RHEO-DIELECTRIC BEHAVIOR OF UNENTANGLED POLY (BUTADIENE OXIDE) UNDER STEADY SHEAR

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ABSTRACT

A rheo-dielectric test for a type-A unentangled melt, poly(butylene oxide), was performed to measure η, Ψ_1, and ε_y'' in the velocity gradient (y) direction. Analyzing these ε_y'', η, and Ψ_1 data, we found that the spring strength κ increases moderately while the off-diagonal components of the friction coefficient tensor $\boldsymbol{\zeta}$ remain negligibly small on an increase of Wi up to 1.2. We also found that the diagonal components ζ_{xx} (with x being the velocity direction) and B_{yy} hardly change while ζ_{yy} decreases moderately. These results, suggesting the onset of the finite extensive nonlinear elasticity and violation of a relationship $B_{yy} \propto \zeta_{yy}$, serve as a starting point for deeper investigation of κ, $\boldsymbol{\zeta}$, and $\mathbf{B}$.

INTRODUCTION

Recently, extensive studies have been made for flow-induced changes in the local properties of polymer chains. In the bead-spring chain model, these changes can be expressed as changes in the spring constant κ, the bead friction ζ, and the mean-square intensity B of the Brownian force acting on the bead. An experimental evaluation of the magnitude of flow-induced changes in these parameters is desired. In this regard, we have recently conducted the Rouse analysis of dielectric and diffusion properties measurable with Lab devices under shear.[1] Based on this analysis, we have performed the rheo-dielectric measurement for a typical type-A polymer, poly(butylene oxide) (PBO), in the unentangled melt.[2]

EXPERIMENTAL

A linear unentangled polybutylene oxide (PBO) ($M_\mathrm{w} = 16\times10^3$, $M_\mathrm{w}/M_\mathrm{n} = 1.30$) was used. Linear viscoelasticity and rheo-dielectric measurements were performed on a rheometer ARES-G2 (TA Instruments) using a parallel plate (5ϕ) and a homemade cone-plate electrode (10ϕ, 0.025 rad), respectively. In the rheo-dielectric measurements, the cone-plate electrode was connected to a dielectric bridge (ModuLab XM MTS; Solartron Analytical) *via* a Hg reservoir, and dielectric frequency sweep tests were performed in the range of $10^4 \geq f/\mathrm{Hz} \geq 1$ under steady shear flow.

RESULTS AND DISCUSSION

The rheo-dielectric measurements of PBO-16k were performed at −20°C and the resulting steady-state viscosity η, first normal stress difference coefficient Ψ_1, and dielectric loss ε_y'' in the velocity gradient direction are summarized in **Figs. 1 and 2**. For comparison, complex viscosity |η*| and elastic factor 2G'/ω^2 obtained from the linear viscoelastic measurements are also shown in **Fig. 1**.

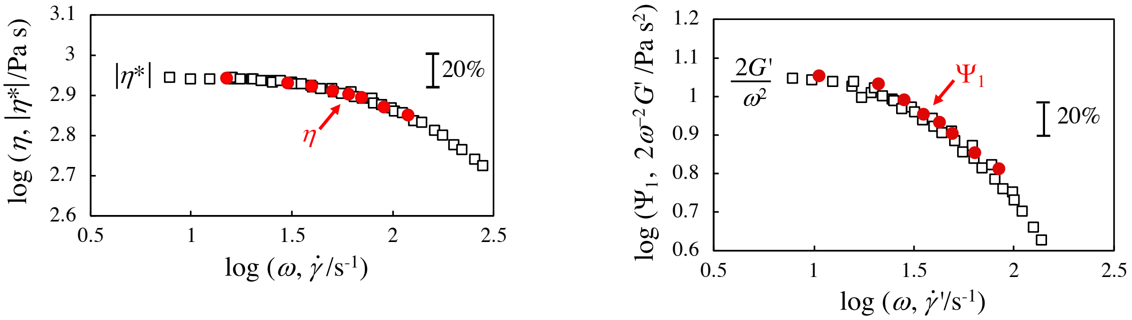

Figure 1: (left) η of PBO-16k at −20˚C against $\dot{\gamma}$ in filled circles. |η*| against ω is shown with open squares. **(right)** Ψ_1 against $\dot{\gamma}' = \dot{\gamma}/1.4$ in filled circles. 2G'/ω^2 against ω is shown with open squares.

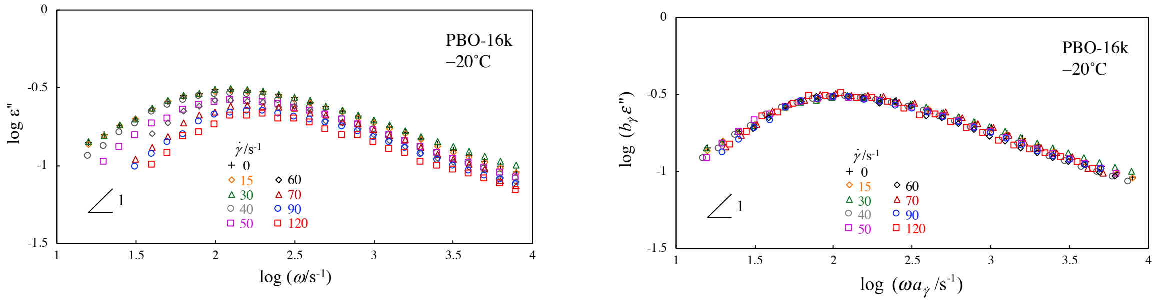

Figure 2: (**left)** ε" of PBO-16k at −20˚C measured under steady shear at the rate $\dot{\gamma}$ as indicated is plotted against ω.**(right)** Normalized plots of the rheo-dielectric ε" data.

We have solved the equation of motion of the type-A Rouse chain to express its ε" analytically in terms of κ and **ζ**.[1] (The mean-square intensity of the Brownian force **B** vanishes on the averaging of the first order moments, and is not included in this expression.) The key quantities in that expression are the non-equilibrium parameter r defined for κ and **ζ**:

$$r_{\kappa} \equiv \kappa_{\mathrm{sf}} / \kappa_{\mathrm{eq}} \tag{1a}$$

$$r_{\zeta,ij} \equiv \zeta_{ij,\mathrm{sf}} / \zeta_{\mathrm{eq}} \tag{1b}$$

Here, the subscripts "sf" and "eq" stand for the quantities under steady flow and at equilibrium, respectively. ζ_{ij} is the ij component of the friction coefficient tensor **ζ** ($i,j = x$: velocity direction, y: velocity gradient direction, z: vorticity direction). If ζ_{yx} is negligibly small, the dielectric mode distribution is not affected by the shear and ε_y" is simply related to ε_{eq}"(ω) as[1]

$$\varepsilon_y''(\omega) = \frac{1}{r_\kappa}\varepsilon_{\mathrm{eq}}''(\omega\{r_{\zeta,yy}/r_\kappa\}) \tag{2}$$

The experimentally observed shear-insensitivity of the dielectric mode distribution (**Fig. 2**) strongly suggests that our PBO-16k sample had negligibly small ζ_{yx} at $\dot{\gamma}$ examined. Then, the intensity factor $b_{\dot{\gamma}}$, used for the vertical shift in **Fig. 2**, coincides with the non-equilibrium parameter r_κ (Eq. 1a), and the frequency shift factor $a_{\dot{\gamma}}$ is identical to the $r_{\zeta,yy}/r_\kappa$ (Eq. 2). These relationships allow us to evaluate $r_{\zeta,yy}$ and r_κ. The results are shown in **Fig. 3**.

As mentioned earlier, dielectric data are independent of **B**. However, the rheological data depend on **B**, so that combination of dielectric and rheological data allows us to obtain the non-equilibrium parameter for **B**:

$$r_{B,ij} \equiv B_{ij,\mathrm{sf}} / B_{\mathrm{eq}} \; (i,j = x, y, z) \tag{3}$$

By solving the Rouse equation of motion, η and Ψ_1 can be expressed analytically in terms of r_κ, $r_{\zeta,ij}$, $r_{B,ij}$. When $r_{\zeta,yx} \sim 0$ as in the present experiment, r_κ and $r_{\zeta,yy}$ obtained from the dielectric data (**Fig. 2**) and the rheological η/η_0 and $\Psi_1/\Psi_{1,0}$ data give $r_{\zeta,xx}$ and $r_{B,yy}$ as

$$r_{\zeta,xx} = \frac{\{\Psi_1/\Psi_{1,0}\}}{\{\eta/\eta_0\}} r_\kappa \tag{4}$$

$$r_{B,yy} = \frac{r_\kappa}{2}\left\{\frac{\eta}{\eta_0}\right\}\left(1 + \frac{r_{\zeta,yy}}{r_\kappa}\frac{\{\eta/\eta_0\}}{\{\Psi_1/\Psi_{1,0}\}}\right) \tag{5}$$

The non-equilibrium parameters r_κ, $r_{\zeta,yy}$, $r_{\zeta,xx}$, and $r_{B,yy}$ thus evaluated are summarized as a function of Weissenberg number $Wi = \tau_1^{[\mathrm{G}]}\dot{\gamma}$ in **Fig. 3**. ($\tau_1^{[\mathrm{G}]}$: the longest linear viscoelastic relaxation time). $r_{\zeta,xx}$ and $r_{B,yy}$ remain close to unity, whereas r_κ and $r_{\zeta,yy}$ increases and decreases, respectively, on an increase of Wi up to 1.2. This nonlinearity of r_κ and $r_{\zeta,yy}$ is just moderate (possibly because Wi is not increased well beyond unity). Nevertheless, the following features are worth noting: the increase of r_κ suggests the *onset* of finite extensible nonlinear elasticity, and the difference between $r_{B,yy}$ and $r_{\zeta,yy}$ suggests a violation of the proportionality, $B_{yy} \propto \zeta_{yy}$, naively expected from the fluctuation-dissipation theorem. In addition, for $Wi \leqq 1.2$, $\eta/\eta_0 \cong 2/\{r_\kappa(1 + r_{\zeta,yy})\}$, $\Psi_1/\Psi_{1,0} \cong 2/\{r_\kappa^2(1 + r_{\zeta,yy})\}$.[2] Namely, the thinning of η and Ψ_1 is determined by a delicate balance between the increase of r_κ and decrease of $r_{\zeta,yy}$. Further rheo-dielectric experiments covering larger Wi are desired for a deeper understanding of these features of η, Ψ_1 and r, and are now being planned with a setup of a CPP shearing fixture/electrode.

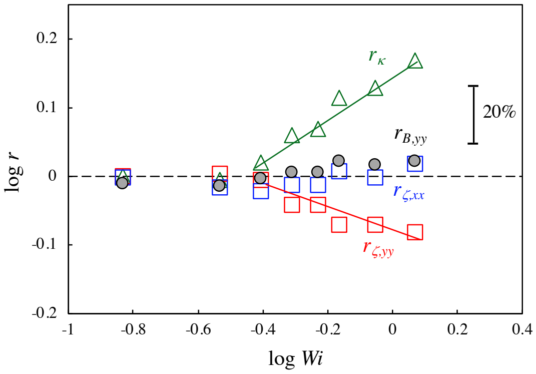

Figure 3: Changes of non-equilibrium parameters *r's* with the Weissenberg number *Wi.*

REFERENCES

1. Sato, T.; Matsumiya, Y.; Watanabe, H., Rheo-Dielectrics and Diffusion of Type-A Rouse Chain under Fast Shear Flow: Method of Evaluation of Non-Equilibrium Parameters for FENE, Friction-Reduction, and Brownian Force Intensity Variation*, Nihon Reoroji Gakkaishi* (*J. Soc. Rheol. Jpn.*), **50**, 253-268, 2022. https://doi.org/10.1678/rheology.50.253.
2. Matsumiya, Y.;Sato, T.; Chen, Q.; Watanabe, H., Rheo-dielectric Behavior of Unentangled Poly(butylene oxide) under Steady Shear: Non-equilibrium Parameters at the Onset of Nonlinearity, *Nihon Reoroji Gakkaishi* (*J. Soc. Rheol. Jpn.*), **50**, 371-385, 2022. https://doi.org/10.1678/rheology.50.371.