

Division of Multidisciplinary Chemistry – Molecular Rheology –

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



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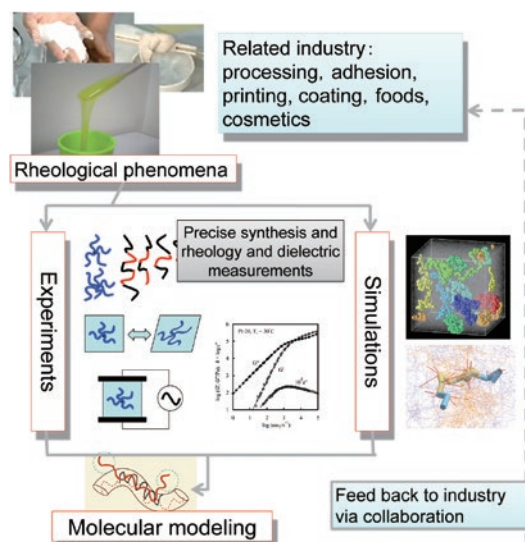
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Scope of Research

Research focus is placed on the molecular origin of rheological properties of various materials. 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 these features, the molecular motion and structures at various scales are studied for polymeric systems in deformed state. Rheological measurements are performed with various rheometers. Auto-correlation of the molecular orientation is also investigated with dynamic dielectric spectroscopy. Analysis of rheological and dielectric behavior elucidates new aspect of softmatter physics.

KEYWORDS

Rheology Dielectric Spectroscopy Softmatter

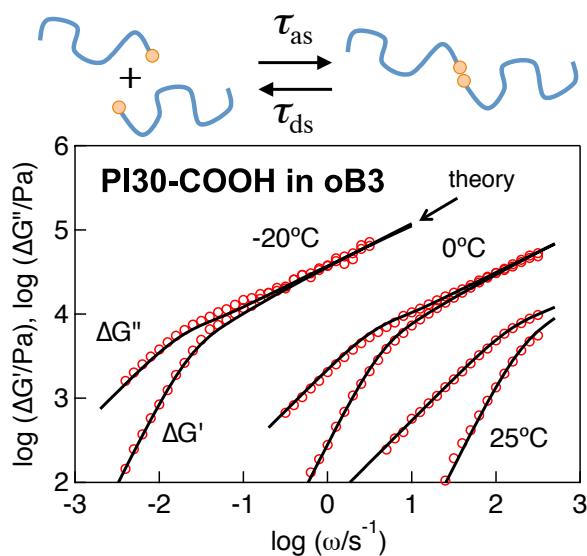


Selected Publications

- Ankiewicz, S.; Orbey, H.; Watanabe, H.; Lentzakis, H.; Dealy, J., On the Use of Continuous Relaxation Spectra to Characterize Model Polymers, *J. Rheol.*, **60**, 1115-1120 (2016).
- Matsumiya, Y.; Watanabe, H.; Urakawa, O.; Inoue, T., Experimental Test for Viscoelastic Relaxation of Polyisoprene Undergoing Monofunctional Head-to-Head Association and Dissociation, *Macromolecules*, **49(18)**, 7088-7095 (2016).
- Matsumiya, Y.; Watanabe, H., Nonlinear Stress Relaxation of Miscible Polyisoprene/Poly(p-tert-butylstyrene) Blends in Pseudomonodisperse State, *Macromolecules*, **49(12)**, 4544-4556 (2016).
- Kwon, Y.; Matsumiya, Y.; Watanabe, H., Viscoelastic and Orientational Relaxation of Linear and Ring Rouse Chains Undergoing Reversible End-Association and Dissociation, *Macromolecules*, **49(9)**, 3593-3607 (2016).
- Doi, Y.; Iwasa, Y.; Watanabe, K.; Nakamura, M.; Takano, A.; Takahashi, Y.; Matsushita, Y., Synthesis and Characterization of Comb-Shaped Ring Polystyrenes, *Macromolecules*, **49**, 3109-3115 (2016).

Experimental Test for Viscoelastic Relaxation of Polyisoprene Undergoing Monofunctional Head-to-Head Association and Dissociation

A viscoelastic test was made for end-carboxylated polyisoprene (PI-COOH) of the molecular weight $M = 30.5 \times 10^3$ that underwent the interchain association and dissociation through hydrogen bonding of the COOH groups at the chain end. As a reference, the test was made also for neat PI unimer (with no COOH group at the chain end) and for PI₂ dimer (with $M = 61.0 \times 10^3$), the latter being synthesized through end-coupling of PI⁻ anions (precursor of the PI-COOH sample). The PI-COOH, neat unimer, and dimer samples were diluted in oligomeric butadiene (oB) to a concentration of 10 wt %. The neat unimer and dimer exhibited nonentangled Rouse behavior at this concentration, as expected from their molecular weights. At low temperatures ($T \leq 0$ °C) the PI-COOH sample relaxed slower than the reference unimer but faster than the dimer, whereas the relaxation of PI-COOH approached that of the unimer with increasing $T > 0$ °C, and this change of the relaxation time of PI-COOH was associated with changes in the angular frequency (ω) dependence of the dynamic modulus. This behavior of PI-COOH was well described by a recently proposed theory considering motional coupling between the end-associating unimer and its dimer at chemical equilibrium. On the basis of this result, an effect of the polymeric character of PI-COOH chain on the viscoelastically detected association/dissociation of the hydrogen bonding of the COOH groups was discussed.



Viscoelastic and Orientational Relaxation of Linear and Ring Rouse Chains Undergoing Reversible End-Association and Dissociation

For dilute telechelic linear and ring Rouse chains undergoing reversible end-association and dissociation, the time (t) evolution equation was analytically formulated for the bond vector of the subchain (or segment), $\mathbf{u}^{[c]}(n,t)$ with n being the subchain index and the superscript c specifying the chain ($c = L$ and R for the linear and ring chains). The end-association of the linear chain (i.e., ring formation) occurs only when the ends of the linear chain come into close proximity. Because of this constraint for the ring formation, the time evolution equation for $\mathbf{u}^{[L]}(n,t)$ of the linear chain was formulated with a conceptually new, two-step expansion method: $\mathbf{u}^{[L]}(n,t)$ was first expanded with respect to its sinusoidal Rouse eigenfunction, $\sin(p\pi n/N)$ with $p = \text{integer}$ and N being the number of subchains *per* chain, and then the series of odd sine modes is re-expanded with respect to cosine eigenfunctions of the ring chain, $\cos(2\alpha\pi n/N)$ with $\alpha = \text{integer}$, so as to account for that constraint. This formulation allowed analytical calculation of the orientational correlation function, $S^{[c]}(n,m,t) = b^{-2} \langle u_x^{[c]}(n,t) u_y^{[c]}(m,t) \rangle$ ($c = L, R$) with b being the subchain step length, and the viscoelastic relaxation function, $g^{[c]}(t) \propto \int_0^N S^{[c]}(n,n,t) dn$. It turned out that the terminal relaxation of $g^{[R]}(t)$ and $g^{[L]}(t)$ of the ring and linear chains is retarded and accelerated, respectively, due to the motional coupling of those chains occurring through the reaction. This coupling breaks the ring symmetry (equivalence of all subchains of the ring chain in the absence of reaction), thereby leading to oscillation of the orientational anisotropy $S^{[R]}(n,n,t)$ of the ring chain at long t with the subchain index n . The coupling also reduces a difference of the anisotropy $S^{[L]}(n,n,t)$ of the linear chain at the middle ($n \sim N/2$) and end ($n \sim 0$).

