

Division of Multidisciplinary Chemistry – Molecular Rheology –

<http://rheology.minority.jp/en/>



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Durham University, UK, 11–12 August

Université Catholique de Louvain, Belgium, 15–17 August

Seoul National University, Korea, R., 8–9 August

Shanghai Jiao Tong University, China, P.R., 8–10 August

Sungkyunkwan University, Korea, R., 8–10 August

Shanghai Jiao Tong University, China, P.R., 8–10 August

Stanford University, USA, 8–10 August

Kyungpook National University, Korea, R., 8–10 August

Shanghai Jiao Tong University, China, P.R., 20 March – 20 June, 8–10 August

University of Washington, USA, 8–10 August

McGill University, Canada, 8–10 August

Federal University of Rio de Janeiro, Brazil, 8–10 August

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 basic understanding of the features, the molecular motion and structures at 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.

Selected Publications

Uno A, Matsumiya Y, Masubuchi Y, Watanabe H: Rheological and Dielectric Behavior of Polyisoprene under Pressurized Carbon Dioxide, *J. Soc. Rheol. Jpn.*, **38(3)**, 117-123 (2010).

Furuichi K, Nonomura C, Masubuchi Y, Watanabe H: Chain Contraction and Nonlinear Stress Damping in Primitive Chain Network Simulations, *J. Chem. Phys.*, **133**, [174902-1]-[174902-10] (2010).

Chen Q, Uno A, Matsumiya Y, Watanabe H: Viscoelastic Mode Distribution of Moderately Entangled Linear Polymers, *J. Soc. Rheol. Jpn.*, **38(5)**, 187-193 (2010).

KEYWORDS

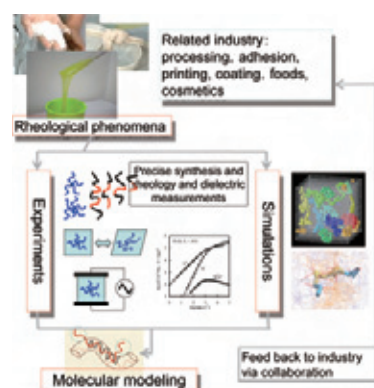
Rheology

Softmatters

Polymers

Emulsions

Suspensions



Rheological and Dielectric Behavior of Polyisoprene under Pressurized Carbon Dioxide

For a well-entangled polyisoprene (PI; molecular weight = 260k) equilibrated under pressurized carbon dioxide (CO₂) at 25 °C, linear viscoelastic and dielectric data, respectively, were measured with a stress-controlled rheometer and a dielectric bridge being equipped with respective high-pressure cells. The viscoelastic and dielectric data shifted to higher frequencies with increasing CO₂ pressure, indicating that the pressurized CO₂ dissolved into PI thereby accelerating the global motion of PI. For those data at various CO₂ pressure, time-CO₂ pressure superposition held well and a single master curve was obtained, and the horizontal/vertical shift factors were consistent for the viscoelastic and dielectric data. These results indicated that the dissolved CO₂ behaved just as an ordinal solvent to accelerate the global motion of PI as in ordinary solutions. In fact, the dynamic tube dilation (DTD) relationship between the viscoelastic and dielectric data, known to be valid for ordinary solutions/bulk of linear PI, was found to work also the PI/CO₂ system, which confirmed the simple solvent role of the pressurized CO₂ for the global motion of PI. Thus, the knowledge for ordinary polymer solutions would work for processing of polymer/CO₂ systems.

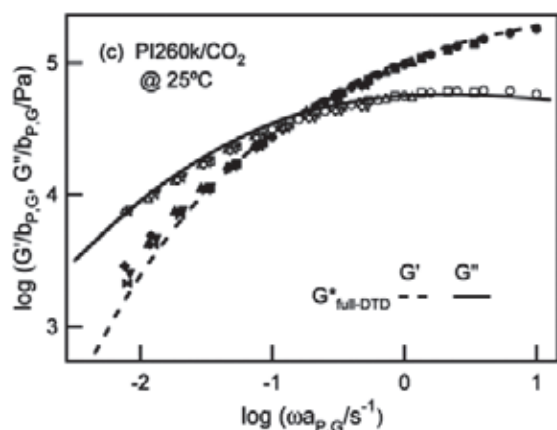


Figure 1. Linear viscoelastic storage and loss moduli measured for PI260k equilibrated under various pressures of CO₂ at 25 °C after time-CO₂ pressure superposition. Dashed and solid curves show G' and G'' calculated from the dielectric data through the full-DTD relationship.

Chain Contraction and Nonlinear Stress Damping in Primitive Chain Network Simulations

Doi and Edwards (DE) proposed that the relaxation of entangled linear polymers under large deformation occurs

in decoupled two steps: the fast chain contraction (via the longitudinal Rouse mode of the chain backbone) and the slow orientational relaxation (due to reptation). However, this decoupling is invalid for a generalized convective constraint release (CCR) mechanism that releases the entanglement on every occasion of the contraction of surrounding chains. Thus, we conducted primitive chain network simulations to investigate the chain contraction under step shear. The simulation quantitatively reproduced experimental features of the nonlinear relaxation modulus $G(t, \gamma)$. Namely, $G(t, \gamma)$ was cast in the time-strain separable form, $G(t, \gamma) = h(\gamma)G(t)$ with $h(\gamma)$ =damping function and $G(t)$ =linear modulus, but this rigorous separability was valid only at times t comparable to the terminal relaxation time, although a deviation from this form was rather small (within 10%) at $t > \tau_R$ (longest Rouse relaxation time). A molecular origin of this delicate failure of time-strain separability at $t \sim \tau_R$ was examined for the chain contour length. The contributions of the terminal reptative mode to the chain length relaxation emerged because the sliplinks (entanglement) were removed via the generalized CCR mechanism and the reformation of the sliplinks was slow at around the chain center. The number of monomers in the subchain was kept larger at the chain center than at the chain end, thereby reducing the tension at the chain center compared to the DE prediction. This reduction of the tension prevented completion of the length equilibration at $t \sim \tau_R$ and it forced the equilibration to complete through the reptative mode. The delicate failure of time-strain separability seen for $G(t, \gamma)$ at $t \sim \tau_R$ reflects this retarded length equilibration.

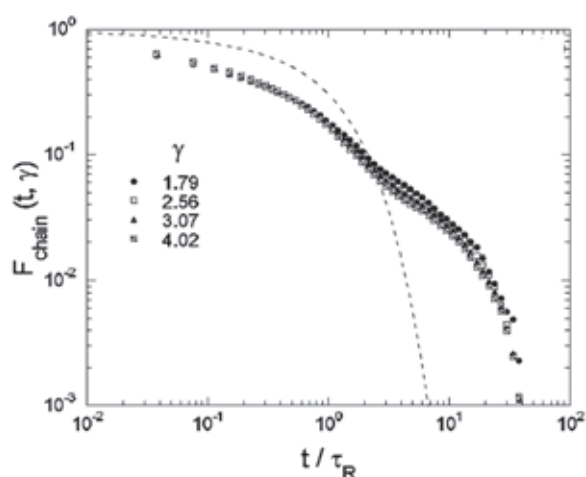


Figure 2. Relaxation of contour length of the chain after various step shear deformations with strain at γ . Dashed lines indicate the prediction of DE theory.