of the polyelectrolyte. The higher $D_{\text{obsd}}$ values for the 6-6 ionene as compared to the 3-3 ionene are believed to be due to a collision of the more flexible polyelectrolyte due to divalent counterion condensation. As $X$ is decreased from about $2 < X < 3$ to $X = 0.1$, $D_{\text{obsd}}$ increases. This is probably due to both the $\text{SO}_4^{2-}$ ions in the ionic atmosphere and the condensed $\text{SO}_4^{2-}$ ions since the equivalent concentration ratio of salt to polyelectrolyte increases as $X$ decreases. Thus, the tracer and nonradioactive $\text{SO}_4^{2-}$ ions are distributed between the polyelectrolyte and the simple salt at low $X$ values according to their weighted concentrations.

It is desirable to obtain the counterion tracer diffusion coefficient for those ions in the ionic atmosphere, for this is a measure of the long-range ion-polyion interaction. For high molecular weight polyelectrolytes with diffusion coefficients very much smaller than those for small ions, the condensed radioactive small ions would not contribute appreciably to the measured counterion tracer diffusion coefficients. If the diffusion coefficient of the polyelectrolyte is not negligible compared to that of the counterions if counterion condensation takes place, then the measured counterion diffusion coefficient $D_{\text{obsd}}$ is

$$D_{\text{obsd}} = D^{(c)}_{\text{i,eff}} + D^{(i)}_{\text{i,eff}}$$

where $D^{(c)}_{\text{i,eff}}$ and $D^{(i)}_{\text{i,eff}}$ are the effective diffusion coefficients of the condensed counterions and uncondensed counterions, respectively. To determine the desired quantity $D^{(i)}_{\text{i,eff}}$, the weighted concentration average of $D^{(c)}_{\text{i,eff}}$, is used, i.e.,

$$D^{(c)}_{\text{i,obsd}} = D^{(c)}(1 - (Z_i \xi)^{-1})/(N_c/N_i)$$

where $D^{(c)}_{\text{i,obsd}}$ is the diffusion coefficient of the condensed counterions and hence of the polyelectrolyte. Values of $D^{(c)}_{\text{i,obsd}}$ can be obtained from tracer diffusion measurements of divalent (or higher valent) counterions when they are added to a polyelectrolyte whose counterions are monovalent. Recently, direct evidence has been reported\(^{28}\) that shows tracer values of radioactive Ca\(^{2+}\) ion condensed onto sodium heparin, and the values observed for $D_{\text{Ca}^{2+}}$ were very close to the values obtained for the tracer diffusion coefficient of the polyelectrolyte itself. Also the replacement of monovalent counterions by trace amounts of divalent and trivalent counterions has been confirmed indirectly from tracer diffusion measurements\(^{11-16}\) and from potentiometric measurements.\(^{20,27}\) In the absence of direct experimental information pertaining to the charge fraction of the ionene halides, an assumption had to be used in eq 4 to evaluate the weighted contribution of counterions dissociated from the polyelectrolyte. The validity of the Manning theoretical charge fraction of the polyelectrolyte was assumed for $\xi > \xi_0$, i.e., $(1 - (Z_i \xi)^{-1})$.\(^{17}\)

To determine the appropriate values to use for $D^{(c)}_{\text{i,obsd}}$ in eq 4, it is noted from Table II that in the range $3 < X < 10$, fairly constant $D_{\text{obsd}}$ values for $\text{SO}_4^{2-}$ are observed. At high $X$ values, where there is an excess of polyelectrolyte to salt, the small amounts of $\text{SO}_4^{2-}$ ions replace the condensed $\text{Br}^{-}$ ions, so that the measured diffusion is due to the diffusion of the polyelectrolyte in this region. Then $D^{(c)}_{\text{i,obsd}} = D_{\text{obsd}}$ in the range $3 < X < 10$. These values are the ones listed in Table IV and are used in eq 4 to calculate $D^{(i)}_{\text{i,obsd}}$.

References and Notes


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Crossover Behavior for the Directed Lattice Animals Model of Anisotropic Polymers\(^{1}\)

JOHN M. DEUTCH

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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I. Introduction

Recently, Daoud et al.\(^{1}\) have examined the collapse and phase separation of linear and randomly branched polymers by a scaling analysis. In this note, the analysis of

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Table IV

<table>
<thead>
<tr>
<th>$N_s$</th>
<th>$N_i$</th>
<th>$D_{\text{SO}_4^{2-}}$</th>
<th>$D_{\text{obsd}}$</th>
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<td>0.0050</td>
<td>0.100</td>
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</table>

Limiting Values for $N_s-N_i$ Solutions Used for $D^{(c)}_{\text{i,obsd}}$ in Eq 4

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these authors is extended to so-called directed lattice animals,6 which speculatively may serve as a model for composite polymeric materials. The free energy is constructed so that the polymer tends to align as a linear chain in the $R_i$ direction and as a randomly branched polymer in the remaining $d-1$ directions.

The mean field free energy for the model anisotropic polymer under consideration is

$$ F = \frac{R_i^2}{a^2 N} + \frac{R_{\perp}^2}{a^2 N^{1/2}} + \frac{\nu N^3}{R_i R_{\perp}^{d-1}} + \frac{\nu N^3}{R_i R_{\perp}^{2d-1}} $$  

where $N$ is the number of segments of length $a$ in the polymer and $\nu(\omega)$ denotes the interaction energy between pairs (triples) of monomers.

In a good solvent, $\nu > 0$ and minimization of the free energy with respect to $R_i$ and $R_{\perp}$ leads to the results of Redner and Coniglio3

$$ R_i \sim N^{1/2} $$
$$ R_{\perp} \sim N^{1/2} $$

with

$$ \nu_i (d) = \frac{(d + 11)}{[4(d + 2)]} $$
$$ \nu_{\perp} (d) = \frac{9}{[4(d + 2)]} $$

The critical dimension is $d_c = 7$, above which the polymer adopts its classical conformation, $\nu_i = 1/2$ and $\nu_{\perp} = 1/4$.

In a poor solvent, $\nu < 0$ and $\omega > 0$, the polymer collapses, and we find

$$ \nu_i = \nu_{\perp} = 1/d $$

At $T_o$, the $\Theta$ point, $\nu = 0$ and $\omega > 0$. In this case, one finds3

$$ \nu_i (d) = \frac{(d + 11)}{[4(d + 2)]} $$
$$ \nu_{\perp} (d) = \frac{3}{[2(d + 1)]} $$

with $d_c = 5$.

II. Crossover Behavior in the $\Theta$ Region

We proceed to apply the crossover scaling analysis of Daoud et al.1 in the $\Theta$ region. One assumes the $\Theta$ region is approached according to $\nu \sim \tau$, with $\tau = \{T - T_o\}/T_o$. The crossover region is defined by the condition that the repulsive term $\nu N^3/R_i R_{\perp}^{d-1}$ is $1$. Accordingly, for small $\tau$, we must have $\nu \sim N^{1/3}$. An expression for the crossover exponent $\phi$ is determined by replacing $R_i$ and $R_{\perp}$ by eq 2 but with use of the $\Theta$-point exponents in eq 5. One finds

$$ \phi (d) = 2 - \frac{\nu_i (d) - (d - 1)\nu_{\perp} (d)}{(d + 1)} $$

For $d = 3$ this predicts $\tau \sim N^{5/6}$, in contrast to the result1 for a linear chain, $\tau \sim N^{1/2}$, and for the branched chain, $\tau \sim N^{11/16}$.

The crossover in the transition region is determined by

$$ R_o = N^{\alpha} f_o (1/\nu N^{1/3}) $$
$$ \alpha = ||, \perp $$

where $f_o (z) \rightarrow z^\sigma$ for large $z$. The exponent $x_o$ is determined by the condition in the collapsed state $R_o \sim N^{1/3}$ according to eq 4. The result for the collapsed state is

$$ R_i \sim N^{1/3} d_{\perp}^{-1} [d(d+1)/d(d+7)] $$

and

$$ R_{\perp} \sim N^{1/3} d_{\perp}^{-1} [2d(d+1)/d(d+7)] $$

For $d = 3$ the predictions are $R_i \sim N^{1/3} \tau^{7/15}$ and $R_{\perp} \sim N^{1/3} \tau^{11/15}$, in contrast to the result1 for a linear chain, $R \sim N^{1/3} \tau^{1/3}$, and for the branched chain, $R \sim N^{1/3} \tau^{5/33}$.

An identical procedure leads to results for transition into the good solvent region. The result is

$$ R_i = N^{\nu_i (3d-7)/(d+2) \phi (d+7)} $$

and

$$ R_{\perp} = N^{\nu_{\perp} (3d-1)/(d+2) \phi (d+1)} $$

where $\nu_i$ and $\nu_{\perp}$ are given by eq 3. For $d = 3$ the predictions are $R_i \sim N^{16/30,1/25}$ and $R_{\perp} \sim N^{16/20,3/10}$, in contrast to the result for a linear chain, $R \sim N^{16/30,1/25}$, and for a branched chain, $R \sim N^{16/30,3/10}$.

III. Simple Prediction for Coexistence Curve

Daoud et al.1 also propose a simple argument for determining phase separation for linear and branched polymers. For the anisotropic polymer considered here the coexistence curve of $\tau$ vs. monomer concentrations is determined by assuming that phase separation occurs when the volume fraction $\phi = c/NR_i R_{\perp}^{d-1}$ reaches some constant. Use of eq 8 and 9 leads to the curve

$$ \tau \sim \phi^{(d+7)/(3d-1)} $$

For $d = 3$ the prediction is $\tau \sim c^{9/2}$, compared to the classical result1 for the linear chain, $\tau \sim c$, and for the branched chain, $\tau \sim c^{1/3}$. Note that according to eq 12 at the critical dimension $d_c = 5$, one regains the classical result $\tau \sim c$.

IV. Transition to Isotropic Single-Chain Behavior

The transition from directed polymer behavior to isotropic single-chain behavior can be examined by the method of Daoud and Janny.4 One modifies the mean square radius of gyration in the denominator of the transverse elastic energy in eq 1 only. In the second term on the right-hand side of eq 1, the expression for the square radius of gyration for a random network where branching occurs at every step $[a^2 N^{1/2}]$ is replaced by the expression when there are, on the average, $n$ segments between branching sites $[a^2 (nN)^{1/2}]$. Minimization of the free energy leads to

$$ R_i = a N^{\nu_i (1-2d)/(d+2)} $$
$$ R_{\perp} = a N^{\nu_{\perp} (1-2d)/(d+2)} $$

In the limit $n \rightarrow N$, one approaches single-chain behavior $R_i \sim R_{\perp} \sim a N^{\nu_i (1-2d)/(d+2)}$ and $d_c \rightarrow 4$.

One can also employ a "blob" picture1,5 to determine $R_i$ and $R_{\perp}$, for $4 < d < 7$. If the blobs of monomer are considered to consist of $n$ segments of size $\xi$, one may write

$$ R_i = \xi (N/n)^{\nu_i} $$
$$ R_{\perp} = \xi (N/n)^{\nu_{\perp}} $$

For $4 < d < 7$, one expects ideal blob behavior $\xi = an^{1/2}$, and one finds

$$ R_i = a N^{\nu_i (4-2d)/[d(d+2)]} $$
$$ R_{\perp} = a N^{\nu_{\perp} (4-2d)/[d(d+2)]} $$

Evidently $R_i = R_{\perp} a N^{1/2}$ for $n \rightarrow N$. For $d < 4$ one expects swollen blobs $\xi = an^{1/4}$ and the result eq 13 is regained. Similar arguments can be constructed to examine the transition to pure branched behavior and transitions at the $\Theta$ point.

V. Conclusion

In this note, we have shown how scaling arguments may be applied to the mean field theory model of directed
such variety of electron acceptors results in highly conductive crystalline solutions, which can be wet-spun into strong, sulfonic acid at 80°C. Partial oxidation of the former with a significant advance has recently been made in understanding and modifying the properties of electrically conductive molecular and macromolecular solids. Nevertheless, many of these substances exhibit limitations with regard to chemical/structural control at the molecular level, mechanical stability, air, water, and temperature stability, solubility and processability, and ease of synthesis. In the present communication, we address some of these limitations and describe an approach to the formation of a new class of hybrid molecular/macromolecular solids that can be spun into flexible, oriented, electrically conductive fibers. The approach capitalizes upon similar solubility characteristics yet complementary electrical and structural properties of a well-characterized, chemically flexible, dopable “molecular metal” and a robust, processable, and in this case orientable, macromolecule. Although we illustrate with phthalocyanine molecular conductors and a high-modulus “aramid” polymer, the approach would appear to have considerable generality.

Metallophthalocyanines (A) and Kevlar (B) are soluble in strong acids. Partial oxidation of the former with a variety of electron acceptors results in highly conductive solids (e.g., Ni(Pc): $\sigma$ (crystal) $\approx$ 500 $\Omega^{-1}$ cm$^{-1}$, $\sigma$ (powder) $\approx$ 5 $\Omega^{-1}$ cm$^{-1}$ at 300 K), while the latter forms liquid crystalline solutions which can be wet-spun into strong, crystalline, highly oriented fibers. Thus in a typical experiment, solutions of vacuum-sublimed phthalocyanine (e.g., Ni(Pc) and H$_2$(Pc), 5-18% by weight) and Kevlar-29 (3-7% by weight) were prepared in trifluoromethane-sulfonic acid at 80°C under an inert atmosphere. Fibers were then wet-spun from this viscous solution by extrusion (e.g., Ni(Pc) and H$_2$(Pc), $\approx$ 100 R$^{-1}$ cm$^{-1}$) to form a high-modulus “aramid” polymer: the approach capitalizes upon structurally interesting and modifying the properties of electrically conductive molecular and macromolecular solids. Nevertheless, many of these substances exhibit limitations with regard to chemical/structural control at the molecular level, mechanical stability, air, water, and temperature stability, solubility and processability, and ease of synthesis. In the present communication, we address some of these limitations and describe an approach to the formation of a new class of hybrid molecular/macromolecular solids that can be spun into flexible, oriented, electrically conductive fibers. The approach capitalizes upon similar solubility characteristics yet complementary electrical and structural properties of a well-characterized, chemically flexible, dopable “molecular metal” and a robust, processable, and in this case orientable, macromolecule. Although we illustrate with phthalocyanine molecular conductors and a high-modulus “aramid” polymer, the approach would appear to have considerable generality.

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