How Entangled Polymer Chains Relax

RICHARD WOOL, Department of Chemical Engineering, Univ Delaware — It will be shown through a series of experiments with selectively deuterated model polymers that stress relaxation occurs through a mechanical percolation process which permits large clusters of entangled polymers to stress relax before their conformations are fully relaxed. We find that:

(a) Reptating homopolymer chains with molecular weight $M >> M_c$ appear to be non-Reptating as their ends and centers relax at the same rate in a Rouse-like manner during percolation. (b) The mechanical relaxation time $\tau(M)$ is related to the Reptation time $T_r \sim M^3$ by $\tau(M) = T_r [(1-M_c/M) M_e/M_c]^2$, which is the origin of the viscosity behaving as $\eta \sim M^{3.4}$. (c) During stress relaxation, the random coil dimensions $R_g(//)$ and $R_g(\perp)$ are significantly not relaxed when the stress and birefringence relax to zero.

(d) Matrix molecular weight $P$ effects on relaxation time $\tau(M)$ of the probe chain $M$ are as follows: When the probe chain $M >> P$, the matrix $P$-chains percolate and Rouse-like dynamics is observed for the $M$-Reptating chains with $\tau(M) \sim P^1 M^2$. (e) When the matrix $P >> M$, percolation does not occur for the $M$-chain and the relaxation time of the probe chain $\tau(M) \sim P^0 M^3$ is in accord with DeGennes Reptation theory. These results clearly suggest that current notions of polymer rheology involving chain end fluctuation and constraint release need to be reconsidered.

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