Quiz 5 Polymer Properties September 27, 2013

1) Polyelectrolytes display an enhanced persistence length associated with charged groups on the polymer chain. The enhancement in persistence length is associated with a balance between three size scales important to calculation of the persistence length.
   a) Name the three size scales important to persistence length in polyelectrolytes?
   b) Explain what charge screening caused by increasing counter ion concentration means. What is "screening" in this context?
   c) Why would the distribution of charge along the chain need to be smaller than r_D in order for charge to change the persistence length?
   d) The parameter "u" is a ratio of two energy terms related to counter ions associated with a polyelectrolyte chain. Describe these two energy terms as best you can.
   e) The plot below from Murnen et al. *Soft Matter* **9** 90 (2013) shows the electrostatic contribution to persistence, l_e, as a function of the Debye screening length κ^{-1} for a polyelectrolyte. Explain why you might expect l_e to drop with decreasing κ^{-1}. (The slope of the line is about -2.)

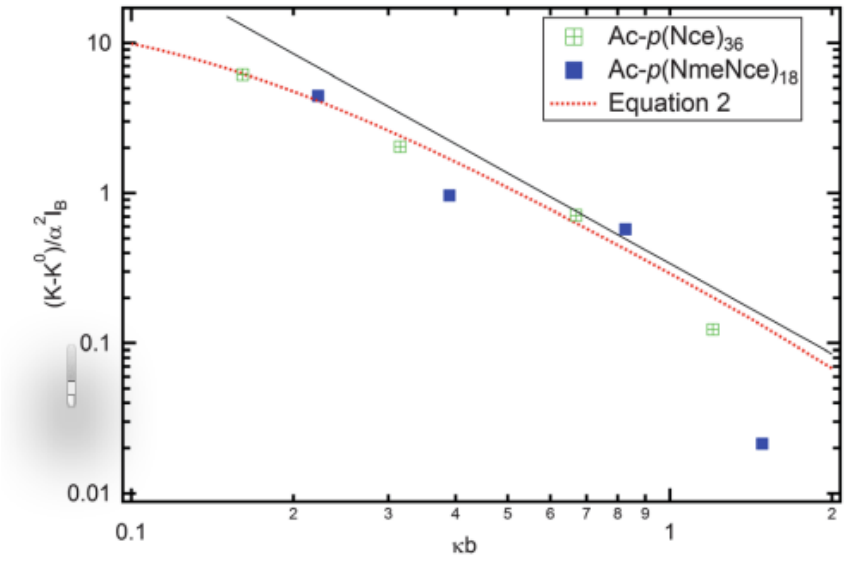

Fig. 4 Electrostatic contribution to the chain persistence length as a function of the reduced Debye screening length. Experimental data for Ac-p(NmeNce)$_{18}$ are shown as open circles and those for Ac-p(Nce)$_{36}$) shown as filled circles. Dashed red line corresponds to eqn (3). The solid black line illustrating a quadratic scaling serves as a guide to the eye.

2) Polymer melts and concentrated solutions display three characteristic distances on a small scale associated with static and dynamic properties.

   a) List these three distances that are important to polymer melts.
   b) Which of these distances can be measured using static neutron scattering? Why can't the others be measured?

c) The following plot from quasielastic neutron scattering measurements of Richter was used to define one of these distances. Explain this plot.

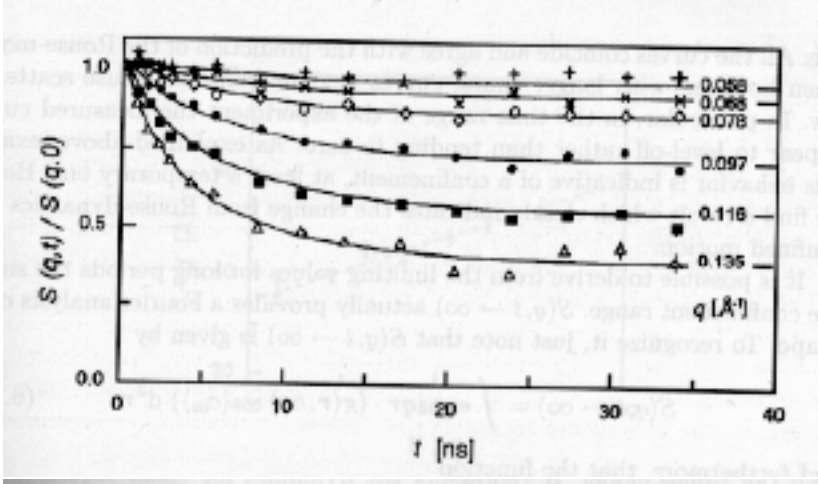

Fig. 6.8. Results of a quasielastic neutron scattering experiment on a melt of poly(ethylene-*co*-propylene) at 199 °C (10% protonated chains dissolved in a deuterated matrix; $M = 8.6 \cdot 10^4$): Intermediate scattering laws measured at the indicated scattering vectors (*top*); data representation using the dimensionless variable $x = q^2(12kTa_n^2t/\zeta_n)^{1/2}$ (*bottom*). From Richter et al.[67]

d) A microphase separated block copolymer displays nanoscale domains. Explain the area and volume terms that are needed to calculate the phase size. How are these parameters related to a local scale size parameter that can predict mechanical properties of polymers?

e) What is the plateau modulus and how is it related to the size parameter of part d?

ANSWERS: **Quiz 5 Polymer Properties September 27, 2013**

1) a) Spacing distance for charges along the chain, "a"; The Debye screening length $r_D = \kappa^{-1} = (\varepsilon kT/(4\pi ne^2))^{1/2}$; and the bare persistence length with no charge, l_0.
b) The force or energy between a charge on the chain and a test charge in the solution are reduced by the presence of counter ion charges in the solution. The counter ion charges screen the interaction. The higher the counter ion concentration, the weaker the interaction. The Debye screening length is a measure of the distance over which this interaction energy is important. It decreases with increasing counter ion charge, $r_D = \kappa^{-1} = (\varepsilon kT/(4\pi ne^2))^{1/2}$.
c) r_D is the distance over which the charge is felt so if "a" is smaller than r_D the charges can be felt by each other. If "a" is larger then the charges have no effect.
d) The counter ions tend to disperse to increase entropy and tend to condense on the chain driven by enthalpic interactions. The ratio of the enthalpic (coalescing) to the entropic (randomizing) energy is termed u. $u = e^2/(\varepsilon akT)$. For $u < 1$ the counter ions disperse, for $u > 1$ the counter ions coalesce. The chain is neutralized when $u = 1$.
e) As the screening length decreases the interaction between charges along the chain are felt less since the effective distance of interaction is dropping and the charges begin to not be felt by other charges. The power decay of 2 could be related to binary interactions.

2) a) The Kuhn, l_K, or persistence, l_p, length; the packing length, p or l_p; and the tube diameter, d_t.
b) Static neutron scattering can measure the persistence or Kuhn length. It can not measure dynamic parameters since it is not sensitive to motion of poymer chains.
c) The plot shows the exponential decay of scattered intensity as a function of time in a dynamic measurement of the autocorrelation function. More rapid decay relates to faster molecular motion. The different curves are for different values of $q = (4\pi/\lambda)\sin\theta = 2\pi/d$. Slow decay occurs for small q or large size and rapid decay occurs for large q or small size. The transition between these different dynamic regimes is the definition of the tube diameter. This is direct evidence for the existence of the tube and of reptation.
d) The area at the interface associated with a single chain, A, (packing area); and the occupied volume of a Kuhn unit, V_c, (packing volume). $V_c = p\, l_K^2$ and $A = \pi p^2$
e) In a plot of the storage modulus versus frequency, at low frequency the material displays viscous flow and the storage modulus scales with ω^2. At the high frequency near the glass transition the storage modulus follows Rouse behavior scales with $\omega^{1/2}$. At intermediate frequency for high molecular weight, molecular weight above the entanglement molecular weight, the modulus is constant in frequency and a plateau modulus is observed that scales with $G_0 \sim 3kT/(M_e l_K^2)$.

The storage modulus scales with $G_0 \sim kT/p^3$.

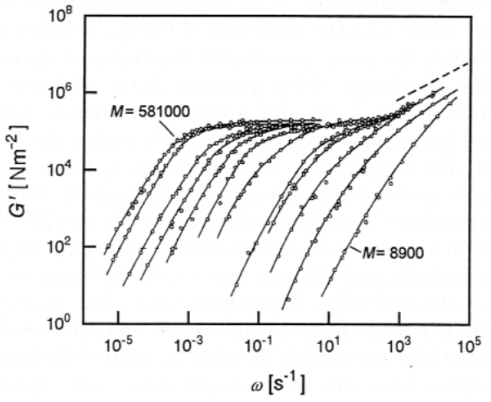

Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range $M = 8.9 \cdot 10^3$ to $M = 5.81 \cdot 10^5$. The *dashed line* in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of the glass-transition. Data from Onogi et al.[54]