

Division of Multidisciplinary Chemistry

– Molecular Rheology –

<https://molrheo.kuicr.kyoto-u.ac.jp/en/>



Prof
WATANABE, Hiroshi
(D Sc)



Assoc Prof
MATSUMIYA, Yumi
(D Eng)



Assist Prof
SATO, Takeshi
(D Eng)

Students

EBARA, Shunsuke (UG)

KAWAKATSU, Hikaru (UG)

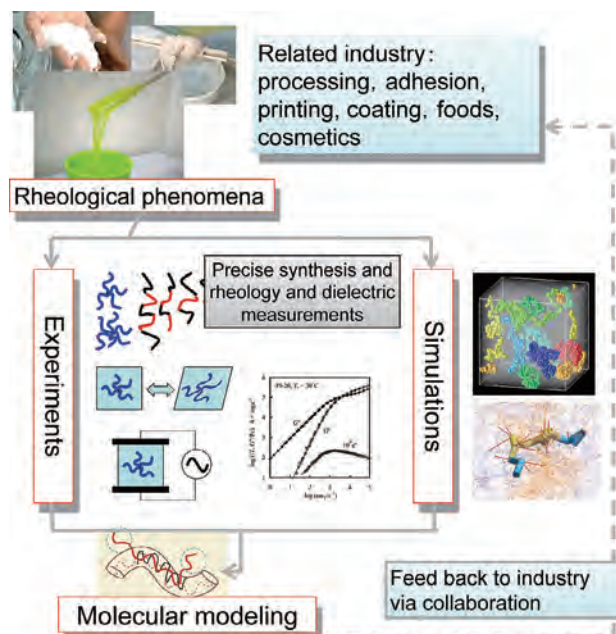
OHARA, Miu (UG)

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 Softmatter



Recent Selected Publications

Sato, T.; Kwon, Y.; Matsumiya, Y.; Watanabe, H., A Constitutive Equation for Rouse Model Modified for Variations of Spring Stiffness, Bead Friction, and Brownian Force Intensity Under Flow, *Phys. Fluids*, **33**, 063106 (2021).

Matsumiya, Y.; Watanabe, H.; Sukhonthamethirat, N.; Vao-Soongnern, V., Viscoelastic and Dielectric Behavior of Polyisoprene Monofunctionally Head-Modified with Associative Metal-Carboxylate Group, *J. Soc. Rheol. Jpn.*, **49**, 189-197 (2021).

Shimada, R.; Urakawa, O.; Inoue, T.; Watanabe, H., Phase Equilibrium and Dielectric Relaxation in Mixture of 5CB with Dilute Dimethyl Phthalate: Effect of Coupling between Orientation and Composition Fluctuations on Molecular Dynamics in Isotropic One-Phase State, *Soft Matter*, **17**, 6259-6272 (2021).

Watanabe, H.; Matsumiya, Y.; Sato, T., Revisiting Nonlinear Flow Behavior of Rouse Chain: Roles of FENE, Friction-Reduction, and Brownian Force Intensity Variation, *Macromolecules*, **54**, 3700-3715 (2021).

Matsumiya, Y.; Watanabe, H., Non-Universal Features in Uniaxially Extensional Rheology of Linear Polymer Melts and Concentrated Solutions: A Review, *Prog. Polym. Sci.*, **112**, 101325 (2021).

Revisiting Nonlinear Flow Behavior of Rouse Chain: Roles of FENE, Friction-Reduction, and Brownian Force Intensity Variation

The local elastic strength κ , segmental friction coefficient ζ , and the Brownian force intensity B of polymer chains in a melt are expected to change under fast flow. This study examined the effects of those changes on rheological and structural properties of the Rouse model, the most frequently utilized model for unentangled melts. Specifically, the Langevin equation of the Rouse model was solved with the decoupling and preaveraging approximations to derive analytical expressions of nonlinear rheological properties and the end-to-end stretch ratio under steady shear and extension. The expressions explicitly included nonequilibrium parameters r_κ , r_ζ , and r_B defined as the ratios of κ , ζ , and B under flow to those at equilibrium, thereby offering a method of evaluating each of r_κ , r_ζ , and r_B from rheological and structural data under flow within the framework of those approximations. Data of extensional viscosity η_E and the relaxation rate of the tensile stress decay coefficient η_E^- reported for the unentangled polystyrene melt (PS-27k; $M = 27.1 \times 10^3$) and data of shear viscosity η and the first normal stress difference coefficient Ψ_1 reported for the PS-14k melt ($M = 13.7 \times 10^3$) were analyzed with this method to evaluate the r_ζ/r_κ ratio under respective flow conditions. The r_ζ/r_κ ratios thus obtained under extension and shear were found to exhibit the same dependence on the Weissenberg number Wi , given that Wi was reduced to an iso-local stretch state wherein the local elastic unit of the chain (Rouse spring) is stretched to the same extent under extension and shear. The analytical expressions of the rheological properties also enabled a preliminary test

of the behavior of r_B . This test, made for the η_E , η_E^- , η , and Ψ_1 data mentioned above, posed a serious question about the relationships under fast flow often assumed in molecular models, $r_B = r_\zeta$ (proportionality between B and ζ not affected by flow) and $r_B = 1$ (no flow effect on B).

Viscoelastic and Dielectric Behavior of Polyisoprene Monofunctionally Head-Modified with Associative Metal-carboxylate Group

For moderately entangled high-*cis* polyisoprene (molecular weight = 30.5×10^3) head-modified with an associative metal-carboxylate (salt) group, PI30-COOM with $M = \text{Li, Na, and K}$, linear viscoelastic and dielectric measurements were conducted to examine an effect(s) of the head-to-head association on the chain dynamics. The PI30-COOM chains had type-A dipoles so that their large-scale dynamics was reflected in both viscoelastic and dielectric data at low angular frequencies. The salt groups associate and dissociate (without ionization) with a rate that changes with the temperature T , as known for ionomers having non-polar backbones. Correspondingly, PI30-COOM exhibited failure of the time-temperature superposition for both viscoelastic and dielectric data. This failure was characterized through comparison with non-associative reference homo-PI, the PI30 unimer (a precursor of PI30-COOM), (PI30)₂ dimer, and (PI30)₆ star-type hexamer. It turned out that the viscoelastic data of PI30-COOLi at low and intermediate T (-20° and 20°C), respectively, were close to those of the star-hexamer and dimer data in the iso-frictional state, and a further increase of T resulted in deviation from the dimer data toward the unimer data. This “crossover” was observed also for PI30-COONa and PI30-COOK but at lower T , which possibly reflected a barrier for the dissociation of the COOM groups lowering in the order of COOLi > COONa > COOK. The dielectric data of PI30-COOM showed a qualitatively similar crossover but at higher T compared to the viscoelastic crossover. This difference between the viscoelastic and dielectric behavior was discussed in relation to the dynamic tube dilation mechanism and also to the motional coupling (conformational transfer) among the PI30-COOM chains coexisting in different association forms.

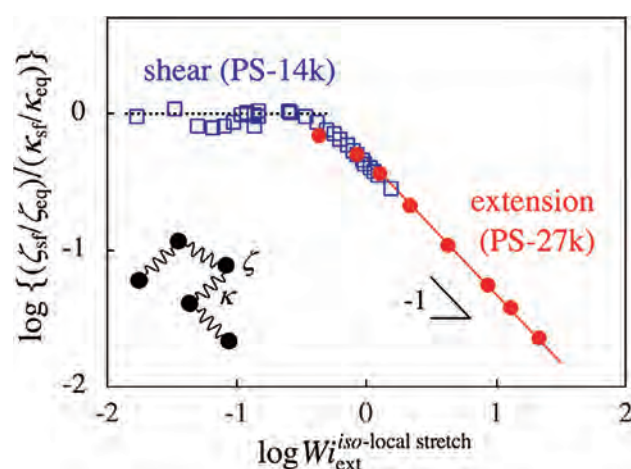


Figure 1. Comparison of the ratio of friction reduction factor ζ_{sf}/ζ_{eq} and spring strength reduction factor κ_{sf}/κ_{eq} against extensional Weissenberg number in the iso-local stretch condition Wi_{ext}^{iso-lu} for PS-14k under shear and PS-27k under extension.