# Rheo-Dielectric Behavior of Oligostyrene and Polyisoprene

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## Introduction

Viscoelastic relaxation of flexible polymer chains is determined by thermal motion of the chain. The relaxation spectrum has a considerably broad distribution of relaxation modes over a wide range of time scales, and the fast and slow modes reflect the chain motion at small (segmental) and large (global) length scales, respectively. Recent rheo-optical studies by Inoue, Okamoto, and Osaki revealed that the viscoelasticity−structure relationship is not identical for these fast and slow modes (the glassy and rubbery modes according to their terminology).[1] For the slow modes observed in the rubbery to terminal flow regime, 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 fast modes seen at around the long time end of the glassy regime is related to an anisotropy of the planar orientation of the monomeric units (or the segments): most of the polymers have a rather flat (planar) structure in their monomers, and the rotation of the monomers around the backbone axis decreases this anisotropy and results in the fast mode relaxation.

Inoue, Ryu, and Osaki also found that the glassy mode of polystyrene ($M$ = 270k) exhibits strong nonlinearity (thinning) under elongational flow at rates well below the characteristic frequency of this mode.[3] This type of nonlinearity under such *slow* flow can be observed for systems of some heterogeneous structure, but not for homogeneous polymeric systems. The thinning behavior of the glassy mode, noted not only for polystyrene but also for inorganic glasses,[4] is of particular interest in a sense that the behavior could provide us with detailed insight for (dynamic) structures of glassy materials.

Dielectric techniques are useful in challenges to these types of problems. 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.[5] Comparison of the dielectric and viscoelastic data for the same polymer system can provide us with detailed information for the chain motion, for example, the information about short time coherence of the equilibrium chain motion for the case of polymers having the parallel dipoles.[6]

On the basis of the above background, we have utilized rheo-dielectric techniques and compared the dielectric and viscoelastic behavior under steady flow. We chose oligostyrene (OS) and *cis*-polyisoprene (PI) as the model materials for which the viscoelastic quantities at long time scales are dominated by the glassy and rubbery modes, respectively. The OS has the perpendicular dipoles, and its segmental motion is dielectrically detected in the terminal flow regime, while the PI has the parallel dipoles and its dielectric dispersion in this regime reflects the global motion. Considering these features, this paper examines the flow effects on the dielectric responses of these materials and discusses the nonlinearity for the glassy mode as well as a difference between the glassy and rubbery modes.

## Experimental Section

**Materials.** The oligostyrene sample (OS-1) having $M_w$ = 0.95k and $M_w/M_n$ = 1.13 (manufacture's designation) was purchased from Tosoh Co. Ltd. and used as received. The *cis*-polyisoprene sample (PI-8; $M_w$ = 8.2k, $M_w/M_n$ = 1.05) was anionically synthesized in this study. Heptane and *sec*-butyllithium were used as the polymerization solvent and initiator, respectively. The molecular characteristics of PI-8 were determined with GPC (HLC-802UR, Tosoh) equipped with an on-line low-angle laser light scattering photometer (LS-8000, Tosoh).

**Measurements.** Dielectric and rheological measurements were carried out at temperatures $T$ well above $T_g$ (∼7 °C for OS-1 and ∼−75 °C for PI-8). For OS-1 and PI-8 under steady shear flow at $T_r$ = 42 and 23 °C, respectively, dielectric loss $\epsilon''$ was determined with a transformer bridge (GR 1648A, General Radio). Cone-plate type electrodes (of cone angle = 2.6° and diameter = 3 cm) mounted on a laboratory rheometer (Autoviscometer L-III, Iwamoto Seisakusho, Kyoto) were used to detect dielectric responses in the shear gradient direction. This rheometer was modified to include a mercury reservoir for electrical contact so that the dielectric measurements were conducted without mechanical disturbance. Details of the electrodes and rheometer were described elsewhere.[7]

Rheological data were obtained with a high-precision rheometer (ARES, Rheometrics). For comparison with the $\epsilon''$ data, steady-state viscosity $\eta$ was determined in a cone-plate geometry (of cone angle = 5.7° and diameter = 2.5 cm) for OS-1 and PI-8 at respective $T_r$ (42 and 23 °C). Linear viscoelastic measurements were also carried out in cone-plate and parallel plate geometries to determine complex moduli $G^*$ ($=G' + iG''$) at various temperatures $T$ ($> T_g$) including the $T_r$ where $\epsilon''$ and $\eta$ were determined.

## Results and Discussion

**Linear Viscoelastic Behavior.** Figure 1 shows master curves of storage and loss moduli, $G'$ and $G''$, for OS-1 (part a) and PI-8 (part b) reduced at $T_r$ = 42 and 23 °C, respectively. Corresponding shift factors $a_T$ are shown in Figure 2. Both OS-1 and PI-8 have the molecular weight below a characteristic $M_c$ for entanglements (=31k and 10k for polystyrene and polyisoprene),[8] and their dynamic behavior is free from the entanglement effects.

The $G_G^*$ due to the glassy mode is thermo-rheologically simple (unless $T$ is very close to $T_g$), and this simplicity holds for the $G_R^*$ for the rubbery mode as well.[1] However, the shift factors $a_{T,G}$ and $a_{T,G}$ for $G_G^*$ and $G_R^*$ usually have different $T$ dependence, and the

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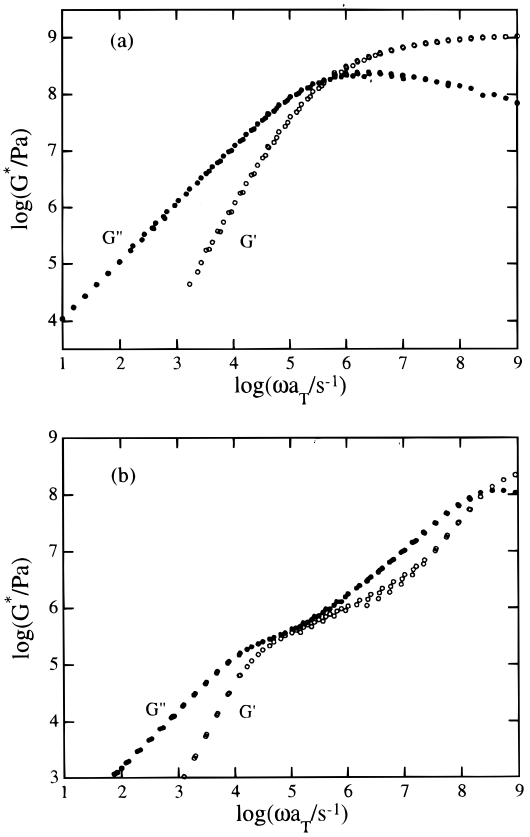


**Figure 1.** Linear viscoelastic moduli $G'$ and $G''$ for (a) OS-1 and (b) PI-8. Master curves are constructed with the data at $T_r$ (=42 and 23 °C for OS-1 and PI-8) being used as the reference. For PI-8, the time−temperature superposition becomes poor at high $\omega$ and low $T$ because of comparable contributions from the glassy and rubbery modes to $G^*$. However, the master curve is constructed in the entire range of $\omega$ and $T$ for the purpose of demonstrating the wide separation of these modes.

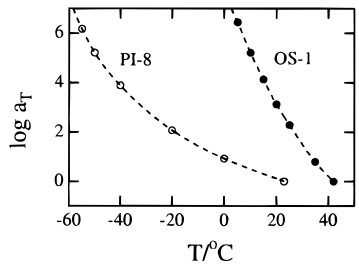


**Figure 2.** Shift factors for the master curves shown in Figure 1.

time−temperature superposition fails for the $G^*$ data if the glassy and rubbery modes have comparable contributions to the data.[1] This is the case for PI-8 at $\omega a_T = 10^6 - 10^7$ s$^{-1}$ where only poor superposition can be achieved; see the branch in the $G'$ curve in part b of Figure 1. Thus the superposition for PI-8 is valid only at low $\omega a_T$ ($<10^6$ s$^{-1}$) where the rubbery mode dominates the $G^*$ data and the Rouse-like shoulder of $G'$ and $G''$ followed by the terminal tails ($G' \propto \omega^2$, $G'' \propto \omega$) are observed. (Despite the failure of the superposition at high $\omega$, the master curve for PI-8 is constructed in the entire range of $\omega$ to demonstrate the wide separation of the glassy and rubbery modes of PI-8.)

In contrast, for OS-1, $G^*$ immediately exhibits the terminal tails on a decrease of $\omega$ from the glassy plateau regime (where $G' \cong 10^9$ Pa), and no Rouse-like shoulder is observed. This fact indicates that $G^*$ of OS-1 is

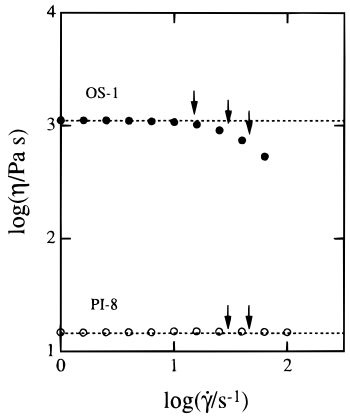


**Figure 3.** Steady-state viscosity $\eta(\dot\gamma)$ for OS-1 at 42 °C and PI-8 at 23 °C. Plots of $|\eta^*(\omega)|$ against $\omega$ are also shown (dashed lines). The arrows indicate the shear rates for the rheo-dielectric data shown in Figure 4.

dominated by the glassy mode at all $\omega$ examined. Correspondingly, the time−temperature superposition works well in the entire range of $\omega$; see part a of Figure 1.

From the $G^*$ data shown in Figure 1, we evaluated the terminal relaxation time in the linear viscoelastic regime, $\tau_1 = [G'/\omega G'']_{\omega\to 0}$. The results are

$$\tau_1 = 1.3 \times 10^{-5} \text{ s for the segmental mode of OS-1 at 42 °C} \quad (1)$$

$$\tau_1 = 4.0 \times 10^{-5} \text{ s for the global mode of PI-8 at 23 °C} \quad (2)$$

These $\tau_1$ characterize the equilibrium motion of OS-1 and PI-8.

**Steady Flow and Rheo-Dielectric Behavior.** Figure 3 shows the shear rate ($\dot\gamma$) dependence of the steady-state viscosity $\eta(\dot\gamma)$ measured for OS-1 at 42 °C and PI-8 at 23 °C. For comparison, plots of the magnitude of complex viscosity $|\eta^*(\omega)|$ against $\omega$ are also shown (dashed line). Figure 4 demonstrates the dielectric loss $\epsilon''$ data in the quiescent state and under steady flow at representative $\dot\gamma$. The $\dot\gamma$ values for these rheo-dielectric data are specified with the arrows in Figure 3.

As seen in Figure 4, the $\epsilon''$ curves of both OS-1 and PI-8 exhibit a peak followed by a low-$\omega$ terminal tail ($\epsilon'' \propto \omega$). The peak corresponds to the segmental motion for OS-1 (having dipoles perpendicular to the backbone) and the global motion for PI-8 (having the parallel dipoles). In fact, a characteristic relaxation time $\tau_{peak} = 1/\omega_{peak}$ evaluated from the $\epsilon''$-peak frequency $\omega_{peak}$ in the quiescent state ($\dot\gamma = 0$), $\tau_{peak} \cong 3 \times 10^{-5}$ s for OS-1 and $\tau_{peak} \cong 7 \times 10^{-5}$ s for PI-8, is close to the linear viscoelastic $\tau_1$ for the equilibrium motion (eqs 1 and 2). (A perfect agreement is not found between $\tau_{peak}$ and $\tau_1$ because of a difference in fundamental features of dielectric and viscoelastic quantities.[6] However, this difference is beyond a scope of this paper and not discussed here.)

For PI-8, the shear rates examined are much smaller than the frequency $\tau_1^{-1}$ for the equilibrium global motion ($\dot\gamma\tau_1 < 0.002$, cf. eq 2). Thus, this motion is not affected by such slow flow, naturally resulting in the $\dot\gamma$-independent $\epsilon''$ data (part b of Figure 4) and in the Newtonian $\eta(\dot\gamma)$ that coincides with $|\eta^*(\omega)|$ at $\omega = \dot\gamma$ (Figure 3).

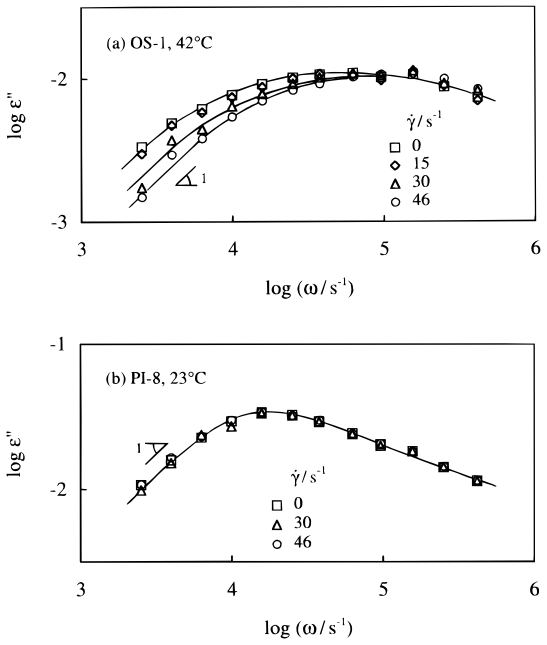


**Figure 4.** Dielectric loss $\epsilon''$ for OS-1 at 42 °C and PI-8 at 23 °C determined under steady shear flow. For comparison, the data in the quiescent state ($\dot{\gamma} = 0$) are also shown.

For OS-1 (part a of Figure 4), no detectable flow effect for the $\epsilon''$ data is found at $\dot{\gamma} < 15$ s$^{-1}$. However, with further increase of $\dot{\gamma}$ up to 46 s$^{-1}$, the terminal tail of the $\epsilon''$ curve is shifted to higher $\omega$ 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 of OS-1 ($\dot{\gamma}\,\tau_1 < 0.001$, cf. eq 1). As noted in Figure 3, the steady $\eta(\dot{\gamma})$ deviates from the $|\eta^*(\omega)|$ data and exhibits thinning at $\dot{\gamma} \geq 15$ s$^{-1}$. This thinning behavior quite possibly results from the acceleration of the segmental motion under flow.

**Origin of Thinning for OS-1.** For homogeneous polymeric liquids, the thinning is usually observed under fast flow (at $\dot{\gamma}\tau_1 > 1$) that overwhelms the equilibrium molecular motion.[8] Nevertheless, the thinning for OS-1 is observed under much slower flow. Similar thinning behavior has been noted also for the glassy mode of polystyrene under very slow elongational flow.[3]

The thinning behavior of the OS-1 system suggests that the 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 $\eta$. (Related thinning behavior is found in molecular dynamics simulation for cluster-forming, supercooled liquids.)[9]

The dynamically heterogeneous structure in OS-1 might be a cooperative domain structure[10] (or the conformer domain structure)[11] characteristic to glassy materials. At time scales of the segmental motion, this dynamic structure could have survived in the OS-1 system even at $T_r = 42$ °C $\gg T_g$ ($\sim$7 °C). 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 $\eta$ for the glassy mode. At this moment, no structural data proving/disproving this speculation is available. Further studies are desired for the structure under flow.

Finally, a brief comment needs to be added for the behavior of PI-8. For PI-8, $\epsilon''$ and $\eta$ in our experimental window reflect the global chain motion, and no flow effect is found at $\dot{\gamma}\tau_1 < 0.002$. Since the thinning behavior of $\eta$ for the rubbery (global) mode is generally determined by the product $\dot{\gamma}\tau_1$,[8,12] the $\eta$ and $\epsilon''$ of PI-8 should be insensitive to $\dot{\gamma}$ ($<0.002\tau_1^{-1}$) at any $T$ well above $T_g$, e.g., at $T = T_g + 35$ °C (where the flow effects for OS-1 were examined). Thus, the findings of this paper, the difference in the flow effects for PI-8 and OS-1, should indicate an essential difference between the rubbery and glassy modes. From this point of view, the dynamic heterogeneity seen at short time scales (glassy regime) appears to be smeared at longer time scales. In other words, the PI-8 system would be in a dynamically homogeneous state at time scales of the global motion so that its $\epsilon''$ and $\eta$ are insensitive to the slow flow at $\dot{\gamma}\tau_1 < 0.002$.

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