The molecular origin of various rheological properties of materials is studied. 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 a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of auto-correlation of the orientation with dynamic dielectric spectroscopy.

**Scope of Research**

**Presentations**

- Dynamics of Monofunctional Polybutadienyl Lithium Chains Aggregated in Benzene, Watanabe H, AERC06, Hersonisos, Crete, Greece, April 2006.
- Non-Newtonian Behavior of Diblock and Triblock Copolymer Solutions, Matsumiya Y, AERC06, Hersonisos, Crete, Greece, April 2006.
- Transient Conformational Change of Bead-spring Ring Chain during Creep Process, Watanabe H, SOR Meeting, Portland, MA, USA, October 2006.

**Grants**

- Watanabe H, Creation of Non-equilibrium Soft Matter Physics: Structure and Dynamics of Mesoscopic Systems, Grant-in-Aid for Scientific Research on Priority Areas,
Constraint Release in Moderately Entangled Monodisperse Star Polyisoprene Systems

For examination of a constraint release (CR) contribution to relaxation in monodisperse systems of moderately entangled 6-arm star polyisoprenes (PI), viscoelastic measurements were conducted for blends of these star PI and a high molecular weight (M) linear PI. In the blends, the linear PI was dilute and entangled only with the matrix star chains. The terminal relaxation of this dilute linear probe occurred through competition of reptation and Rouse-type CR, as confirmed from its relaxation mode distribution. The probe relaxation time $\tau_{\text{probe}}$ measured in the blends was utilized in the following way to elucidate the CR relaxation of the star matrices. Since the CR time $\tau_{\text{CR}}$ of the star matrix is expressed as $(2N_a)^2\tau_{\text{life}}$ with $2N_a$ and $\tau_{\text{life}}$ being the entanglement number per two arms (span length) and the effective entanglement lifetime in the system, $\tau_{\text{CR}}$ can be evaluated if the $\tau_{\text{life}}$ value is known. For determination of the $\tau_{\text{life}}$ value, the $\tau_{\text{probe}}$ data of the linear probe in the star matrices was compared with the $\tau_{\text{probe}}$ data of the same probe in linear PI matrices (Figure 1) under a molecular idea that $\tau_{\text{life}}$ should be the same in a pair of star and linear matrices giving the same $\tau_{\text{probe}}$ value. The molecular weight $M_{L,\text{mat}}$ of the linear matrix paired with each star matrix was thus specified as indicated with the filled squares in Figure 1, and the value of $\tau_{\text{life}}$ in the star matrix was determined by utilizing this $M_{L,\text{mat}}$ value in an empirical equation of $\tau_{\text{life}}$ in the linear matrices ($\tau_{\text{life}}=2.5\times10^{-18}M_{L,\text{mat}}^3$ s at 40°C). For the monodisperse systems of the star PI, the $\tau_{\text{CR}} = (2N_a)^2\tau_{\text{life}}$ thus evaluated was close to the measured relaxation time (Figure 2), indicating that the CR mechanism significantly contributes to the star relaxation. This result was in harmony with the validity of the molecular picture of partial dynamic-tubedilation (p-DTD) confirmed for the star PI.

Figure 1. Plots of the terminal viscoelastic relaxation time $\tau_{\text{probe}}$ of the dilute linear probe in 6-arm star PI matrices (large unfilled squares) and/or linear PI matrices (circles) at 40°C. The symbols with pip indicate that the probe exhibited pure CR behavior in the given matrices.

Figure 2. Comparison the viscoelastic CR relaxation time $\tau_{\text{CR}}$ for monodisperse systems of star and linear PI chains with the observed terminal relaxation time $\tau_{\text{obs}}$ (circles) at 40°C.

October 2006–March 2011.

Watanabe H, Grant-in-Aid for Scientific Research (B), Relationship between Loop Content and Rheological Behavior of Multi-block Copolymer System, 1 April 2005–31 March 2007.


Matsumiya Y, Grant-in-Aid for Young Scientists (B), Rheo-dielectric Study on Non-equilibrium Dynamics of Polyether/lithium Salt Mixture Systems, 1 April 2005–31 March 2007.