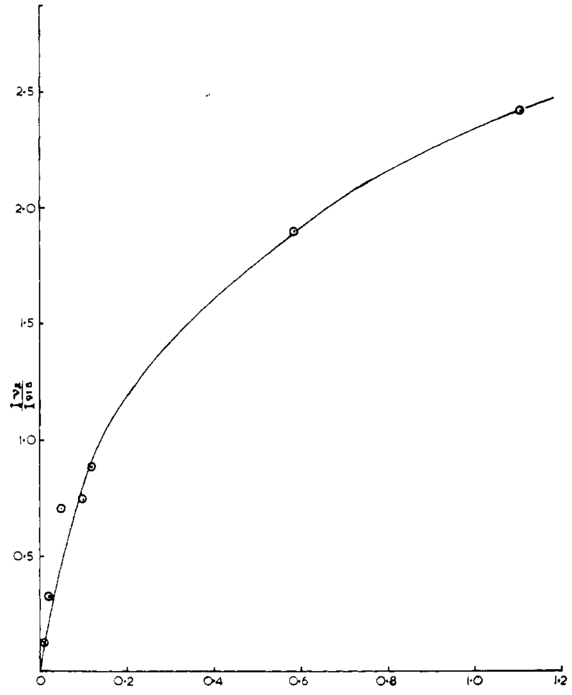

Figure 7. Intensity of the resonance Raman line ν_1 as a function of percentage degradation for PVC samples degraded at 190°.

as its very high sensitivity is concerned, is that it permits solution studies on comparatively insoluble samples with normal levels of degradation. It is interesting to note that the results obtained from measurements on solid samples enable values to be obtained for the approximate degree of degradation of the samples examined by Liebman, *et al.* The most heavily degraded of these contains about 0.003% of conjugated polyenes only, making the assumption that the distribution of sequence lengths is not markedly different from that of the samples examined in the present work. This provides another cogent example of the very high sensitivity of the technique.

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Partially Melted Rodlike Molecules. Light-Scattering and Translational Diffusion

S. A. Adelman and J. M. Deutch*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received May 30, 1974.*

ABSTRACT: A simple method is presented for determining physical properties of partially melted polymers. The model employed treats "unmelted" regions as rigid rods and "melted" regions as Gaussian random coils. The regions are separated by universal joints. The physical properties explicitly considered are the structure factor for scattered light intensity and the Kirkwood translational diffusion coefficient. Four cases of melting are considered: melting at one end into a single strand; melting at one end into two strands; melting at both ends; and interior melting.

We present a method for determining physical properties of partially melted polymers. The simple model we employ replaces the "unmelted" regions by rigid rods and the "melted" regions by Gaussian random coils. The two properties that are explicitly considered are the Debye intramolecular structure factor $P_n(\theta)$ for the angular distribution of scattered light intensity from a single chain[1]

$$P_n(\theta) = \frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\langle\exp[i\mathbf{q}\cdot\mathbf{R}_{ij}]\rangle \tag{1}$$

and the Kirkwood expression[2] for the translational diffusion coefficient D

$$D = \frac{kT}{n\zeta}\left[1 + (\zeta/6\pi\eta_0 n)\sum_{i=1}^{n}\sum_{j=1(\neq i)}^{n}\langle\mathbf{R}_{ij}^{-1}\rangle\right] \tag{2}$$

In eq 1 n is the number of segments in the chain; the sums are over all the segments; $|\mathbf{q}| = (4\pi/\lambda_0)\sin\theta$ is the scattering wave vector for light of wavelength λ_0, scattered at angle θ; and $\mathbf{R}_{ij}$ is the vector position between segments i and j. In eq 2 T is the temperature, k is Boltzmann's constant, ζ is the friction coefficient for an individual segment, and η_0 is the solvent viscosity. While the expression for D

is known not to be exact[3] it is believed to have practical value.[4] In the absence of hydrodynamic interactions

$$D = D_0 = (kT/n\zeta) \tag{3}$$

In these two expressions the averages are defined by

$$\langle f_{ij}\rangle = \int f(\mathbf{R})P_{ij}(\mathbf{R})\mathrm{d}\mathbf{R} \tag{4}$$

where $p_{ij}(\mathbf{R})$ is the probability density for the distance between segments i and j. For a rigid rod composed of segments of length a

$$P_{ij}{}^{\mathrm{r}}(\mathbf{R}) = [4\pi(|i-j|a)^2]^{-1}\delta[\mathbf{R} - |i-j|a] \tag{5}$$

For a Gaussian coil

$$P_{ij}{}^{\mathrm{G}}(\mathbf{R}) = [{}^3\!/_2\,\pi\langle\mathbf{R}_{ij}{}^2\rangle]^{3/2}\exp[-3\mathbf{R}^2/2\langle\mathbf{R}_{ij}{}^2\rangle] \tag{6}$$

where

$$\langle\mathbf{R}_{ij}{}^2\rangle = a^2|i-j| \tag{7}$$

Excluded volume effects might be crudely taken into account, as usual, by replacing $|i-j|$ by $|i-j|^{1+\epsilon}$ in this expression for $\langle\mathbf{R}_{ij}{}^2\rangle$, but we will not explore the consequences of this modification here.

Expressions for $P(\theta)$ and D are known for a rigid rod[1,2]

$$P_n{}^{\mathrm{r}}(\theta) = (2/n\mathbf{q}a)[Si(n\mathbf{q}a) + (n\mathbf{q}a)^{-1}(\cos n\mathbf{q}a - 1)] = \mathbf{R}(n\mathbf{q}a) \tag{8}$$

$$D^{\mathrm{r}} = D_0[1 + (\zeta/6\pi\eta_0 a)(\ln n - 1 + \gamma)] \tag{9}$$

the Gaussian coil[1,2]

$$P_n{}^{\mathrm{G}}(\theta) = \left(\frac{2}{u}\right)[1 + u^{-1}(e^{-u} - 1)] \qquad u = (n\mathbf{q}^2a^2/b) \tag{10}$$

$$D^{\mathrm{G}} = D_0\left[1 + (\zeta/6\pi\eta_0 a)\left(\frac{8}{3}\right)(6n/\pi)^{1/2}\right] \tag{11}$$

and the "once broken" rod[5,6] with a universal joint at position (σna) on the rod $\frac{1}{2} \leq \sigma \leq 1$.

$$P_n{}^{\mathrm{b}}(\theta) = \sigma^2\mathbf{R}[\sigma\mathbf{q}na] + (1-\sigma)^2\mathbf{R}[(1-\sigma)n\mathbf{q}a] + \frac{2}{(\mathbf{q}an)^2}Si(\sigma\mathbf{q}an)Si[(1-\sigma)\mathbf{q}an] \tag{12}$$

$$D^{\mathrm{b}} = D_0\{1 + (\zeta/3\pi\eta_0 a)[\ln n - 1 + \gamma + (g/\sigma)]\} \tag{13}$$

where

$$g(\sigma) = 2(1-\sigma) + \ln\sigma; \quad Si(x) = \int_0^x \frac{\sin Z}{Z}\mathrm{d}Z \tag{14}$$

and γ = Euler's constant. Our expression for $P_n{}^{\mathrm{b}}(\theta)$ is an obvious generalization of the expression obtained by Pecora[7] for the special case $\sigma = \frac{1}{2}$.

Here we consider the calculation of $P_n(\theta)$ and D for macromolecules composed of two or more portions at least one of which is a rigid rod and one a random coil. Our motivation for presenting these results is that many macromolecules undergo shape transitions from rodlike to flexible coil when temperature or solution pH is varied. In the melting region the sample will contain macromolecules in intermediate conformations containing both rodlike and random coil regions. An experiment will measure an average property of the sample with a particular weighting of the different conformations. The appropriate average will depend on the experiment, *e.g.*, quasi-elastic light scattering, and the characteristic time of the measurement compared to the interconversion rate of the conformations. The method and results we present indicate how to determine properties for the different conformations of the macromolecule in the intermediate melting region.

Method

Consider a single macromolecule divided into two portions containing respectively n_{A} and n_{B} segments. For convenience we locate at position $(n_{\mathrm{A}} + 1)$ a segment which serves as the joint separating the two sections. Thus the polymer contains $n = n_{\mathrm{A}} + n_{\mathrm{B}} + 1 \approx n_{\mathrm{A}} + n_{\mathrm{B}}$ segments. It is clear that the average of any function $f(\mathbf{R}_{ij})$ of the distance of separation $\mathbf{R}_{ij}$ of two segments on the chain may be expressed as

$$\langle f\rangle = \sum_{i,j}\langle f_{ij}\rangle = \sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=1}^{n_{\mathrm{A}}}\langle f_{ij}\rangle^{\mathrm{A}} + \sum_{i=n_{\mathrm{A}}+2}^{n_{\mathrm{A}}+n_{\mathrm{B}}+1}\sum_{j=n_{\mathrm{A}}+2}^{n_{\mathrm{A}}+n_{\mathrm{B}}+1}\langle f_{ij}\rangle^{\mathrm{B}} + 2\sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=n_{\mathrm{A}}+2}^{n_{\mathrm{A}}+n_{\mathrm{B}}+1}\langle f_{ij}\rangle^{\mathrm{AB}} \tag{15}$$

where the superscript A(B) on $\langle f_{ij}\rangle$ denotes the average in eq 4 with a probability density $P_{ij}{}^{\mathrm{A}}(\mathbf{R})[P_{ij}{}^{\mathrm{B}}(\mathbf{R})]$ appropriate to the pure chain section. The superscript AB on the last term in eq 15 refers to the probability density $P_{ij}{}^{\mathrm{AB}}(\mathbf{R})$ of separations between segment i on chain A and segment j on chain B. Clearly the first two terms on the right-hand side of eq 15 give the contribution to $\langle f\rangle$ of two unconnected pure chains A and B of length n_{A} and n_{B}, respectively; the last term gives the interference contribution due to the chain connection.

For light scattering $f_{ij} = \exp[i\mathbf{q}\cdot\mathbf{R}]$ and for diffusion $f_{ij} = \mathbf{R}^{-1}$. The calculation of the pure chain contributions proceeds as usual and our problem is reduced to consideration of the cross term.

Our method for determining the cross term is based on the observation that for chains with a universal joint where excluded volume effects are ignored

$$P_{ij}{}^{\mathrm{AB}}(\mathbf{R}) = \int P_{i,n_{\mathrm{A}}+1}{}^{\mathrm{A}}(\mathbf{R}')P_{n_{\mathrm{A}}+1,j}{}^{\mathrm{B}}(\mathbf{R}-\mathbf{R}')\mathrm{d}\mathbf{R}' \tag{16}$$

The convolution form of this expression suggests employing Fourier transforms to compute the cross term X_f

$$X_f = \sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=n_{\mathrm{A}}+2}^{n_{\mathrm{A}}+n_{\mathrm{B}}+1}\langle f_{ij}\rangle^{\mathrm{AB}} \tag{17}$$

With the definition

$$\hat{G}(\mathbf{q}) = \int\mathrm{d}\mathbf{R}\,\exp[i\mathbf{q}\cdot\mathbf{R}]G(\mathbf{R}) \tag{18}$$

one easily finds that

$$\hat{P}_{ij}{}^{\mathrm{AB}}(\mathbf{q}) = \hat{P}_{i,n_{\mathrm{A}}+1}{}^{\mathrm{A}}(\mathbf{q})\hat{P}_{n_{\mathrm{A}}+1,j}{}^{\mathrm{B}}(\mathbf{q}) \tag{19}$$

and

$$X_f = (2\pi)^{-3}\sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=n_{\mathrm{A}}+2}^{n_{\mathrm{A}}+n_{\mathrm{B}}+1}\int\mathrm{d}\mathbf{q}_0\hat{P}_{i,n_{\mathrm{A}}+1}{}^{\mathrm{A}}(\mathbf{q}_0)\hat{P}_{n_{\mathrm{A}}+1,j}{}^{\mathrm{B}}(\mathbf{q}_0)\hat{f}(\mathbf{q}_0) \tag{20}$$

For the case of light scattering $\hat{f}(\mathbf{q}_0) = (2\pi)^3\delta(\mathbf{q}-\mathbf{q}_0)$ and the cross term is

$$X_{\mathrm{L}} = \sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=2}^{n_{\mathrm{B}}+1}\hat{P}_{1,i}{}^{\mathrm{A}}(\mathbf{q})\hat{P}_{1,j}{}^{\mathrm{B}}(\mathbf{q}) \tag{21}$$

while for the case of translation diffusion the cross term is

$$X_{\mathrm{D}} = (2\pi^2)^{-1}\sum_{i=1}^{n_{\mathrm{A}}}\sum_{j=2}^{n_{\mathrm{B}}+1}\int\hat{P}_{1,i}{}^{\mathrm{A}}(\mathbf{q})\hat{P}_{1,j}{}^{\mathrm{B}}(\mathbf{q})\mathbf{q}^{-2}\mathrm{d}\mathbf{q} \tag{22}$$

where we have set the Fourier transform of $f(\mathbf{R}) = \mathbf{R}^{-1}$ equal to $\hat{f}(\mathbf{q}) = 4\pi\mathbf{q}^{-2}$.

Evaluation of these formulas is relatively straightforward. For example for the case of the once-broken rod we

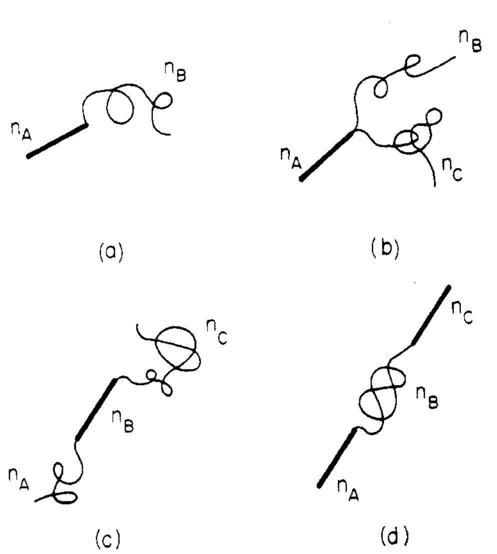

Figure 1. Cases considered for partially melted polymers: (a) rod with n_A sigments melted at one end into coil of n_B segments; (b) rod melted at one end into two coils; (c) rod melted at both ends into coils; (d) rod with interior melting into coil.

take both A and B to be rods and from eq 5 we find

$$\hat{P}_{ij}{}^{r}(\mathbf{q}) = \frac{\sin[\mathbf{q}a(i-j)]}{(i-j)\mathbf{q}a} \tag{23}$$

Substitution of this expression into eq 21 and 22 and subsequent evaluation of the integral and sums leads to values of $X_D{}^b$ and $X_L{}^b$. When these values are combined in eq 15 with the rigid rod results and use is made of the definition of $P_n(\theta)$ and D one obtains the results for $P_n{}^b(\theta)$ and D^b displayed in eq 12 and 13, respectively.

Results for Partially Melted Chains

For the case where A is a rigid rod and B a random coil (see Figure 1a) the light scattering cross term is

$$X_L = \sum_{i=1}^{n_A}\sum_{j=1}^{n_B} \frac{\sin \mathbf{q}ai}{\mathbf{q}ai} \exp[-\mathbf{q}^2a^2j/6] \tag{24}$$

Here we have used eq 9 and the fact that (see eq 6, 7, and 18)

$$\hat{P}_{ij}{}^{G}(\mathbf{q}) = \exp[-\mathbf{q}^2a^2|i-j|/6] \tag{25}$$

Replacement of the sums by integrals leads to the results

$$X_L = \frac{Si(n_A\mathbf{q}a)}{n_A\mathbf{q}a} u_B{}^{-1}(1 - e^{-u_B})n_An_B \tag{26}$$

where $u_B = (\mathbf{q}^2a^2n_B/6)$. Consequently the structure factor for light scattering is

$$P_n(\theta) = \left[\left(\frac{n_A}{n}\right)^2 P_{n_A}{}^{r}(\theta) + \left(\frac{n_B}{n}\right)^2 P_{n_B}{}^{r}(\theta) + 2\left(\frac{n_An_B}{n^2}\right)\frac{Si(n_A\mathbf{q}a)}{n_A\mathbf{q}a} u_B{}^{-1}(1 - e^{-u_B})\right] \tag{27}$$

In the limit $\mathbf{q}an_A \ll 1$ and $\mathbf{q}an_B \ll 1$ we find

$$P_n(\theta) = 1 - \mathbf{q}^2a^2n^2\kappa + 0(\mathbf{q}^4) \tag{28}$$

where

$$\kappa = y_A{}^2\left[\frac{1}{36}y_A{}^2 + \frac{1}{9}y_Ay_B\right] + n^{-1}y_B{}^2\left[\frac{1}{18}y_B + \frac{1}{6}y_A\right] \tag{29}$$

with $y_A = (n_A/n)$ and $y_B = (n_B/n)$. In passing we note that the coefficient of the $\mathbf{q}^2$ term in the expansion of $P_n(\theta)$ equals $(-\frac{1}{3})$ times the radius of gyration of these partially melted chains.

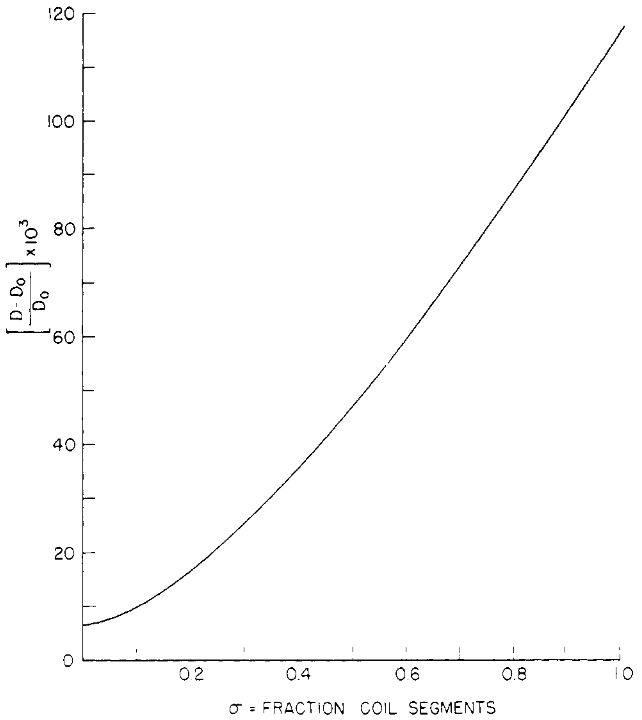

Figure 2. Diffusion coefficient of a partially melted rod. The fractional hydrodynamic contribution to the Kirkwood translational diffusion coefficient is plotted *vs.* the degree of melting $\sigma = (n_B/n)$ for $n = 1000$. Here n_B is the number of coil segments and $(n - n_B)$ the number of rod segments. The polymer is melting at one end as exhibited in Figure 1a.

The calculation of the cross term for diffusion X_D is a bit more lengthy. From eq 22, 23, and 25 we find

$$X_D = \left(\frac{2}{n}\right)\sum_{j=1}^{n_B}\sum_{i=1}^{n_A}\int_0^\infty d\mathbf{q}\frac{\sin(\mathbf{q}ai)}{\mathbf{q}ai}\exp[-\mathbf{q}^2a^2j/6] \tag{30}$$

and the integral over $\mathbf{q}$ can be performed to yield

$$X_D = \left(\frac{2}{\pi}\right)\sum_{i=1}^{n_A}\sum_{j=1}^{n_B}\left[\frac{1}{2a}\left(\frac{6\pi}{j}\right)^{1/2}\int_0^1 \exp[-3i^2Z^2/2j]dZ\right] \tag{31}$$

A convenient expression for calculational purposes is obtained by replacing the sum over i by an integral; one obtains

$$X_D = a^{-1}\phi(n_A, n_B) = \frac{2}{\sqrt{\pi}}a^{-1}\sum_{j=1}^{n_B}\left\{\ln\left[\sqrt{3/2}\frac{n_A}{\sqrt{j}}\right] \times \int_0^{\sqrt{3/2}n_A/\sqrt{j}} dZ\exp(-Z^2) - \int_0^{\sqrt{3/2}n_A/\sqrt{j}} dZ\ln Z\exp(-Z^2)\right\} \tag{32}$$

The function $\phi(n_A,n_B)$ can be evaluated asymptotically for $n_A \geq n_B \gg 1$. Under these circumstances (incomplete melting) the upper limits on the above integrals can be extended to infinity. One finds

$$\phi(n_A, n_B) = n_B\left\{\ln\left(\frac{n_A}{n_B{}^{1/2}}\right) + \frac{1}{2}\left[\frac{1}{2}\ln\left(\frac{3}{32}\right) + 1 - \gamma\right]\right\} \tag{33}$$

The general expression for the translational diffusion coefficient of the partially melted chain may be expressed as

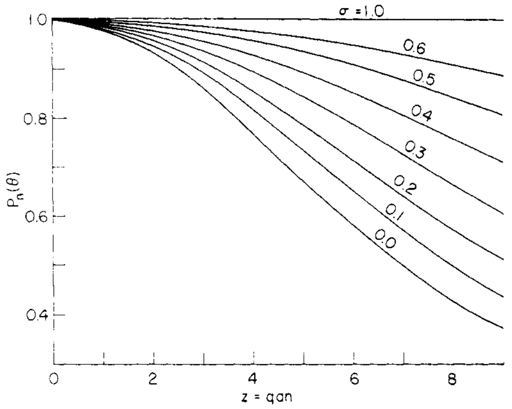

Figure 3. Structure factor $P_n(\theta)$ for interior melting. $P_n(\theta)$ is plotted *vs.* $Z = \mathbf{q}an$ for several values of $\sigma = (n_B/n)$; n_B is the number of coil segments and $n_A = n_C = \frac{1}{2}(n - n_B)$ are the number of rod segments. The polymer melting is symmetric and corresponds to Figure 1d. For $\sigma = 0$ the result reduces to the once broken rod with its joint in the center.

$$\frac{\Delta D}{D_0} = \frac{D - D_0}{D_0} = \left[\frac{\zeta}{6\pi\eta_0 an}\right]\left\{\frac{8}{3}\left(\frac{6n_B{}^3}{\pi}\right)^{1/2} + n_A \ln n_A - n_A + \gamma n_A + 2\phi(n_A, n_B)\right\} \quad (34)$$

In Figure 2 $\Delta D/D_0$ is plotted for $n = 1000$ with the assumption of Stokes law $[\zeta = 6\pi\eta_0 a]$ as a function of $\sigma = (n_B/n)$. The asymptotic expression for $\phi(n_A,n_B)$ (eq 33) is completely adequate representation of $(\Delta D/D_0)$ to values of σ beyond 0.95. For larger values of σ an adequate approximation to $(\Delta D/D_0)$ is the contribution from the Gaussian portion of the coil.

More Complex Cases

Once the method is established for determining $P_n(\theta)$ and D for a chain with one break into a rod and random coil portion it is clear that the same technique may be used for chains with more breaks or with several branches. Any particular case may easily be examined. For example Figure 1b presents a crude model of a double helix melted from one end. We consider a rigid (helical)length of n_A segments attached to two coil lengths of n_B and n_C segments. In addition to the two pure coil and one pure rod contributions to $P_n(\theta)$ and D one must consider cross terms between the two coils as well as between each coil and the rod. It is an easy matter to show by the method developed above that the two pure coil contributions and the coil–coil cross term combine to give a single contribution of an effective coil with $(n_B + n_C)$ segments. This result is physically reasonable and one may immediately conclude that the structure factor $P_n{}^h(\theta)$ for this case is

$$P_n{}^h(\theta) = \left[\left(\frac{n_A}{n}\right)^2 P_{n_A}{}^r(\theta) + \left(\frac{n_B + n_C}{n}\right)^2 P_{n_B+n_C}{}^G(\theta) + 2\sum_{\alpha=B,C}\left(\frac{n_A n_\alpha}{n^2}\right)\frac{Si(n_A\mathbf{q}a)}{n_A\mathbf{q}a}u_\alpha{}^{-1}(1 - e^{-u_\alpha})\right] \quad (35)$$

where $n = n_A + n_B + n_C$ and $u_\alpha = (\mathbf{q}^2a^2n_\alpha/6)$. Similarly the translation diffusion coefficient D^h will be given by

$$\frac{D^h - D_0}{D_0} = \left[\frac{\zeta}{6\pi\eta_0 an}\right]\left\{n_A \ln n_A - n_A + \gamma n_A + \frac{8}{3}\left[\frac{6(n_B + n_C)^3}{\pi}\right]^{1/2} + 2\phi(n_A, n_B) + 2\phi(n_A, n_C)\right\} \quad (36)$$

The analysis for a chain with several breaks composed of many rigid rod and random coil links is more involved, especially for the calculation of D. For illustrative purposes we consider two cases: melting of a rodlike macromolecule at its ends and also interior melting of the rodlike macromolecule. We idealize a polymer undergoing melting at its ends as two random coils joined by a rod, Figure 1c. Similarly we regard a polymer undergoing interior melting as two rods linked by a coil portion, Figure 1d.

For both cases we require $P_{ij}{}^{AC}(\mathbf{R})$, the probability that segment i on end portion A with n_A segments will be a distance $\mathbf{R}$ from segment j on end portion C with n_C segments given that the central link B contains n_B segments. With our previous assumption that the different portions are connected by universal joints we see that

$$P_{ij}{}^{AC}(\mathbf{R}) = \int d\mathbf{R}'d\mathbf{R}''P_{i,n_A+1}{}^A(\mathbf{R}')P_{n_A+1,n_A+n_B+2}{}^B(\mathbf{R}'') \times P_{n_A+n_B+2,j}{}^C(\mathbf{R} - \mathbf{R}' - \mathbf{R}'') \quad (37)$$

Accordingly we find

$$\hat{P}_{ij}{}^{AC}(\mathbf{q}) = \hat{P}_{i,n_A+1}{}^A(\mathbf{q})\hat{P}_{n_A+1,n_A+n_B+2}{}^B(\mathbf{q})\hat{P}_{n_A+n_B+2,j}{}^C(\mathbf{q}) \quad (38)$$

The contribution to a property $f(\mathbf{R})$ from the cross terms between segments on end A and segments on end C is thus (*cf. eq* 21 and 22)

$$X_f{}^{(3)} = (2\pi)^{-3}\sum_{i=1}^{n_A}\sum_{j=1}^{n_C}\int d\mathbf{q}_0\hat{f}(\mathbf{q}_0)\hat{P}_{1,i}{}^A(\mathbf{q}_0) \times \hat{P}_{1,n_B+1}{}^B(\mathbf{q}_0)\hat{P}_{1,j}{}^C(\mathbf{q}_0) \quad (39)$$

For the case of a macromolecule melting at its ends (Figure 1c), the structure factor and Kirkwood diffusion coefficient can be written as a sum of two pure coil terms, a pure rod term, two rod–coil terms, and also the cross contribution of eq 39. We find for the structure factor for end melting

$$P_n{}^e(\theta) = \left[\left(\frac{n_A + n_C}{n}\right)^Z P_{n_A+n_C}{}^G(\theta) + \left(\frac{n_B}{n}\right)^2 P_{n_B}{}^r(\theta) + 2\sum_{\alpha=A,C}\frac{n_B n_\alpha}{n^2}\frac{Si(n_B\mathbf{q}a)}{n_B\mathbf{q}a}u_\alpha{}^{-1}(1 - e^{-u_\alpha}) + 2\frac{n_A n_C}{n^2}\left[\frac{\sin(n_B\mathbf{q}a)}{n_B\mathbf{q}a} - 1\right]\frac{(1 - e^{-u_a})(1 - e^{-u_c})}{u_A u_C}\right] \quad (40)$$

To obtain the diffusion coefficient, one must evaluate eq 39 with $\hat{f}(\mathbf{q}) = 4\pi q^{-2}$. This can be accomplished for end melting if $(n_A + n_C)^{1/2} \ll n_B$, that is when the melting is incomplete. One finds

$$X_D{}^{(3)} = n_A n_C/n_B a \quad (41)$$

Thus

$$\frac{\Delta D^e}{D_0} = \left[\frac{\zeta}{6\pi\eta_0 an}\right]\left\{n_B \ln n_B - n_B + \gamma n_B + \frac{8}{3}\left[\frac{6n_A{}^3}{\pi}\right]^{1/2} + \frac{8}{3}\left[\frac{6n_C{}^3}{\pi}\right]^{1/2} + 2\phi(n_B, n_A) + 2\phi(n_B, n_C) + 2\frac{n_A n_C}{n_B}\right\} \quad (42)$$

The structure factor for interior melting (Figure 1d) can also be easily worked out. One finds

$$P_n{}^I(\theta) = \left(\frac{n_B}{n}\right)^2 P_{n_B}{}^G(\theta) + \sum_{\alpha=A,C}\left[\left(\frac{n_\alpha}{n}\right)^2 P_{n_\alpha}{}^r(\theta) + 2\frac{n_\alpha n_B}{n^2}\frac{Si(n_\alpha\mathbf{q}a)}{n_\alpha\mathbf{q}a}u_B{}^{-1}(1 - e^{-u_B})\right] + \frac{2n_A n_C}{n^2}\frac{Si(n_A\mathbf{q}_a)}{n_A\mathbf{q}_a}\frac{Si(n_C\mathbf{q}_a)}{n_C\mathbf{q}_a}e^{-u_B} \quad (43)$$

We expect on physical grounds that the structure factor for interior melting should reduce to that for a once broken rod, eq 12, when $n_B \to 0$. From eq 43 we see that this is indeed true. Calculation of the diffusion coefficient for interior melting involves more labor since the integral in eq 39 is difficult to evaluate analytically for this case. One can, however, perform the double sum analytically and evaluate the remaining integral over $\mathbf{q}_0$ numerically.

In Figure 3 the structure factor for interior melting is plotted against $Z = \mathbf{q}an$ for several values of the melting parameter $\sigma = (n_B/n)$ with $n_A = n_C = (n/2)(1 - \sigma)$. The figure has been constructed for the regime where Z is of order unity but $u = (n\mathbf{q}^2a^2/6) = Z^2/6n^2 \ll 1$ so that the structure facture depends only on Z. Physically this condition states that the wavelength of light is large compared with all possible coil lengths but comparable to possible rod lengths. The curve $\sigma = 0$ corresponds to the once-broken rod case.

Concluding Remarks

We have presented a simple method for determining the properties of partially melted macromolecules when these properties depend upon some function of the distance between pairs of segments of the polymer. We find that in partially melted conformations the macromolecule exhibits significantly different behavior than in the extreme circumstances of no melting or complete melting. Quantitative results are displayed for the light-scattering structure factor and the translational diffusion coefficient for a number of cases.

The analysis may be extended in a number of ways, *e.g.*, to heterogeneous chains, to polydisperse systems, or to other hydrodynamic or equilibrium properties. Experimentalists should note that the proper interpretation of measurements in the melting region must take into account the variation of partially melted chains as discussed here. A particular measurement will require an appropriate average over the different conformations represented in the system during the process of melting.

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References and Notes

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Thermal Transition Behavior of Polyurethanes Based on Toluene Diisocyanate

N. S. Schneider,* C. S. Paik Sung, R. W. Matton, and J. L. Illinger

Polymer and Chemistry Division, Army Materials and Mechanics Research Center, Watertown, Massachusetts 02172, and Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01002. *Received May 1, 1974*

ABSTRACT: The thermal transition behavior of two series of polyurethane block copolymers, one based on 2,4-toluene diisocyanate, the other on 2,6-toluene diisocyanate, was studied to determine the influence of an asymmetric diisocyanate structure, such as that represented by 2,4-toluene diisocyanate, on domain organization and polyurethane properties. The 2,4-TDI polyurethanes were transparent and amorphous, and the properties varied progressively with urethane concentration; the 2,6-TDI polyurethanes were opaque, semicrystalline, and hard but tough. In the 2,4-TDI samples the glass transition T_g was a strong function of urethane concentration. Similar behavior was shown by an intermediate temperature transition T_2. A higher temperature transition T_3 was detected only in the samples of highest urethane content and then only on the initial heating. In the 2,6-TDI samples T_g was generally independent of urethane concentration. No T_2 transition was observed. The T_3 transition was repeatable and increased with urethane concentration. It is suggested that the T_2 transition which occurs in the 2,4-TDI polyurethanes is indicative of weak domain structure and that the increase in T_g with urethane concentration is due to extensive hard segment mixing with the soft segment phase. The absence of a T_2 transition in 2,6-TDI is taken to indicate that all domain structure which occurs is highly ordered and, therefore, that hard segment–soft segment mixing is minimal. This is in keeping with the strong T_3 transition and observed crystallinity and could account for the invariance of T_g with urethane concentration.

The thermoplastic polyurethanes are linear segmented copolymers which consist of alternating soft and hard segment units. The soft segment is commonly a low molecular weight polyether or polyester whereas the hard segment generally consists of an aromatic diisocyanate condensed with a low molecular weight diol. It is now generally accepted that the properties of these materials are primarily due to the phase segregation of soft and hard segments leading to the formation of hard segment domains which are dispersed in the rubbery matrix. The polyurethanes based on diphenyl methyl diisocyanate (MDI) have been the subject of intensive investigation by a variety of techniques. Three characteristic endothermic transitions have been detected by differential scanning calorimetry and penetrometer techniques:[1-3] a transition at 80° which is attributed to the disruption of domains with limited short-range order; a transition at 130 to 150° which represents the dissociation of domain structure with improved short-range order; and a transition above 200° which is due to the melting of crystalline structure in samples with sufficiently long hard segments. Annealing studies[2] have shown that the lower sitions can be shifted continuously upward to merge with

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* Army Materials and Mechanics Research Center.