

# Division of Multidisciplinary Chemistry – Molecular Rheology –

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## Scope of Research

The molecular origin of various rheological properties of material 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. Direct observation of molecular motion is also carried out with fluorescent microscopy and molecular simulations.

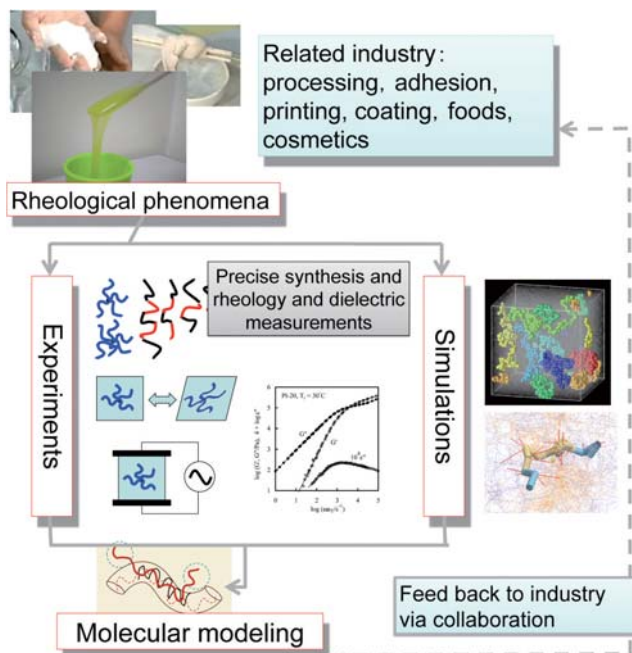
### KEYWORDS

Rheology

Softmatter

Dielectric Spectroscopy

Primitive Chain Network Simulation



## Selected Publications

Masubuchi, Y.; Watanabe, H., Origin of Stress Overshoot under Start-up Shear in Primitive Chain Network Simulation, *ACS Macro Letters*, **3**, 1183-1186 (2014).

Matsumiya, Y.; Masubuchi, Y.; Inoue, T.; Urakawa, O.; Liu, C.-Y.; van Ruymbeke, E.; Watanabe, H., Dielectric and Viscoelastic Behavior of Star-Branched Polyisoprene: Two Coarse-Grained Length Scales in Dynamic Tube Dilution, *Macromolecules*, article ASAP DOI: 10.1021/ma501561y.

van Ruymbeke, E.; Shchetnikava, V.; Matsumiya, Y.; Watanabe, H., Dynamic Dilution Effect in Binary Blends of Linear Polymers with Well-Separated Molecular Weights, *Macromolecules*, article ASAP DOI: 10.1021/ma501566w.

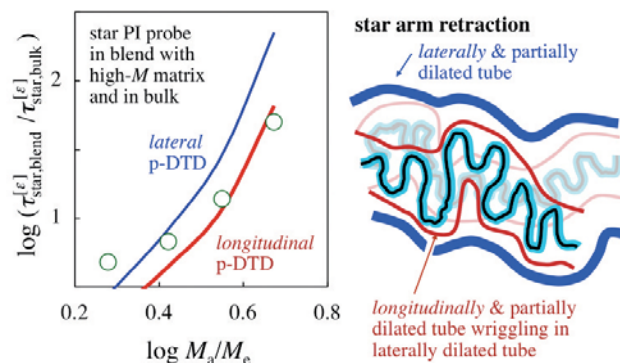
Masubuchi, Y.; Matsumiya, Y.; Watanabe, H., Test of Orientation/Stretch-Induced Reduction of Friction via Primitive Chain Network Simulations for Polystyrene, Polyisoprene, and Poly (n-butyl acrylate), *Macromolecules*, **47(19)**, 6768-6775 (2014).

Masubuchi Y.; Matsumiya, Y.; Watanabe, H.; Marrucci, G.; Ianniruberto, G., Primitive Chain Network Simulations for Pom-Pom Polymers in Uniaxial Elongational Flows, *Macromolecules*, **47(10)**, 3511-3519 (2014).

## Dielectric and Viscoelastic Behavior of Star-Branched Polyisoprene: Two Coarse-Grained Length Scales in Dynamic Tube Dilution

cis-Polyisoprene (PI) chain has the type A dipole parallel along the backbone so that its large-scale (global) motion results in not only viscoelastic but also dielectric relaxation. Utilizing this feature of PI, we examined dielectric and viscoelastic behavior of star PI probe chains (arm molecular weight  $10^{-3}M_a = 9.5\text{--}23.5$ , volume fraction  $v_1 = 0.1$ ) blended in a matrix of long linear PI ( $M = 1.12 \times 10^6$ ). The constraint release (CR)/dynamic tube dilation (DTD) mechanism was quenched for those dilute probes entangled with the much longer matrix, as evidenced from coincidence of the frequency dependence of the dielectric and viscoelastic losses of the probe in the blend. Comparison of the probe data in the blend and in monodisperse bulk revealed that the star probe relaxation is retarded and broadened on blending and the retardation/broadening is enhanced exponentially with  $M_a$ . This result in turn demonstrates significant CR/ DTD contribution to the dynamics of star PI in bulk. The magnitude of retardation was quantitatively analyzed within the context of the tube model, with the aid of the dielectrically evaluated survival fraction of the dilated tube,  $\phi'(t)$ , and the literature data of CR time,  $\tau_{CR}$ . In the conventional molecular picture of partial-DTD, the tube is assumed to dilate laterally, but not coherently along the chain backbone. The corresponding lateral partial-DTD relationship between  $\phi'(t)$  and the normalized viscoelastic relaxation function  $\mu(t)$ ,  $\mu(t) = \phi'(t)/\beta(t)$  with  $\beta(t)$  being the number of entanglement segments per laterally dilated segment (that was evaluated from the  $\phi'(t)$  and  $\tau_{CR}$  data), held for the  $\mu(t)$  and  $\phi'(t)$  data of star PI in bulk. Nevertheless, the observed retardation of the star probe relaxation on blending was less significant compared to the retardation expected for the arm motion (retraction) along the laterally dilated tube in bulk PI. This result suggests that the relaxation time of the probe in bulk is governed by the longitudinal partial-DTD that occurs coherently along the chain backbone. In fact, the magnitude of retardation evaluated from the  $\phi'(t)$  and  $\tau_{CR}$  data on the basis of this longitudinal partial-DTD picture was close to the observation. These results strongly suggest that the star PI chains in monodisperse bulk have two different coarse-grained length scales: the diameter of laterally dilated tube that determines the modulus level and the diameter of longitudinally dilated tube that reflects the path length for the arm retraction and determines the relaxation time.

Thus, the star PI chains in bulk appear to move along the longitudinally dilated tube that wriggles in the laterally dilated tube. This molecular scenario is consistent with the previous finding for bulk linear PI [Matsumiya et al., *Macromolecules*, 2013, **46**, 6067-6080 (2013)].



## Origin of Stress Overshoot under Start-up Shear in Primitive Chain Network Simulation

Birefringence measurement demonstrates that the segment orientation of entangled polymers overshoots on start-up of fast shear [Pearson et al., *J. Rheol.*, **33**, 517-536 (1989)]. The stress-optical rule holds for those polymers, so that the overshoot of orientation results in the overshoot of shear stress. On the other hand, an opposite result was deduced from the recent molecular dynamics simulation for bead-spring chain [Lu et al., *ACS Macro Lett.*, **3**, 569-573 (2014)]: the evolution of segment orientation does not overshoot but the chain stretch induces the stress overshoot, even at the shear rate  $\dot{\gamma}$  smaller than the reciprocal Rouse time,  $1/\tau_R$ . In this study, we performed the primitive chain network simulation to find that our simulation reproduces the overshoot of both stress and orientation and the chain stretch exhibits a slight, monotonic increase but no overshoot. Our result is thus fully consistent with the experiment.

