Division of Multidisciplinary Chemistry
– Molecular Rheology –

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Visitors

Prof HASSAGER, Ole	Technical University of Denmark, Denmark, 12 March
Prof LIKHTMAN, Alexey	University of Reading, U.K., 1 April–30 June
Dr SHAUKAT, Asima	University of Leeds, U.K., 22 June–20 July, 17–30 December
Prof MCKENNA, Greg	Texas Tech University, U.S.A.,12 November
Prof MCLEISH, Tom	Durham University, U.K., 27–29 November
Prof KUNIN, Seth	Durham University, U.K., 27–29 November
Prof ASUTAY, Mehmet	Durham University, U.K., 27–29 November
Prof PETLEY, David	Durham University, U.K., 27–29 November
Prof SAUL, Nicholas	Durham University, U.K., 27–29 November
Prof HENDRY, Robin	Durham University, U.K., 27–29 November
Prof QUINLAN, Roy	Durham University, U.K., 27–29 November
Prof BENHAM, Adam	Durham University, U.K., 27–29 November
Prof STRANG, Veronica	Durham University, U.K., 27–29 November
Prof GARNETT, Philip	Durham University, U.K., 27–29 November
Prof ROBERTS, David	Durham University, U.K., 27–29 November
Prof PETEKIDIS, George	University of Crete, Greece, 30 November
Prof LODGE, Tim	University of Minnesota, U.S.A., 10 December

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 Dielectric Spectroscopy Softmatter
Primitive Chain Network Simulation

Selected Publications

Yaoita, T.; Isaki, T.; Masubuchi, Y.; Watanabe, H.; Ianniruberto, G.; Marrucci, G., Primitive Chain Network Simulation of Elongational Flows of Entangled Linear Chains: Stretch/Orientation-induced Reduction of Monomeric Friction, *Macromolecules*, **45,** 2773-2782 (2012).

Masubuchi, Y.; Matsumiya, Y.; Watanabe, H.; Shiromoto, S.; Tsutsubuchi, M.; Togawa, Y., Primitive Chain Network Simulations for Comb-branched Polymer under Step Shear Deformations, *Rheo. Acta*, **51,** 193-200 (2012).

Suzuki, S.; Uneyama, T.; Inoue, T.; Watanabe, H., Nonlinear Rheology of Telechelic Associative Polymer Networks: Shear Thickening and Thinning Behavior of Hydrophobically Modified Ethoxylated Urethane (HEUR) in Aqueous Solution, *Macromolecules*, **45,** 888-898 (2012).

Matsumiya, Y.; Chen, Q.; Uno, A.; Watanabe, H.; Takano, A.; Matsuoka, K.; Matsushita, Y., Dielectric Behavior of Styrene–Isoprene (SI) Diblock and SIIS Triblock Copolymers: Global Dynamics of I Blocks in Spherical and Cylindrical Domains Embedded in Glassy S Matrix, *Macromolecules*, **45,** 7050-7060 (2012).

Uneyama, T.; Masubuchi, Y., Multi-chain Slip-spring Model for Entangled Polymer Dynamics, *J. Chem. Phys.*, **137,** 154902 (2012).

Primitive Chain Network Simulation of Elongational Flows of Entangled Linear Chains: Stretch/Orientation-induced Reduction of Monomeric Friction

Well-entangled monodisperse linear polystyrene melts exhibit monotonic thinning of the steady state elongational viscosity with increasing the strain rate $\dot{\varepsilon}$ even beyond the Rouse relaxation frequency, τ_R^{-1}. This behavior is quite different from the thinning followed by hardening at $\dot{\varepsilon}>\tau_R^{-1}$ observed for entangled semidilute solutions. We attempt to elucidate the molecular origin of this difference by focusing on the concept of stretch/orientation-dependent monomeric friction ζ recently proposed by Ianniruberto and co-workers. Specifically, literature data of the stress relaxation after cessation of transient elongational flow, reported for both PS melts and solutions, are analyzed to evaluate the stretch/orientation-dependent decrease of ζ. In our working hypothesis, ζ is expressed as a function of the factor $F_{so} = \tilde{\lambda}^2\bar{S}$, where $\tilde{\lambda}$ is the normalized stretch ratio of entangled subchains defined with respect to the fully stretched state, and $\bar{S}$ is an average orientational anisotropy of the components (polymer plus solvent if any) in the system. The factor F_{so} was estimated from the stress decay data after flow cessation. The resulting functional form of $\zeta(F_{so})$ was then used in the primitive chain network (PCN) simulation including finite extensible nonlinear elasticity (FENE) to examine the elongational behavior of melts and solutions. For melts the simulation indicates that ζ decreases significantly under fast elongation because the entangled subchains are short and approach the fully stretched (and fully oriented) limit rather easily. Hence, the steady elongational viscosity η_E follows this decrease of ζ to exhibit the monotonic thinning even at $\dot{\varepsilon}>\tau_R^{-1}$. In contrast, for solutions, the simulated η_E exhibits thickening at $\dot{\varepsilon}>\tau_R^{-1}$ because the average anisotropy $\bar{S}$ is governed by the solvent and remains small, thus overwhelming the increase of the subchain stretch $\tilde{\lambda}$. The simulated results proved to be in satisfactory agreement with the experiments.

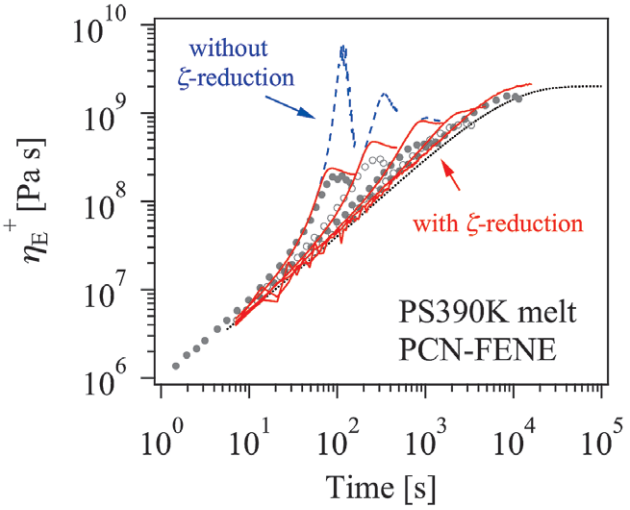

Figure 1. Uniaxial viscosity growth data for linear polymer melt (PS, M = 390K) at various strain rates (open circles). Simulation results with (red solid curves) and without (black dash curves) stretch/orientation-dependent monomeric friction reduction are shown. The former agrees well with the experimental data.