

Division of Multidisciplinary Chemistry

– Molecular Rheology –

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



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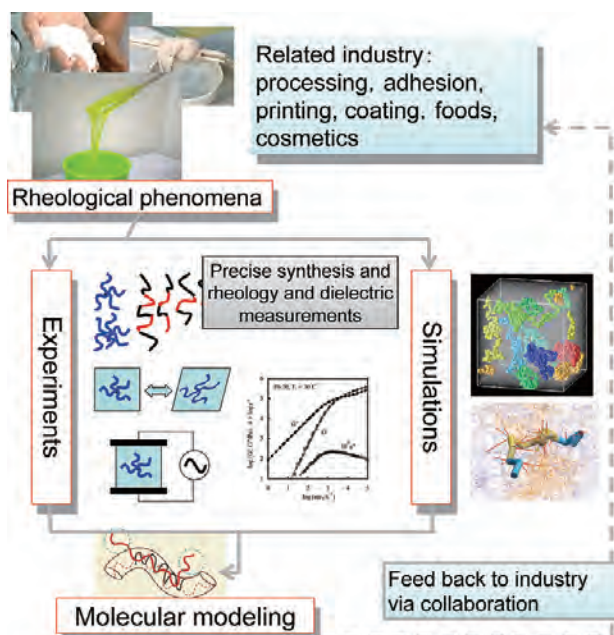
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Scope of Research

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 a new aspect of softmatter physics.

KEYWORDS

Rheology Dielectric Spectroscopy Softmatter



Selected Publications

Iwawaki, H.; Urakawa, O.; Inoue, T.; Nakamura, Y.; Matsumiya, Y.; Watanabe, H., Rheo-Optical and Dielectric Study on Dynamics of Bottlebrush-like Polymacromonomer Consisting of a Polyisoprene Main Chain and Polystyrene Side Chains, *Macromolecules*, **53**, 7096-7106 (2020).

Matsumiya, Y.; Watanabe, H., Entanglement-Loosening Dynamics Resolved through Comparison of Dielectric and Viscoelastic Data of Type-A Polymers: A Review, *Rubber Chemistry and Technology*, **93**, 22-62 (2020).

Zhao, X.; Yu, W.; Matsumiya, Y.; Watanabe, H.; Kwon, Y., Dielectric Relaxation of Type-A Rouse Chains Undergoing Reversible End-Adsorption and Desorption, *J. Soc. Rheol. Jpn.*, **48**, 27-35 (2020).

Matsumiya, Y.; Watanabe, H.; Urakawa, O.; Inoue, T.; Kwon, Y., Effect of Head-to-Head Association/Dissociation on Viscoelastic and Dielectric Relaxation of Entangled Linear Polyisoprene: An Experimental Test, *Macromolecules*, **53**, 1070-1083 (2020).

Effect of Head-to-Head Association/Dissociation on Viscoelastic and Dielectric Relaxation of Entangled Linear Polyisoprene: An Experimental Test

For linear high-*cis* polyisoprene having a monofunctionally associative carboxyl group at the chain head (PI30-COOH; $M = 30.5 \times 10^3$), linear viscoelastic and dielectric behavior was examined in its entangled bulk system. The PI30-COOH unimer chain had type-A dipoles aligned from the tail to head so that its large-scale motion (over the tail-to-head distance) activated not only viscoelastic but also dielectric relaxation. Consequently, the head-associated dimer of PI30-COOH had symmetrically inverted type-A dipoles, and its large-scale motion also activated both viscoelastic and dielectric relaxation. These unimer and dimer were coexisting in the system at equilibrium because of the association/dissociation reaction at the carboxyl group, and this reaction strongly affected the viscoelastic and dielectric behavior. Experimentally, the reaction effect was examined by utilizing two reference polyisoprenes undergoing no reaction, PI30 and (PI30)₂: PI30 was a prepolymer of PI30-COOH before introducing the carboxyl group at the head, and (PI30)₂ was a head-to-head dimer of PI30 prepared by coupling of the PI30 anion. The viscoelastic and dielectric relaxation was found to be faster for the PI30-COOH system than for a reference PI30/(PI30)₂ blend having the unimer/dimer composition identical to that in the PI30-COOH system (determined from Fourier transform infrared measurement), and this difference between the PI30-COOH system and the blend was more significant for the viscoelastic relaxation than for the dielectric relaxation. This experimental fact unequivocally indicates that the reaction induces motional coupling between the unimer and dimer to significantly affect the relaxation behavior of these chains. This result lends support to a recent model analyzing this coupling for entangled (reptating) unimer and dimer. In fact, the model described low-frequency asymptotes of the viscoelastic and dielectric losses of PI30-COOH surprisingly well, given that the viscoelastic and dielectric asymptotes of the reference PI30 bulk system were separately fitted by the model to determine the terminal relaxation times in the model calculation in the absence of reaction. This success of the model strongly suggests that the difference of the reaction effects on the dielectric and viscoelastic relaxation reflects the vectorial and tensorial nature of the

respective relaxation processes. The dielectric relaxation reflects the (vectorial) first-moment average of bond vectors $\mathbf{u}$ of the chain so that the dipole inversion of the dimer leads to pairwise coupling of the dielectric modes of the unimer and dimer under the reaction, thereby allowing the reaction to affect the dielectric relaxation just moderately. In contrast, the viscoelastic relaxation detects the (tensorial) second-moment average of $\mathbf{u}$ so that the reaction results in multiple coupling of the viscoelastic modes of the unimer and dimer to strongly affect the viscoelastic relaxation.

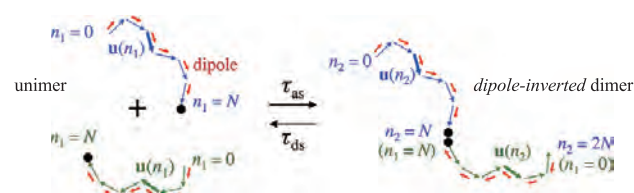


Figure 1. Illustration of head-to-head associating unimers and dissociating dimer at equilibrium. Purple circles at 0-th segments of the blue and green unimers (A and B) indicate the associative heads. The unimers and dimer have type-A dipoles aligned along the chain backbone without and with inversion, respectively.

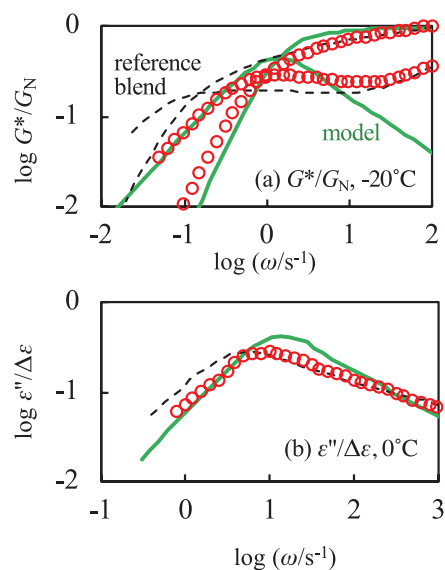


Figure 2. Comparison of (a) viscoelastic and (b) dielectric data (red circles) of PI30-COOH bulk system, model calculation (green solid curves), and data of the reference blend systems (thin dashed curves).