

Division of Multidisciplinary Chemistry - Molecular Rheology -

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DEMÉ, Bruno Institut Laue-Langevin, Grenoble, France, July 2006
SUN, Kang Shanghai Jiao Ton University, China, P.R., 24–28 July 2006

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.

Research Activities (Year 2006)

Presentations

Non-Newtonian Behavior of Diblock and Triblock Copolymer Solutions, Watanabe H, APS Annual Meeting, Baltimore, MD, USA, March 2006.

Constraint Release in Star/Star Blends and Partial-DTD in Monodisperse Star Systems, Watanabe H, AERC06, Hersonisos, Crete, Greece, April 2006.

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.

Dielectric Studies for Predicting Viscoelastic Properties of Polymers under Supercritical CO₂, Inoue T, Macro 2006, Rio de Janeiro, Brazil, July 2006.

Non-Newtonian Behavior of Diblock and Triblock

Copolymers, Watanabe H, PPS 22, Yamagata, July 2006.

Molecular Picture of Dynamic Tube Dilution for Entangled Polymers –Coarse-Graining of Length Scale Consistent with Time Scale–, Watanabe H, Yukawa Institute for Theoretical Physics (YITP) Workshop, Kyoto, July 2006.

Transient Conformational Change of Bead-spring Ring Chain during Creep Process, Watanabe H, SOR Meeting, Portland, MA, USA, October 2006.

Constraint Release in Star/Star Blends and Partial-DTD in Monodisperse Star Systems, 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 τ_{probe} measured in the blends was utilized in the following way to elucidate the CR relaxation of the star matrices. Since the CR time τ^{CR} of the star matrix is expressed as $(2N_a)^2\tau_{\text{lifc}}$ with $2N_a$ and τ_{lifc} being the entanglement number per two arms (span length) and the effective entanglement lifetime in the system, τ^{CR} can be evaluated if the τ_{lifc} value is known. For determination of the τ_{lifc} value, the τ_{probe} data of the linear probe in the star matrices was compared with the τ_{probe} data of the *same* probe in linear PI matrices (Figure 1) under a molecular idea that τ_{lifc} should be the same in a *pair* of star and linear matrices giving the same τ_{probe} value. The molecular weight $M_{\text{L,mat}}$ 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 τ_{lifc} in the star matrix was determined by utilizing this $M_{\text{L,mat}}$ value in an empirical equation of τ_{lifc} in the linear matrices ($\tau_{\text{lifc}} = 2.5 \times 10^{-18} M_{\text{L,mat}}^3$ s at 40°C). For the monodisperse systems of the star PI, the $\tau^{\text{CR}} (= (2N_a)^2\tau_{\text{lifc}})$ 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.

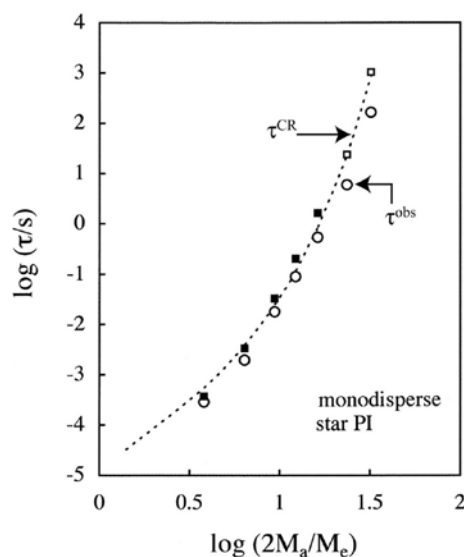


Figure 1. Plots of the terminal viscoelastic relaxation time τ_{probe} of the dilute linear probe in 6-arm star PI matrices (large unfilled squares) and/or linear PI matrices (circles) at 40°C. The symbols with pip indicate that the probe exhibited pure CR behavior in the given matrices.

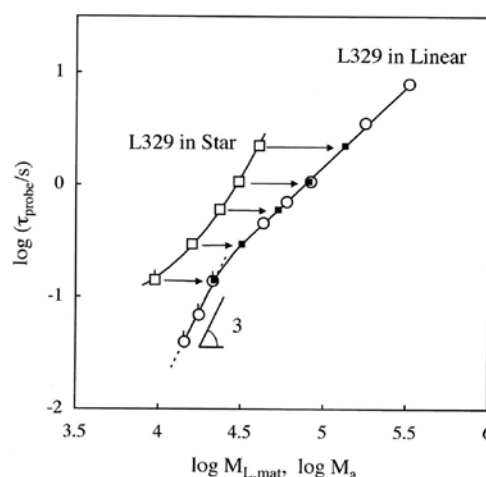


Figure 2. Comparison the viscoelastic CR relaxation time τ^{CR} for monodisperse systems of star and linear PI chains with the observed terminal relaxation time τ^{obs} (circles) at 40°C.

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.

Inoue T, Grant-in-Aid for Scientific Research (C), Rheology of Surfactant Solution: Nonlinear Elongation

and Shear-induced Structure of Thread-like Micelles, 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.