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Form Birefringence of Block Copolymer Melts under Oscillatory Shear

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ABSTRACT: When block copolymer melts are subjected to an external flow field, such as simple shear flow, composition fluctuations are distorted by the velocity field and take on an anisotropic character. This leads to anisotropy in the macroscopic dielectric tensor, which is manifested in optical experiments as form birefringence or dichroism. At temperatures near the microphase separation transition in block copolymer melts, the amplitudes of the fluctuations become very large, giving rise to singular behavior of the birefringence. We employ a mean field theory for the dynamics of homogeneous block copolymer melts to calculate the form birefringence of a diblock melt subjected to low-amplitude oscillatory shear. In the limit of low frequencies we find that the in-phase component of the birefringence approaches a constant value that is predicted to diverge like $\mu^{-3/2}$ [$\mu = (T - T_c)/T_c$] as the temperature is lowered toward its critical value T_c. The limiting slope of the out-of-phase component at zero frequency is even more singular, scaling like $\mu^{-5/2}$. We find no substantial form dichroism from diblock melts at visible wavelengths.

In a recent paper[1] we developed a mean field theory for the dynamics of homogeneous block copolymer melts. The theory is capable of describing collective diffusion processes on time scales longer than the reptation time τ and incorporates the effect of systematic flows, such as simple shear or extensional flow. The only restrictions on the flow field are that it be homogeneous (i.e. a linear flow) and that the characteristic Deborah number $D = \dot{\gamma}\tau$ must be small compared with unity. (Here $\dot{\gamma}$ is a rate that describes the magnitude of velocity gradients in the appropriate flow. $\dot{\gamma}$ is the shear rate in simple shear flow.) In ref 1 the theory was used to study the nonequilibrium steady state of a diblock copolymer melt in the presence of time independent shear. The scattering function that describes the composition fluctuations at such a steady state was found to be highly anisotropic, with composition patterns in the plane of shear distorted to a large extent by the flow. Fluctuations with wavenumbers close to q^*, the wavenumber at which the equilibrium scattering function has its maximum,[3] are most strongly affected by the flow because such fluctuations are the longest lived. The equation of motion for the scattering function derived in ref 1 permits quantitative interpretation of neutron and X-ray scattering experiments on block copolymers under steady or time-dependent deformations. The formulae can also be applied to binary homopolymer blends by inserting the appropriate equilibrium structure factor.[10]

In ref 2 the formalism was employed to compute the contribution of composition fluctuations to the dynamic shear modulus for a diblock copolymer melt subjected to low amplitude oscillatory shear. Near the critical point for the microphase separation transition (MST)[3] and at low frequencies, the critical contributions to the modulus were found to dominate over the usual (noncritical) contributions from the terminal relaxation mechanism. These theoretical results are in qualitative agreement with dynamical mechanical measurements on a 1,2-/1,4-polybutadiene diblock copolymer by Bates.[4] For the case of slow steady shear, expressions were also derived[5] for the fluctuation contributions to the three viscometric coefficients: the viscosity, the first normal stress coefficient, and the second normal stress coefficient. These coefficients were found to be singular as the critical temperature is approached.

In the present communication we consider the form birefringence of block copolymer melts under shear. Because of the anisotropy of composition fluctuations in the presence of flow, the dielectric tensor is rendered anisotropic. This optical anisotropy gives rise to form birefringence and form dichroism.[6,7] Near the MST in the disordered phase the amplitudes of the composition fluctuations become very large and the optical anisotropy becomes very pronounced. In this regime the form contributions to the birefringence and dichroism will dominate the intrinsic contributions, which are important in conventional flow birefringence experiments on noncritical polymeric systems.[15,16] The intrinsic contributions arise from the orientation of polymer segments induced by the macroscopic flow. Because we restrict consideration to temperatures near the MST, these contributions to the birefringence and dichroism will not be considered in this paper.

The system of interest is that studied previously.[1-3,5] We consider a diblock copolymer melt, each molecule having Nf statistical segments of monomer A and $N(1 - f)$ statistical segments of monomer B. The melt is assumed incompressible, and the segment lengths and specific volumes of the two species are taken to be the same. The order parameter field $\psi(\mathbf{x}) = \rho_A(\mathbf{x})/\rho - f$ describes the fluctuation of the local A species density $\rho_A(\mathbf{x})$ from its average value ρf. In the subsequent analysis all lengths will be expressed in units of $\rho^{-1/3}$, where ρ is the total segment density.

Onuki and Kawasaki[6] and Onuki and Doi[7] have derived an expression for the form contribution to the dielectric tensor in terms of the order parameter correlation function (scattering function) in the presence of flow. For the present case of a diblock copolymer melt the expression can be written

$$\epsilon_{\alpha\beta} = -\frac{A_0}{(2\pi)^3}\int \mathrm{d}\mathbf{q}\; C(\mathbf{k} - \mathbf{q},t)\frac{q_\alpha q_\beta - k^2\delta_{\alpha\beta}}{q^2 - k^2 - i\eta} \qquad (1)$$

where

$$A_0 = \frac{1}{\epsilon_0}\left(\frac{\partial\epsilon_0}{\partial f}\right)^2 \qquad (2)$$

η is a positive infinitesimal, and $\epsilon_0 = \epsilon_0(f)$ is an effective dielectric constant for the melt. The dielectric tensor in eq 1 has explicit dependence on the wavevector of the incident radiation $\mathbf{k}$ and on the time t that enters in the correlation function

$$C(\mathbf{q},t) = \langle \psi(\mathbf{q},t)\psi(-\mathbf{q},t)\rangle \qquad (3)$$

The average in eq 3 is taken with the distribution function of order parameter fluctuations at time t and $\psi(\mathbf{q})$ is the Fourier transform of $\psi(\mathbf{x})$.

In this paper we consider the case of low-amplitude oscillatory simple shear flow in the x–y plane, characterized by the velocity field components: $v_x(t) = \dot{\gamma} y \cos \omega t$, $v_y = v_z = 0$. For simplicity the incident radiation will be taken in the z direction. In this case the form birefringence Δn and the form dichroism $\Delta\kappa$ are obtained from eq 1 by means of the relations[7] ($n_0 = \epsilon_0^{1/2}$)

$$\Delta n = \frac{1}{n_0} \operatorname{Re} \epsilon_{xy} \tag{4}$$

$$\Delta\kappa = \frac{1}{n_0} \operatorname{Im} \epsilon_{xy} \tag{5}$$

For the usual situation of visible incident radiation, the wavelength of the light, $2\pi/k$, is much larger than the wavelength of the dominant order parameter fluctuations in a diblock melt, $2\pi/q^*$. (Leibler[3] has shown that q^*, the wavenumber of the peak in the equilibrium scattering function, is of order the reciprocal of the radius of gyration.) Hence, the limit $k/q^* \rightarrow 0$ may be taken, reducing eq 1 to ($\hat{q}_\alpha \equiv q_\alpha/|\mathbf{q}|$)

$$\Delta n(t) = -\frac{A_0}{(2\pi)^3 n_0} \int \mathrm{d}\mathbf{q}\; C(\mathbf{q},t) \hat{q}_x \hat{q}_y \tag{6}$$

The form dichroism can be shown to be very small, scaling like $\Delta\kappa \sim (k/q^*)^5$ for $k/q^* \rightarrow 0$ (in the present regime of weak shear), and thus will be given no further consideration.

An equation of motion for $C(\mathbf{q},t)$ was derived in ref 1 to describe flows with shear rates satisfying $\dot{\gamma} \ll \tau^{-1}$, where τ is the terminal relaxation (reptation) time of the melt. In principle, this equation can be solved numerically and the results used in eq 6 to evaluate the form birefringence. However, to obtain analytical results we restrict consideration to the linear regime of low-amplitude flows for which $\dot{\gamma} \ll \Gamma(q^*) \ll \tau^{-1}$. Here $\Gamma(q^*)$ is the value of the thermal decay rate $\Gamma(q) = q^2\lambda(q)/C_0(q)$ at the wavenumber corresponding to the peak in the equilibrium scattering function $C_0(q)$. The thermal decay rate[1,8-11] describes the rate at which composition fluctuations of wavenumber q relax at equilibrium (in the absence of flow) and is proportional to a phenomenological transport coefficient $\lambda(q)$.

In the present linear regime, $\dot{\gamma} \ll \Gamma(q^*) \ll \tau^{-1}$, the correlation function $C(\mathbf{q},t)$ can be expanded in powers of $\dot{\gamma}$

$$C(\mathbf{q},t) = C_0(q) + \dot{\gamma} \operatorname{Re} [C^*(\omega,\mathbf{q}) e^{-i\omega t}] + \mathcal{O}[(\dot{\gamma})^2] \tag{7}$$

with

$$C^*(\omega,\mathbf{q}) = \frac{q_x}{2\Gamma(q) - i\omega} \frac{\partial}{\partial q_y} C_0(q) \tag{8}$$

We retain only terms linear in the amplitude $\dot{\gamma}$ and express the form birefringence in terms of a complex mechano-optical coefficient[7] $S^*(\omega)$ by the relation

$$\Delta n(t) = \frac{A_0 \dot{\gamma} \tau}{5\pi^2 n_0 R \rho^{1/3}} \operatorname{Re} [S^*(\omega) e^{-i\omega t}] \tag{9}$$

where $R^2 = N\rho^{-2/3}/6$ is the mean-squared radius of gyration of diblock molecule.

We adopt Leibler's expression[3] for the equilibrium scattering function, $C_0(q)/N = 1/[F(x,f) - 2\chi N]$, where $x = q^2R^2$ and χ is the Flory interaction parameter. The function $F(x,f)$ is defined elsewhere.[1-3,5] Following previous work, the thermal decay rate is assumed to have the form[1,2,5] $\Gamma(q) = (x/2\tau)g(x)[F(x,f) - 2\chi N]$, where $g(x)$ is the Debye function $2x^{-2}[x + e^{-x} - 1]$. Combining eq 6–9, expressions for the real and imaginary parts of $S^*(\omega) = S'(\omega) + iS''(\omega)$ are found to be ($\Omega = \omega\tau$):

$$S'(\Omega) = \int_0^{x_c} \mathrm{d}x\, \frac{x^{5/2} g(x) \partial F(x,f)/\partial x}{\{\Omega^2 + x^2 g^2(x)[F(x,f) - 2\chi N]^2\}\{F(x,f) - 2\chi N\}} \tag{10}$$

$$S''(\Omega) = \Omega \int_0^{x_c} \mathrm{d}x\, \frac{x^{3/2} \partial F(x,f)/\partial x}{\{\Omega^2 + x^2 g^2(x)[F(x,f) - 2\chi N]^2\}\{F(x,f) - 2\chi N\}^2} \tag{11}$$

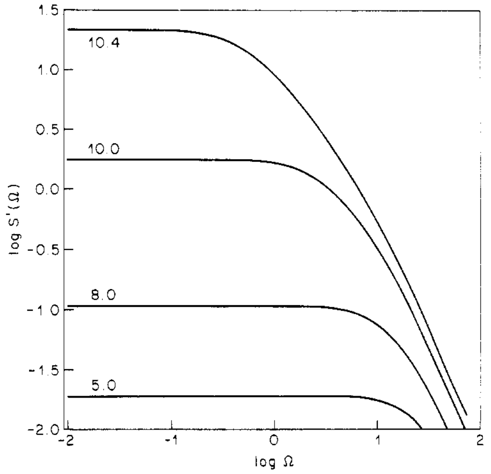

Figure 1. Frequency dependence of the real part of the mechano-optical coefficient $S^*(\Omega)$ for the case of symmetric diblock molecules ($f = 1/2$). A cutoff at $x_c = 10.0$ is taken in the numerical evaluation of eq 10. $S'(\Omega)$ describes the component of the form birefringence that is in-phase with the imposed oscillatory shear. The labels on the curves correspond to the respective values of χN. The low-frequency plateau is seen to rise dramatically as the critical point is approached, scaling as $S'(\Omega) \sim a^{-3/2}$, where $a = 2[10.5 - \chi N]$.

In eq 10 and 11 we have introduced a cutoff in the integrals at $x_c = q_c^2R^2$. (See discussion in ref 2.) Although not necessary at finite Ω, the cutoff renders the integrals convergent in the limit $\Omega \rightarrow \infty$. The behavior of $S^*(\Omega)$ for the frequencies of interest ($\Omega < 1$), however, is independent of the choice of cutoff (provided it is sufficiently large).

In Figures 1 and 2 we illustrate the results of numerically integrating eq 10 and 11 for a symmetric diblock melt ($f = 1/2$) at various values of χN. Figure 1 shows that $S'(\Omega)$, the component of the birefringence that is in-phase with the oscillatory shear, approaches a constant value in the limit of low frequencies and, as the frequency is increased, crosses over to an Ω^{-2} scaling regime. As χN is increased toward its critical value of 10.5 (where the homogeneous phase becomes unstable),[3] either by lowering the temperature or by increasing molecular weight, the crossover region between the two types of frequency dependence moves to lower Ω. Furthermore, the limiting low-frequency plateau of $S'(\Omega)$ is seen to increase dramatically as the critical point (or spinodal for the case of asymmetric diblocks) is approached.

Figure 2 illustrates the behavior of the out-of-phase component of the form birefringence, $S''(\Omega)$, as a function of frequency and χN. In the limit of low frequency, we find $S''(\Omega) \sim \Omega$ scaling, with the coefficient becoming very large near the spinodal $(\chi N)_s = 10.5$. At higher frequencies, $S''(\Omega)$ attains a maximum value and then decreases like $S''(\Omega) \sim \Omega^{-1}$ on further increasing the frequency. The location of the maximum moves to lower Ω as the spinodal temperature is approached.

The scaling properties of the low-frequency behavior of $S'(\Omega)$ and $S''(\Omega)$ can be obtained by the method discussed

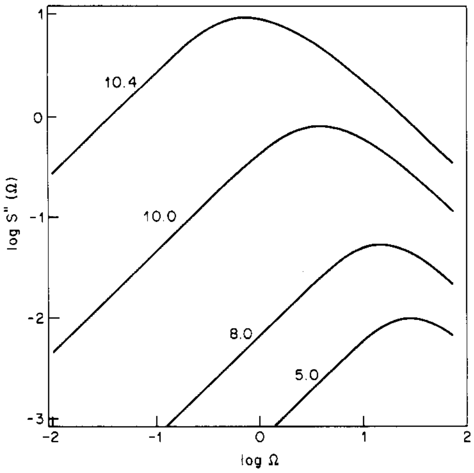

Figure 2. Frequency dependence of the imaginary part of the mechano-optical coefficient $S^*(\Omega)$ for the case of symmetric diblock molecules ($f = 1/2$). A cutoff at $x_c = 10.0$ is taken in the numerical evaluation of eq 11. $S''(\Omega)$ describes the component of the form birefringence that is out-of-phase with the imposed oscillatory shear. The labels on the curves correspond to the respective values of χN. The linear low-frequency regime and maximum exhibited by the curves are seen to be strongly affected as the critical point is approached, scaling as $S''(\Omega) \sim \Omega a^{-5/2}$, where $a = 2[10.5 - \chi N]$.

in ref 2 and 5. We adopt the following approximation for the reciprocal of the equilibrium scattering function[2,5,12,13]

$$F(x,f) - 2\chi N \approx \frac{[x^* - x]^2}{2f(1-f)x} + a \qquad (12)$$

where $x^* = [3/f(1-f)]^{1/2}$ is an approximation for $(q^*)^2R^2$ and $a = 2[(\chi N)_s - \chi N]$ is a measure of the distance from criticality. To extract the limiting behavior of eq 10 and 11 for a, $\Omega \to 0$, we make the change of variables $y = a^{-1/2}[x - x^*]$ and expand the integrand in powers of Ω and $a^{1/2}$. After substantial algebraic manipulations we find the following leading order behavior

$$S'(\Omega) \approx \frac{\sqrt{6}\pi[1 - 2x^*g'(x^*)/g(x^*)]}{4x^*g(x^*)a^{3/2}} \qquad (13)$$

$$S''(\Omega) \approx \frac{\sqrt{6}\pi\Omega[-1 - 4x^*g'(x^*)/g(x^*)]}{16[x^*g(x^*)]^2a^{5/2}} \qquad (14)$$

with $g'(x) \equiv dg(x)/dx$. For the symmetric case of $f = 1/2$ we find that both expressions are positive because $x^*g'(x^*)/g(x^*) = -0.655$, leading to $[1 - 2x^*g'(x^*)/g(x^*)] = 2.31$ and $[-1 - 4x^*g'(x^*)/g(x^*)] = 1.62$.

These mean field predictions for the low-frequency, low-amplitude form birefringence of diblock melts could be tested in systems such as the 1,2-/1,4-polybutadiene copolymer studied rheologically by Bates,[4] for which the disordered phase is easily attained. The strong singular character of the mechano-optical coefficients $S'(\Omega) \sim a^{-3/2}$, $S''(\Omega) \sim \Omega a^{-5/2}$, should be observed as the temperature is lowered to closely approach the spinodal for the microphase separation transition.

A remarkable relationship known as the stress optical law[7,15,16] is found experimentally as a proportionality between the *intrinsic* contributions to the anisotropic parts of the dielectric tensor and the stress tensor. This relationship is understood theoretically as a consequence of the fact that both tensorial quantities have the same microscopic expression, apart from a proportionality constant. A reasonable question to consider is whether a similar relationship holds between the *form* contribution to the dielectric tensor and the contribution to the stress tensor arising from composition fluctuations. Equation 1 in the $k \to 0$ limit gives for the form contribution to $\epsilon_{\alpha\beta}$

$$\epsilon_{\alpha\beta} = -\frac{A_0}{(2\pi)^3}\int d\mathbf{q}\; C(\mathbf{q},t)\hat{q}_\alpha\hat{q}_\beta \qquad (15)$$

while the expression for the fluctuation contribution to the stress is[2,5]

$$\sigma_{\alpha\beta} = -\frac{k_BT}{(2\pi)^3}\int d\mathbf{q}\; C(\mathbf{q},t)q_\alpha q_\beta\frac{\partial}{\partial q^2}C_0^{-1}(q) \qquad (16)$$

Because of the differences between the two expressions, there is no general stress optical law for the form birefringence. However, the fluctuation contributions to various optical and mechanical coefficients exhibit the same scaling behavior in the a, Ω, $\dot{\gamma} \to 0$ limit, being related by proportionality constants. An example of such a relationship that could be tested experimentally is between the shear viscosity[2,5] η and the low-frequency behavior of $S'(\Omega)$ given in eq 13 ($a \to 0$)

$$\eta = A_1 \lim_{\Omega \to 0} S'(\Omega) \qquad (17)$$

A second proportionality exists between the first normal stress coefficient[5] Ψ_1 and the limiting slope of $S''(\Omega)$ given in eq 14

$$\Psi_1 = \lim_{\omega \to 0} 2\frac{G'(\omega)}{\omega^2} = A_2 \lim_{\Omega \to 0}\frac{S''(\Omega)}{\Omega} \qquad (18)$$

The dynamic storage modulus $G'(\omega)$ was studied in ref 2 and the relationship between the fluctuation contributions to Ψ_1 and $G'(\omega)$ was established in ref 5. The coefficients A_1 and A_2 appearing in eq 17 and 18 are given by

$$A_1 = \frac{k_BT\tau(x^*)^3}{90\pi^2R^3[1 - 2x^*g'(x^*)/g(x^*)]}$$

$$A_2 = \frac{2k_BT\tau^2(x^*)^3}{45\pi^2R^3[-1 - 4x^*g'(x^*)/g(x^*)]}$$

Finally, we comment that the present mean field theory does not properly treat composition fluctuations at temperatures very near the spinodal. We have recently considered corrections to mean field theory for the bulk equilibrium properties of diblock melts[14] and have found that a more sophisticated treatment of fluctuations leads to several important changes. First, we find a fluctuation-induced first-order transition for a *symmetric* diblock melt in place of the second-order transition predicted by mean field theory. The value of χN at the predicted microphase separation transition (MST), $10.5 + 41.0N^{-1/3}$, is larger than Leibler's critical value of 10.5. Because the transition is first order, the peak in $C_0(q)$ does not diverge at the transition temperature but instead attains a maximum value of $0.123N^{1/3}$. As a result, the critical singularities predicted for the form birefringence and viscometric functions in mean field theory will be cutoff near the MST. For high molecular weight symmetric diblocks, however, the fluctuation corrections are small and the MST is close to being second-order. Hence, we expect to observe the scaling relations predicted here and in ref 2 and 5 at temperatures near the transition, except in the narrow non-mean field regime $a \lesssim 40N^{-1/3}$. A reasonable method of treating the cutoff of the singularities near the MST is to replace $a = 2[(\chi N)_s - \chi N]$ in the scaling laws derived above (eq 13 and 14) by the renormalized variable ϵ, which satisfies the following algebraic equation[14]

$$\epsilon = a + c^3d\lambda/(\epsilon N)^{1/2} \qquad (19)$$

The parameters c, d, and λ are f-dependent dimensionless constants that are tabulated in ref 14. For a symmetric diblock, ϵ has the value $8.11N^{-1/3}$ at the MST.

After this paper was completed, the author received a preprint from A. Onuki[17] that has a brief discussion of the form birefringence of diblock melts. Because of slightly different assumptions, he finds results qualitatively similar to those reported here, but they differ in quantitative detail.

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References and Notes

(1) Fredrickson, G. H. *J. Chem. Phys.* **1986**, *85*, 5306.
(2) Fredrickson, G. H.; Larson, R. G. *J. Chem. Phys.* **1987**, *86*, 1553.
(3) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(4) Bates, F. S. *Macromolecules* **1984**, *17*, 2607.
(5) Larson, R. G.; Fredrickson, G. H. *Macromolecules* **1987**, *20*, 1897.
(6) Onuki, A.; Kawasaki, K. *Physica A (Amsterdam)* **1982**, *11*, 607.
(7) Onuki, A.; Doi, M. *J. Chem. Phys.* **1986**, *85*, 1190.
(8) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(9) Hohenberg, P. C.; Halperin, B. I. *Rev. Mod. Phys.* **1977**, *49*, 435.
(10) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(11) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.
(12) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.
(13) Olvera de la Cruz, M.; Sanchez, I. C. *Macromolecules* **1986**, *19*, 2501.
(14) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.
(15) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(16) Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence*; Springer: Berlin, 1983.
(17) Onuki, A., preprint.

Correlation between Crystallinity and Ethylene Content in LLDPE and Related Ethylene Copolymers. Demonstration of the Applicability of a Simple Empirical Relationship

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ABSTRACT: Calorimetric data on six distinct series of ethylene copolymers have been examined and shown to fit the empirical relationship $\log(\Delta H_m) = \log k + n \log x_E$, where ΔH_m is the heat of fusion, k a constant, n the critical sequence length for crystallization, and x_E the mole fraction of ethylene. For olefin copolymers values of $n = 8$–16 are observed, whereas a series of vinyl chloride copolymers shows a value of $n = 5$. These are generally in accord with literature data. The analysis of co- and terpolymers based on a range of olefinic comonomers strongly suggests that the number and distribution of noncrystallizable units are more important than size in the inhibition of crystallization.

Introduction

The copolymer melting of polyethylene is a fascinating topic which has been studied for many years and has attracted attempts to provide some quantitative theoretical basis.[1-3] The development of the commercial ethylene copolymer LLDPE has led to a renewed interest in this topic, and recently several calorimetric studies of ethylene copolymers have been published.[4-10] A common feature of all of these studies is that the level of crystallinity, as measured by the enthalpy of fusion (ΔH_m), decreases as the level of comonomer is increased. In an earlier publication[8] we proposed a simple empirical relationship for the dependence of crystallinity of the mole fraction of ethylene in the copolymer and showed it to be applicable to calorimetric data on one series of LLDPE samples. We now wish to provide further results and an analysis of published data to show that the proposed relationship has general applicability to a wide range of ethylene copolymers.

Experimental Section

The parent polyethylene and derived 4-methyl-1-pentene copolymers were prepared with a $TiCl_3$ 1.1 Stauffer catalyst by procedures to be described elsewhere.[11]

Calorimetric measurements were made with a Perkin-Elmer Model DSC-2C instrument on 5-mg samples as detailed earlier.[8] Samples were inserted into the instrument at 310 K and heated at 20 K/min over the range 310–450 K (as-polymerized samples). Subsequently the cooling curve was obtained by cooling the sample at 20 K/min with data acquisition (*cooling run*). Finally the sample was rescanned over the temperature range 310–450 K (*rerun sample*).

Results and Discussion

For the purpose of analysis an ethylene copolymer may be treated as being composed of crystallizable ethylene units and noncrystallizable comonomer units. Long sequence runs of ethylene are presumed to crystallize whereas short sequences are inhibited from so doing. The lamellar thickness of the formed crystallites will be determined in part by the sequence length of ethylene units providing that the comonomer unit is excluded from the structure. It is known that the melting point of the crystallites is related to the lamellar thickness and it follows therefore that at any given temperature there is a certain minimum thickness required to provide a stable crystallite. Consequentially it is not unreasonable to suppose that there is also a corresponding critical ethylene sequence length (n) below which chains will not crystallize.

In an earlier publication[8] it was suggested that for a random copolymer the enthalpy of fusion (ΔH_m) should be related to the ethylene mole fraction (x_E) by the relationship

$$\Delta H_m = k x_E^{\,n} \qquad (1)$$

where k is a constant related to the enthalpy of fusion of the parent homopolymer. The constant k is likely to be affected by parameters such as MW and MWD, heterogeneity of copolymer composition, thermal history of sam-

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