

Division of Multidisciplinary Chemistry - Molecular Rheology -

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Università degli studi di Napoli "Federico II", Italy, 15 March–15 April 2008

Illinois Institute of Technology, USA, 17–30 March 2008

Università degli studi di Napoli "Federico II", Italy, 1–7 June 2008

California Institute of Technology, USA, 1–9 June 2008

University of Montpellier, France, 1–13 June 2008

Seoul National University, Korea, 25 March–28 August 2008

University of Leeds, UK, 21 May–25 November 2008

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 2008)

Publications

Chen Q, Matsumiya Y, Masubuchi Y, Watanabe H, Inoue T: Component Dynamics in Polyisoprene/Poly(4-tert-butylstyrene) Miscible Blends, *Macromolecules*, **41**(22), 8694-8711 (2008).

Masubuchi Y, Watanabe H, Ianniruberto G, Greco F, Marrucci G: Comparison among Slip-Link Simulations of Bidisperse Linear Polymer Melts, *Macromolecules*, **41**(21), 8275-8280 (2008).

Watanabe H, Matsumiya Y, van Ruymbeke E, Vlassopoulos D, Hadjichristidis N: Viscoelastic and Di-

electric Relaxation of a Cayley-Tree-Type Polyisoprene: Test of Molecular Picture of Dynamic Tube Dilation, *Macromolecules*, **41**, 6110-6124 (2008).

Presentations

Dielectric and Viscoelastic Investigation of Entanglement Relaxation, Watanabe H, 2008 APS March Meeting, New Orleans, 13 March 2008 (Invited).

Molecular Simulations of Polymers with Primitive Chain Network Model, Masubuchi Y, MSSMBS2008, 12 September 2008, Dubna, Russia (keynote, invited).

Viscoelastic and Dielectric Relaxation of a Cayley-Tree Type Polyisoprene: Test of Molecular Picture of Dynamic Tube Dilation

We have experimentally elucidated that entangled polymer chains with multi-branched structure relax through the constraint release mechanism. This result provided us with significant progress in our understanding of entanglement dynamics.

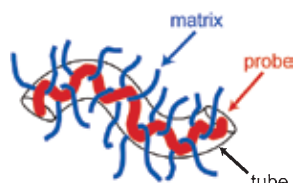


Figure 1. Schematic illustration of tube model.

The entanglement between polymer chains strongly affects the global (large scale) thermal motion of the chains governing their flow behavior. In the widely utilized tube model (cf. Figure 1), the entanglement effect for a focused chain (probe) is represented by a tube along the probe backbone formed by the surrounding chains (matrix) and the probe motion is constrained in this tube. The current tube model incorporates fluctuation of the probe length measured along the tube axis as well as the removal/reformation of the tube wall resulting from motion of the tube-forming matrix chains. The probe motion activated by this wall removal/reformation, referred to as the *constraint release* (CR) motion, represents the motional cooperativity of the chains within the context of the mean-field tube model. On an increase of the time scale of observation, the effective tube dilates as a result of the CR motion. The current tube model regards the relaxed portion of the chains as a simple solvent to evaluate the diameter of the dilated tube. This model describes the viscoelastic data of polymers well, but the validity of the model for the chain dynamics itself remains unclear.

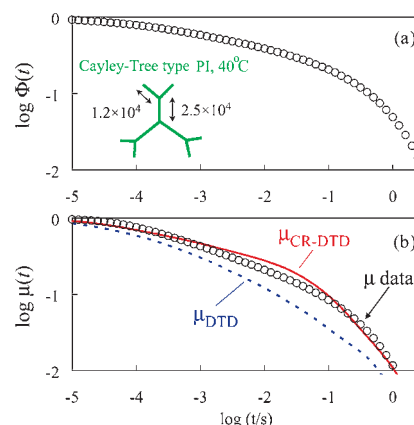


Figure 2. Dielectric relaxation function (a) and viscoelastic relaxation function (b) of Cayley-tree cis-polyisoprene.

For this problem, we focused on a fact that the viscoelastic and dielectric relaxation functions, $\mu(t)$ and $\phi(t)$, of chains having the type-A electrical dipoles (parallel along the chain backbone) detect the same global motion with different averaging moments to formulate a relationship of these functions, $\mu_{\text{DTD}}(t) = \{\phi(t)\}^d + \text{minor contribution from fluctuation at tube edge}$ ($d = 1-1.3$), that should hold if the relaxed portion is equivalent to the simple solvent. They tested this relationship for a representative multi-branched chain having the type-A dipoles, a Cayley-tree cis-polyisoprene (CT-PI), to find that the above relationship does not hold for the $\mu(t)$ and $\phi(t)$ data of CT-PI and thus the relaxed portion is not equivalent to the solvent. This result demonstrated that the widely utilized, current tube model includes a flaw. Furthermore, we derived the other type of $\mu(t)$ - $\phi(t)$ relationship that should hold whenever the tube dilates consistently with the CR mechanism and demonstrated its validity. This result offered an experimental basis for accurate description of the entanglement effect on the motion of multi-branched chains.

Nonlinear Rheology of Multiblock Copolymer Solutions, Matsumiya Y, JAPAN-KOREA Polymer Young Scientist Symposium, Green-pia in Tsunan (Niigata), 24 October 2008 (Invited).

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, 1 October 2006–31 March 2011.

Masubuchi Y, Multi-scale Simulations for Soft Matters, Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, 1 October 2006–

31 March 2012.

Masubuchi Y, New Molecular Model for Branched Polymer Chains, Grant-in-Aid for Scientific Research (B), 1 April 2008–31 March 2010.

Matsumiya Y, Dynamics of Ionic Liquids in Polymer Networks, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Award

Watanabe H, The Award of the Society of Polymer Science, Japan, “Molecular Dynamics and Rheology of Homogeneous and Inhomogeneous Polymer Liquids”, The Society of Polymer Science, Japan, 29 May 2008.