Rheo-Dielectrics: Its Applicability

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For a wide variety of systems, structures under flow have been investigated with rheo-optical techniques. It is of particular interest and importance to examine the flow effects on structures and dynamics with different techniques. A rheo-dielectric technique, that detects dynamic dielectric responses under flow, is complementary to rheo-optical techniques and provides us with a very useful method of investigating these effects. This article gives a brief review of rheo-dielectric features of some model systems revealed in recent studies to demonstrate the applicability of the rheo-dielectric technique.

Key Words: Rheo-dielectrics / Polyisoprene / SIS copolymer / 5CB

1. INTRODUCTION

Rheo-optical techniques have been applied to a wide variety of materials and their importance in rheological research has been widely recognized.^{1),2)} These techniques have spatial and time resolutions that depend on the nature of an optical quantity measured under strain/flow: Scattering measurements resolve spatial distribution of a scattering power (structures) but usually have no resolution of time scales for molecular motion. In contrast, dichroism measurements enable us to follow time-dependent changes in orientational anisotropy of particular probes but usually have no spatial resolution. Thus, despite the usefulness of the rheo-optical techniques, the techniques have their intrinsic limitations and are not appropriate for some purposes.

From this point of view, it is desirable to detect molecular motion with different techniques and, if possible, combine the resulting information with the rheo-optical data. Our recent studies^{3)~5)} revealed that a *rheo-dielectric* technique detecting this motion is one of the important techniques complementary to the rheo-optical techniques. This article briefly summarizes rheo-dielectric features of some model materials found in those studies to demonstrate the applicability and limitations of the rheo-dielectric technique.

2. PRINCIPLE AND EXPERIMENTAL SET-UP

2.1 Principle

In general, molecular motion results in dielectric relaxation if the molecules have permanent dipoles. Under an electric field with a sufficiently small magnitude E , the molecular motion is negligibly disturbed and the equilibrium

dynamics is dielectrically detected. The resulting *linear* dielectric responses are discussed in this article.

In steady states, i.e., in quiescent states and under steady flow, the normalized dielectric relaxation function in the linear regime is given by⁶⁾

$$\Phi(t) = \langle P_E(t)P_E(0) \rangle / \langle P_E^2 \rangle \quad (1)$$

where $P_E(t)$ is the component of the polarization of the system at a time t in the direction of the electric field. We can use this Φ also under oscillatory flow when the oscillation is much slower than the relaxation (decay) of Φ .

The complex dielectric constant detected under the oscillatory electric field, $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, is given by the Fourier transform of a time derivative of Φ ,

$$\epsilon^*(\omega) = \epsilon_\infty - \Delta\epsilon \int_0^\infty \frac{d\Phi(t)}{dt} \exp[-i\omega t] dt \quad (2)$$

Here, ϵ_∞ is the high-frequency dielectric constant. $\Delta\epsilon$ is the dielectric intensity determined by the number density of molecules, magnitudes of their dipoles, and amplitudes of orientational fluctuation of the dipoles that are in turn determined by molecular interactions.⁷⁾ Thus the molecular motion inducing the fluctuation of $P_E(t)$ is observed as the dispersion of ϵ^* .

2.2 Experimental set-up

Our experiments utilized guarded cone-plate type electrodes schematically shown in Figure 1. The cone radius was 1.5 cm, and the angle between the cone and plate was 2.6°. The electrodes were mounted on a laboratory rheometer (Auto-viscometer, Iwamoto Seisakusho) that was modified to make an electrical contact to the moving

Fig. 1 A schematic illustration of the rheo-dielectric cell.

electrode (plate) through a mercury reservoir.⁴⁾ This reservoir enabled us to detect the dielectric signals without disturbance from the electrode motion. Automated transformer bridges (GR 1689, General Radio; HP 4285A, Hewlett-Packard) were used to measure ϵ^* .

In a first attempt, we made the electrical connection to the moving electrode with a metal brush similar to that in a motor. However, for nonpolar materials, the measurements of ϵ^* under flow were significantly disturbed by noises due to the frictional motion of the brush against this electrode. The mercury reservoir was found to be very useful to avoid this difficulty.

Under steady shear flow, the set-up shown in Figure 1 allows us to measure ϵ^* in the *shear gradient* direction. In other words, the molecular motion inducing fluctuation of the polarization in this direction is dielectrically detected. At this moment, it is difficult to detect the motion in the flow and vorticity directions, although modification of the electrodes may allow the detection in the latter direction.

3. RESULTS AND DISCUSSION

3.1 Rheo-dielectric behavior of polyisoprene

Figure 2 shows the $\epsilon''(\omega)$ data at 23°C obtained for a bulk *cis*-polyisoprene (PI-8; $M_w = 8.2 \times 10^3$, $M_w/M_n = 1.05$) in the quiescent state and under steady shear flow at $\dot{\gamma} = 46 \text{ s}^{-1}$.³⁾ The PI chain has the so-called type-A dipoles⁸⁾ parallel along the chain backbone, and the global chain motion (end-to-end vector fluctuation) is observed as the dielectric dispersion at the frequencies ω examined.⁹⁾ (The

Fig. 2 Dielectric behavior of PI-8 in the quiescent state and under steady shear flow. (Redrawn, with permission, from Ref. 3)

segmental motion is too rapid to be detected at those ω .)

The dispersion seen in the quiescent state reflects the equilibrium motion of the PI chains. In Figure 2, the terminal tail ($\epsilon'' \propto \omega$) is observed soon after ω is decreased from the ϵ'' -peak frequency ω_p . This peak corresponds to the slowest mode of the chain motion, and its relaxation time is

$$\tau_1 = 1/\omega_p \cong 7 \times 10^{-5} \text{ s} \quad (3)$$

As seen in Figure 2, the steady shear has no effects on the ϵ'' data. (Although not shown here, no effects were found also for ϵ' .) This result is a natural consequence of a fact that the applied shear is much slower than the equilibrium chain motion (i.e., $\dot{\gamma} \ll \tau_1^{-1}$; cf. eq 3) and thus has no effect on this motion. In fact, Newtonian flow behavior, demonstrating lack of the flow effects on the equilibrium dynamics, was confirmed from rheological measurements.³⁾ (Note, however, that the shear slower than the molecular motion could induce dielectric changes if a system has a heterogeneous texture, as explained later for Figure 4.)

We have tried the rheo-dielectric measurements on PI-8 at lower temperatures (T), i.e., at effectively higher shear rates. However, at the rates well above τ_1^{-1} at those T , ϵ'' was not measured accurately because the material was viscoelastic and did not stay in the gap between the cone and plate electrodes. Thus flow geometries other than the cone-plate geometry are required to dielectrically examine the effects of such fast flow on the global motion of the PI chain. One possible geometry is a coaxial capillary geometry (coaxial cylinder geometry with the flow in the direction of the cylinder axis). Rheo-dielectric measurements in this geometry are now being attempted.

3.2 Rheo-dielectric behavior of SIS copolymer

Figure 3 shows the $\epsilon''(\omega)$ data at 50°C (circles) obtained for a styrene-isoprene-styrene (SIS) triblock copolymer ($M_w = 60.2 \times 10^3$, $M_w/M_n = 1.07$, S content = 29 wt%)

Fig. 3 Dielectric behavior of a SIS/tetradecane system in the quiescent state and under steady shear flow. (Redrawn, with permission, from Ref. 4)

dissolved in tetradecane ($c_{\text{SIS}} = 50 \text{ wt\%}$).⁴⁾ The I block has the type-A dipoles and its end-to-end vector fluctuation, if it occurs, leads to the dielectric dispersion at ω examined. In fact, at $T \geq 90^\circ\text{C}$ where the I blocks were uniformly mixed with the S blocks to exhibit this fluctuation, a significant dispersion was observed.⁴⁾ In Figure 3, the dashed curve indicates the dispersion curve expected for the I blocks that are *hypothetically* in this mixed state at 50°C . (This curve was obtained from extrapolation of the $\varepsilon''(\omega)$ data at $T \geq 90^\circ\text{C}$ to 50°C .)

In reality, microphase separation took place at 50°C , and the S blocks formed spherical domains.⁴⁾ These domains, being plasticized with tetradecane to have $T_g = 34 \pm 4^\circ\text{C}$,⁴⁾ were inter-connected by the I blocks. Corresponding to this network structure, the system exhibited elastic behavior under small strains while it flew plastically under steady shear.⁴⁾ The S blocks can be pulled out from one domain and transferred to the others when the steady shear enhances the tension of the connected I blocks, and this chain pull-out/transfer process has been considered to be the mechanism of the plasticity of triblock copolymers.¹⁰⁾

With this mechanism, no significant dielectric dispersion is expected in the quiescent state where the I blocks do not pull out the S blocks and the end-to-end vector fluctuation of the I blocks is essentially frozen. In contrast, this fluctuation should be activated under flow. Thus, for the chain-pull out mechanism, the dielectric dispersion should be induced under the plastic flow and the ε'' data should tend to exhibit up-turn at low ω and approach the dashed curve shown in Figure 3. (If all I blocks pull out the S blocks, the dispersion peak height would be close to that for the dashed curve.)

In Figure 3, no significant dielectric dispersion is seen in the quiescent state, as expected above. However, we also note that the flow has no detectable effects on the dielectric behavior. This result led us to modify the above molecular picture by incorporating heterogeneities in the flow profile

Fig. 4 Dielectric behavior of nematic 5CB in the quiescent state and under steady shear flow.

and existence of loop-type I blocks.⁴⁾ In general, microphase-separated block copolymers form multi-grain structures with many defects^{11,12)} and the deformation/flow tends to occur mostly in defect regions containing only a small fraction of the I blocks. Thus the number of the I blocks pulling out the S blocks in these regions (and exhibiting the dispersion) is much smaller than the total number, and the flow-induced dielectric dispersion appears to be too weak to be detected. In addition, the loop-type I blocks (dielectrically estimated to have $\approx 60\%$ population¹³⁾), having its ends on the same S domain, are not significantly strained under shear and hardly pull out the S blocks if the loops are not mutually interdigitating. Existence of these dangling loops further reduces the intensity of the flow-induced dispersion.¹³⁾

The above arguments in turn demonstrate that the rheo-dielectric technique may allow us to examine the heterogeneity in the deformation/flow profile in the SIS system. This feature of the technique is believed to be useful in studies of systems that exhibit a flow-induced dispersion with the intensity being determined by this heterogeneity, for example, semi-crystalline polymer systems exhibiting characteristic dispersions due to crystallites.

3.3 Rheo-dielectric behavior of nematic 5CB

3.3.1 overview

Figure 4 shows the ε' and ε'' data of 4-4'-n-pentyl-cyanobiphenyl ($\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}\equiv\text{N}$; abbreviated as 5CB) in a stably supercooled nematic state at 5°C . (The data at higher temperatures were published elsewhere.⁵⁾) This 5CB system was prepared by cooling from an isotropic state (45°C) and had a nematic texture.⁵⁾ In this texture, the 5CB

molecules are coherently orientated only within small length scales, and the director specifying this local orientation gradually changes its direction over larger scales.¹⁴⁾ The 5CB molecule has a large dipole along the molecular axis (in the direction of the C≡N bond), and the slow dielectric dispersion essentially detects fluctuation of this axis due to the molecular motion in the texture.

At low $\omega < 10^5 \text{ s}^{-1}$, ϵ'' of our 5CB system is dominated by the direct current (DC) conductance, $\epsilon'' \propto \omega^{-1}$ (cf. Figure 4). In contrast, ϵ' is not affected by this conductance under the experimental conditions examined. Clearly, ϵ' is independent of ω and no dielectric dispersion is observed at $\omega < 10^5 \text{ s}^{-1}$. Thus the dispersion seen at $\omega = 10^5 - 10^8 \text{ s}^{-1}$ is the terminal dispersion of the 5CB molecules in the nematic phase.⁵⁾

In the quiescent state, this dispersion has a very narrow mode distribution and is close to the Debye relaxation. The terminal relaxation time evaluated from the ϵ'' -peak frequency is

$$\tau_1 \cong 3 \times 10^{-7} \text{ s} \quad (4)$$

In contrast, the mode distribution becomes broad and the terminal relaxation intensity is significantly decreased under the slow steady shear at $\dot{\gamma} \ll \tau_1^{-1}$. However, the flow does not change the longest relaxation time τ_1 that determines a frequency at the onset of the terminal behavior, $\epsilon'' \propto \omega$.

The flow effects on ϵ^* disappeared and the behavior of the quiescently prepared nematic 5CB system was recovered within 30 min after cessation of flow. Thus the rheo-dielectric changes seen in Figure 4 correspond to non-permanent structural changes.

3.3.2 assignment of dispersion

Molecular motion in nematic systems is highly anisotropic with respect to the director.^{14)~16)} Thus the dielectric response of the 5CB molecules is dependent on the relative alignment of the director and the electric field E .

For a model system containing only two types of nematic domains having the director parallel or perpendicular to E , ϵ^* can be written in a simple form. If the domains are packed side by side along the electrode surface and each domain extends throughout the gap between the electrodes, ϵ^* is written as⁵⁾

$$\epsilon^*(\omega) = \tilde{v}_{\parallel} \tilde{\epsilon}_{\parallel}^*(\omega) + \tilde{v}_{\perp} \tilde{\epsilon}_{\perp}^*(\omega) \quad (5)$$

On the other hand, if the domains are vertically stacked from one electrode to the other, ϵ^* is⁵⁾

$$\frac{1}{\epsilon^*(\omega)} = \frac{\tilde{v}_{\parallel}}{\tilde{\epsilon}_{\parallel}^*(\omega)} + \frac{\tilde{v}_{\perp}}{\tilde{\epsilon}_{\perp}^*(\omega)} \quad (6)$$

In eqs. (5) and (6), $\tilde{\epsilon}_x^*$ is the complex dielectric constant for

the domains having the director parallel ($x = \parallel$) or perpendicular ($x = \perp$) to E , and $\tilde{v}_x$ is the number fraction of the molecules in respective domains. $\tilde{\epsilon}_{\parallel}^*$ and $\tilde{\epsilon}_{\perp}^*$ can be replaced by the ϵ^* data of a macroscopic monodomain measured in respective directions.

The nematic texture in our 5CB system can be dielectrically regarded as an ensemble of domains that have randomly distributed directors and are packed/stacked in various ways. For this multi-domain structure, ϵ^* is between those given by eqs. (5) and (6), and the molecules in domains having the director not exactly parallel and/or perpendicular to E contribute to both $\tilde{v}_{\parallel}$ and $\tilde{v}_{\perp}$.

For 4-4'-n-heptyl-cyanobiphenyl cyanobiphenyl (7CB) chemically very similar to 5CB, Davies et al.¹⁵⁾ and Lippens et al.¹⁶⁾ indicated that the relaxation of $\tilde{\epsilon}_{\parallel}^*$ is much slower than that of $\tilde{\epsilon}_{\perp}^*$. Thus the terminal dispersion of 7CB having the nematic texture corresponds to the relaxation of $\tilde{\epsilon}_{\parallel}^*$. This should be the case also for our 5CB system. In fact, the τ_1 value of 5CB (eq. (4)) was found to be close to the literature data of τ_1 for $\tilde{\epsilon}_{\parallel}^*$ of 7CB (extrapolated to 5°C).⁵⁾ Thus the dispersion seen in Figure 4 is assigned to the relaxation of $\tilde{\epsilon}_{\parallel}^*$ for the 5CB system. (The faster relaxation of $\tilde{\epsilon}_{\perp}^*$ is hardly observed in our experimental window.)

3.3.3 origin of rheo-dielectric changes

On the basis of the above assignment, the rheo-dielectric changes seen in Figure 4 are attributed to a flow-induced decrease of $\tilde{v}_{\parallel}$ (cf. eqs. (5) and (6)). This decrease results in an increase of $\tilde{v}_{\perp}$ that leads to the up-turn of the ϵ'' data at $\omega > 10^7 \text{ s}^{-1}$ under flow. This up-turn corresponds to the terminal tail of $\tilde{\epsilon}_{\perp}''$ ($\propto \omega$). In relation to these changes of $\tilde{v}_{\parallel}$ and $\tilde{v}_{\perp}$, we emphasize that the flow at $\dot{\gamma} \ll \tau_1^{-1}$ has no detectable effect on the molecular motion and thus on τ_1 , as observed.

The decrease of $\tilde{v}_{\parallel}$ is related to the flow-induced orientation of the nematic director. For nematic 5CB homeotropically aligned on a lecithin-treated parallel-plate fixture, Mather et al.¹⁷⁾ rheo-optically found that the director is orientated toward the flow direction within a plane formed by the velocity gradient and flow axes. This director orientation should have been more easily attained in our 5CB system having no homeotropic alignment in the initial state. Clearly, the orientation in the flow direction (perpendicular to the electric field) leads to the decrease of $\tilde{v}_{\parallel}$ and results in the observed rheo-dielectric changes.

4. CONCLUDING REMARKS

We have demonstrated the importance of the rheo-dielectric technique in investigation of flow effects on the textures and molecular motion. This technique is useful in

particular for molecules exhibiting anisotropic motion (e.g., 5CB). At the same time, it should be noted that a direct effect of flow on the molecular motion has not been observed for *any* of the three systems examined in this article: The flow examined was too slow to raise this effect. To detect the flow effects on the molecular motion, we are now attempting rheo-dielectric measurements under fast flow in geometries other than the cone-plate geometry, e.g., the coaxial capillary geometry.

REFERENCES

- 1) Fuller GG, *Optical Rheometry*, Oxford, New York, 1995.
- 2) Janeschitz-Kriegl H, *Polymer Melt Rheology and Flow Birefringence*, Springer, New York, 1983.
- 3) Matsumiya Y, Watanabe H, Inoue T, Osaki K, Yao ML, *Macromolecules*, **31**, 7973 (1998).
- 4) Sato T, Watanabe H, Osaki K, *Macromolecules*, **29**, 6231 (1996).
- 5) Watanabe H, Sato T, Hirose M, Osaki K, Yao ML, *Rheol Acta*, **37**, 519 (1998).
- 6) Cole RH, *J Chem Phys*, **42**, 637 (1965).
- 7) Fröhlich H, *Theory of Dielectrics* (Second Ed), Clarendon, Oxford, 1960.
- 8) Stockmayer WH, *Pure Appl Chem*, **15**, 539 (1967)
- 9) Adachi K, Kotaka T, *Prog Polym Sci*, **18**, 585 (1993).
- 10) Watanabe H, Kuwahara S, Kotaka T, *J Rheol*, **28**, 393 (1984).
- 11) Koppi KA, Tirrell M, Bates FS, *Phys Rev Lett*, **70**, 1449 (1993).
- 12) Balsara NP, Hammouda B, Kesani PK, Jonnalagadda SV, Straty GC, *Macromolecules*, **27**, 2566 (1994).
- 13) Watanabe H, Sato T, Osaki K, Yao ML, Yamagishi A, *Macromolecules*, **30**, 5877 (1997)
- 14) de Jeu WH, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, New York, 1980.
- 15) Davies M, Moutran R, Price AH, Beevers MS, Williams G, *J Chem Soc Faraday II*, **72**, 1447 (1976).
- 16) Lippens D, Parneix JP, Chapoton A, *J de Physique*, **38**, 1465 (1977).
- 17) Mather PT, Pearson DS, Larson RG, *Liquid Crystals*, **20**, 527 (1996).