Abstract Submitted
for the MAR17 Meeting of
The American Physical Society

Viscoelastic Relaxation of Mono-functionally End-Associating Rouse Chains: Experimental Test HIROSHI WATANABE, YUMI MATSUMIYA, Institute for Chemical Research, Kyoto University — Viscoelastic test was made for end-calboxylated polyisoprene (PI-COOH) of the molecular weight M = 30.5k that underwent the inter-chain 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 and PI2 dimer (both having no COOH group at the chain end). These samples were diluted in oligomeric butadiene (oB) to a concentration of 10 wt%. The neat unimer and dimer exhibited non-entangled 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 relaxation mode distribution. 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 COOH groups is discussed.

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Date submitted: 06 Nov 2016 Electronic form version 1.4