Dielectric and Viscoelastic Investigation of Entanglement Relaxation

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For a chain (probe) entangled with surrounding chains (matrix), the entanglement is released on large-scale motion of the matrix chains. This constraint release (CR) mechanism plays a central role in the current tube model for entangled chains. Since the distance for the lateral motion of the probe (= tube diameter) increases on CR, the tube model often utilizes the molecular picture of dynamic tube dilation (DTD) to represent the CR effect on the probe dynamics. In the simplest case of full-DTD, the relaxed portion behaves as a solvent giving no constraint and the tube diameter increases to the diameter in the corresponding solution. This talk utilizes cis-polyisoprene (PI) having the type-A dipole to test the validity of the DTD picture with the following strategy. The type-A dipole allows us to dielectrically evaluate the survival fraction $f(t)$ of the dilated tube at time $t$. The full-DTD picture can be unequivocally tested by comparing the normalized viscoelastic modulus deduced from this picture ($2.0-2.3$th power of $f(t)$) with the viscoelastic data. The comparison indicated that the full-DTD picture works satisfactorily for monodisperse linear PI but not for blends of linear PI as well as for monodisperse star PI. The failure of the full-DTD picture for the last two systems is related to the fast relaxation modes in these systems. These modes leads to a significant increase of the fully dilated tube diameter over which the CR motion of the probe cannot occur in time, which naturally results in the failure of the full-DTD picture. Even for this case, the tube diameter increases to a level accepted by the CR motion. The partial-DTD picture considering this consistency with the CR motion was found to be valid for blends and star chains.