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Thermorheological Complexity in Polystyrene Melt YN-HWANG LIN, National Chiao Tung University — Using the successful description of creep compliance$J(t)$ of nearly monodisperse polystyrene melts[1] in terms of the extended reptation theory[2] (ERT) in the rubber(like)-fluid region as the *reference frame* in time, the analysis of the glassy-relaxation process$A_G u_G(t)$ that occurs in the short-time region of $J(t)$ in terms of a stretched exponential form incorporated into ERT reveals that the temperature dependence of the $A_G u_G(t)$ process being stronger in a simple manner than that of the *entropy-derived* ERT processes accounts fully for the uneven thermorheological complexity in the $J(t)$. The results being displayed in the modulus $G(t)$ form, it is shown that at T_g, the contribution from$A_G u_G(t)$ to $G(t)$ at the time scale corresponding to the highest Rouse-Mooney normal mode greatly exceeds that derived from entropy, indicating vitrification at the Rouse-segmental level. At the same time the Rouse-Mooney normal modes provide an internal yardstick for estimating the length scale of the polymer at T_g, giving 3 nm for polystyrene. Based on the obtained results, the basic mechanism for the thermorheological complexity is analysed, showing that the break-down of Stoke-Einstein relation in glass-forming liquids, such as OTP, should occur for a similar reason. Ref: (1) D. J. Plazek, *J. Phys. Chem.* **1965**, 69, 3480; *J. Polym. Sci. A*-2 **1968**, 6, 621. (2) Y.-H. Lin, *Macromolecules* **1984**, 17, 2846; **1986**, 19, 159; 168; **1987**, 20, 885; **1999**, 32, 181; *Polymer Viscoelasticity*: *Basics, Molecular Theories and Experiments*; World Scientific: Singapore, 2003.

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