

Rheo-Dielectric Behavior of Oligostyrene and Polyisoprene

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Flow effects were examined for dielectric behavior of oligostyrene (OS; $M = 950$) and *cis*-polyisoprene (PI; $M = 8200$). OS-1 has monomeric dipoles perpendicular to its backbone and the terminal dielectric relaxation results from the segmental motion, while for PI-8 having parallel dipoles this relaxation reflects the global chain motion. The dielectric loss ϵ'' and viscosity η were measured for OS and PI at T well above respective T_g under steady shear flow at rates $\dot{\gamma} \ll 1/\tau_1$, with τ_1 being the linear viscoelastic terminal relaxation time. The ϵ'' and η of PI were independent of $\dot{\gamma}$, as usually expected under such slow flow. In contrast, OS exhibited acceleration of the dielectric relaxation and the shear-thinning of η at $\dot{\gamma} \ll 1/\tau_1$. This thinning was related to flow-induced changes in some sort of dynamic structure, probably a cooperative domain structure, and the dielectric change detected acceleration of the segmental motion due to this structural change.

Keywords : Rheo-dielectric behavior/ Global mode/ Segmental mode/ Shear-thinning/ Cooperative domain structure

Viscoelastic relaxation of flexible polymer chains has a considerably broad distribution of relaxation modes, and the fast and slow modes reflect the chain motion at small (segmental) and large (global) length scales, respectively. A recent rheo-optical study [1] revealed that the viscoelasticity-structure relationship is not identical for these fast and slow modes (the segmental and global modes). For the global mode, the mechanical stress is in proportion to an anisotropy of axial orientation of the chain backbone and the conventional stress-optical rule [2] is valid. In contrast, the segmental mode is related to an anisotropy of the planar orientation of the segments.

The segmental mode of polystyrene has been found to exhibit strong thinning under elongational flow at rates much smaller than the characteristic frequency of this

mode [3]. This result is of particular interest in a sense that the thinning behavior could provide us with detailed insight for a *dynamic structure* in glassy materials.

Dielectric techniques are useful in investigation of this structure. For polymer chains having electrical dipoles, the chain motion results in not only viscoelastic but also dielectric relaxation. Specifically, the segmental motion is observed as the dielectric dispersion (often referred to as the α dispersion) if the chains have the dipoles perpendicular to their contour, while the global motion is dielectrically detected if the chains have the parallel dipoles [4]. Taking advantage of these dielectric features, we have carried out rheo-dielectric measurements for model materials, oligostyrene (OS) of the molecular weight $M_w = 950$ ($M_w/M_n = 1.13$) and *cis*-

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Rheology —

Scope of research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.



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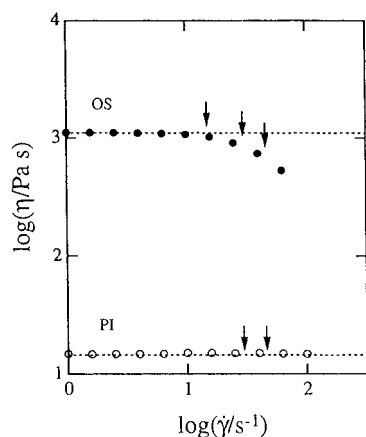


Fig.1 Steady state viscosity of OS at 42°C and PI at 23°C. The arrows indicate the shear rates for the rheo-dielectric data shown in Figure 2.

polyisoprene (PI) of $M_w = 8200$ ($M_w/M_n = 1.05$) [5]. The results are summarized here.

For the low-M OS molecules having the perpendicular dipoles, both of the terminal viscoelastic and dielectric relaxation processes reflect the segmental mode. In contrast, the PI chains have the parallel dipoles and their terminal processes are dominated by the global mode. The terminal relaxation time τ_1 at equilibrium was viscoelastically determined as [5]

$$\tau_1 = 1.3 \times 10^{-5} \text{ s for OS at } T_r = 42^\circ\text{C} \quad (1)$$

$$\tau_1 = 4.0 \times 10^{-5} \text{ s for PI at } T_r = 23^\circ\text{C} \quad (2)$$

The reference temperatures T_r are well above respective T_g ($\cong 7^\circ\text{C}$ for OS and $\cong -75^\circ\text{C}$ for PI).

For OS and PI at respective T_r , Figure 1 shows the steady state shear viscosity $\eta(\dot{\gamma})$ determined at shear rates $\dot{\gamma} \ll 1/\tau_1$. The dashed lines indicate plots of the magnitude of complex viscosity $|\eta^*(\omega)|$ against the angular frequency ω . The corresponding dielectric loss ϵ'' , measured in the quiescent state and under steady shear flow at $\dot{\gamma}$ indicated with the arrows in Figure 1, are shown in Figure 2.

For PI, completely Newtonian behavior is observed and the Cox-Merz rule is valid at $\dot{\gamma}$ examined (cf. Figure 1). This result indicates that the equilibrium global motion is not affected by the slow flow at $\dot{\gamma} \ll 1/\tau_1$. Correspondingly, the ϵ'' data detecting the global chain motion are insensitive to $\dot{\gamma}$ (cf. Figure 2).

For OS, Figure 2 demonstrates no detectable flow effect on the ϵ'' data at $\dot{\gamma} < 15 \text{ s}^{-1}$. However, with further increase of $\dot{\gamma}$ up to 46 s^{-1} , the terminal tail of the ϵ'' curve (where $\epsilon'' \propto \omega$) is shifted to higher ω side and the dielectrically detected segmental motion becomes faster, despite a fact that the flow at those $\dot{\gamma}$ is still much slower than the equilibrium segmental motion. As noted in Figure 1, the $\eta(\dot{\gamma})$ data of OS deviate from the $|\eta^*(\omega)|$ data

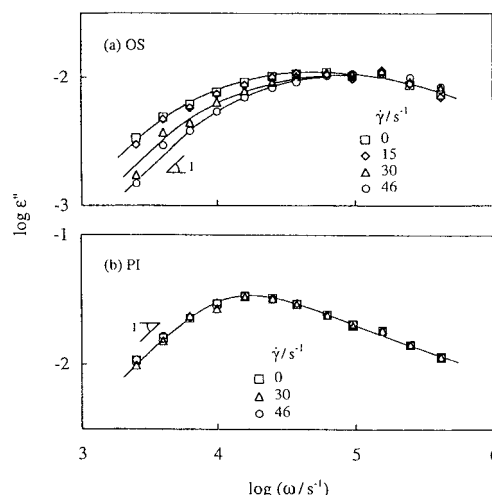


Fig.2 Dielectric loss ϵ'' of OS at 42°C and PI at 23°C determined under steady shear flow. For comparison, the data in the quiescent state are also shown.

and exhibit thinning at $\dot{\gamma} \geq 15 \text{ s}^{-1}$. This thinning for the segmental mode, noted also for polystyrene under very slow elongational flow [1], quite possibly results from the flow-induced acceleration of the segmental motion.

This result suggests that the OS system includes some sort of *dynamically heterogeneous* structure: Such a structure can be distorted under the slow flow, thereby affecting the segmental motion therein and inducing the thinning of η . This dynamic structure might be a cooperative domain structure [6] characteristic to glassy materials. At time scales of the segmental motion, the dynamic heterogeneity could have survived in the OS system even at $T_r > T_g$. We speculate that the flow may reduce the cooperative domain size thereby weakening the cooperativity in the segmental motion to accelerate this motion and induce the thinning of η . At this moment, no structural data proving/disproving this speculation are available. Further studies are desired for the structure under flow.

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