

Division of Multidisciplinary Chemistry – Molecular Rheology –

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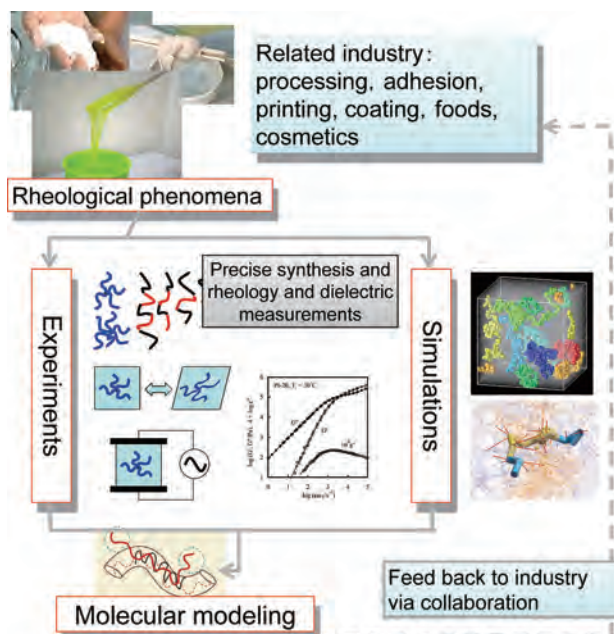
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Scope of Research

Research focus is placed on the molecular origin of rheological properties of various materials. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For basic understanding of these features, the molecular motion and structures at various scales are studied for polymeric systems in deformed state. Rheological measurements are performed with various rheometers. Auto-correlation of the molecular orientation is also investigated with dynamic dielectric spectroscopy. Analysis of rheological and dielectric behavior elucidates a new aspect of softmatter physics.

KEYWORDS

Rheology Dielectric Spectroscopy
Soft Matter Mesoscopic Model



Recent Selected Publications

Sato, T.; Matsumiya, Y.; Watanabe, H., Experimental Study of Phase Separation in Dynamically Asymmetric Unentangled Polymer Blend, *J. Chem. Phys.*, **157**, 224908 (2022).

Matsumiya, Y.; Sato, T.; Chen, Q.; Watanabe, H., Rheo-Dielectric Behavior of Unentangled Poly(butylene oxide) under Steady Shear: Preliminary Evaluation of Non-Equilibrium Parameters at the Onset of Nonlinearity, *Nihon Reoroji Gakkaishi*, **50(5)**, 371-385 (2022).

Sato, T.; Larson, R. G., Nonlinear Rheology of Entangled Wormlike Micellar Solutions Predicted by a Micelle-Slip-Spring Model, *J. Rheol.*, **66**, 639-656 (2022).

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, *Nihon Reoroji Gakkaishi*, **50**, 253-268 (2022).

Sato, T., Modeling Techniques for the Rheology of Wormlike Micellar Solutions, *Nihon Reoroji Gakkaishi*, **50**, 9-13 (2022).

Rheo-Dielectric Behavior of Unentangled Poly(butylene oxide) under Steady Shear: Preliminary Evaluation of Non-Equilibrium Parameters at the Onset of Nonlinearity

For a type-A Rouse chain, a recent study derived an analytical expression of its dielectric loss ε'' under steady shear in terms of the Rouse parameters, the spring strength κ , the friction coefficient ζ , and the mean-square Brownian force intensity \mathbf{B} , all being allowed to arbitrarily change with the Weissenberg number Wi (i.e., shear rate multiplied by the longest relaxation time at equilibrium) and the latter two having a tensorial form. Here, we have conducted a rheo-dielectric test for a type-A unentangled melt, poly(butylene oxide) to measure ε_y'' in the velocity gradient (y) direction as well as the viscosity η and the first normal stress difference coefficient Ψ_1 . Both dielectric relaxation time and intensity were found to decrease on an increase of Wi up to the onset of rheological nonlinearity where η and Ψ_1 exhibited moderate thinning, but the dielectric relaxation mode distribution was not affected by this increase of Wi . Analyzing those ε_y'' , η , and Ψ_1 data on the basis of the above expressions, we found that κ increases moderately but the off-diagonal components of ζ remains negligibly small on that increase of Wi . We also found that the diagonal components ζ_{xx} (with x being the velocity direction) and B_{yy} hardly change but ζ_{yy} decreases moderately. These results serve as a starting point for deeper investigation of κ , ζ , and \mathbf{B} .

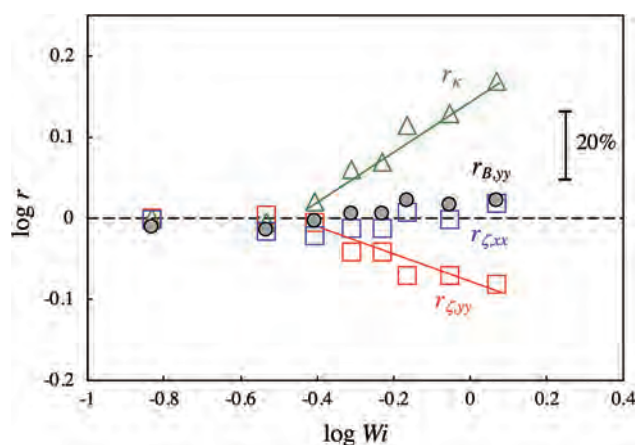


Figure 1. Changes of non-equilibrium parameters r 's with the Weissenberg number Wi defined with respect to the longest viscoelastic relaxation time in the LVE regime.

Experimental Study of Phase Separation in Dynamically Asymmetric Unentangled Polymer Blend

We examined a phase separation process of a dynamical asymmetric blend of unentangled polyisoprene (PI) and poly(4-ethylstyrene) (PC2St) exhibiting the upper critical solution temperature (UCST). PI having the type-A dipole was the dielectrically active fast component, whereas PC2St was the dielectrically inert slow component whose dynamics can be detected by rheological measurements. To precisely model the phase separation process, it is important to estimate the composition-dependence of the mobility which is needed to describe the phase separation dynamics. For that purpose, we conducted dielectric and rheological measurements to determine the friction coefficient of each component in a homogeneous state sufficiently above the phase separation temperature. The temperature dependence of the friction coefficient of each component was reasonably expressed by the Williams-Landel-Ferry (WLF) equation. Extrapolating this dependence obtained for blends of various compositions to the test temperature T^* below the phase separation temperature, we were able to estimate the friction coefficient of the chain at T^* as a function of the composition. This friction coefficient was then used to determine the mobility Λ defined for the material fluxes at T^* . The time-dependent Ginzburg-Landau (TDGL) equation incorporating this Λ well described the experimentally observed phase separation dynamics. In particular, the 2D TDGL simulation with this Λ qualitatively captured the phase-separated structure observed with the optical microscope as well as broad dielectric mode distribution of the blend at T^* .

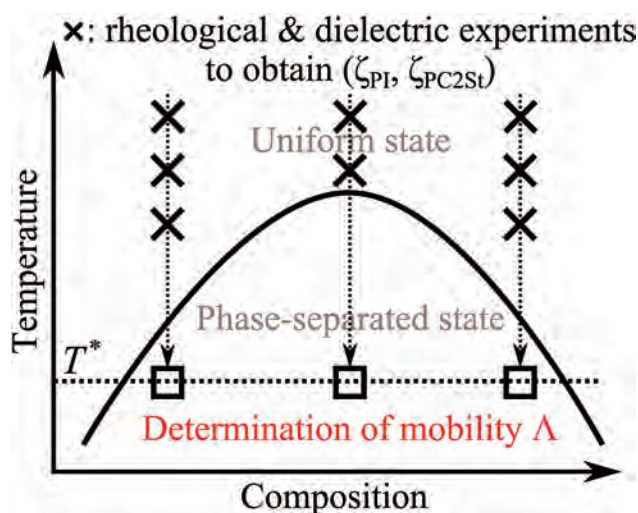


Figure 2. Schematic illustration of the experimental strategy to obtain the mobility.