Relaxation Modulus of Polymer Melt [pln53]

In a monodisperse polymer melt, the relaxation modulus $G(t)$ exhibits distinct behavior on three different time scales:

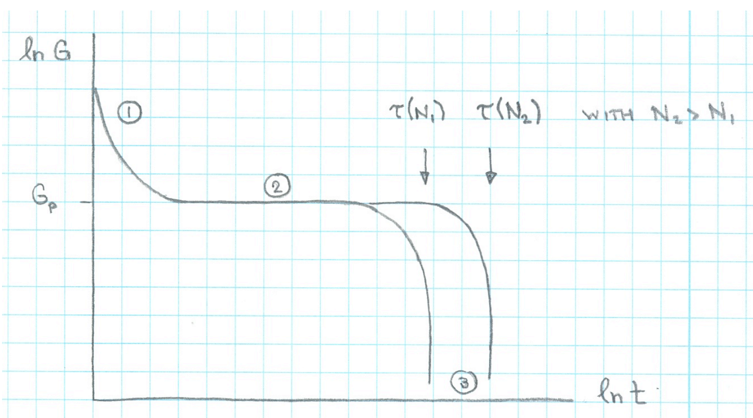
(1) The high initial value at short time reflects stiff *glassy* behavior.

(2) The plateau modulus G_p at intermediate times reflects *rubbery* elastic behavior. Entanglement produces contacts that act like temporary cross-links.

(3) At long times *viscous* behavior is in evidence with a strong dependence on N (degree of polymerization). The terminal time $\tau(N)$ is related to the zero shear viscosity introduced in [pln52]:

$$\eta_0 = \int_0^\infty dt\, G(t) \simeq G_p \tau(N).$$

Experimental evidence suggests that $\eta_0 \sim N^{3.4}$. [psl9]



Reptation: diffusion of polymers along tubular space.

- mobility: $\mu_{pol} = \mu_{mon}/N$,
- diffusivity: $D_{pol} = k_B T \mu_{pol} \sim N^{-1}$,
- effective random walk:[1] $\langle L^2 \rangle = D_{pol}\tau(n) \sim N^2$,
- terminal time: $\Rightarrow \tau(N) \sim N^3$ (exp. evidence: $\sim N^{3.4}$ [psl9]),
- self diffusion: $D_s \sim \dfrac{\langle x^2 \rangle}{\tau} \sim \dfrac{N}{N^3} \sim N^{-2}$ (exp. evid.: $\sim N^{-2.3}$ [psl9]).

[extracted in part from Jones 2002]

[1]using $L \propto N$.