Division of Multidisciplinary Chemistry
– Molecular Rheology –

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Assoc Prof
MATSUMIYA, Yumi
(D Eng)

Assist Prof
SATO, Takeshi
(D Eng)

Students

MATSUTO, Naoki (M2)   YAMAMOTO, Ayumu (M1)
TOSAKI, Tomohiro (M2)   KITAGAWA, Yoshifumi (UG)

Guest Scholars

KWON, Youngdon (Ph D)   Sungkyunkwan University, Korea, 15 January 2023–20 January 2023
LIM, KyungKon (Ph D)   Ewha Womens University, Korea, 15 January 2023–18 January 2023

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
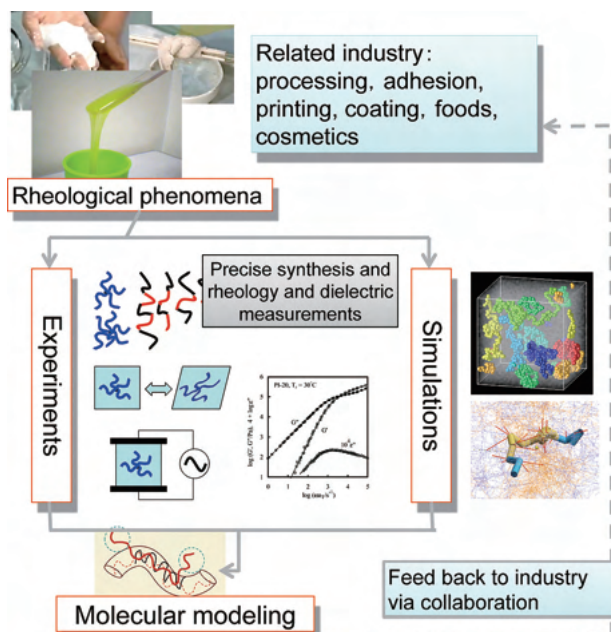
Recent Selected Publications

Sato, T.; Gong, Y.; Larson, R. G., Testing the Ability of the Slip-Spring Model to Describe Constraint Release Effects Using Experimental Linear and Nonlinear Rheology, *Macromolecules*, **56,** 8116-8132 (2023).

Miyamoto, S.; Sato, T.; Taniguchi, T., Stretch-Orientation-Induced Reduction of Friction in Well-Entangled Bidisperse Blends: a Dual Slip-Link Simulation Study, *Rheologica Acta*, **62,** 57-70 (2023).

Matsumiya, Y.; Sato, T.; Chen, Q.; Watanabe, H., Rouse Analysis of Nonlinear Rheology of Unentangled Polymer Melts under Fast Shear: Viscoelastic Response to Superposed Oscillatory Strain, *Macromolecules*, **56,** 2930-2983 (2023).

Topics

Rouse Analysis of Nonlinear Rheology of Unentangled Polymer Melts under Fast Shear: Viscoelastic Response to Superposed Oscillatory Strain

Nonlinear rheological behavior of unentangled polymer melts can be described by the Rouse model given that its parameters, spring strength κ, bead friction coefficient ζ, and mean-square Brownian force intensity B, are allowed to change under fast flow/large strain (and to take anisotropic tensorial forms when necessary). Within this model, analytic expressions in terms of those parameters have been obtained for measurable quantities that include viscosity η, the first normal stress difference coefficient Ψ_1, and complex dielectric permittivity ε^*. Those expressions in turn enable us to extract κ, ζ, and B from experimental data of unentangled melts. In particular, the rheo-dielectric ε^* data under shear, recently obtained for unentangled low-M poly (butylene oxide) melt having type-A dipoles (PBO-16k; $M = 16 \times 10^3$), suggest that the tensorial ζ and B have negligibly small off-diagonal components in a range of Weissenberg number Wi up to 1.2. On the basis of that study, we here focus on the complex shear moduli $G_\parallel^*$ and $G_\perp^*$ of the Rouse chain defined as responses to a small oscillatory strain superposed on the steady shear flow, with $\parallel$ and $\perp$ representing parallel and perpendicular superposition, respectively. In the case of negligible off-diagonal components of ζ and B, the Rouse analysis gave a very simple expression of those moduli, $G_X^*(\omega) = b_X^{[G]} G_{eq}^*(\omega\alpha_X^{[G]})$ with X = $\parallel$ and $\perp$, where $G_{eq}^*(\omega)$ is the linear viscoelastic (LVE) complex modulus at an angular frequency ω. Namely, in that case, the relaxation time of G_X^* decreases by a factor of $\alpha_X^{[G]}$ (<1) and its terminal relaxation intensity is enhanced by a factor of $b_X^{[G]}$ (>1), but a relative distribution of the relaxation modes exhibits no change. Furthermore, the Rouse parameters obtained from the η, Ψ_1, and ε^* data of PBO-16k were found to satisfy a specific empirical relationship, $\{b_\parallel^{[G]}\}^2 \cong 1/\alpha_\parallel^{[G]}$. Because $G_{eq}'(\omega) \cong G_{eq}''(\omega) \propto \omega^{1/2}$ at high ω where the LVE Rouse relaxation has not completed, this relationship suggests $G_\parallel''(\omega) = G_{eq}''(\omega)$ at $\omega > 1/\tau_\parallel^{[G]}$ and $G_\parallel''(\omega) < G_{eq}''(\omega)$ at $\omega < 1/\tau_\parallel^{[G]}$, where $\tau_\parallel^{[G]}$ is the terminal viscoelastic relaxation time defined for $G_\parallel^*(\omega)$. This behavior of $G_\parallel''(\omega)$ is superficially equivalent to that expected for a case of disappearance of viscous contributions of low-order Rouse eigenmodes under fast shear discussed in the literature on the basis of the concept of Pincus blob. However, the current Rouse analysis clearly indicated that all eigenmodes keep their viscous contributions with a magnitude determined by ζ and κ under flow, confirming the importance of nonequilibrium changes of ζ and κ in the nonlinear flow behavior of unentangled melts.