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Microphase Separation in Block Copolymer/Homopolymer Blends

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Phase separation in a blend of long polymers is properly described by mean field theory.[1] The phase diagram may be obtained from a lattice model free energy of mixing (Flory–Huggins free energy)

$$f[\phi(\mathbf{r})] = \frac{\phi(r)}{N_A} \ln \phi(\mathbf{r}) + \frac{(1-\phi(\mathbf{r}))}{N_B} \ln (1-\phi(\mathbf{r})) + \chi\phi(\mathbf{r})(1-\phi(\mathbf{r})) \quad (1)$$

where ϕ is the concentration of component A, N_A and N_B are the number of monomers in the A and B chains, respectively, and χ is the usual interaction parameter.

The mixture is homogeneous at high temperatures where the entropic term dominates the free energy. The blend phase separates into two systems, one richer in component A and the other richer in component B when the temperature is lowered below $\chi_t(\phi)$. For a blend with $N_A = N_B$ the critical value at which immiscibility first occurs is $\chi_c = 2/N$ and $\phi_c = {}^1/_2$. The system with original concentration ϕ_0 is metastable for $\chi > \chi_t(\phi_0)$. The limit of metastability for a given ϕ_0 is at the spinodal point $\chi_s(\phi_0)$; below $\chi_s(\phi_0)$ the system is unstable. The spinodal point is an inflexion point in the free energy

$$\left.\frac{\partial^2 f}{\partial \phi^2}\right|_{\phi=\phi_0} = S^{-1}(\mathbf{q}{=}0) = 0 \quad (2)$$

$S(\mathbf{q})$ is the Fourier transform of the density–density correlation function and can be obtained directly from scattering experiments

$$S(\mathbf{r}-\mathbf{r}') = \langle \Delta\phi(\mathbf{r})\Delta\phi(\mathbf{r}') \rangle$$

$$S(\mathbf{q}) = \int \exp(i\mathbf{q}\cdot\mathbf{r}) S(\mathbf{r})\, d\mathbf{r}$$

with $\Delta\phi(\mathbf{r}) = \phi_0 - \phi(\mathbf{r})$.

The scattering function for this blend is[2]

$$S^{-1}(\mathbf{q}) = \frac{1}{\phi_0 D(x_A) N_A} + \frac{1}{(1-\phi_0) D(x_B) N_B} - 2\chi \quad (3)$$

where $x_i = q^2 R_i^2$ with $R_i^2 = (l^2/6)N_i$ (i = A, B) the radius of gyration, and $D(\mu)$ is the Debye function defined as

$$D(\mu) = (2/\mu^2)[\mu + e^{-\mu} - 1] \quad (4)$$

In the limit $x_i = q^2 R_i^2 \ll 1$ (i = A, B) the scattering function takes on the Ornstein–Zernike form

$$S^{-1}(\mathbf{q}) \propto (\xi^{-2} + q^2) \quad (5)$$

where the correlation length ξ measures the intensity of the light scattered at $\mathbf{q} = 0$. The correlation length diverges at the spinodal point $\chi_s(\phi_0)$ as

$$\xi^{-2} = 2[\chi_s(\phi_0) - \chi] \frac{18}{l^2} \phi_0(1-\phi_0) \quad (6)$$

where

$$\chi_s(\phi_0) = \frac{1}{2N_A\phi_0} + \frac{1}{2N_B(1-\phi_0)} \quad (7)$$

In the case where the A and B chains are chemically linked at the end points, the phase separation occurs on length scales of the order of the radius of gyration of the block copolymer, $R^2 = l^2N/6$ with $N = N_A + N_B$. Let f be the fraction of A monomers along the block copolymer. If the melt is quenched below $\chi_t(f)$, the block copolymer microphase separates into an ordered structure.[3] Leibler found that for $f \neq 0.5$ a body-centered cubic microphase structure is formed at $\chi = \chi_t(f)$, for deeper quenches a hexagonal cylinder, and for quenches $\chi \geq \chi_s(f)$ the microphase separation proceeds by spinodal decomposition and forms a one-dimensional lamellar structure. He found that the critical point is at $\chi_c = 10.5/N$ and $f_c = 0.5$; at this point the phase separation proceeds by spinodal decomposition to a lamellar structure. The spinodal point for microphase separation $\chi_s(f)$ is determined by the condition

$$S^{-1}(\mathbf{q})|_{\mathbf{q}=\mathbf{q}^*} = 0 \quad (8)$$

where $\mathbf{q}^*$ determines the wave vector at which the concentration fluctuations are maximum. The scattering function for a block copolymer is[3]

$$S(x) = \frac{N}{\dfrac{D_1}{D_f D_{1-f} - \Delta D^2} - 2\chi N} \quad (9a)$$

where

$$D_\alpha = \alpha^2 D(\alpha x) \quad (9b)$$

$$\alpha = f,\ (1-f),\ \text{or } 1 \qquad x = q^2R^2$$

with $D(\mu)$ given by eq 4 and

$$\Delta D = \Delta D(x,f) = \tfrac{1}{2}[D_1 - (D_f + D_{1-f})] \quad (10)$$

When homopolymer is added to a block copolymer, the phase diagram is very rich and complicated. For example, when the concentration of homopolymer is low, there can be transitions to different ordered morphologies, and as the homopolymer concentration increases, transitions to micellar structures are possible. Let ϕ be the concentration of homopolymer made of N_C monomers of type C and $(1 - \phi)$ the concentration of block copolymer with degree of polymerization N and with the fraction of A monomers along the chain given by f. An inspection of the lattice model free energy for such systems[4]

$$f[\phi(\mathbf{r})] = \frac{\phi(\mathbf{r})}{N_C} \ln \phi(\mathbf{r}) + \frac{(1-\phi(\mathbf{r}))}{N} \ln (1-\phi(\mathbf{r})) + [\chi_{AC} f + \chi_{BC}(1-f) - \chi_{AB} f(1-f)]\phi(\mathbf{r})(1-\phi(\mathbf{r})) \quad (11)$$

where χ_{ij} is the usual net interaction between ij monomers, reveals an immiscibility curve or liquid–liquid phase transition.

From eq 11 the spinodal temperature of a system with mean concentration $\phi_0 = \phi$ can be calculated by using eq 2. The spinodal temperature is given by the familiar expression

$$2\chi_s(f,\phi) = \frac{1}{N_C\phi} + \frac{1}{N(1-\phi)} \quad (12)$$

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where the net interaction parameter χ is now given by

$$\chi(f) = \chi_{\mathrm{BC}}(1 - f) + \chi_{\mathrm{AC}}f - \chi_{\mathrm{AB}}f(1 - f) \quad (13)$$

The Flory–Huggins free energy eq 11 does not give information about the microphase separation transition or the formation of micelles. The simplest case to study is when the homopolymer is made by B type monomers, so $\chi(f)$ is simply $\chi_{\mathrm{AB}}f^2$. Leibler et al.[5] have analyzed micelle formation for $\phi > 0.5$ and $N_{\mathrm{C}}/N = r > 2$. They found that the formation of micelles occurs well before (at higher temperatures) the χ_c predicted by the lattice model (eq 11). Because the system is inhomogeneous due to the micelles well before the predicted critical point, the Flory–Huggins free energy eq 11 cannot predict the true liquid–liquid phase diagram. Neither would the phase diagram be correctly predicted by a microscopic theory that expands the free energy of the homogeneous block copolymer–homopolymer melt in powers of, say, the concentration fluctuations of homopolymer $\Delta\phi(\mathbf{r}) = \phi - \phi(\mathbf{r})$.

However, when the concentration of homopolymer is very low and f is around 0.5, the system is close to the critical point of the pure block copolymer melt. Near the critical point the spinodal and the first-order-transition lines are very close together, and an expansion of the free energy of the homogeneous melt in powers of the concentration fluctuations can describe the microphase separation. At the critical point, the wave vector at which the scattering function diverges dominates the transition. So, it is reasonable to assume that near the critical point[5,6] the free energy is also dominated by the concentration fluctuations of wave vector $q^*(f)$. Within this assumption the third- and fourth-order terms in the free energy expansion in the concentration fluctuations can be evaluated at q^* for different structures, and the structure that minimizes the free energy is determined. So only in the vicinity of the critical point ($\phi = 0$ and $f = 0.5$) can the spinodal lines, which determine q^*, reveal information about the coexistence curves; away from this point the first-order transition $\chi_t(f, \phi)$ can be very distant from the spinodal, and the assumption that a single wave vector q^* dominates the free energy is not valid.

In this paper we analyze the variations of the spinodal line and the value of q^* as a function of ϕ, r, and f near $\phi = 0$ and $f = 0.5$. We first calculate the scattering function for an A–B block copolymer with C homopolymer melt, then we discuss in detail the case C = B. Throughout the calculation the chains are assumed to be Gaussian.

Let us consider a system consisting of n_{AB} block copolymer chains of degree of polymerization $N = N_{\mathrm{A}} + N_{\mathrm{B}}$ with $N_{\mathrm{A}} = fN$ and $N_{\mathrm{B}} = (1 - f)N$ and n_{C} chains of length $N_{\mathrm{C}} = rN$. In order to construct the partition function Z, a continuous model for n_{i} Gaussian chains of contour length $L_{\mathrm{i}} = N_{\mathrm{i}}l_{\mathrm{i}}$ (i = A, B, C) was used. The short-range interaction energy was represented as a delta function interaction of magnitude w_{ij} between ij monomer,[7] where $w_{\mathrm{ij}}\bar{\rho}$, with $\bar{\rho}$ the total density, is related to ϵ_{ij}, the interaction between ij monomers. In the continuous representation the i = A, B, C chains are given as continuous curves in space as $\int_0^{L_{\mathrm{i}}}\delta(\mathbf{r} - \mathbf{r}(s))\,\mathrm{d}s/l_{\mathrm{i}}$. So the microscopic concentration is

$$\phi_{\mathrm{i}}(\mathbf{r}) = \frac{1}{\bar{\rho}}\sum_{\alpha=1}^{n_{\mathrm{i}}}\int_0^{L_{\mathrm{i}}}\delta(\mathbf{r} - \mathbf{r}^{\alpha}(s))\,\frac{\mathrm{d}s}{l_{\mathrm{i}}} = \sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{r})\phi_{\mathrm{i}\mathbf{q}} \quad (14)$$

where the $\phi_{\mathrm{i}\mathbf{q}}$, the collective coordinates, are given by

$$\phi_{\mathrm{i}\mathbf{q}} = \frac{1}{\bar{\rho}}\sum_{\alpha=1}^{n}\int_0^{L_{\mathrm{i}}}\exp(i\mathbf{q}\cdot r_{\mathrm{i}}^{\alpha}(s))\,\frac{\mathrm{d}s}{l_{\mathrm{i}}} \quad (15)$$

where $\bar{\rho} = \bar{\rho}_{\mathrm{A}} + \bar{\rho}_{\mathrm{B}} + \bar{\rho}_{\mathrm{C}}$ and $\bar{\rho}_{\mathrm{i}} = n_{\mathrm{i}}N_{\mathrm{i}}/V$ for i = A, B, C.

Introducing the collective coordinates, eq 15, into the partition function Z, one can express the partition function as[8]

$$Z = \mathcal{N}(q{=}0)\int\exp\left\{-\frac{1}{2\bar{\rho}V}\sum_{\mathbf{q}}\sum_{\mathrm{ij}}\phi_{\mathrm{i}\mathbf{q}}\phi_{\mathrm{j}\mathbf{q}}\left[S_{\mathrm{ij}}^{-1} + \frac{w_{\mathrm{ij}}\bar{\rho}}{k_{\mathrm{b}}T}\right]\right\}\prod_{q\neq0}\delta(\phi_{\mathrm{A}\mathbf{q}} + \phi_{\mathrm{B}\mathbf{q}} + \phi_{\mathrm{C}\mathbf{q}})\,\mathrm{d}\phi_{\mathrm{A}\mathbf{q}}\,\mathrm{d}\phi_{\mathrm{B}\mathbf{q}}\,\mathrm{d}\phi_{\mathrm{C}\mathbf{q}} \quad (16)$$

where S_{ij}^{-1} is the ij element of the inverse of the matrix S

$$S = N\begin{pmatrix} (1 - \phi)D_f & (1 - \phi)\Delta D & 0 \\ (1 - \phi)\Delta D & (1 - \phi)D_{1-f} & 0 \\ 0 & 0 & \phi D_r/r \end{pmatrix} \quad (17)$$

$D_\alpha = \alpha^2D(\alpha x)$ is defined in eq 9b, ΔD in eq 10, and $D(\mu)$ in eq 4 with $x = q^2R^2$, $R^2 = Nl^2/6$, and ϕ is the concentration of homopolymer in the system, and where we have simplified eq 16 by assuming that the step lengths of the A, B, and C polymers are equal.

Integrating out $\mathrm{d}\phi_{\mathrm{B}\mathbf{q}}$ and $\mathrm{d}\phi_{\mathrm{C}\mathbf{q}}$, one obtains

$$Z = \mathcal{N}\int\exp\left\{-\frac{1}{\bar{\rho}V}\sum_{\mathbf{q}}\phi_{\mathrm{A}\mathbf{q}}^2/S_{\mathrm{A}}(\mathbf{q})\right\}\prod_{\mathbf{q}}\mathrm{d}\phi_{\mathrm{A}\mathbf{q}}$$

where the scattering function for component A is

$$\begin{aligned} S_{\mathrm{A}}(\mathbf{q}) = \Bigg\{ & N\phi(1 - \phi)D_f\frac{D_r}{r} + (1 - \phi)^2[D_fD_{1-f} - \Delta D^2] \times \left[1 - 2\chi_{\mathrm{BC}}N\frac{D_r}{r}\right]\Bigg\}\Bigg\{(1 - \phi)D_1 + \phi\frac{D_r}{r} - 2\chi_{\mathrm{BC}}N\phi(1 - \\ & \phi)D_1\frac{D_r}{r} - 2(1 - \phi)^2(D_fD_{1-f} - \Delta D^2) \times \left[\chi_{\mathrm{AB}}N + \left(\frac{\chi_{\mathrm{ABC}}^2}{2} - 2\chi_{\mathrm{AB}}\chi_{\mathrm{BC}}\right)N\phi\frac{D_r}{r}\right] - \\ & 2\chi_{\mathrm{AB}}(1 - \phi)\phi ND_f\frac{D_r}{r} + 2\chi_{\mathrm{ABC}}N\phi(1 - \phi)\frac{D_r}{r}(D_f + \Delta D)\Bigg\}^{-1} \end{aligned} \quad (18)$$

with $\chi_{\mathrm{ij}} = \bar{\rho}/k_{\mathrm{b}}T(w_{\mathrm{ij}} - {}^1/_2(w_{\mathrm{jj}} + w_{\mathrm{ii}}))$ and $\chi_{\mathrm{ABC}} = \chi_{\mathrm{AB}} + \chi_{\mathrm{BC}} - \chi_{\mathrm{AC}}$. Equation 18 reduces to eq 9 in the limit of $\phi = 0$, as required. Also in the limit when $f = 1$ (and $\chi_{\mathrm{AB}} = \chi_{\mathrm{BC}} = 0$), eq 18 reduces to eq 4. Equation 18 is in agreement with previous theories.[9,10]

Let us concentrate on the case where the homopolymer of length rN is made of B monomers so $\chi_{\mathrm{BC}} = 0$ and $\chi_{\mathrm{AB}} = \chi_{\mathrm{AC}} = \chi$. Then eq 18 reduces to

$$S_{\mathrm{A}}(\mathbf{q}) = N/(F(x, \phi, f, r) - 2\chi) \quad (19)$$

where

$$F(x, \phi, f, r) = \frac{(1 - \phi)D_1 + \phi D_r/r}{\phi(1 - \phi)\dfrac{D_fD_r}{r} + (1 - \phi)^2(D_fD_{1-f} - \Delta D^2)} \quad (20)$$

The scattering function eq 19 for small ϕ has a broad peak at $x^* \neq 0$ even at high temperatures ($\chi \sim 0$). When ϕ is small, the concentration fluctuations are maximum at x finite, while when ϕ is large, concentration fluctuations of infinite wavelength ($x = 0$) dominate the scattered intensity.

The broad peak of eq 19 at $\chi = 0$ is at the minimum of $F(x, \phi, f, r)$; i.e., when

$$\left.\frac{\partial F(x, \phi, f, r)}{\partial x}\right|_{x=x^*} = 0 \qquad (21)$$

One approaches the spinodal point by lowering the temperature or increasing χ. The broad peak becomes sharper as in the case of pure block copolymer with the difference that now the scattering function has a finite intensity at $x = 0$ that represents the concentration fluctuations of infinite wavelength. At the spinodal point $(\chi N)_s$, the scattering function diverges and

$$(\chi N)_s = \tfrac{1}{2}F(x^*, \phi, f, r) \qquad (22)$$

The concentration fluctuations are localized in domains with a periodic structure of wave vector $q^* = (x^*)^{1/2}/R$. When ϕ increases, the scattering intensity at $x = 0$ increases until eventually it dominates and the spinodal is found at $x = 0$. The homogeneous state is then unstable against concentration fluctuations of infinite wavelength.

We are interested in the values of $(\chi N)_s$ and x^* for small values of ϕ near $f = 0.5$. Leibler[3] found for $\phi = 0$ the critical point at $f_c = 0.5$ with $x_c^* = 3.78$. In order to calculate the variation of $(\chi N)_s$ when $\phi = 0$, we differentiate eq 22 and solve the resulting equation numerically to find in general agreement with a previous study[1] that

$$\begin{aligned}(\partial(\chi N)_s/\partial\phi)|_{\phi=0,f_c,x_c^*} &= -18.1 \quad r \to \infty \\ &= 0.0 \quad r = 0.257 \\ &= 10.5 \quad r \to 0\end{aligned} \qquad (23)$$

The entropy of mixing homopolymer with block copolymer increases with respect to its value at $\phi = 0$ because adding homopolymer increases the number of degrees of freedom. The shorter (small r) the homopolymer added, the larger the entropy of mixing. A system with homopolymer made of short chains is more stable in the disordered state than when it is made of long chains because entropically it is more difficult to localize short chains in a domain. So one would expect $(\chi N)_s$ to increase as ϕ increases, and at fixed ϕ, one would expect $(\chi N)_s$ to increase as r decreases. On the other hand, the energy of mixing, U_{mix}, increases as ϕ increases independent of r, $\partial U_{\text{mix}}/\partial\phi > 0$. According to eq 23 when $r > 0.257$, the energy coming from adding more AB contacts between different chains dominates the entropy term. The disordered state for $r > 0.257$ and $f = 0.5$ becomes unstable at $(\chi N)_s < 10.5$. The numerical solution of $(\chi N)_s$ as a function of ϕ from eq 22 for $f = 0.5$ and $r = 1.6$, 1.0, and 0.15 is plotted in Figure 1A.

We also found the variation of x^* for $f = 0.5$ in the limit $\phi \to 0$:

$$\begin{aligned}(\partial x^*/\partial\phi)|_{\phi=0,f_c} &= -19.7 \quad r \to \infty \\ &= -12.1 \quad r \to 1 \\ &= 0.0 \quad r = 0.181 \\ &= 3.35 \quad r \to 0\end{aligned} \qquad (24)$$

In figure 1B x^* is plotted against ϕ for $f = 0.5$ for $r = 1.6$, 1.0, and 0.15; x^* was determined by finding the maximum in eq 19 numerically. The above result that x^* decreases with ϕ for sufficiently large values of r is in qualitative agreement with the results of Hong and Noolandi.[10] What is new is the result that when the added homopolymer is sufficiently small ($r < 0.18$), x^* can increase with ϕ. Indeed, it has been mentioned[10,13] that, when short homopolymer chains are present, the periodicity of the ordered structure may decrease. It is believed that in the absence of a diluent ($\phi = 0$) interfacial forces and the condition of constant density leads to a situation where the block copolymer chains are stretched well beyond their normal Gaussian dimensions. It is probable that by adding a diluent, say, a short-chain homopolymer, the strectched chains might relax, which would decrease the periodicity.

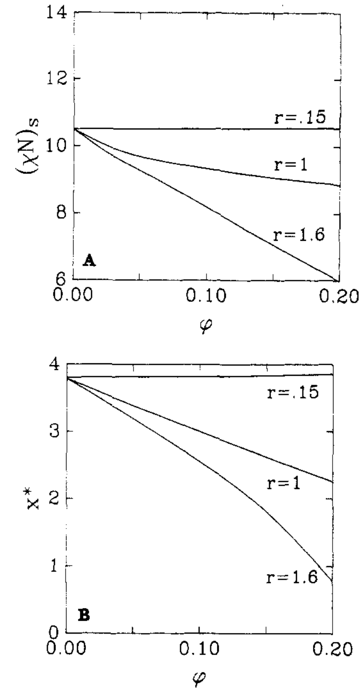

Figure 1. Block copolymer (A–B)–homopolymer (B) blend: (A) spinodal temperature $(\chi N)_s$; (B) x^* as a function of ϕ, for $f = 0.5$ and $r = 1.6$, 1.0, and 0.15.

In our calculation the chains are always assumed to be Gaussian and in the homogeneous one-phase region of the phase diagram, so this "relaxation" is not the origin of the effect; instead it arises because x^* is an inverse measure of the range of possible concentration fluctuations.[8] In general, x^* varies inversely as the radius of gyration of the polymer chains. Adding a small amount of short homopolymer chains effectively reduces the radius of gyration of the chains and the range of concentration fluctuations (or increases x^*). However, there is an important caveat. It is well-known that adding solvent to a melt will cause the polymer chains to swell. Self-excluded volume effects will not be screened if the added homopolymer is very short ($r \ll 1$). Therefore, the effect of the excluded volume interaction is in the opposite direction and may significantly reduce (or eliminate) the predicted increase in x^* with ϕ. Although there are experimental reports of periodicity spacings decreasing upon addition of low molecular weight diluents[14-16] in agreement with the present theory, the agreement may be fortuitous. A true test of the theory requires measurements in the neighborhood of the microphase transition temperature but still in the one-phase region of the phase diagram.

The influence of f, ϕ, and r on $(\chi N)_s$ can be determined by expanding eq 22 in a Taylor series around $f = 0.5$, $\phi = 0$, and $r = 0.257$:

$$(\chi N)_s = 10.5\{1 + 0.486\phi^2 + 7.63(f - 1/2)^2 - 4.58\phi(f - 1/2) - 2.83\phi(r - 0.257) + ...\} \qquad (25)$$

In parts A and B of Figure 2 we have plotted $(\chi N)_s$ and x^*, respectively, against ϕ for $f = 0.25$, 0.5, and 0.75 with $r = 1$. Notice that x^* goes to zero faster for $f > 0.5$, because when $f > 0.5$ the number of repulsive contacts (A, B) between homopolymer and block copolymer is higher than when $f < 0.5$, favoring immiscibility at infinite wavelength. Equation 25 is in qualitative agreement with the experiments of Roe and Zin[13] in polystyrene–polybutadiene block

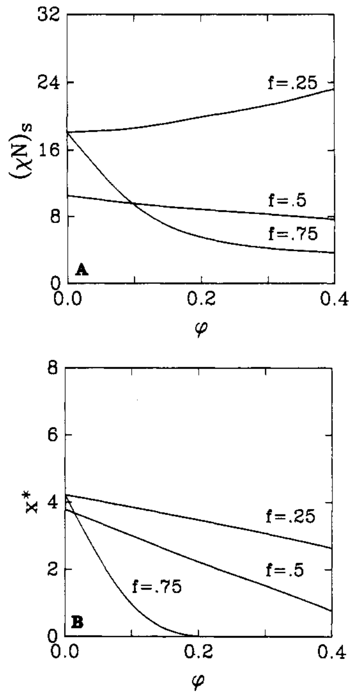

Figure 2. Block copolymer (A–B)–homopolymer (B) blend: (A) spinodal temperature $(\chi N)_s$; (B) x^* as a function of ϕ for $r = 1$ and $f = 0.25$, 0.5, and 0.75.

copolymers mixed with polystyrene or polybutadiene.

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Gelation and Solubilization of Aliphatic Polyamides in Tetrahydrofuran Using Lithium Perchlorate

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Mixtures of nylon 6 and inorganic salts, mainly metal halides such as LiCl, KI, and KBr, have been extensively studied over the past decade (see, for example, ref 1). In these efforts, the emphasis has been on the changes in the physical properties of nylon 6 arising from the solubility of these salts in nylon 6 even in the absence of any liquid diluent. Further, nylon 6 and other nylon type polyamides have been shown to be soluble in $CaCl_2$–methanol solutions.[2,3] We now report the swelling and eventual dissolution of aliphatic polyamides (nylons) in tetrahydrofuran (THF) in the presence of $LiClO_4$. The possibility of using the $LiClO_4$ complex of nylon 6 as a solid electrolyte and of drawing a fiber from nylon 6 gel were the motives behind this study.

Nylon 6 films (Type 77A) produced commercially by Allied Corp. were used in all our experiments ($[\eta] = 1.33$ dL/g, $M_n = 20\,000$, $M_w/M_n \approx 2$). Nylon 6,9 was obtained from Aldrich Chemical Co., nylon 6,10, nylon 11, and nylon 6,12 were purchased from Polysciences, Inc., nylon 12 was purchased from Emser Industries, and nylon 3 was obtained from H. K. Reimschuessel (Allied). X-ray diffraction (XRD) patterns were obtained at room temperature on a Philips automated powder diffractometer in the parafocus mode using Cu Kα radiation. Viscosities were determined with a capillary viscometer, using both *m*-cresol (a standard solvent) and the $THF/LiClO_4$ solution as solvents. Differential scanning calorimeter scans (DSC) were obtained on a Du Pont 9900 DSC apparatus. Infrared spectra were obtained on a Perkin-Elmer 953 spectrometer both in the ATR mode on a thick film and in the transmission mode on thin films sandwiched between KBr plates.

Polyamides do not dissolve in THF and it also was found that nylon 6 films changed very little when immersed in a solution of 0.25 M $LiClO_4$ in THF. At a salt concentration of 0.5 M, the nylon 6 film became whitish, at 0.75 M $LiClO_4$ the film lost its shape, and at 1.0 M $LiClO_4$ the film became a gel and did not dissolve in the solvent. The gel exhibited an ionic conductivity similar to that of the $LiClO_4/THF$ solution, and this conductivity disappeared as the gel was dried. At a salt concentration of 1.5 M or higher, nylon 6 dissolved. At least 18 wt % of nylon 6 could be dissolved in a 2.0 M $LiClO_4/THF$ solution (ca. 12 wt % in *m*-cresol). We also found that other nylons dissolved in THF at the following approximate concentrations of $LiClO_4$: nylon 3 at 2 M, nylon 6,6 at 4 M, nylon 6,9 at 2.5 M, and nylon 6,10 at 2.0 M. However, nylons with 10 or more CH_2 units, nylon 6,11 and nylon 11, dissolved very slowly over a period of several days in ~6 M $LiClO_4/THF$ solution, and nylon 12 did not dissolve even in saturated (6–8 M) $LiClO_4/THF$ solutions. We limited our detailed investigation to nylon 6.

Viscosity measurements were done to follow the changes in the molecular weight and the conformation of nylon 6 in solution. The intrinsic viscosity of a sample of nylon 6 in *m*-cresol was 1.33 dL/g. The intrinsic viscosity of nylon 6 in THF with 2.0 M $LiClO_4$ was 0.88 dL/g. The lower intrinsic viscosity in $LiClO_4/THF$ as compared to that in *m*-cresol suggests a smaller spatial extension of nylon 6 in $LiClO_4/THF$. The viscosities of nylon 6 reprecipitated from the gel and from the solution ($LiClO_4/THF$) as measured in *m*-cresol are similar to that of the original nylon 6 (1.38 vs. 1.32 dL/g; thus in fact slightly higher), suggesting that nylon 6 was not degraded in the $LiClO_4/THF$ solvent.

X-ray diffraction scans of nylon 6 variously treated with $LiClO_4/THF$ solutions are shown in Figure 1. The gel freshly prepared by immersing nylon 6 in 1.0 M $LiClO_4/THF$ for ~15 h was amorphous (Figure 1a). Drying the gel under vacuum at 22 °C crystallized $LiClO_4{\cdot}3H_2O$ but nylon 6 apparently was still complexed with Li^+ and ClO_4^- ions and thus remained amorphous (Figure 1b). The

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