Division of Multidisciplinary Chemistry
– Molecular Rheology –

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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   Softmatter
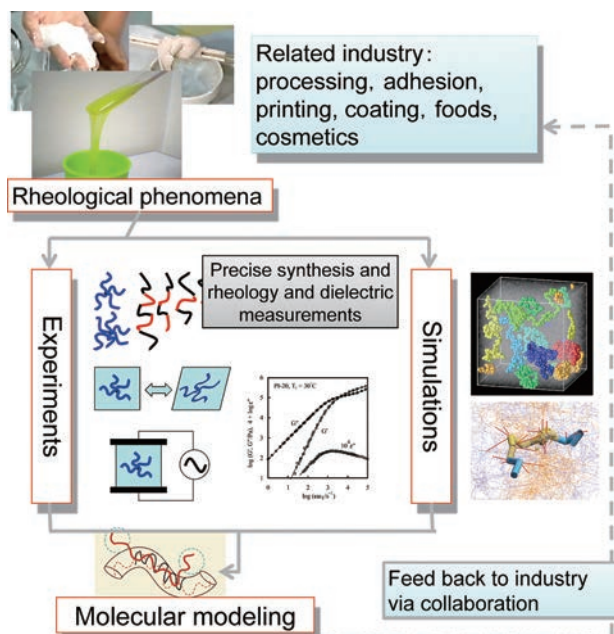
Selected Publications

Mongcopa, K. I. S.; Tyagi, M.; Mailoa, J. P.; Samsonidze, G.; Kozinsky, B.; Mullin, S. A.; Gribble, D. A.; Watanabe, H.; Balsara, N. P., Relationship between Segmental Dynamics Measured by Quasi-Elastic Neutron Scattering and Conductivity in Polymer Electrolytes, *ACS Macro Lett.*, **7**, 504-508 (2018).

Wu, S.; Cao, X.; Zhang, Z.; Chen, Q.; Matsumiya, Y.; Watanabe, H., Molecular Design of Highly Stretchable Ionomers, *Macromolecules*, **51**, 4735-4746 (2018).

Watanabe, H.; Matsumiya, Y.; Kwon, Y., Iscoelastic and Dielectric Relaxation of Reptating Type-A Chains Affected by Reversible Head-to-Head Association and Dissociation, *Macromolecules*, **51**, 6476-6496 (2018).

Matsumiya, Y.; Watanabe, H.; Masubuchi, Y.; Huang, Q.; Hassager, O., Nonlinear Elongational Rheology of Non-Entangled Polystyrene and Poly(p-tert-butylstyrene) Melts, *Macromolecules*, **51**, 9710-9729 (2018).

Topics

Nonlinear Elongational Rheology of Non-Entangled Polystyrene and Poly(*p-tert*-butylstyrene) Melts

Nonlinear rheological behavior under uniaxial elongation was examined for unentangled melts of polystyrene (PS27; M = 27k) and poly(*p-tert*-butyl styrene) (PtBS53; M = 53k) having nearly the same number of Kuhn segments *per* chain, n_K = 30 and 35 for PS27 and PtBS53, respectively. For both materials, the steady-state elongational viscosity η_E exhibited strain-rate-hardening and then strain-rate-softening on an increase of the Weissenberg number $Wi \geq 0.3$ ($Wi = \dot{\varepsilon}\tau_1^{eq}$, with τ_1^{eq} and $\dot{\varepsilon}$ being the longest relaxation time in the linear viscoelastic regime and the Hencky strain rate, respectively). For the unentangled melts, the hardening and softening were free from any entanglement nonlinearity, so that the hardening was unequivocally related to the finite extensible nonlinear elasticity (FENE) of the chain, and the softening, to suppression of the FENE effect due to reduction of the segmental friction ζ occurring for the highly stretched and oriented chain. Thus, the ζ-reduction, speculatively discussed for entangled melts so far, was experimentally confirmed, to the first time, for unentangled melts. Quantitatively, the hardening at intermediate Wi was stronger and the softening at higher Wi was weaker for PtBS53 than for PS27 despite the similarity of their n_K values, which suggested that the magnitude of ζ-reduction depends on the chemical structure of the chains. For estimation of this magnitude, the well-established FENE bead-spring model (FENE-PM model) was modified for the ζ-reduction in an empirical way with an *assumption* that ζ at a given time is fully determined by the chain stretch/orientation and thus by the elongational stress σ_E at that time. This modified model was able to mimic the steady state η_E data excel-

lently, and the ζ-reduction utilized in the modification was weaker for PtBS53 than for PS27k to confirm the dependence of the ζ-reduction on the chemical structure of the chain. Nevertheless, the same modified model failed to accurately describe the transient stress growth and relaxation data on start-up and cessation of fast flow (at $Wi \geq 4$), despite its success in description of the transient stress data for slow flow as well as the steady-state η_E data in the entire range of Wi. Specifically, changes of ζ in the unentangled melts with time during the relaxation for large Wi were delayed compared to the model calculation. This result suggests that ζ is determined not only by the chain stretch/orientation (*i.e.*, by σ_E) at respective times but also by the transient changes of the stretch/orientation (by $\dot{\sigma}_E$), with those changes vanishing in the steady state thereby allowing the model to describe the η_E data. The origin of the change of ζ with the transient changes of the stretch/orientation is discussed in relation to the local motion of the chain necessary for adjusting its friction to the changes of the stretch/orientation environment.
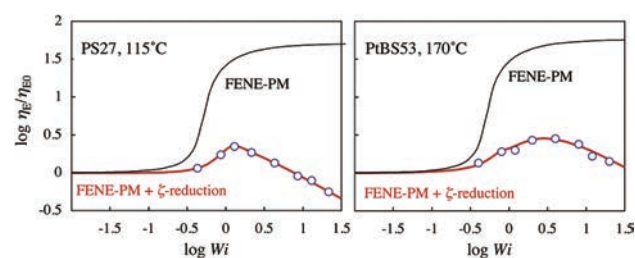

Figure 1. Steady state elongational viscosity η_E of PS27 at 115°C (left) and PtBS53 at 170°C (right). The η_E data are normalized by $\eta_{E0} = 3\eta_0$ (η_0 = zero-shear viscosity) and plotted against the Weissenberg number $Wi = \dot{\varepsilon}\tau_1^{eq}$, with τ_1^{eq} being the longest relaxation time in the LVE regime measured after cessation of elongational flow. The small red circle and red curve indicate the η_E/η_{E0} ratio calculated from FENE-PM model modified for anisotropic and isotropic ζ-reduction, respectively. Black curve shows the FENE-PM calculation without ζ-reduction.