

Dynamics of Polymer and Solvent in Poly (Vinyl Pyrrolidone)/Alcohol Mixtures Studied by Broadband Dielectric Spectroscopy

N. Shinyashiki, D. Imoto, and S. Yagihara

Department of Physics, Tokai University, Hiratsuka, Kanagawa 259-1292 Japan

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 liquid state physics. Poly(vinyl pyrrolidone) (PVP) is an amorphous and nontoxic synthetic polymer, which has a randomly coiled and highly flexible chain in polar solvents.

In order to observe the local chain motion of PVP and get the information of the effects of polymer to the polar molecular liquids in polymer solutions, broadband dielectric measurements of PVP/alcohol mixtures with various alcohol structures were made in the frequency range of 2mHz-10GHz at 25°C. The alcohols used in this experiments are mono-alcohols, diols, and triols with the number of carbon of an alcohol molecule are one to ten. Poly (vinyl pyrrolidone) (PVP) with weight average molecular weight of 40,000 was used for all the PVP/alcohol mixtures. PVP and alcohols were mixed in the PVP concentration of 10-50 wt%. Dielectric measurements were performed in the frequency range of 2 mHz to 20 GHz using a time domain reflectometry (TDR) (100 MHz–20 GHz), an impedance/material analyzer (Hewlett Packard 4291A) (1MHz–1.8 GHz), a precision impedance analyzer (Agilent Technologies 4294A)(40 Hz–110 MHz), an LCR meter (Hewlett Packard 4284A)(20 Hz–1 MHz), and an AC phase analysis (ACPA) method (2 mHz–1 kHz) at 25°C.

Figure 1 shows dielectric constant and loss for PVP/1-heptanol mixtures with various PVP concentrations at 25°C by way of example of concentration dependence of PVP/alcohol mixture. The frequency dependence of the dielectric constant and loss for the PVP/alcohol mixtures are composed of three relaxation processes and contribution of dc conductivity. The high-frequency-process (h-process) observed in a frequency range between 10MHz and 1GHz is a primary relaxation process of alcohol. The middle-frequency-process (m-process) observed in a frequency range between 1kHz and 10MHz is attributed to the local chain motion of PVP. In the frequency range below 1 kHz for the dielectric constant and below 100 kHz for the dielectric loss, huge electrode polarization (l-process) and dc conductivity are recognized.

For the PVP/mono-hydroxyl alcohol mixtures, the concentration dependence of the relaxation time of the h-process strongly depends on the alcohol structure. For the mixtures with water, methanol, and ethanol, the relaxation time of the h-process increases with increasing PVP concentration. In these cases, the relaxation time of alcohol molecule shows a large concentration dependence. On the other hand, for the mixtures of propanol and buthanol, the relaxation time of the h-process is independent of PVP concentration.

In the case for the mixtures with alcohol larger than buthanol, the relaxation time of the h-process decreases with increasing PVP concentration up to 30 or 40 wt% of PVP. The PVP concentration dependence of the relaxation time of the h-process can be explained by the hydrogen bond acceptor density determining the relaxation time of the h-process. An increase in the PVP concentration changes the hydrogen bond acceptor density in the mixture. It is very interesting that the polymer chain does not always make the solvent motion slower.

On the other hand, the relaxation times of the m-process increases with increasing PVP concentration for all the mixtures. In the case for the relaxation time of the isolated PVP molecule in infinite dilution of PVP, the local chain motion of PVP depends on the viscosity of pure alcohol. This characteristic behavior also appears for the local chain motion of polymer in non-polar solvent.

More detailed explanation of the alcohol structure dependence of the dynamics of polymer and alcohol will be discussed in our presentation.

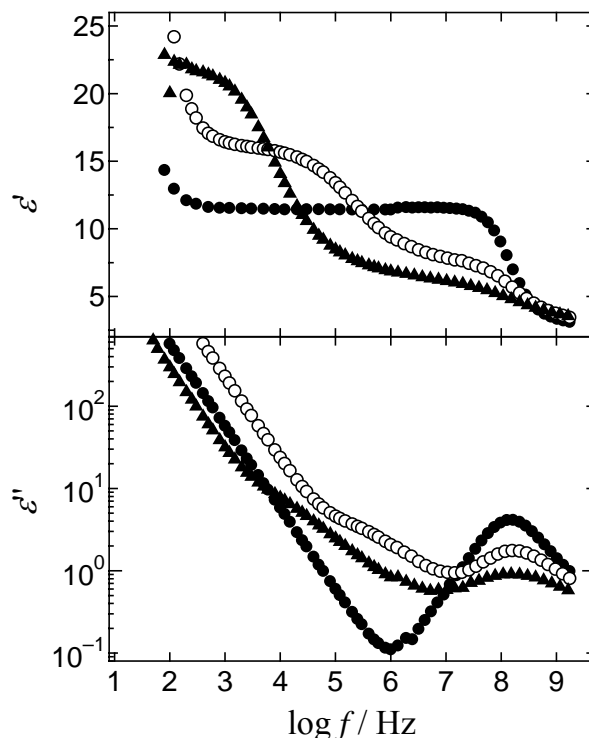


Fig. 1. Dielectric constant and loss for PVP/1-heptanol mixtures with various PVP concentrations at 25°C. The symbols in the figure indicate the PVP concentrations of the PVP-heptanol mixtures as 0 wt% (pure heptanol); ●, 30 wt%; ○, 50 wt%; ▲.