation time at an infinite dilution of PVP, C_∞ is the polymer concentration at which relaxation time tends to infinity, and B is a parameter of the degree of the concentration

dependence of relaxation time. τ_{m0} implies the relaxation time of the isolated PVP molecule at an infinite dilution of PVP. τ_{m0} is plotted against viscosity, η_s , of the solvents, i.e., pure alcohols, as shown in Figure 5. τ_{m0} depends on η_s and its

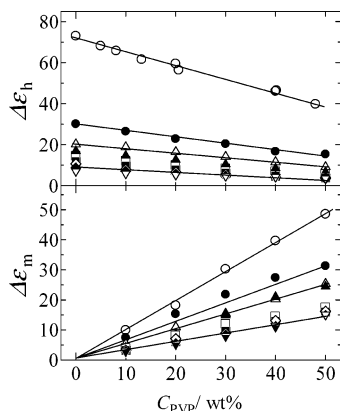


Figure 3. PVP concentration dependences of relaxation strengths of the h-process, $\Delta\epsilon_h$, and of the m-process, $\Delta\epsilon_m$, at 25 °C for PVP mixtures with water (○), methanol (●), ethanol (△), propanol (▲), butanol (□), heptanol (◇), heptanol (◆), octanol (▽), and nonanol (▼).

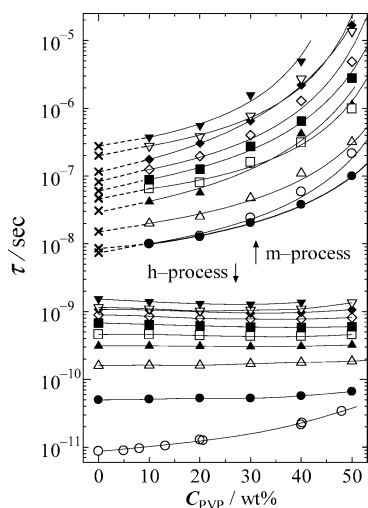


Figure 4. PVP concentration dependences of the relaxation times of the h-process, τ_h , and of the m-process, τ_m , at 25 °C for PVP mixtures with water (○), methanol (●), ethanol (△), propanol (▲), butanol (□), heptanol (◇), heptanol (◆), octanol (▽), and nonanol (▼). The crosses are the extrapolated values of the relaxation time of the m-process to the pure alcohols.

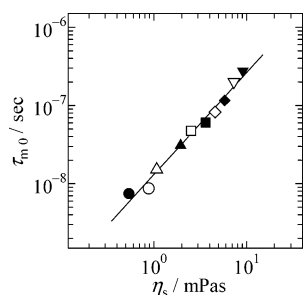


Figure 5. Plots of extrapolated relaxation time of the m-process to zero PVP concentration, τ_{m0} , against solvent viscosity, η_s . The solvents of the PVP mixtures are water (○), methanol (●), ethanol (△), propanol (▲), butanol (□), heptanol (◇), heptanol (◆), octanol (▽), and nonanol (▼).

relationship was obtained from the plots in Figure 5 by least-squares fitting as

$$\tau_{m0} \propto \eta_s^{1.3} \quad (3)$$

The relationship between the dielectric relaxation time of the local chain motion of an isolated polymer, τ_0 , and the viscosity

of solvent has been discussed.⁴⁶ According to the Debye–Stokes equation,⁴⁷ this relationship is given by

$$\tau_0 = \frac{V\eta_s}{k_B T} \quad (4)$$

where 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 an isolated polymer and the viscosity of a solvent has been obtained experimentally for polymer solutions with nonpolar solvents, as determined by dielectric⁴³ and fluorescence depolarization spectroscopies.⁴⁸ Adolf et al. reported that $\tau_0 \approx \eta_s^{0.74}$.⁴⁹ Recently, we have proposed that the exponent obtained for the local chain motion of PVP in PVP–EGO blends is 0.87.¹⁵ This value is the same as those for the nonpolar solvent polymer mixtures. On the other hand, the exponent obtained for the PVP–alcohol mixtures is larger than that for the nonpolar solvent.

The local chain motion of PVP in alcohol mixtures is treated in almost the same way as the motion in homogeneous viscous media, similarly to the polymer chain motion in a nonpolar solvent, in spite of the existence of hydrogen bonds between PVP and alcohol molecules. The difference between the exponents of the relationship between the dielectric relaxation time of the polymer and the solvent viscosity from our result and those from other studies^{15,42,48,49} is thought to be due to the difference in the dynamics of the bulk solvent and the solvent in the vicinity of polymer chains.

B. Relaxation Process of Alcohol. The concentration dependence of the relaxation time of the h-process depends strongly on the alcohol structure. In the cases of mixtures with water, methanol, and ethanol, τ_h increases with increasing PVP concentration. In these cases, the τ_h values of the mixtures with smaller alcohol molecules show strong concentration dependence. On the other hand, for the mixtures of propanol and butanol, τ_h is independent of PVP concentration. In the cases of alcohol molecules larger than butanol, τ_h decreases with increasing PVP concentration up to 30 wt % of PVP. The larger alcohol molecules show larger decreases in τ_h with increasing PVP concentration. In the concentration range higher than 30 wt % of PVP, τ_h increases with increasing PVP concentration.

Alcohols are one of the molecular liquids most comprehensively investigated by dielectric spectroscopy. The primary relaxation process of alcohol is considered to be due to the cooperative dynamics of molecules accompanying the formation and deformation of intermolecular hydrogen bonds. Models that can describe well the primary dielectric relaxation time of alcohols have been proposed.^{19,50} Murthy⁵⁰ synthesized the ideas based on the “–OH flipping process” in Hassion and Cole’s model,⁵¹ and proposed a model of the primary relaxation process of monohydroxyl alcohols between 270 and 77 K. Kaatz et al.¹⁹ developed the “wait-and-switch (WS) model”, which is based on the ideas of the dipole reorientational motion in alcohols as well as on computer simulation studies of water, in order to describe the molecular structure dependence of the relaxation times for the primary relaxation process of normal alcohols and water at 25 °C. The interpretation of the mechanism of relaxation of alcohols given by the WS model,¹⁹ which follows the model proposed by Murthy,⁵⁰ is as follows: Owing to thermal activation, the bond strength of the hydrogen network fluctuates rapidly. For water correlation times as small as 0.1–1.0 ps, results for these fluctuations were obtained from computer simulations.^{52–54} The reorientation of a dipolar group

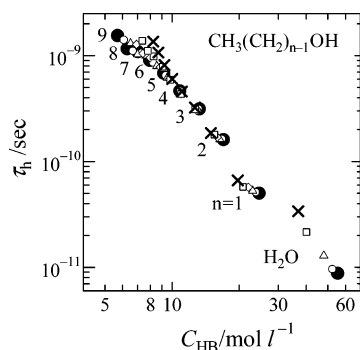


Figure 6. Plots of relaxation time of the h-process against concentration of hydrogen-bonding partners, C_{HB} , for pure alcohols and water (●) and for PVP–alcohol mixtures with PVP concentrations of (○) 10, (△) 20, (◇) 30, (□) 40, and (×) 50 wt %.

or molecule through a significant angle occurs only if an additional neighbor exists in a suitable position.^{55–57} The dielectric relaxation time is mainly determined by the period for which a dipolar group or molecule has to wait until favorable conditions for the reorientation arise. The reorientational motion is initiated by the presence of an additional neighbor molecule at a position that first flattens the potential energy barrier for the reorientation of a given dipole moment and simultaneously offers a site for the formation of a new hydrogen bond. For this reason, the period of approach of an additional neighbor is determined by the concentration of hydrogen-bonding species and the diffusion coefficient of hydrogen-bonding molecules. Thus, these two parameters are important factors controlling the dielectric relaxation time of hydrogen-bonding liquids.

According to the WS model, the main factor for determining the relaxation time of neat alcohols is the concentration of hydrogen-bonding partners, C_{HB} , in the system. From the concentration dependence of the relaxation time of alcohol, C_{HB} of the PVP–alcohol mixture seems to also determine the relaxation time. We calculated the C_{HB} values of PVP–alcohol mixtures. Although the number of hydrogen bonds per alcohol molecule and that of the repeat unit of PVP are still controversial, each alcohol molecule and each repeat unit of PVP are assumed to have one hydrogen-bonding partner, following the assumption of Kaatze et al.¹⁹ We also assumed that the number of hydrogen-bonding sites for the repeat unit of PVP was one. Under these assumptions, we calculated the C_{HB} values of PVP–alcohol mixtures as

$$C_{HB} = \rho \left(\frac{C_a}{M_a} + \frac{C_{PVP}}{M_{PVP}} \right) \quad (5)$$

where ρ is the density of the mixture, C_a and C_{PVP} are the weight fractions of the alcohol and PVP, respectively, M_a is the molecular weight of the alcohol, and M_{PVP} is the molecular weight of a repeat unit of PVP.

Figure 6 shows plots of τ_h against C_{HB} for various alcohol mixtures and PVP concentrations. The plots of τ_h for the pure alcohols given by filled circles are on a single smooth curve, as predicted by the WS model. The value of the slope being approximately -2 implies that τ_h is determined by the probability of meeting a new hydrogen-bonding partner. Note that not only the relaxation times of the pure alcohols but also those of the mixtures are on the same line, as shown in Figure 6. In the cases of the alcohol mixtures with alcohol molecules smaller than propanol, an increase in PVP concentration reduces C_{HB} . The high C_{HB} of water shows the largest change in τ_h . The mixtures with methanol and ethanol show smaller changes than

the water mixtures because the PVP concentration dependences of the C_{HB} values of these mixtures are small. For propanol and butanol, C_{HB} is not changed by the addition of PVP, so τ_h remains approximately constant. For the alcohol molecules larger than butanol, the addition of PVP increases C_{HB} and results in a decrease in τ_h .

Although τ_h decreases with increasing PVP concentration up to 30 wt % for the mixtures with alcohols larger than propanol, τ_h increases above 30 wt % PVP. In this higher PVP concentration region, an increase in the volume fraction of PVP reduces the free volume available for the translational motion of alcohol molecules. Then, the microscopic diffusion of alcohol molecules should be restricted. The restricted diffusion of alcohol molecules increases the waiting time for obtaining a new hydrogen-bonding partner. Then, not only the concentration of hydrogen-bonding sites but also the microscopic diffusion of alcohol molecules affects the dielectric relaxation time of alcohol. The concentration dependence of the relaxation time of the primary relaxation process of alcohols (h-process) is explained by the WS model without discrepancies between the increase and decrease in relaxation time with increasing PVP concentration. It is very interesting that a polymer chain does not always magnify the relaxation time of the solvent.

Conclusion

Two relaxation processes, caused by the rotational motion of dipole moments on alcohol molecules and the local chain motion of PVP for PVP–monohydroxyl alcohol mixtures, were observed by broadband dielectric spectroscopy at 25 °C. Note that different time scales of the molecular motions of polymers and the solvent coexist in homogeneous mixtures with hydrogen-bonded solvents and polymers. The relaxation time of PVP is more than hundred times larger than that of alcohol. The solvent behaves almost as a homogeneous viscous medium for the motion of a polymer chain. The relaxation time of alcohols depends strongly on the alcohol structure. For the mixtures with alcohol molecules smaller than propanol, the concentration of hydrogen-bonding partners decreases and the relaxation time of alcohol increases with increasing PVP concentration. On the other hand, for the mixtures with alcohol molecules larger than butanol, the concentration of hydrogen-bonding partners increases and the relaxation time of alcohols decreases with increasing PVP concentration.

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