COMPONENT DYNAMICS IN MISCIBLE BLENDS

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Viscoelastic, dielectric, and rheo-optical behavior was examined for miscible blends of high-M *cis*-polyisoprene (PI) and poly(*p*-*tert*-butyl styrene) (PtBS). The slow dielectric relaxation detected the global motion of the PI chains having the type-A dipoles. The PI and PtBS chains were the fast and slow component chains entangling with each other.

At high T, the blend exhibited two-step plateau of the storage modulus $G'(\omega)$, and the plateaus at high and low angular frequencies (ω) were attributed, with the aid of the dielectric data, to the entanglement among all chains and that between the PtBS chains, respectively; see the 100˚C data in Fig.1. The entanglement length a characterizing the high-ω plateau was described by a simple mixing rule, $a = \Sigma_X n_X a_X$, based on the number fraction n of the Kuhn segments. The complex moduli G^* of the blends as well as the rheo-optical data in the high-ω plateau zone were well described by this mixing rule combined with a simple blending law of the component moduli; see curves for the high-ω data at 100˚C.

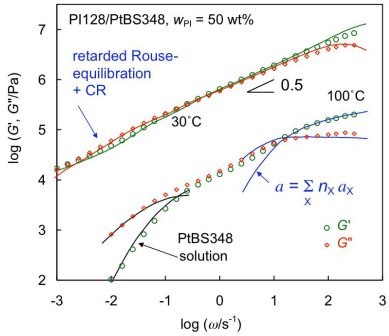

Fig.1 Viscoelastic behavior of a PI/PtBS blend. The sample code numbers indicate $10^{-3}M$.

At low T, the blend exhibited the Rouse-like behavior of storage and loss moduli, $G' = G'' \sim \omega^{1/2}$, in the range of ω where the high-ω plateau was supposed to emerge (see the 30˚C data). This lack of high-ω plateau was attributed to retardation of the Rouse equilibration of the PI chain within the entanglement length due to the hindrance from the slow PtBS chains. The Rouse equilibration time was just moderately shorter than the dielectrically determined terminal relaxation time of PI. Thus, the high-ω plateau zone was too narrow to be resolved experimentally, and the PI chains relaxed almost immediately after their Rouse equilibration (retarded by PtBS). This PI relaxation activated the CR relaxation of PtBS to dilate the entanglement mesh for PtBS. A model considering the Rouse equilibration and CR/dilation processes (solid curves attached to the 30˚C data in Fig.1) described the G^* data as well as the rheo-optical data, lending support to the above molecular picture.