Home assignments for the Course of Polymer Physical Chemistry

Section VI: Polymer Viscoelasticity

1. Estimate diffusion coefficient of PS molecule with molecular weight M=100,000 g/mol in dilute Θ-solution. The solvent viscosity η_S=1cP. Assume that hydrodynamic radius R_h is about radius of gyration R_g.

$D = \frac{kT}{6\pi\eta_S R_h}$; We need to estimate the hydrodynamic radius.

$R_h = R_g \approx l(nC_\infty/6)^{1/2} \approx 1.5*(2000*9.5/6)^{1/2} \approx 8.45$ nm;
From here, assuming room T=300K, we can estimate
$D \approx 1.38*10^{-23}*300/(6\pi*10^{-3}*8.45*10^{-9}) \approx$ **$2.6*10^{-11}$ [m^2/s]**

2. Estimate molecular weight between entanglement M_e for a polymer if it has rubbery plateau value G_N=1 MPa at T=400K. Assume that the density of the polymer is 1g/cm^3.

$M_e = \frac{\rho RT}{G_N} \approx$ **3320 [g/mol]**

3. Estimate the viscosity of the PDMS melt with molecular weight M=10^6 g/mol and the modulus plateau level G_N=0.2 MPa at room T. Assume that relaxation time of a segment at room T is $\tau_0=10^{-10}$ s, mass of a single segment is M_S=250 g/mol and the melt density is ρ=0.97 g/cm^3. Using all these parameters, estimate:
   - M_e;
   - viscosity and
   - how extended in time is the rubbery plateau.

$M_e = \frac{\rho RT}{G_N} \approx$ **12,077 [g/mol]**

$\eta = \frac{\pi^2}{12} G_N \tau^* \approx \frac{\pi^2}{12} G_N \frac{M^3}{M_e M_S^2}\tau_0 \approx 0.822*0.2*10^6*1.32*10^9*10^{-10} \approx$ **21,700 [Pa*s]**

The rubbery plateau extends from the Rouse time of the chain with $M \sim M_e$, τ_a, till the reptation time τ^*.

$\tau_a \approx \frac{M_e^2}{M_S^2}\tau_0 \approx$ **$2.3*10^{-7}$ [s]**

$\tau^* \approx \frac{M^3}{M_e M_S^2}\tau_0 \approx$ **0.132 [s]**. So, the plateau extends for almost 6 orders in time.