(14) (a) Marucci, G.; Grizzuti, N. *J. Rheol.* **1983**, *27*(5), 433. (b) Doi, M.; Edwards, S. M. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 918.
(15) In a recent, parallel effort on mutual diffusion in glassy mixtures, Jackle and Frisch[10b,c] develop the same integrodifferential equation and provide some analytical solutions complementing those in section VI.
(16) Hildebrand, F. B. *Advanced Calculus for Applications*, 2nd ed.; Prentice Hall: Englewood, NJ, 1976; Chapter 5.
(17) Carslaw, H. S.; Jeager, J. C. *Conduction of Heat in Solids*, 2nd ed.; Oxford University Press: London, 1959; p 105.
(18) Ni, L. W., Ph.D. Thesis, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA, 1984.
(19) Kishimoto, A.; Maekawa, E.; Fujita, H. *Bull. Chem. Soc. Jpn.* **1968**, *33*, 988.
(20) Ninomiya, K.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 2292.
(21) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(22) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 417.
(23) Fujita, H.; Kishimoto, A. *J. Polym. Sci.* **1967**, *28*, 547.
(24) Kovacs, A. J.; Stratton, R. A.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 152.

Effect of Electrostatic Interaction on the Liquid Crystal Phase Transition in Solutions of Rodlike Polyelectrolytes[†]

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ABSTRACT: It is shown that the effect of electrostatic interactions on the liquid crystal phase transition in solutions of rodlike polyelectrolytes can be characterized by two parameters, one describing the increase of the effective diameter and the other the twisting action. The dependence of these parameters on the charge density and the salt concentration is studied both for weakly charged polyelectrolytes, for which the Debye–Hückel approximation applies, and for highly charged polyelectrolytes, for which the full Poisson–Boltzmann equation has to be used. The isotropic–nematic phase transition cannot be described solely in terms of an effective diameter as has always been done before but one must also take the twisting effect into account. This effect, which enhances the concentrations at the transition, is particularly marked for weakly charged polyions.

I. Introduction

Above a critical concentration solutions of rodlike particles undergo a phase separation into an isotropic phase and an anisotropic phase, coexisting in equilibrium. In the latter phase, which is usually referred to as a lyotropic liquid crystal, the particles have a preferred orientation. This phase separation was first explained by Onsager[1] as the result of the competition between the orientational entropy favoring orientational disorder and the entropy effect associated with the orientation-dependent excluded volume of the rodlike particles which favors orientational order. Onsager calculated explicitly the concentrations of the coexisting phases for the case of monodisperse hard rigid rods. However, many of the particles that form lyotropic liquid crystals are in fact polyelectrolytes, e.g., V_2O_5,[2] γ-AlOOH,[3,4] TMV,[5-9] DNA,[10,11] cellulose microcrystals,[12] Schizophyllan,[13] Scleroglucan,[14] and sickel cell hemoglobin.[15,16] The electrostatic repulsion between the particles influences strongly the formation of the anisotropic liquid crystal phase, as has been particularly well documented for the case of TMV.[6-8] For example, Oster[6] noted that whereas an aqueous solution of TMV freshly purified by ultracentrifugation will separate into isotropic and anisotropic phases if the virus concentration exceeds 2.3%, salts at ionic strengths above 0.005 M cause the system to be fully isotropic. Onsager[1] already indicated that the effect of the electrostatic repulsion will be equivalent to an increase of the effective diameter. This effective diameter will be dependent on the thickness of the electric double layer and thus on the ionic strength. However, the electrostatic repulsion also depends on orientation and thus the effect of the electrostatic repulsion will be different in the isotropic phase from that in the anisotropic phase. Actually the electrostatic interaction favors perpendicular orientation of the particles.

In this paper we take this twisting effect quantitatively into account in the calculation of the isotropic–liquid crystal phase equilibria in solutions of rodlike polyelectrolytes. From our calculations it follows that the importance of the twisting effect is determined by the ratio of the thickness of the electric double layer and the effective diameter of the rods as defined by Onsager.

This paper is organized as follows. In section II we present the relevant theoretical framework that is applied in section III to calculate numerically the concentrations of the coexisting phases. To analyze the results we present in section IV an analytic perturbation treatment of the influence of the twisting effect, and in section V we apply our calculations to some representative systems. The conclusions that can be drawn from this work are collected in section VI.

II. Formalism

We consider a solution of N rodlike polyelectrolytes of length L and diameter D interacting not only electrostatically but also via the hard-core repulsion. There is an excess of 1–1 electrolyte present. The electrostatic interaction between two rods can be written approximately in the form[1,17-19]

$$\frac{w}{k_B T} = \frac{A e^{-\kappa x}}{\sin \phi} \qquad (1)$$

[†] A preliminary version of this paper was reported at the Faraday Discussion on Polymer Liquid Crystals, Cambridge, April 1985.

0024-9297/86/2219-2232$01.50/0

Here, x is the shortest distance between the center lines of the polyion cylinders, κ^{-1} is the Debye screening length, and ϕ is the angle between the rods. The $\sin^{-1}\phi$ term signifies that the rods want to twist toward mutually perpendicular directions, a fact that we shall take into account explicitly. We defer discussion of the proportionality constant A and its dependence on the polyelectrolyte parameters to section V because the precise nature of A need not be specified in a calculation of polyelectrolyte nematics. The connection between w and the second virial coefficient is also outlined in section V. Here we simply give the expression for the Helmholtz free energy, which is identical with Onsager's except for the fact that we have $A' = Ae^{-\kappa D}$ instead of his A.

$$\frac{\Delta F}{Nk_BT} = \frac{F(\text{solution}) - F(\text{solvent})}{Nk_BT} = \frac{\mu^\circ(T,\mu_\mathrm{O})}{k_BT} - 1 + \ln c' + \int f(\Omega)\ln(4\pi f(\Omega))\,\mathrm{d}\Omega + c'L^2D\int\int\left\{1 + \frac{1}{\kappa D}(\ln A' + \gamma - \ln(\sin\phi))\right\}(\sin\phi)f(\Omega)f(\Omega')\,\mathrm{d}\Omega\,\mathrm{d}\Omega' \quad (2)$$

Here $\gamma = 0.577\,215\,665...$ denotes Euler's constant, $\mu^\circ(T,\mu_\mathrm{O})$ represents the standard chemical potential of the particles at the temperature T in a solvent with chemical potential μ_O, and $c' = N/V$ is the number density.

In the isotropic state $f_i(\Omega) = 1/(4\pi)$ and taking into account that

$$\langle\langle\sin\phi\rangle\rangle_i = \int\int f_i(\Omega)f_i(\Omega')\sin\phi\,\mathrm{d}\Omega\,\mathrm{d}\Omega' = \pi/4 \quad (3)$$

$$\langle\langle -\sin\phi\ln(\sin\phi)\rangle\rangle_i = \frac{\pi}{4}\left[\ln 2 - \frac{1}{2}\right] \quad (4)$$

we obtain

$$\frac{\Delta F_i}{Nk_BT} = \frac{\mu^\circ}{k_BT} - 1 + \ln c' + \frac{\pi}{4}c'L^2D\left(1 + \frac{\ln A' + \gamma + \ln 2 - 1/2}{\kappa D}\right) \quad (5)$$

The second term in the parentheses on the right-hand side of eq 5 represents the effect of the electrostatic interaction on the free energy. We see that this contribution can be interpreted as an increase of the diameter of the rods in the isotropic phase by a factor

$$\delta = \frac{\ln A' + \gamma + \ln 2 - 1/2}{\kappa D} \quad (6)$$

Introducing the effective diameter

$$D^{\mathrm{eff}} = D(1 + \delta) \quad (7)$$

and the effective excluded volume

$$b^{\mathrm{eff}} = \frac{\pi}{4}L^2D^{\mathrm{eff}} \quad (8)$$

we can write the free energy in the isotropic phase as

$$\frac{\Delta F_i}{Nk_BT} = \frac{\mu^\circ}{k_BT} - 1 + \ln c' + b^{\mathrm{eff}}c' \quad (9)$$

In the anisotropic phase we have

$$\frac{\Delta F_a}{Nk_BT} = \frac{\mu^\circ}{k_BT} - 1 + \ln c' + \sigma + b^{\mathrm{eff}}c'(\rho(f) + h\eta(f)) \quad (10)$$

where $\sigma = \langle\ln(4\pi f)\rangle_a$,

$$\rho(f) = (4/\pi)\langle\langle\sin\phi\rangle\rangle_a \quad (11)$$

and

$$\eta(f) = (4/\pi)\langle\langle -\sin\phi\ln(\sin\phi)\rangle\rangle_a - [\ln 2 - 1/2]\rho(f) \quad (12)$$

Furthermore, the parameter h is the ratio of the Debye length κ^{-1} and the effective diameter D^{eff}

$$h = \frac{1}{\kappa D^{\mathrm{eff}}} = \frac{1}{\kappa D(1 + \delta)} \quad (13)$$

In the isotropic state $\rho = 1$ and $\eta = 0$ and thus we recover from eq 10 the free energy in the isotropic state (9) if we put $f = 1/(4\pi)$. Note that whereas in the isotropic phase the effect of the electrostatic interaction can be taken into account by an increase of the effective diameter, leading to an effective excluded volume, in the anisotropic phase the angular dependence of the electrostatic interaction explicitly plays a role in the form of the term $b^{\mathrm{eff}}c'h\eta(f)$. This contribution we shall refer to as the twisting effect. Evidently the parameter h is a very important one. Its behavior for some representative systems will be considered in section V.

The orientation distribution function $f(\Omega)$ is determined by minimizing the free energy with respect to variations in this distribution. This leads to the integral equation

$$\ln(4\pi f(\Omega)) = C - \frac{8}{\pi}b^{\mathrm{eff}}c'\int[1 + h(-\ln(\sin\phi) - [\ln 2 - 1/2])](\sin\phi)f(\Omega')\,\mathrm{d}\Omega' \quad (14)$$

where C is a constant that is determined by applying the normalization condition

$$\int f(\Omega)\,\mathrm{d}\Omega = 1 \quad (15)$$

Once the minimization problem has been solved, the concentrations of the coexisting phases are found by applying the coexistence conditions, i.e., the equality of the osmotic pressure Π' and the chemical potential μ' in the two coexisting phases

$$\Pi' = -\left(\frac{\partial\Delta F}{\partial V}\right)_{T,\mu_0,N} = k_BTc'(1 + b^{\mathrm{eff}}c'[\rho + h\eta]) \quad (16)$$

$$\mu' = \left(\frac{\partial\Delta F}{\partial N}\right)_{T,\mu_0,V} = \mu^\circ + k_BT(\ln c' + \sigma + 2b^{\mathrm{eff}}c'[\rho + h\eta]) \quad (17)$$

At this point it is convenient to introduce dimensionless variables. In the following c denotes the dimensionless concentration $b^{\mathrm{eff}}c'$, Π the dimensionless osmotic pressure $(b^{\mathrm{eff}}\Pi'/k_BT)$, and μ the dimensionless chemical potential $((\mu' - \mu^\circ)/k_BT + \ln b^{\mathrm{eff}})$.

III. Calculations of the Coexisting Concentrations

In order to calculate the coexisting concentrations we expand $\sin\phi$ and $-\sin\phi\ln(\sin\phi)$ in terms of Legendre polynomials $P_{2n}(\cos\phi)$.

$$\sin\phi = \sum_{n=0}^{\infty}c_{2n}P_{2n}(\cos\phi) \quad (18)$$

$$-\sin\phi\ln(\sin\phi) = \sum_{n=0}^{\infty}c_{2n}'P_{2n}(\cos\phi) \quad (19)$$

Substitution of the above expansions in the integral equation (14) yields, using the addition theorem for spherical harmonics,

$$f(\Omega) = \exp\left[\sum_{n=0}^{\infty}\alpha_{2n}P_{2n}(\cos\theta)\right]/Z \quad (20)$$

Table I
Coefficients c_{2n} and c_{2n}' Appearing in the Expansion of sin ϕ and -sin ϕ ln (sin ϕ) in Terms of Legendre Polynomials

n	c_{2n}	c_{2n}'
0	$\pi/4$	$c_0[\ln 2 - 1/2]$
1	$-5\pi/32$	$c_2[\ln 2 - 5/4]$
2	$-9\pi/256$	$c_4[\ln 2 - 1/12]$
3	$-65\pi/4096$	$c_6[\ln 2 + 3/8]$
4	$-595\pi/65536$	$c_8[\ln 2 + 27/40]$
5	$-3087\pi/524288$	$c_{10}[\ln 2 + 5299/5880]$
6	$-17325\pi/4194304$	$c_{12}[\ln 2 + 30041/27720]$
7	$-410553\pi/134217728$	$c_{14}[\ln 2 + 1961633/1585584]$

where Z is the normalization constant. The form of $f(\Omega)$ is determined by the coefficients α_{2n} that follow from the consistency equations

$$\alpha_{2n} = -\frac{8}{\pi}c\langle P_{2n}\rangle[c_{2n} + h(c_{2n}' - [\ln 2 - \tfrac{1}{2}]c_{2n})] \tag{21}$$

The quantities

$$\langle P_{2n}\rangle = \int P_{2n}(\cos\theta)f(\Omega)\,\mathrm{d}\Omega \tag{22}$$

are zero in the isotropic phase and positive in the anisotropic phase.

The consistency equations (21) have a trivial solution $\alpha_{2n} = 0$, $\langle P_{2n}\rangle = 0$, $n = 1, 2, ...$ for all concentrations. However, for sufficiently high concentrations c the consistency equations (21) also have a nontrivial solution $\alpha_{2n} > 0$, $\langle P_{2n}\rangle > 0$, $n = 1, 2, ...$ This solution corresponds to the anisotropic phase, where the orientation distribution function is peaked around $\theta = 0$ and $\theta = \pi$. In order to find the coexisting concentrations c_i and c_a in the isotropic and anisotropic phases, one has to solve the coexistence equations

$$\Pi_i = \Pi_a \tag{23}$$

$$\mu_i = \mu_a \tag{24}$$

In terms of the dimensionless quantities introduced at the end of section II, the coexistence equations can be written as

$$c_i\{1 + c_i\} = c_a\{1 + c_a[\rho_a + h\eta_a]\} \tag{25}$$

$$\ln c_i + 2c_i = \ln c_a + \sigma + 2c_a[\rho_a + h\eta_a] \tag{26}$$

We note again that the only parameter causing the twisting effect is h (and not other combinations of D, κ, and A'). The accuracy with which the phase transition can be located is essentially determined by the number of terms used in the expansions (18) and (19), because this determines how accurate the functions sin ϕ and -sin ϕ ln (sin ϕ) are represented. For the case $h = 0$, i.e., the hard-rod model, effectively full covergence was reached for $n = 7$.[20] We investigated whether for the present case this number of terms is also sufficient.

The coefficients c_{2n} and c_{2n}', which can be calculated by standard techniques, are collected in Table I. The results of the calculations with respectively 1, 2, ..., 7 terms in the expansions (18) and (19) are presented in table II for $h = 0.25$, which is a reasonable value for h as will become apparent in section V. Although the covergence is less fast than in the case for hard rods without electrostatic interaction, taking into account terms up to P_{14} leads to satisfactory convergence.

In Table III we present the results for the phase transition for values of h up to 0.50. The values for $h = 0$ have been added for the sake of reference. All calculations were done with terms up to P_{14} in the expansions for sin ϕ and -sin ϕ ln (sin ϕ). It is clear that the twisting term, which hinders the phase transition, leads to higher coexisting concentrations (when scaled with respect to b^{eff}).

Table II
Convergence of the Concentrations, Order Parameter, and Orientation-Dependent Free Energy Terms of the Coexisting Isotropic and Anisotropic Phase, Using the Expansion of sin ϕ in Legendre Polynomials $P_{2n}(\cos\phi)$ Truncated at Different Values of n, for h = 0.25

n	c_i	c_a	$\langle P_2\rangle$	σ	ρ	η	Π	μ
1	4.348	4.675	0.543	0.674	0.816	0.138	23.26	10.17
2	4.056	4.791	0.748	1.384	0.622	0.251	20.51	9.51
3	3.986	4.951	0.813	1.727	0.537	0.286	19.87	9.35
4	3.966	5.052	0.838	1.894	0.499	0.298	19.69	9.31
5	3.960	5.101	0.848	1.965	0.483	0.302	19.64	9.30
6	3.958	5.120	0.851	1.992	0.478	0.304	19.63	9.29
7	3.958	5.126	0.853	2.000	0.476	0.304	19.63	9.29

Table III
Composition, Concentration, Order Parameters, and Orientation-Dependent Free Energy Terms in the Coexisting Isotropic and Anisotropic Phase for h Values up to 0.50

h	c_i	c_a	$\langle P_2\rangle$	σ	ρ	η
0.00	3.290	4.191	0.792	1.602	0.565	
0.05	3.410	4.340	0.800	1.650	0.554	0.278
0.10	3.536	4.506	0.811	1.711	0.540	0.283
0.15	3.669	4.690	0.823	1.787	0.522	0.289
0.20	3.810	4.895	0.837	1.882	0.501	0.296
0.25	3.958	5.126	0.853	2.000	0.476	0.304
0.30	4.114	5.385	0.870	2.146	0.446	0.312
0.35	4.275	5.676	0.889	2.321	0.412	0.318
0.40	4.441	5.996	0.908	2.522	0.376	0.323
0.45	4.610	6.335	0.924	2.738	0.340	0.325
0.50	4.782	6.682	0.938	2.953	0.307	0.325

Table IV
Increase of the Coexisting Concentrations c_i and c_a as a Function of the Parameter h

h	$\delta c_i = c_i - c_{i,0}$	$\delta c_a = c_a - c_{a,0}$	$\delta c_i/h$	$\delta c_a/h$
0.05	0.119	0.149	2.38	2.99
0.10	0.245	0.315	2.45	3.15
0.15	0.379	0.499	2.52	3.32
0.20	0.520	0.704	2.60	3.52
0.25	0.668	0.935	2.67	3.74
0.30	0.823	1.194	2.74	3.98
0.35	0.984	1.485	2.81	4.24
0.40	1.150	1.805	2.88	4.51
0.45	1.320	2.144	2.93	4.77
0.50	1.492	2.491	2.98	4.98

In Table IV we present the increase of c_i and c_a with respect to the values $c_{i,0}$ and $c_{a,0}$, the values of the coexisting concentration for $h = 0$. We see that the increase is approximately proportional to h. Using an analytic theory we shall investigate this in the next section, where we devise a perturbation theory for the proportionality constants.

IV. Analytical Theory

The best way to proceed analytically is to choose a trial function for f that is physically reasonable yet simple enough. We shall use Onsager's original choice,[1] which is still one of the best, although others have also proved convenient.[21-24] This normalized function f_0 depends on the adjustable parameter α.

$$f_0(\Omega) = f_0(\theta) = \frac{\alpha\cosh(\alpha\cos\theta)}{4\pi\sinh\alpha} \tag{27}$$

Note that this function can easily accommodate isotropic, weakly anisotropic, or fully anisotropic states (see in this regard also note 12 of ref 20). In view of the numerical results of the previous section, we anticipate that for the nematic phase the α values ought to be quite high. In that case we already know the following asymptotic expansions for the anisotropic entropic terms calculated with the use of eq 27:[1]

$$\sigma(\alpha) \sim \ln \alpha - 1 \tag{28}$$

$$\rho(\alpha) \sim 4(\pi\alpha)^{-1/2}\left[1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3} + \ldots\right] \tag{29}$$

The term η containing the awkward logarithmic function can likewise be expanded for large α by a suitable extension of the calculations in he appendix to ref 1. Onsager was able to show that for any function H depending on sin x only and for which $H(0) = 0$, one has

$$\langle\langle H(\sin x)\rangle\rangle_{\mathrm{a}} = 2e^{-2\alpha}\int_{x=0}^{\pi} \cosh\,(2\alpha \cos {}^1\!/_2 x)\;\mathrm{d}H(\sin x) \tag{30}$$

For $H_{\mathrm{e}} = -(4/\pi)(\sin x)\ln(\sin x)$ eq 30 yields

$$\langle\langle H_{\mathrm{e}}\rangle\rangle_{\mathrm{a}} \sim -\rho(\alpha) - (8/\pi)e^{-2\alpha}I(2\alpha) \tag{31}$$

where the integral I is defined by

$$I(y) \equiv \int_0^{\pi} \cosh\,(y \cos {}^1\!/_2 x)(\cos x)\ln(\sin x)\;\mathrm{d}x \tag{32}$$

In order to perform the asymptotic expansion of $I(y)$ for large y, one starts with the substitution $\cos {}^1\!/_2 x = 1 - z$ and expands the slowly varying functions occurring in the integrand in powers of z. In the explicit calculation of the resulting integrals one notes that the presence of a logarithmic singularity is no problem at all because of a well-established theorem.[25] Furthermore, several properties of the Psi and Gamma functions[26] greatly simplify the analysis. The final result is

$$I(y) \sim \frac{e^y\pi^{1/2}}{(2y)^{1/2}}\left\{({}^1\!/_2 \ln 2 - {}^1\!/_2 \ln y - {}^1\!/_2\gamma)\left(1 - \frac{15}{8y} + \frac{105}{128y^2} + \frac{315}{1024y^3}\right) + \left[-\frac{5}{2y} + \frac{67}{16y^2} + \frac{307}{256y^3}\right] + \ldots\right\} \tag{33}$$

Accordingly, eq 12, 29, 31, and 32 yield the twisting term η valid for large α

$$\eta(\alpha) \sim 2(\pi\alpha)^{-1/2}\left\{(\ln \alpha - 2\ln 2 - 1 + \gamma)\left(1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + \frac{315}{8192\alpha^3}\right) + \left[\frac{5}{2\alpha} - \frac{67}{32\alpha^2} - \frac{307}{1024\alpha^3}\right] + \ldots\right\} \tag{34}$$

We have also calculated $\eta(\alpha)$ numerically by expanding H_{e} in terms of Legendre polynomials just as in the previous section. As can be seen from Table V, the difference between eq 34 and $\eta_{\mathrm{num}}(\alpha)$ from numerical analysis is always less than 10^{-5} for $10 < \alpha < 40$. This incidentally proves the adequacy of our earlier expansions of the logarithm. For $\alpha > 40$, it is clear that eq 34 increases considerably in accuracy whereas the expansion of H_{e} up to only P_{14} starts becoming dubious as is evidenced by the enhanced divergence between $\eta(\alpha)$ and $\eta_{\mathrm{num}}(\alpha)$. We have remarked before[23] on the possibility of an increasingly poor convergence of Legendre polynomial expansions as α attains higher and higher values.

Obviously the presence of the ln α term in eq 34 precludes a series solution of the coexistence equations like the one discussed in ref 1. Bearing in mind that in practice h is relatively small (see next section), we can profitably try a perturbation theory. From eq 10 we know that the term proportional to the second virial coefficient $B_2{}^a$ can be expressed as

Table V
Comparison of the Approximate Numerical and Analytical Calculation of $\rho(\alpha)$ and $\eta(\alpha)$

	ρ		η	
α	numerical	analytical	numerical	analytical
5	0.82873	0.82861	0.12575	0.12613
10	0.64823	0.64823	0.24158	0.24158
15	0.54682	0.54682	0.29159	0.29159
20	0.48123	0.48123	0.31573	0.31573
25	0.43457	0.43457	0.32813	0.32813
30	0.39925	0.39925	0.33452	0.33452
35	0.37131	0.37130	0.33750	0.33750
40	0.34852	0.34851	0.33850	0.33848
45	0.32948	0.32944	0.33826	0.33822
50	0.31324	0.31319	0.33726	0.33717
70	0.26640	0.26613	0.32989	0.32936
100	0.22456	0.22357	0.31729	0.31535
150	0.18608	0.18312	0.30049	0.29465
200	0.16416	0.15882	0.28870	0.27809

$$c'B_2{}^a = c(\rho(\alpha) + \epsilon(\alpha)) \tag{35}$$

with

$$\epsilon(\alpha) \equiv h\eta(\alpha) \tag{36}$$

If the driving or twisting term $\epsilon(\alpha)$ were zero, we would just have the Onsager calculation for hard rods, identified by the parameter set α_0, $\sigma(\alpha_0)$, $\rho(\alpha_0)$, $c_{\mathrm{i},0}$, and $c_{\mathrm{a},0}$. When we hypothetically switch on the effect of electrostatic twisting forces ($h > 0$), we modify α, σ, and ρ as well as c_{i} and c_{a}. Therefore it is natural to set up the following perturbation scheme: $\epsilon(\alpha) = \epsilon(\alpha_0) + \mathcal{O}(h^2)$, $\alpha = \alpha_0 + \delta\alpha + \mathcal{O}(h^2)$, $\rho(\alpha) = \rho(\alpha_0) + \rho'(\alpha_0)\delta\alpha + \mathcal{O}(h^2)$, $c_{\mathrm{a}} = c_{\mathrm{a},0} + \delta c_{\mathrm{a}} + \mathcal{O}(h^2)$, etc., where we suppose all δ-type terms to be proportional to h. Insertion of these expansions in eq 25 and 26 and systematic linearization lead to two sets of equations—a zero-order set previously established and solved by Onsager[1] and one of first order consisting of two equations that connect the perturbation terms

$$(c_{\mathrm{i},0}{}^{-1} + 2)\delta c_{\mathrm{i}} = (\alpha_0{}^{-1} + 2c_{\mathrm{a},0}\rho'(\alpha_0))\delta\alpha + (c_{\mathrm{a},0}{}^{-1} + 2\rho(\alpha_0))\delta c_{\mathrm{a}} + 2c_{\mathrm{a},0}\epsilon(\alpha_0) \tag{37}$$

$$(1 + 2c_{\mathrm{i},0})\delta c_{\mathrm{i}} = c_{\mathrm{a},0}{}^2\rho'(\alpha_0)\delta\alpha + (1 + 2c_{\mathrm{a},0}\rho(\alpha_0))\delta c_{\mathrm{a}} + c_{\mathrm{a},0}{}^2\epsilon(\alpha_0) \tag{38}$$

The minimization of ΔF_{a} must lead to another expression relating to δ-type terms. We require

$$\sigma'(\alpha) + c_{\mathrm{a}}(\rho'(\alpha) + \epsilon'(\alpha)) = 0 \tag{39}$$

A perturbation expansion of eq 39 is straightforward: $\sigma'(\alpha) = \sigma'(\alpha_0) + \sigma''(\alpha_0)\delta\alpha + \mathcal{O}(h^2)$ and so forth. Of course, the zero-order equation holds automatically

$$\sigma'(\alpha_0) + c_{\mathrm{a},0}\rho'(\alpha_0) = 0 \tag{40}$$

Taking note of the identity $\Delta F_{\mathrm{a},0}''(\alpha_0) = \sigma''(\alpha_0) + c_{\mathrm{a},0}\rho''(\alpha_0)$, with $\Delta F_{\mathrm{a},0}''(\alpha_0) > 0$ pertaining to the hard-rod nematic, we obtain the following first-order expression:

$$\Delta F_{\mathrm{a},0}''(\alpha_0)\delta\alpha + \rho'(\alpha_0)\delta c_{\mathrm{a}} + c_{\mathrm{a},0}\epsilon'(\alpha_0) = 0 \tag{41}$$

The values of the zero-order parameters can be found in ref 1: $c_{\mathrm{a},0} = 4.4858$, $c_{\mathrm{i},0} = 3.3399$, $\alpha_0 = 18.584$, $\rho(\alpha_0) = 0.49740$, and $\sigma(\alpha_0) = 1.9223$. Equations 29, 35, 36, and 40 can be employed to get the other coefficients in eq 37, 38, and 41: $\Delta F_{\mathrm{a},0}''(\alpha_0) = 0.00096042$, $\rho'(\alpha_0) = -0.011996$, $\epsilon(\alpha_0) = 0.31047h$, $\epsilon'(\alpha_0) = 0.0040780h$. We can now derive the modification of the composition at the phase transition by solving eq 37, 38, and 41

$$\delta c_{\mathrm{i}} = 2.37h \tag{42a}$$

$$\delta c_{\mathrm{a}} = 3.01h \tag{42b}$$

These values agree rather well with the numerical results shown in Table IV. As an extra check we have also performed computer calculations of $\delta c_{\mathrm{a}}/h$ and $\delta c_{\mathrm{i}}/h$, starting from the trial function given by eq 27. For small h these functions converge nicely to eq 42. Apparently, this perturbation theory works better than the zero-order or hard-rod theory of ref 1. This phenomenon is perhaps ubiquitous when one recalls the huge success of perturbation theories of the liquid state.[27]

As yet, we have failed to mention whether or not the polyelectrolyte liquid crystal is feasible. First of all, we can state that because the isotropic–nematic phase transition for rods is first order, the polyelectrolyte nematic must also be stable, provided h is small enough. In addition, an explicit calculation shows this to be true for those values of h for which the perturbation theory to order h remains meaningful ($h \lesssim 0.15$).

V. Relation between Electrostatic Potential and Polyelectrolyte Parameters

The interaction w between two skewed, uniformly charged, rodlike polyions is in general a tedious problem to solve. Fortunately, we need solely the Mayer function $1 - \exp(-w/k_{\mathrm{B}}T)$ in our calculations instead of w. Hence, if we replace w by some function v with $v = w$ for w and $v \lesssim 1$ but $w \neq v$ for w and $v > 1$, the errors incurred will be exponentially small. This is precisely the motivation of Brenner and Parsegian[17] to replace the charges on the cylindrical surfaces by effective line charges at the center lines of the polyelectrolytes in such a way that the outer double layers match. Thus, a line charge of effective density ν_{eff} (i.e., number of charges per unit length) and scaled potential $\Phi_{\mathrm{l}}(\kappa r)$ is associated with every polyelectrolyte which exerts the scaled potential $\Phi(\kappa r)$ at a distance r from its center line

$$\frac{e\psi}{k_{\mathrm{B}}T} = \Phi \sim \Phi = 2\nu_{\mathrm{eff}} Q K_0(\kappa r) \qquad (\kappa r \gtrsim {}^1\!/_2\kappa D + 1) \tag{43}$$

Since only the outer parts of the double layers are important, the line potential Φ_{l} is conveniently calculated within the Debye–Hückel approximation. The superposition of Debye–Hückel potentials from an infinite line gives rise to the zero-order modified Bessel function K_0. In eq 43 we have introduced the quantities elementary charge e, Bjerrum length $Q = e^2/\epsilon k_{\mathrm{B}}T$, the permittivity of the solvent ϵ, and the Debye radius κ^{-1}, with $\kappa^2 = 8\pi Q n_{\mathrm{s}}$ and $\mathrm{n_s}$ the 1–1 electrolyte concentration.

The electrostatic interaction between cylinders is now modeled by that between two equivalent line charges which, again, need only be done within the Debye–Hückel approximation. For long cylinders this calculation has been carried out by several authors,[17,18] although most straightforwardly by Fixman and Skolnick[19]

$$\frac{w}{k_{\mathrm{B}}T} = \frac{2\pi \nu_{\mathrm{eff}}{}^2 Q e^{-\kappa x}}{\kappa \sin \phi} \tag{44}$$

implying

$$A = 2\pi \nu_{\mathrm{eff}}{}^2 Q \kappa^{-1} \tag{45}$$

as can be seen from eq 1. Here, x is the shortest distance between the lines and ϕ is the angle between them. In a calculation of the electrostatic excluded volume we stress that one has to integrate the exponent in eq 44 from $x = D$ to ∞, which yields

$$B_{2,\mathrm{el}}(\sin \phi) = 2L^2 \sin \phi \int_D^\infty (1 - e^{-w/k_{\mathrm{B}}T})\, \mathrm{d}x = \frac{2L^2 \sin \phi}{\kappa}\left[\ln A' + \gamma - \ln (\sin \phi) + \mathcal{O}\left(\frac{\sin(\phi) e^{-A'/\sin \phi}}{A'}\right)\right] \tag{46}$$

with

$$A' = A e^{-\kappa D} \tag{47}$$

This expression which holds for $A' \gtrsim 2$ has been used in eq 2. We note that eq 45 is physically plausible for line charges: when two line charges start interacting ($x = \mathcal{O}(\kappa^{-1})$), the interaction interface between them has an area of order $\kappa^{-2} \sin^{-1} \varphi$ so that the number of interacting charges is $(\kappa^{-1}\nu)^2 \sin^{-1} \phi$. Hence, we get eq 44 because the interaction between two charges scales as $(e^2/\epsilon_0 \kappa^{-1} k_{\mathrm{B}}T)$.

Next, let us apply this procedure to weakly charged cylindrical polyelectrolytes. In the Debye–Hückel approximation we have the well-known formula[28]

$$\Phi_{\mathrm{DH}} = \frac{2\nu Q K_0(\kappa r)}{\kappa a K_1(\kappa a)} \qquad (\Phi_{\mathrm{DH}} < 1) \tag{48}$$

where ν is the number of charges per unit length viewed along the cylinder, a is the cylinder radius equal to ${}^1\!/_2D$, and K_1 is the first-order modified Bessel function. The derivative of Φ_{DH} at the polyion surface is connected to the surface density $\sigma_{\mathrm{s}} = \nu/2\pi D$ via Gauss's law. Equations 43 and 48 imply $\nu_{\mathrm{eff}} = \nu(\kappa a K_1(\kappa a))^{-1}$ and we immediately obtain A' from eq 45 and 47

$$A'_{\mathrm{DH}} = 2\pi \nu^2 Q \kappa^{-1} g^{-1}(\kappa a) \tag{49}$$

with $g(z) = z^2 K_1{}^2(z) e^{2z}$, $g(0) = 1$, and $g(z) \sim {}^1\!/_2\pi z$ ($z \gtrsim 2$). If the cylinders are relatively thick, this equation reduces to

$$A'_{\mathrm{DH}} \sim \frac{4\nu^2 Q}{a\kappa^2} \qquad (\kappa a \gtrsim 2) \tag{50}$$

From a physical point of view, eq 50 is also sound: once two thick cylinders start interacting, the interaction interface has an area scaling like $l^2 \sin^{-1} \phi \simeq D\kappa^{-1} \sin^{-1} \phi$, where $l^2 \simeq D\kappa^{-1}$ follows from simple geometrical arguments. There are $\sigma l^2 \sin^{-1} \phi$ charges on one surface, each of which interact with $\sigma \kappa^{-2}$ on the other. Accordingly, the total scaled electrostatic energy is $(\sigma\kappa^{-2})(\sigma l^2 \sin^{-1} \phi)(e^2/\epsilon_0 \kappa^{-1} k_{\mathrm{B}}T)$, i.e., of the same order of magnitude as eq 50. Onsager originally used the Derjaguin approximation,[29] which gives the result in eq 50 provided one divides his potential by a factor of 4 (see ref 18). Onsager suggested that multiplying eq 50 by $D/(D + \kappa^{-1})$ should give the correct result for thick double layers (eq 45) as it does, in fact, apart from the numerical factor. In summary, combination of the Brenner–Parsegian[17] and Fixman–Skolnick[19] procedures leads to an approximate but realistic expression for A' valid for all κD.

For highly charged cylinders ($\nu Q \gtrsim 1$) we know the Poisson–Boltzman equation is reasonably accurate.[30] Because of the nonlinear screening the counterions buffer the high surface charge to a large extent so that the potential is quite a deal lower than naively expected from eq 48. Thus, it is expedient to write

$$\Phi_{\mathrm{PB}} \sim \Gamma K_0(\kappa r) \qquad (\kappa r > {}^1\!/_2\kappa D + 1) \tag{51}$$

Table VI
Effect of the Electrostatic Interaction on the Isotropic–Anisotropic Phase Transition for a Thin Weakly Charged Polyelectrolyte in a 1-1 Salt Solution

M_{salt}	κa	A'	δ	h	$(\pi/4)L^2Dc_i'$	$(\pi/4)L^2Dc_a'$
A. a = 9.62 Å, ν = 0.05 electron charge/Å						
0.001	0.1	9.5	15	0.31	0.26	0.34
0.004	0.2	4.1	5.5	0.39	0.68	0.91
0.010	0.3	2.4	2.8	0.44	1.20	1.65
B. a = 9.62 Å, ν = 0.1 electron charge/Å						
0.001	0.1	38	22	0.22	0.17	0.22
0.004	0.2	17	8.9	0.25	0.34	0.52
0.010	0.3	9.8	5.1	0.27	0.66	0.86

because Γ depends rather weakly on κ, D, and ν. In effect, lower and upper bounds have been devised for Γ[31–34]

$$1.273 < \Gamma < 2K_0^{-1}([1+\xi]a\kappa)\ln\left[\frac{1+e^{-\xi a\kappa}}{1-e^{-\xi a\kappa}}\right] \quad (52)$$

where ξ is a conveniently chosen adjustable parameter. We can now rewrite A' as follows:

$$A'_{\text{PB}} = \tfrac{1}{2}\pi\Gamma^2(Q\kappa)^{-1}e^{-\kappa D} \quad (53)$$

Because we just need the logarithm of A'_{PB} we have found the analytical approximations of Philip and Wooding[31] for the potential precise enough.

When is the effect of twist largest? The κ dependence of A' from eq 45, 49, 50, and 53 can be described in some region of κ values by

$$A' \sim \kappa^{-\omega} \qquad (1 \lesssim \omega \lesssim 2) \quad (54)$$

Equations 6, 13, and 54 can be used to show that h has a maximum when $\kappa^{-1} = D/\omega$; i.e., the Debye radius should be of the order of the diameter of the polyelectrolyte for the twisting effect to be most significant. Since eq 6 is valid only for $A' > 2$ (see eq 46) we have a practical upper bound on h equal to about 0.5. When we let A' be smaller than 2 in the integral of eq 46, we start including terms that cause negligible or no twist. This renders the analysis useless from our point of view.

We now consider the effect of the electrostatic interaction on the isotropic–anisotropic phase transition for some representative cases. First we consider the case of thin weakly charged ($\nu Q < 1$) polyelectrolytes in 1–1 salt solutions varying in concentration from 0.001 to 0.01 M. From the results presented in Table VI it is clear that both the charge density of the polyelectrolyte and the concentration of the salt solution have a pronounced effect on the phase transition concentrations. If we had neglected the twisting effect, the concentrations would have been 20–40% lower. The results presented in Table VI may be relevant for weakly charged rodlike polysaccharides.

As a second case we consider thick highly charged ($\nu Q > 1$) polyelectrolytes. The choice of parameters in Table VII was guided by the values of TMV.[5–9] For this case we have used the approximate analytic solution to the Poisson–Boltzmann equation of Philip and Wooding.[31] Note that an increase of the charge density by a factor 2 changes the electrostatic interaction very little (owing to the nonlinear screening effect of the counterions). Increase of the salt concentration, on the other hand, has as in the case of thin weakly charged polyelectrolytes a marked effect on the phase transition concentrations.

Table VII
Effect of the Electrostatic Interaction on the Isotropic–Anisotropic Phase Transition for a Thick Highly Charged Polyelectrolyte in a 1-1 Salt Solution

M_{salt}	κa	Γ	A'	δ	h	$(\pi/4)L^2Dc_i'$	$(\pi/4)L^2Dc_a'$
A. a = 96.2 Å, ν = 0.5 electron charge/Å							
0.001	1.0	7.31	153	2.90	0.13	0.93	1.18
0.004	2.0	19.7	75.2	1.27	0.11	1.55	1.97
0.010	3.0	50.6	44.8	0.76	0.09	2.02	2.57
B. a = 96.2 Å, ν = 1 electron charge/Å							
0.001	1.0	9.04	234	3.11	0.12	0.88	1.12
0.004	2.0	28.4	145	1.44	0.10	1.47	1.88
0.010	3.0	76.6	103	0.90	0.09	1.85	2.37

After we submitted this work, a paper[35] on nematic polymers appeared containing a short section describing numerical results on the isotropic–nematic transition for charged rods (a preprint had been sent to us but without this specific section). Lee and Meyer use Onsager's expression for the potential, which is a factor of 4 too large and valid only within the limit of the polyion diameter being much greater than the Debye radius. Furthermore, they use the surface potential as an independent variable, which, incidentally, is very dependent on the ionic strength. Polyelectrolyte chemists regard the linear charge density as a fundamental quantity virtually independent of ionic strength. Parenthetically, we note that even for spherical colloids the status of surface and ζ potentials is very unclear at present. These considerations aside, if we temporarily replace our A' by Onsager's A in eq 6, calculate h from eq 13, and obtain c_i, c_a, and order parameter S from Table III by interpolation, we find complete agreement with ref 35.

A referee has queried our insistent use of the scaled parameters c_i, c_a, and h. Equations 14, 25, and 26 show that there is one and only one parameter h that causes deviations from that of the purely hard-rod nematic. Thus, all possible numerical results are compiled in one table, namely Table III, instead of a whole host of tables. Two very different polyelectrolytes could have the same twisting parameter h so that the deviations of their nematic behavior from that of the hard-rod fluid can be identically described provided we insist on using our scaled densities c_i and c_a. In Tables VI and VII we have outlined typical values of the concentrations scaled in the usual way. Because the effects of twist and increase in effective diameter are now intertwined, these figures are not very enlightening. Comparison of the two tables tells us nothing. Scaling the concentrations with respect to the effective diameter would point out the similarity immediately.

VI. Concluding Remarks

In this paper we have shown that within the framework of the Onsager treatment the effect of electrostatic interactions between rodlike polyelectrolytes on the isotropic–anisotropic phase transition can be characterized by two parameters. One of these parameters characterizes the increase of the effective diameter whereas the second parameter characterizes the twisting effect caused by the electrostatic interactions. In previous treatments the latter contribution had not been taken into account. By both numerical and analytical calculations we have shown that the twisting effect is important.

It is well to remember that our quantitative predictions are subject to several limitations. Even a slight flexibility may well increase the concentration at the transition.[22,24] Polydispersity could also muddle the interpretation of experimental results.[20,23] One of us (Th.O.) will deal with these problems in a review to appear shortly. Furthermore, because the effect of twist is largest when the Debye radius is of the order of the polyion diameter, discrete charge effects may possibly not be entirely neglected. Nonetheless, we insist that deviations from the usual lyotropic polymer behavior due to the effect of twist should show up.

As a final comment we remark that there is an urgent need for quantitative experimental data on the isotropic–anisotropic phase transition concentrations as function of charge density and salt strengths. So far nothing of this kind is available in the literature.

References and Notes

(1) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
(2) Zocher, H. *Z. Anorg. Chem.* **1925**, *147*, 91.
(3) Zocher, H.; Török, C. *Kolloid-Z.* **1960**, *170*, 140; **1960**, *173*, 1; **1962**, *180*, 41.
(4) Bugosh, J. *J. Phys. Chem.* **1961**, *65*, 1791.
(5) Bernal, J. D.; Frankuchen, I. *J. Gen. Physiol.* **1941**, *25*, 111.
(6) Oster, G. *J. Gen. Physiol.* **1950**, *33*, 445.
(7) Gregory, J.; Holmes, K. C. *J. Mol. Biol.* **1965**, *13*, 796.
(8) Kreibig, U.; Wetter, G. *Z. Naturforsch., C: Biosci.* **1980**, *35C*, 750.
(9) Fraden, S.; Hurd, A. J.; Meyer, R. B.; Cahoon, M.; Caspar, D. L. D. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, C3-85.
(10) Brian, A. A.; Frisch, H. L.; Lerman, L. S. *Biopolymers* **1981**, *20*, 1305.
(11) Rill, R. L.; Hilliard, P. R.; Levy, G. C. *J. Biol. Chem.* **1983**, *28*, 250.
(12) Marchessault, R. H.; Morehead, F. F.; Walter, N. M. *Nature (London)* **1959**, *184*, 632.
(13) Itou, T.; Teramoto, A. *Polym. J. (Tokyo)* **1982**, *14*, 999; **1984**, *16*, 779.
(14) Yanaki, T.; Norisuye, T.; Teramoto, A. *Polym. J. (Tokyo)* **1984**, *16*, 165.
(15) Perutz, H. F.; Liquori, A.; Eirich, F. *Nature* **1951**, *167*, 929.
(16) Allison, A. C. *Biochem. J.* **1957**, *65*, 212.
(17) Brenner, S. L.; Parsegian, V. A. *Biophys. J.* **1974**, *14*, 327.
(18) Stigter, D. *Biopolymers* **1977**, *16*, 1435.
(19) Fixman, M.; Skolnick, J. *Macromolecules* **1978**, *11*, 863.
(20) Lekkerkerker, H. N. W.; Coulon, Ph.; Haegen, van der R.; Deblieck, R. *J. Chem. Phys.* **1984**, *80*, 3427.
(21) Straley, J. P. *Phys. Rev. A* **1973**, *8*, 2181.
(22) Khokhlov, A. R.; Semenov, A. N. *Macromolecules* **1984**, *17*, 2678.
(23) Odijk, T.; Lekkerkerker, H. N. W. *J. Phys. Chem.* **1985**, *89*, 2090.
(24) Odijk, T. *Polym. Commun.* **1985**, *26*, 197.
(25) Olver, F. W. J. *Asymptotics and Special Functions*; Academic: New York, 1974.
(26) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1970.
(27) McQuarrie, D. A. *Statistical Mechanics*; Harper, and Row: New York, 1976.
(28) Hill, T. L. *Arch. Biochem. Biophys.* **1955**, *57*, 229.
(29) Derjaguin, B. *Kolloid-Z.* **1934**, *69*, 155.
(30) Fixman, M. *J. Chem. Phys.* **1979**, *70*, 4995.
(31) Philip, J. R.; Wooding, R. A. *J. Chem. Phys.* **1970**, *52*, 953.
(32) Russel, W. B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1233.
(33) Odijk, T. *Chem. Phys. Lett.* **1983**, *100*, 145.
(34) Lampert, M. A.; Crandall, R. S. *Chem. Phys. Lett.* **1980**, *72*, 481.
(35) Lee, S. N.; Meyer, R. B. *J. Chem. Phys.* **1986**, *84*, 3443.

Dielectric Relaxation in Poly(ethylene terephthalate)

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ABSTRACT: Dielectric constant and loss have been measured over the frequency range 1 Hz to 100 kHz over a wide temperature range for a series of poly(ethylene terephthalate) (PET) specimens spanning the crystallinity range from essentially amorphous to 62%. The higher crystallinities were achieved via crystallization under pressure. Previous work has indicated that the β subglass process does not extrapolate to zero relaxation strength at 100% crystallinity. Taking advantage of higher crystallinities (and the knowledge that the crystalline density on which some previous crystallinity scales have been based was not completely reliable) we demonstrate here that both the α_a glass–rubber relaxation and the β process extrapolate to zero strength at a density corresponding to 100% crystallinity. This indicates amorphous-phase origin for both processes. The effect of crystallinity on the relaxation parameters for these amorphous-phase processes is discussed. Interpretation of the relaxation strengths in terms of the Onsager–Kirkwood dipolar correlation factor shows that immobilization of amorphous chain segments by connections to the crystals can be detected not only by perturbation of relaxation times but by availability of configurations as well. Specific volumes of the specimens were measured as a function of temperature, and the correlation between the dielectric relaxation results and thermal expansion changes through the relaxation regions is discussed.

Introduction

Poly(ethylene terephthalate) (PET) has served as an important model for studying relaxation processes in semicrystalline polymers.[1-5] The circumstance that it can be quenched into the completely amorphous state as well as isothermally crystallized has allowed direct measurement of the effect of crystallinity presence on relaxations. PET shows two relaxation processes, one designated α_a and the other β. The former is the glass transition (disappearance of long-range segmental motion with lowering temperature) in the completely amorphous material or in the amorphous fraction in semicrystalline specimens. The α_a relaxation is quite sensitive to the presence of the crystalline fraction in that it is dramatically broader in the frequency domain and shifted to higher temperature isochronally in crystalline samples. The β relaxation, occurring at lower temperatures isochronally than the α_a process, has been thought to take place largely in the amorphous phase also and therefore is a "subglass" process. The β relaxation is insensitive to morphology, having virtually the same characteristics (other than strength or intensity) in completely amorphous materials as in semicrystalline ones. This is consonant with the molecular motions associated with it being of shorter range character than those for the α_a process. However, the assignment of the β relaxation as a *purely* amorphous one has been compromised by extrapolation of relaxation strength vs. density to 100% crystallinity. On extrapolation of their β-process strength data Ishida et al.[2] concluded that the process did not disappear at 100% crystallinity. They

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0024-9297/86/2219-2238$01.50/0