

Division of Multidisciplinary Chemistry – Molecular Rheology –

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



Prof

WATANABE, Hiroshi
(D Sc)



Assist Prof

MATSUMIYA, Yumi
(D Eng)



Techn Staff*

OKADA, Shinichi

*Re-employed Staff

Students

HIROTSU, Soichiro (M2)
TANAKA, Takeya (M2)

ISHIBASHI, Takuma (M1)
KUBO, Kosei (M1)

OHKITA, Yuya (M1)
ISHIMOTO, Ryushin (UG)

Guest Scholars

KWON, Youngdon (Ph D)
RAKKAPAO, Natthida (Ph D)

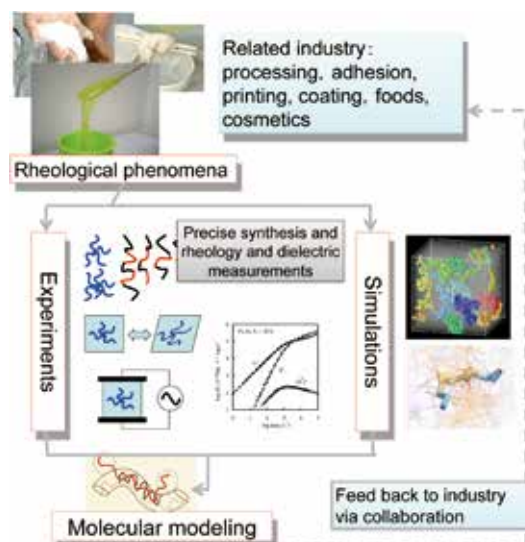
Sungkyunkwan University, Korea, R., 8 April-25 July
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Scope of Research

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

- Matsumiya, Y.; Rakkapao, N.; Watanabe, H., Entanglement Length in Miscible Blends of cis-Polyisoprene and Poly(p-tert-butylstyrene), *Macromolecules*, **48(21)**, 7889–7908 (2015).
- Timachova, K.; Watanabe, H.; Balsara, N. P., Effect of Molecular Weight and Salt Concentration on Ion Transport and the Transference Number in Polymer Electrolytes, *Macromolecules*, **48(21)**, 7882–7888 (2015).
- Watanabe, H.; Matsumiya, Y.; Inoue, T., Revisit the Stress-Optical Rule for Entangled Flexible Chains: Overshoot of Stress, Segmental Orientation, and Chain Stretch on Start-up of Flow, *J. Soc. Rheol. Jpn.*, **43(3-4)**, 105-112 (2015).
- Schauser, N. S.; Harry, K. J.; Parkinson, D. Y.; Watanabe, H.; Balsara, N. P., Lithium Dendrite Growth in Glassy and Rubbery Nanostructured Block Copolymer Electrolytes, *J. Electrochem. Soc.*, **162(3)**, A398-A405 (2015).
- Watanabe, H.; Matsumiya, Y.; Masubuchi, Y.; Urakawa, O.; Inoue, T., Viscoelastic Relaxation of Rouse Chains undergoing Head-to-Head Association and Dissociation: Motional Coupling through Chemical Equilibrium, *Macromolecules*, **48(9)**, 3014–3030 (2015).

Entanglement Length in Miscible Blends of cis-Polyisoprene and Poly (*p*-tert-butylstyrene)

The entanglement length a , being equivalent to the plateau modulus G_N ($\propto M_e^{-1} \alpha a^{-2}$), is one of the most basic parameters that determine the slow dynamics of high molecular weight (M) polymers. In miscible blends of chemically different chains, the components should have the common a value. However, changes of a with the blend composition have not been fully elucidated. For this problem, this study conducted linear viscoelastic tests for miscible blends of high- M *cis*-polyisoprene (PI) and poly(*p*-tert-butylstyrene) (PtBS) and analyzed the storage and loss moduli (G' and G'') data in a purely empirical way, considering the very basic feature that unentangled and entangled blends having the same composition exhibit the same local relaxation. (From a molecular point of view, this local relaxation reflects the chain motion *within* the length scale of a .) On the basis of this feature, a series of barely entangled low- M PI/PtBS blends having various component molecular weights and a given composition were utilized as references for well-entangled high- M PI/PtBS blends with the same composition, and the modulus data of the reference were subtracted from the data of the high- M blends. For an optimally chosen reference, the storage modulus of the high- M blends obtained after the subtraction ($G_{ent}' = G_{high-M blend}' - G_{ref}'$) exhibited a clear plateau at high angular frequencies ω . The corresponding loss modulus G_{ent}'' decreased in proportion to ω^{-1} at high ω , which characterized the short-time onset of the global entanglement relaxation: A mischoice of the reference gave no plateau of $G_{high-M blend}' - G_{ref}'$ and no ω^{-1} dependence of $G_{high-M blend}'' - G_{ref}''$ at high ω , but a survey for various low- M PI/PtBS blends allowed us to find the optimum reference (Figure 1). With the aid of such an optimum reference, the entanglement plateau modulus G_N of the high- M PI/PtBS blends was accurately obtained as the high- ω plateau value of G_{ent}' . G_N thus obtained was well described by a linear mixing rule of the entanglement length a with the weighing factor being equated to the number fraction of Kuhn segments of the components, not by the reciprocal mixing rule utilizing the component volume fraction as the weighing factor (Figure 2). This result, not explained by a mean-field picture of entanglement (constant number of entanglement strands in a volume a^3), is discussed in relation to local packing efficiency of bulky PtBS chains and skinny PI chains.

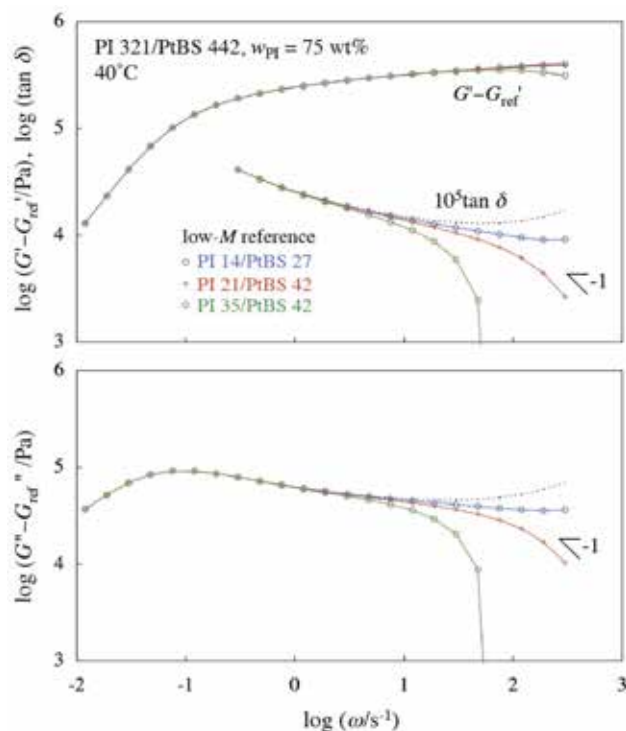


Figure 1. Test of the modulus difference $G^* - G_{ref}^*$ for high- M PI 321/PtBS 442 blend with $w_{PI} = 75$ wt%.

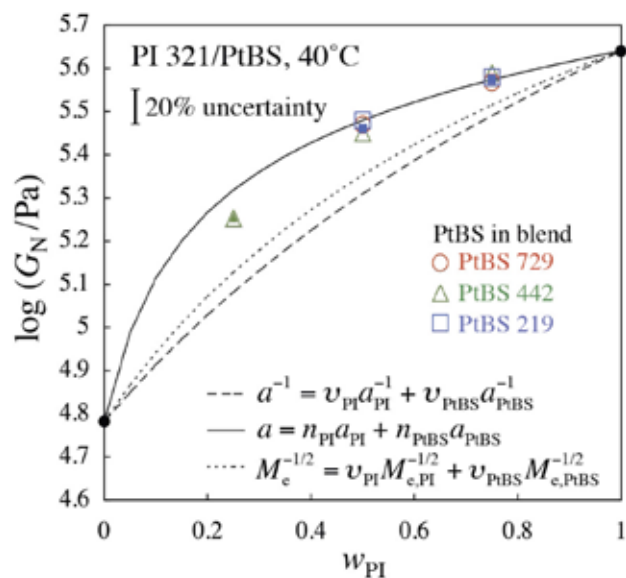


Figure 2. Entanglement plateau modulus G_N of high- M PI/PtBS blends evaluated by subtraction of G^* data of low- M reference blends (large unfilled symbols) and by phenomenological fitting with the aid of G^* data of two PI samples and/or two PtBS samples (small filled squares and small filled triangle).