

## Fundamental Material Properties - Molecular Rheology -



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University of Leeds, UK, 12 January 2001

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## Scope of Research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids 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 autocorrelation of the orientation with dynamic dielectric spectroscopy.

## Research Activities (Year 2001)

### Presentations

Investigation of entanglement dynamics of flexible polymer chains, Watanabe H, Matsumiya Y, APS, 13 March, 3rd PRCR, 9 July, ICAPP, 30 October, 2nd ISAR, 15 November.

Viscoelasticity of polymer solutions, Osaki K, Inoue T, 4th IDMRCs, 22 and 24 June, 3rd PRC R, 9 July.

Rheo-optical studies on amorphous polymers, Inoue T, Osaki K, 3rd PRCR, 10 July.

Rheology of block copolymers, Watanabe H, Matsumiya Y, 3rd PRCR, 10 July, ICAPP, 30 October

### Grants

Osaki K, Molecular rheology of amorphous polymer studied by electric birefringence, Grant-in-Aid for Scientific Research (B) (2), 1 April 2001 - 31 March 2003

Watanabe H, Rheo-dielectric behavior of entangled chains, Grant-in-Aid for Scientific Research (C) (2), 1 April 2000 - 31 March 2002

Inoue T, Molecular rheology of polymer solids, Grant-in-Aid for Scientific Research (C) (2), 1 April 2001 - 31 March 2003

Osaki K, Viscoelasticity of living anionic systems, Grant-in-Aid for Scientific Research, , 1 April 2000 - 31 March 2002

Matsumiya Y, Effect of branching and molecular weight distributions on entanglement relaxation, Grant-in-Aid for Scientific Research, , 1 April 2001 - 31 March 2003

Watanabe H, Development of platform for designing high functional materials, JCII, 1 April 1998 - 31 March 2002

### Award

Osaki K, SROJ Award for 2001, Nonlinear rheology of polymeric systems, Society of Rheology, Japan, 17 May 2001

## Topics

### Equilibrium elasticity of diblock copolymer micellar lattice.

In concentrated solutions of styrene-butadiene (SB) diblock copolymers in a B-selective solvent, n-tetradecane (C14), spherical micelles with S cores and B corona form cubic lattices because of the osmotic constraint for the corona conformation. The equilibrium modulus  $G_e$  of the micellar lattice is proportional to the number density  $\nu$  of the corona blocks but the magnitude of  $G_e$  is smaller, by a factor  $\sim 10$ , than the modulus  $G_e^o (= \nu k_B T; k_B T = \text{thermal energy})$  expected for the simplest case of the entropic elasticity of the corona [1]. The origin of this difference between  $G_e$  and  $G_e^o$  was examined in this study [2]. The  $G_e$  of a model SB/C14 micellar lattice (having deuterated S cores) was measured before and after imposition of steady shear. SANS measurements revealed that the quiescently ordered, polycrystalline lattice was orientated after the shear to have less defects; see Figure. This structural change hardly affected  $G_e$ , suggesting that the defects were not the main factor raising the large difference between  $G_e$  and  $G_e^o$ . Thus, this difference was attributed to the osmotic constraint for the corona conformation [2]: This constraint should force neighboring corona blocks to have mutually correlated conformations (thereby leading to the micellar lattice formation). Such correlated corona blocks cannot behave as independent entropic strands. This correlation possibly reduced the effective number density of the entropic strands to give  $G_e < G_e^o$ .

1. H. Watanabe, *Acta Polymerica*, 48, 215(1997).
2. H. Watanabe, Y. Matsumiya, T. Kanaya, and Y. Takahashi, *Macromolecules*, 34, 6742(2001).

### The significance of the Rouse segment

The Rouse segment is the smallest unit of global motions that are responsible for viscoelastic relaxation. The molecular weight of the Rouse segment,  $M_S$ , can be estimated with rheo-optical methods using birefringence measurements. Measurements on bulk polystyrene showed that  $M_S \sim 900$ . This value agrees with molecular weight of the Kuhn segment size,  $M_K$ , which is a measure of statistical flexibility of the chain.[1] On the other hand, in dilute solutions,  $M_S$  for polystyrene was reported as 5000 although  $M_K$  is almost constant.[2]

Recently, we obtained  $M_S$  data covering the concentration regime  $0.2 \sim 1 \text{ g cm}^{-3}$ . [3] (See Figure)  $M_S$  changes remarkably around  $c = 0.1 \text{ g cm}^{-3}$ , suggesting that screening of the intermolecular interactions may affect the size of the Rouse segment.

The Rouse segment size is related with the initial orientation of chain induced by instantaneous step deformation. Large  $M_S$  in dilute regime implies that deformation of chain in dilute solutions is heterogenous in local scales.

1. T. Inoue and K. Osaki, *Macromolecules*, 29, 1595(1996).
2. D. J. Massa, J. L. Schrag, and J. D. Ferry, *Macromolecules*, 4, 210(1971).
3. T. Inoue, Uematsu, and K. Osaki, *Macromolecules*, in press.

