

Division of Multidisciplinary Chemistry – Molecular Rheology –

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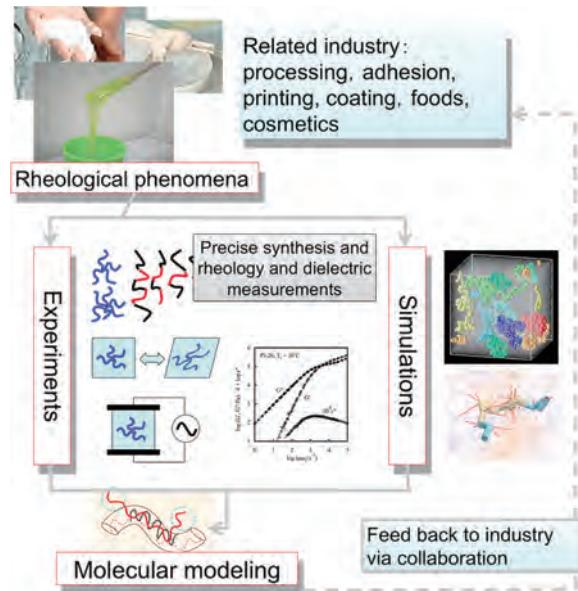
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Pennsylvania State University, U.S.A., 13–17 May
IESL-FORTH and University of Crete, Greece, 13–17 May
Sungkyunkwan University, Korea, R., 18–22 July
Stony Brook University, U.S.A., 25 July

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

- Watanabe, H.; Matsumiya, Y.; van Ruymbeke, E., Component Relaxation Times in Entangled Binary Blends of Linear Chains: Reptation/CLF along Partially or Fully Dilated Tube, *Macromolecules*, **46**, 9296-9312 (2013).
- Huang, Q.; Alvarez, N. J.; Matsumiya, Y.; Rasmussen, H. K.; Watanabe, H.; Hassager, O., Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions, *ACS Macro Letters*, **2**, 741-744 (2013).
- Matsumiya, Y.; Kumazawa, K.; Nagao, M.; Urakawa, O.; Watanabe, H., Dielectric Relaxation of Monodisperse Linear Polyisoprene: Contribution of Constraint Release, *Macromolecules*, **46**, 6067-6080 (2013).
- Masubuchi, Y.; Yaoita, T.; Matsumiya, Y.; Watanabe, H.; Ianniruberto, G.; Marrucci, G., Stretch/orientation Induced Acceleration in Stress Relaxation in Coarse-grained Molecular Dynamics Simulations, *Nihon Reoroji Gakkaishi (J. Soc. Rheol. Jpn.)*, **41**, 35-37 (2013).
- Langloth, M.; Masubuchi, Y.; Böhm, M. C.; Müller-Plathe, F., Recovering the Reptation Dynamics of Polymer Melts in Dissipative Particle Dynamics Simulations via Slip-springs, *J. Chem. Phys.*, **138**, [104907] (2013).

Uniaxial Extensional Behavior of $(SIS)_p$ -Type Multiblock Copolymer Systems: Structural Origin of High Extensibility

Rheological and structural behavior was examined for a series of symmetric styrene (S)–isoprene (I)–styrene (S) multiblock copolymers of $(SIS)_p$ -type ($p = 1, 2, 3$, and 5 corresponding to tri-, penta-, hepta-, and undecablock) in *n*-tetradecane (C14), a selective solvent that dissolves the I block and precipitates (but swells) the S block. The molecular weights of respective blocks were almost identical for these copolymers ($M_I \approx 40$ K for I block; $M_S \approx 20$ K and 10K for inner and outer S blocks, respectively). At 20°C, the $(SIS)_p/C14$ systems with the copolymer concentration $C = 30$ wt % formed a bcc lattice of spherical S domains (with $T_{g,PS} \approx 38$ °C) embedded in the I/C14 matrix. Under small shear and elongation in the linear regime, the systems exhibited gel-like elasticity sustained by the I blocks connecting the S domains. This linear elastic behavior, being associated with affine displacement of the S domains as revealed from small-angle X-ray scattering (SAXS) under small elongation, was very similar for all $(SIS)_p/C14$ systems having the same C . In contrast, a remarkable difference was found for those systems under large (but slow) elongation: The maximum stretch ratio at rupture, λ_{\max} , significantly increased with the repeating number p of the SIS units, $\lambda_{\max} \approx 1.7, 2.2, 6.6$, and ≥ 90 for $p = 1, 2, 3$, and 5, respectively. In particular, $\lambda_{\max} \geq 90$ for $p = 5$ was much larger compared to the full-stretch ratio of the trapped entanglement strand ($\lambda_{\text{full-ent}} \approx 14$) and even to the full-stretch ratio of the $(SIS)_5$ copolymer chain as a whole ($\lambda_{\text{full-copolymer}} \approx 40$). For investigation of the structural origin of such remarkably high extensibility of the undecablock system ($p = 5$), SAXS and rheological tests were made under elongation followed by reversal. The tests

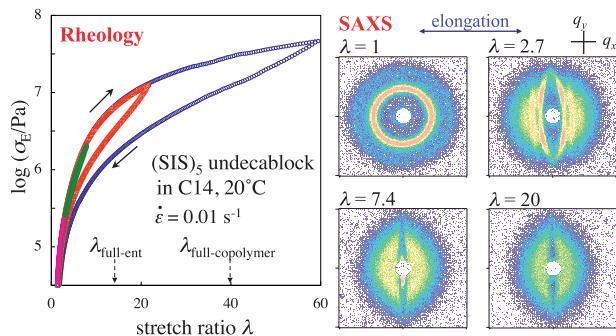


Figure 1. Left: Elongational stress σ_E of the 30 wt% $(SIS)_5/C14$ undecablock systems measured with the reverse mode at 20°C (large unfilled symbols). The strain rate is $\dot{\varepsilon} = 0.01$ s $^{-1}$ for both forward and reverse processes. The σ_E data are plotted against the stretch ratio λ . Right: Two-dimensional SAXS profiles $I(q_x, q_y)$ of the 30 wt% $(SIS)_5/C14$ undecablock system at stretch ratios λ as indicated. The data are shown in the range of $q_x, q_y < 0.5$ nm $^{-1}$.

revealed affine stretching of the lattice (affine displacements of the S domains) and negligible stress-strain hysteresis on reversal of elongation from $\lambda_{\text{rev}} < 3$ (Figure 1). In contrast, on reversal from larger λ_{rev} up to 60, nonaffine stretching of the lattice and the significant stress-strain hysteresis were observed. Thus, under large elongation, some of the S blocks were pulled out from their domains and transferred to the other S domains at 20°C, the experimental temperature not significantly lower than $T_{g,PS} (\approx 38$ °C) of the swollen S domains, to allow the system to deform plasto-elastically. This deformation differed from unrecoverable plastic flow, as evidenced from spontaneous, full recovery of the size, shape, and SAXS profile of the $(SIS)_5/C14$ specimen being kept at rest (without load) at 20°C for a sufficiently long time after the elongation. This recovery strongly suggests that the material preserved some memory of initial connection between the $(SIS)_5$ chains through the S domains, in particular in the direction perpendicular to the elongation, and the corresponding physical network still percolated the whole material even under large elongation (Figure 2). This argument in turn provides us with a clue for understanding the difference of λ_{\max} for the series of $(SIS)_p/C14$ systems. The full percolation can survive and the material can stand with the elongation if at least two PS blocks, on average, remain intact (not pulled out) in each $(SIS)_p$ copolymer backbone. The probability of having such intact S blocks obviously increases with the repeating number p of the SIS units, which possibly resulted in the observed difference of λ_{\max} .

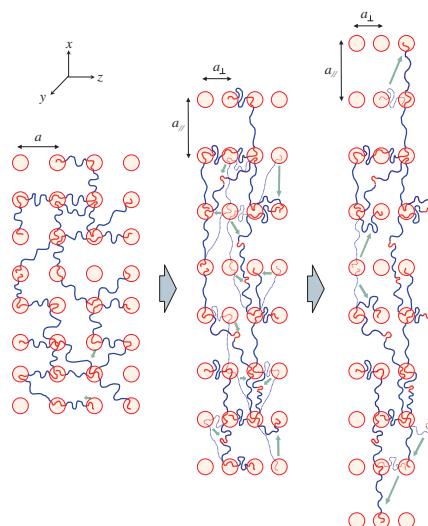


Figure 2. Schematic illustration of possible structural changes in the 30 wt% $(SIS)_5/C14$ undecablock system under large elongation. The macroscopic elongation is applied in x direction, and the width and thickness directions of specimen are chosen to be the y and z direction. The initial network connectivity preferentially surviving in the y and z directions provides the material with the driving force for full structural recovery after elongation.