Description of Entanglement Dynamics of Flexible Polymers:
Self-Consistent Coarse-Graining in Length and Time Scales.

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Viscoelastic and dielectric properties differently reflect the same stochastic motion of the chain, and details of the chain dynamics can be investigated by comparing these properties [1]. For entangled *cis*-polyisoprenes (PI) chains having type-A dipoles parallel along the backbone, this comparison was made to examine validity of the molecular picture of dynamic tube dilation (DTD) in which the length and time scales are simultaneously coarse-grained.

Figure 1 shows the normalized viscoelastic relaxation modulus $\mu(t)$ measured for binary blends of linear PI chains with the molecular weights $M_2 = 308 \times 10^3$ and $M_1 = 21 \times 10^3$ (circles). In these blends, the high-M component chains (with the volume fraction $\upsilon_2 = 0.1$-0.5) are entangled with each other as well as with the low-M component chains. The observed two-step relaxation reflects motion of the low-M and high-M chains occurring in quite different time scales. In time scales *sufficiently* longer than the relaxation time τ_1 of the low-M chains, these chains behave as a simple solvent for the high-M chains and solution-like behavior of the high-M chains prevails. Thus, in this time scale, we expect the validity of the full-DTD molecular picture in which all relaxed portions of the chains are regarded as a solvent and an entanglement mesh size in the corresponding solution is utilized as the coarse-grained length scale in the blends. This expectation was confirmed from dielectric experiments [2]: The normalized dielectric relaxation function $\Phi(t)$ obtained for the PI/PI blends enabled us to evaluate the tube survival fraction and calculate the relaxation modulus for the case of full-DTD as $\mu_{\text{f-DTD}}(t) = \{\Phi(t)\}^{2.3}$ + tube-edge correction term. This $\mu_{\text{f-DTD}}(t)$, shown with the small filled squares in Figure 1, agrees well with the $\mu(t)$ data at long and short times, lending support to the full-DTD picture at those t.

However, at intermediate times that are still much longer than τ_1 of the low-M chain, $\mu_{\text{f-DTD}}(t)$ is smaller than the $\mu(t)$ data and the full-DTD picture fails. This result demonstrates the importance of the consistent coarse-graining in the length and time scales. Namely, for the tube for the high-M chain to dilate to the fully dilated diameter $a_{\text{f}}(t)$ assumed in the full-DTD picture, the entanglement segments of this chain should be mutually equilibrated over the length scale of $a_{\text{f}}(t)$. This equilibration, achieved through the Rouse-like constraint release (CR) mechanism, requires a certain

time $\tau_{\text{R}}(a_{\text{f}})$, and the tube cannot dilate to a_{f} in a time scale of $t < \tau_{\text{R}}(a_{\text{f}}(t))$. Indeed, the failure of the full-DTD picture seen in Figure 1 occurs in this time scale [2].
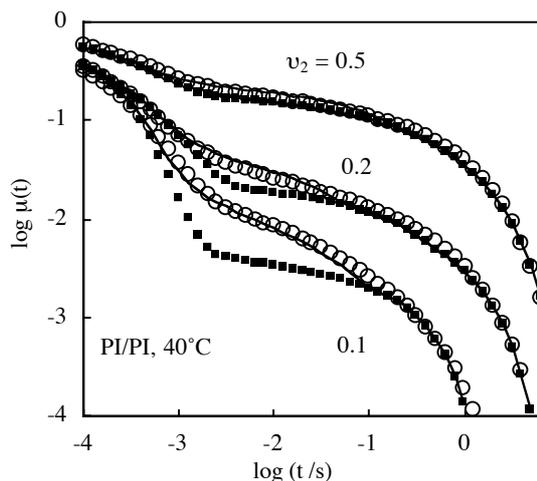
Figure 1: Normalized viscoelastic relaxation function of PI/PI blends at 40°C.

Even for this case, the tube should partially dilate to a diameter $a_{\text{eff}}(t) < a_{\text{f}}(t)$. This $a_{\text{eff}}(t)$ was estimated from the dielectrically obtained tube survival fraction, thereby coarse-graining the length and time scales consistently. The viscoelastic relaxation function for the partial DTD process, $\mu_{\text{p-DTD}}(t)$ calculated from this $a_{\text{eff}}(t)$ [2], is shown in Figure 1 with the solid curves. This $\mu_{\text{p-DTD}}(t)$ agrees well with the $\mu(t)$ data in the entire range of t. Thus, the DTD picture serves as a fundamental basis for description of the dynamics of the entangled chains if the length and time sales are self-consistently coarse-grained and the dilated tube diameter is properly evaluated.

It is known that the full-DTD picture fails for monodisperse star polymers at long t [3]. A recent experiment revealed the same failure also for a dendritic star-burst polymer. A test of the partial-DTD picture for these polymers is now being attempted.

References

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