

Dielectric relaxation strength and magnitude of dipole moment of poly (vinyl pyrrolidone) in polar solutions

Naoki Shinyashiki^{*}, Masahiko Miyara, Shinya Nakano, Wataru Yamamoto, Masahiro Ueshima, Daizo Imoto, Kaito Sasaki, Rio Kita, Shin Yagihara

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

ARTICLE INFO

Article history:

Received 9 August 2012

Received in revised form 16 February 2013

Accepted 27 February 2013

Available online 15 March 2013

Keywords:

Dielectric relaxation strength

Dielectric constant

Dipole moment

Polymer solution

Polar solvent

Poly(vinyl pyrrolidone)

ABSTRACT

Dielectric relaxation caused by the segmental motion of poly(vinyl pyrrolidone) (PVP) was observed in solutions at 25 °C with various solvents, that is, chloroform, water, and mono- and dihydroxyl alcohols with dielectric constants ranging between 5 and 78. The relaxation strength of the segmental motion of PVP varies with the solvent. The magnitudes of the effective dipole moment of the repeat unit of PVP in solutions with various solvents calculated using the Onsager equation depends simply on the dielectric constant of the solvent at higher frequency.

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1. Introduction

There is much literature on the theory and practice of the dependence of dielectric relaxation strength, $\Delta\epsilon$, on the magnitude and density of the dipole moment, the Kirkwood g -factor, internal electric field, and temperature for various systems including polymers [1–7]. The mobility of chains is considered to be limited owing to the entanglement of chains in bulk polymer systems, and the relationship between dielectric relaxation strength and the magnitude of the dipole moment on the polymer has been studied mainly for the relaxation of a polymer in solution. The dielectric relaxation due to the local segmental motion of the polymer had been studied for polymer solutions with nonpolar solvents. The dielectric constants of nonpolar solvents are approximately in the range between 2 and 3. In general, the Kirkwood g -factor has been introduced to interpret the difference between the magnitude of the dipole moment in solution obtained using the Onsager equation [8] and that obtained in gas. In this case, the g -factor has been discussed on the basis of the idea that the estimation of the internal electric field is correct, since this small range of the dielectric constant of the solvent is insufficient to distinguish the effect of the internal electric field from that of the Kirkwood g -factor.

Poly(vinyl pyrrolidone) (PVP) is a semicrystalline synthetic polymer that forms a randomly coiled and highly flexible chain in polar solvents. Moreover, PVP is soluble in various kinds of liquids. The dielectric behavior of PVP solutions in water [9–22], alcohol [20,23], ethylene glycol oligomer (EGO) [24,25], and chloroform [26] has been studied extensively in the frequency range of 20 Hz–20 GHz at 25 °C. Two processes of relaxation due to the reorientation of dipoles on PVP and the solvent were observed. The relaxation process at frequencies higher than 100 MHz is the primary process of solvents, and that at frequencies lower than 10 MHz is attributed to the local segmental chain motion of PVP. Different time scales of the molecular motion of the polymer and solvent coexist in homogeneous mixtures. For these PVP solutions, the dielectric constant of solvents is in the range between approximately 5 and 78. Therefore, we used PVP solutions since they are perfect systems for the investigation of the relationships among the dielectric relaxation strength of the segmental motion of a polymer, the magnitude of the dipole moment of the repeat unit of polymer, and the dielectric constant of the solvent. No one has ever observed the effect of the type of solvent on the relaxation strength of a polymer in solvent with such a wide range of dielectric constant. The details of the structure and dipole moment of a repeat unit of PVP are shown in Fig. 1 in Ref. [26]. The repeat unit of PVP has a permanent dipole moment with a magnitude of 3.53 Debye [26] (1 Debye = 3.33564×10^{-30} C·m). The magnitude of the dipole moment on a repeat unit of PVP can be treated as constant, since the side group of PVP has no internal freedom [26], and PVP possesses only the acceptor of the hydrogen bond,

^{*} Corresponding author. Tel.: +81 463 58 1211; fax: +81 463 50 2013.
E-mail address: naoki-ko@keyaki.cc.u-tokai.ac.jp (N. Shinyashiki).

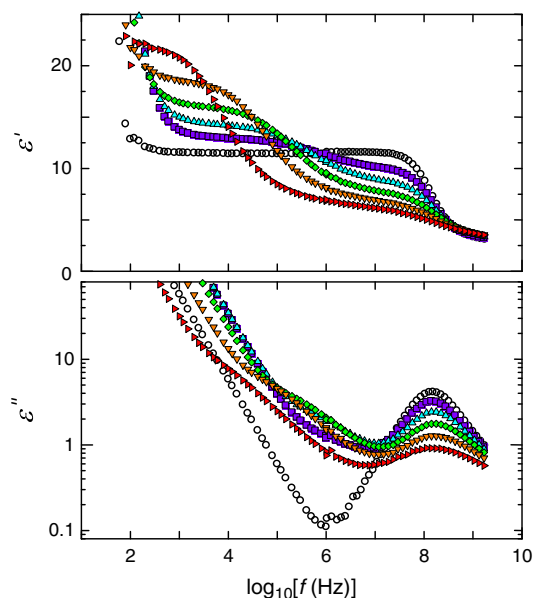


Fig. 1. Dielectric constants and losses for PVP/1-heptanol mixtures with various PVP concentrations at 25 °C. The symbols indicate the following PVP concentrations: 0 wt.% (pure 1-heptanol) (○), 10 wt.% (■), 20 wt.% (▲), 30 wt.% (◆), 40 wt.% (▼), and 50 wt.% (▴).

meaning that we do not need to consider the formation of a complex structure brought about by the inter- and intrachain hydrogen bond.

2. Experimental

PVP with a weight average molecular weight M_w of approx. 4×10^4 was purchased from Sigma. The monohydroxyl alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol) and chloroform used in this experiment are the same to those in the previous study [20]. The dihydroxyl alcohols used in this experiment were ethylene glycol, propylene glycol, tetramethylene glycol, 1,5-pentandiol, and 1,2-hexanediol purchased from Aldrich, 1,2-butanediol and 1,4-butanediol purchased from Wako Pure Chemical Industries, and 1,2-pentanediol and 1,7-heptanediol purchased from Tokyo Chemical Industry. The water contents of the alcohols were less than 1 wt.%. PVP solutions were prepared without further purification with various PVP concentrations from 5 to 50 wt.% with an accuracy better than 0.05 wt.%. Prior to mixing, the PVP was kept in a dry atmosphere in a desiccator with silica gel or P_2O_5 . The apparatus and procedures used for the dielectric measurements have been presented in a previous paper [20].

3. Results and discussion

Fig. 1 shows dielectric constants and losses for PVP/1-heptanol mixtures with various PVP concentrations at 25 °C. The dielectric loss peak for the high-frequency process (h-process) is observed at frequencies around 100 MHz. Its strength decreases and the shape of the loss peak becomes broader with increasing PVP concentration. In the frequency range of 10 kHz–1 MHz, a relaxation process at intermediate frequencies (m-process) 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 solutions

of various concentrations can be described as a simple sum of the three relaxation processes and a contribution of dc conductivity as

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_h}{\left\{1 + (j\omega\tau_h^{\text{HN}})^{\beta_h}\right\}^{\alpha_h}} + \Delta\varepsilon_m \int_0^\infty \left(-\frac{d\Phi_m}{dt}\right) \exp(-j\omega t) dt + \frac{\Delta\varepsilon_l}{1 + (j\omega\tau_l)^{\beta_l}} - j \frac{\sigma}{\varepsilon_0 \omega}, \quad (1)$$

for

$$\Phi_m = \exp\left[-\left(\frac{t}{\tau_m^K}\right)^{\beta_K}\right].$$

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, $\Delta\varepsilon$ 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 [27,28], 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 (HN) equation [29] and the KWW function [27,28], respectively. The h-, m-, and l-processes can be described well by the HN equation, the KWW function, and the Cole–Cole equation [30], respectively. The h-process observed for pure solvents can be described well by the Debye equation without any relaxation time distribution for water, methanol, ethanol, and propanol, and by the Davidson–Cole equation for the other solvents. The h-process is symmetrically broadened by adding PVP. Therefore, to carry out fitting using common shape parameters for all the alcohols and concentrations, the HN equation was used. On the other hand, the m-process is asymmetrically broadened, and the shape was discussed for the PVP–chloroform mixtures in our previous paper [26]. However, the contributions of dc conductivity and the l-process make it difficult to obtain a correct estimation of the shape of the m-process in almost all of the PVP–alcohol and PVP–water mixtures. Thus, we used the KWW equation, which has a single shape parameter for asymmetric broadening of both the low- and high-frequency sides of the loss peak. The origins of the h-, m-, and l-processes were clarified in

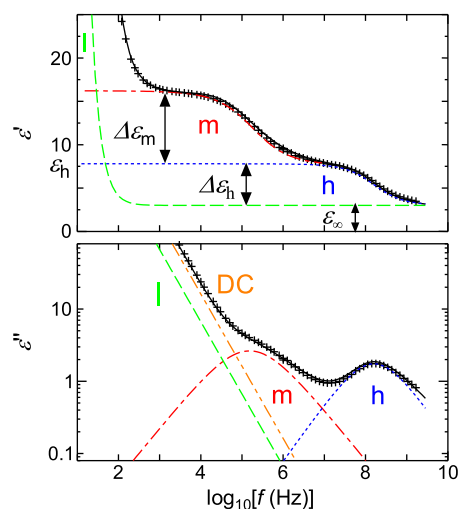


Fig. 2. Dielectric constants and losses for 30 wt.% PVP/1-heptanol mixtures at 25 °C. The values indicated by crosses were obtained experimentally. The lines were drawn using Eq. (1): blue dotted line, h-process; red dot-dash line, m-process; green dashed line, l-process; orange double-dot-dashed line, dc conductivity; black solid line, sum of all the processes. The term ε_∞ obtained by the fitting procedure was added to each curve of dielectric constants.

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