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References and Notes

(1) Bertelson, R. *Tech. Chem. (N.Y.)* **1971**, *3*, 45-293.
(2) Krongauz, V. A.; Parshutkin, A. A. *Photochem. Photobiol.* **1972**, *15*, 503. *Mol. Photochem.* **1974**, *6*, 437.
(3) Krongauz, V. A.; Goldburt, E. S. *Nature (London)* **1978**, *271*, 43.
(4) Krongauz, V. A.; Fishman, S. N.; Goldburt, E. S. *J. Phys. Chem.* **1978**, *82*, 2469.
(5) Krongauz, V. A.; Kiwi, J.; Grätzel, M. *J. Photochem.* **1980**, *13*, 89.
(6) Sturmer, D. M.; Heseltine, D. W. "The Theory of the Photographic Process"; Jammes, H., Ed.; Macmillan: New York, 1977.
(7) Bucher, H.; Kuhn, H. *Chem. Phys. Lett.* **1970**, *6*, 183.
(8) Rosenoff, A. E.; Walworth, V. K.; Bird, G. R. *Photogr. Sci. Eng.* **1970**, *14*, 328.
(9) Bird, G.; Norland, K. S.; Rosenoff, A. E.; Mishaud, H. B. *Photogr. Sci. Eng.* **1968**, *12*, 196.
(10) Ames, K. N.; Taylor, T. *Photogr. Sci. Eng.* **1970**, *14*, 295.
(11) Smets, G. *Pure Appl. Chem.* **1972**, *30*, 1.
(12) Zajtseva, E. L.; Prohoda, A. L.; Kurkovskaya, L. H.; Shifrina, R. R.; Kardash, N. S.; Drapkina, D. A.; Krongauz, V. A. *Khim. Geterotsikl. Soedin.* **1973**, *10*, 1362.
(13) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.
(14) Smith, D. L. *Photogr. Sci. Eng.* **1974**, *18*, 309.
(15) Katchalsky, A.; Eisenberg, H. *J. Polym. Sci.* **1951**, *6*, 145.
(16) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972. Yokota, K.; Ishii, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 771.
(17) Krongauz, V. A.; Goldburt, E. S., unpublished results.
(18) Kardash, N. S.; Krongauz, V. A.; Zaitsera, E. L.; Movshovitch, A. V. *Polym. Sci. USSR (Engl. Transl.)* **1974**, *16A*, 453.
(19) Bohn, C. R.; Schaefgen, J. R.; Statton, W. O. *J. Polym. Sci.* **1961**, *55*, 531.
(20) Ceccarelli, G.; Frosini, V.; Magagnini, P. L.; Newman, B. A. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 101.
(21) Blumstein, A. *Macromolecules* **1977**, *10*, 872.
(22) Wendorff, J. H.; Finkelmann, H.; Ringsdorf, H. *J. Polym. Sci., Polym. Symp.* **1978**, *63*, 245.
(23) Blumstein, A.; Clough, S. B.; Patel, L.; Blumstein, R. B.; Hsu, E. C. *Macromolecules* **1976**, *9*, 243.
(24) Chu, S. C.; Pearce, E. *J. Polym. Sci., Polym Lett. Ed.* **1976**, *14*, 375.
(25) Cheng, C. H.; Pearce, E. M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1871.
(26) Finkelmann, H.; Happ, H.; Portugal M.; Ringsdorf, H. *Macromol. Chem.* **1978**, *179*, 2541.
(27) Finkelman, H.; Naegele, D.; Ringsdorf, H. *Makromol. Chem.* **1979**, *180*, 803.

Effect of Strain Energy in the Theory of Polymer Crystallization

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ABSTRACT: A theory is developed to establish the basic relationship between minimum strain energy and an equilibrium crystal shape in strained states. Changes in crystal shape have been investigated as a major phenomenon in macromolecular crystals. Many familiar observations, such as the thickening of lamellae and extended chain fibers during annealing and stretching, respectively, and the thinning of lamellar crystals under pressure, can be explained adequately by the theory in terms of a single parameter—the strain energy. With irreversible thermodynamics, the nonequilibrium annealing behavior is analyzed with the same strain energy function as the driving force. The theoretical prediction is in good agreement with experimental data and the existing theory of Sanchez, Colson, and Eby which is based on a surface free energy consideration.

Introduction

The thickening of lamellae during annealing and the lengthening of fibrils during stretching are well established in the literature[1,2] and illustrate the important effect of strain energy in the formation of macromolecular crystals. It is generally recognized that polymer crystals are thermodynamically metastable and the crystallization process is controlled by nucleation theory[3,4] under the postulate of local equilibrium. Annealing and stretching may be considered as two opposite irreversible processes.[5,6] The former moves toward the lowest energy state of a crystal and the latter away from it. Energy variations during deformation as a function of crystal shape—the fundamental part of the problem—have not been determined because the role of strain energy in the theoretical treatment of crystallization is not well established.[7] The main objective of this work is to explain the change in shape of polymer crystals in terms of strain energies applied to or released from the system. A functional relationship between the minimum strain energy and the equilibrium shape of a strained crystal is derived for an equilibrium morphology. Assumptions concerning the crystal morphology[8-11] and detailed descriptions of the strain energy are avoided at the present time to preserve the generality of the theory. The fundamental relation between strain energy and crystal shape is applied to interpret various stress effects on crystallization in polymers, such as the crystallization induced by stretching, stress relief by annealing, and the effect of pressure. The theoretical interpretation is then compared with experimental observations. As an example, the strain energy of ultraoriented high-density polyethylene fibers[12] is estimated and the mechanical and thermal implications are discussed.

In the search for a unified approach to the equilibrium and nonequilibrium changes in crystal shape, the time dependence of crystal thickening during annealing was analyzed as an irreversible process driven by the strain energy gradient instead of a surface free energy gradient proposed by Sanchez, Colson, and Eby.[5] The present theory is then compared with their theory and experimental crystal thickening data.

Theoretical Development

The free energy of crystallization from the melt can be written as

$$\Delta G = G_{\text{crystal}} - G_{\text{melt}} \tag{1}$$

The free enthalpy of a crystal consists of bulk and surface contributions

$$G_{\text{crystal}} = G_{\text{bulk}} + \sum_i \gamma_i A_i \tag{2}$$

where γ_i represents the surface free energy per unit area

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and A_i is the corresponding surface area. The surface free energies are always positive and $G_{melt} - G_{bulk}$ is greater than zero for temperatures below the melting point. In the following, our main interest is to investigate the effect of strain energy on overall crystal behavior rather than details of the nucleation process.

1. Unstrained State. Before introducing strain energy into the theoretical treatment, let us define the equilibrium dimensions of a macromolecular crystal. According to ref 1 (Chapter 7), a crystal is either a folded chain lamella or an extended chain fiber, whose equilibrium shape is defined by the ratio of the end (γ_e) and side (γ) surface free energies per unit area. The same definition will be generalized to the strained state where the equilibrium shape of a crystal is determined by the surface free energy ratio and the strain energy. Considering a crystal of thickness l and lateral dimension a, the equilibrium values of a and l are[1,5]

$$a_0^* = 4\gamma/\Delta g_0 \tag{3}$$

$$l_0^* = 4\gamma_e/\Delta g_0 \tag{4}$$

where the subscript 0 refers to the unstrained condition. The thickness of macroscopic crystals is customarily described by l_0^*. The a_0^* is given, by eq 3 and 4, in terms of l_0^* and the ratio of surface free energies and is not related to the ultimate lateral dimensions of macroscopic crystals. The thermodynamic driving force, Δg_0, is given by the familiar expression known as the free energy of fusion per unit volume of the polymer crystal

$$\Delta g_0 = \Delta h_f^\circ (T_m^\circ - T)/T_m^\circ \tag{5}$$

where Δh_f° is the heat of fusion per unit volume of a crystal, T_m° is the melting temperature of the unstrained crystal, and $T_m^\circ - T$ is the degree of supercooling. It follows that a_0^* and l_0^* increase without bound as $T_m^\circ - T$ approaches zero.

2. Strained State. We will now consider the effect of strain energy per unit volume, w, on the equilibrium dimensions a^* and l^* of a crystal. The thermodynamic driving force for crystallization of polymers in the strained state is[8,14]

$$\Delta g = (G_{melt} - G_{bulk})/V = \Delta g_0 + w \tag{6}$$

where V is the crystal volume, Δg_0 is given by eq 5, $w = -T(\Delta S - \Delta S_0) > 0$, and ΔS and ΔS_0 are differences in entropy of fusion in the strained and unstrained states, respectively. Following the procedure used in nucleation theory, the free enthalpy of crystallization, eq 1 and 2, becomes

$$\Delta G = a^2 I(\rho) - a^3 \rho[\Delta g_0 + w(\rho)] \tag{7}$$

where the aspect ratio $\rho = l/a$ characterizes the crystal shape and $I(\rho) = 2\gamma_e + 4\gamma\rho$. The major difference between eq 7 and previous treatments[15] is that the strain energy per unit volume is not a constant but a function of ρ. The equilibrium values of a^* and ρ^* have to simultaneously satisfy the equations

$$(\partial \Delta G/\partial a)_\rho = 0 \tag{8}$$

$$(\partial \Delta G/\partial \rho)_a = 0 \tag{9}$$

Substituting eq 7 into eq 8, one obtains

$$a^* = \frac{2I(\rho^*)}{3\rho^*[\Delta g_0 + w(\rho^*)]} \tag{10}$$

Differentiation of eq 9 leads to

$$I'(\rho^*) = a^*\{[\Delta g_0 + w(\rho^*)] + \rho^* w'(\rho^*)\} \tag{11}$$

where the prime denotes the derivative with respect to ρ^*.

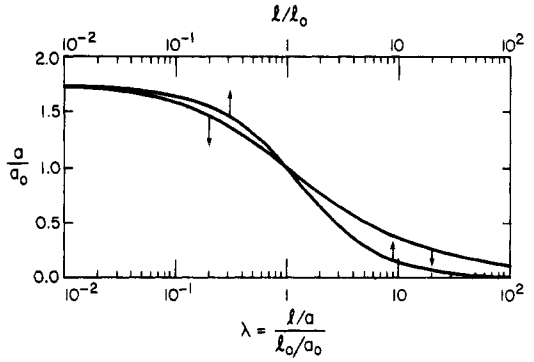

Figure 1. Ratio of strained to unstrained lateral dimensions vs. the relative aspect ratio and thickness ratio.

Eliminating a^* between eq 10 and 11 yields an ordinary differential equation

$$\frac{3}{2} I'(\rho^*) = I(\rho^*)\left[\frac{1}{\rho^*} + \frac{w'(\rho^*)}{\Delta g_0 + w(\rho^*)}\right] \tag{12}$$

With the condition of $w = 0$ at $\rho^* = \rho_0^* \equiv l_0^*/a_0^*$, the solution of eq 12 is

$$I^{3/2}(\rho^*) = \frac{6^{3/2}\gamma\gamma_e^{1/2}}{\Delta g_0}\rho^*[\Delta g_0 + w(\rho^*)] \tag{13}$$

The above equation provides the fundamental relationship between the equilibrium crystal shape and the minimum strain energy in the strained state. Hence the equilibrium values of a^* and ΔG^* can be obtained by substituting eq 13 into eq 10 and then into eq 7. In the rest of the paper, equilibrium values are implied without mentioning equilibrium and the asterisk will be dropped.

Theoretical Interpretation

In order to avoid the need for absolute values of γ, γ_e, T_m°, T, and Δh_f°, it is convenient to introduce the nondimensional parameters

$$\lambda = \frac{\rho}{\rho_0} = \frac{l/a}{l_0/a_0} \tag{14}$$

and

$$\psi = \frac{w}{\Delta h_f^\circ}\frac{T_m^\circ}{T_m^\circ - T} \tag{15}$$

which characterize the crystal shape and strain energy, respectively. Using eq 3 and 4, one finds the aspect ratio for unstrained crystals is $\rho_0 = \gamma_e/\gamma$ and is independent of temperature. One can rearrange eq 10 and 13 in terms of nondimensional parameters as follows:

$$a/a_0 = [3/(1 + 2\lambda)]^{1/2} \tag{16}$$

$$\psi = [\tfrac{1}{3}(1 + 2\lambda)]^{3/2}/\lambda - 1 \tag{17}$$

where λ is related to the thickness ratio l/l_0 by the equation

$$\lambda = \frac{l/l_0}{[(l/l_0)^2 + 3]^{1/2} - l/l_0} \tag{18}$$

The ratio of strained to unstrained lateral dimensions, a/a_0, is plotted in Figure 1 as a monotonic decreasing function of the relative aspect ratio, λ, and thickness ratio, l/l_0, based on eq 16 and 18. In Figure 2 the strain energy function, ψ, computed from eq 17, has the shape of a "potential well" with its minimum at $\lambda = 1$ and increases as λ departs from 1 in both directions ($\lambda < 1$ and $\lambda > 1$).

Our primary interest is to interpret the changes in crystal shape λ in terms of a single driving force ψ during

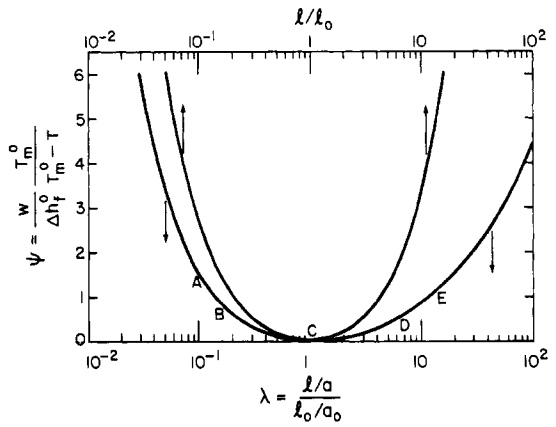

Figure 2. Variation of nondimensional minimum strain energy with equilibrium crystal shape in strained states.

the stressed crystallization of polymers. The strain energy is due to the frozen-in deformation of the polymer crystal and surrounding material on cooling from the melt. The deformation can be induced by external and internal strains, such as mechanical stretching or internal defects. Some familiar effects of stress on the crystallization of polymers can be interpreted by Figure 2.

1. Mechanical Stretching. A tensile stress tends to straighten the polymer chains and orients them preferentially parallel to the stress. The aspect ratio of an extended chain fiber, λ, increases with an increase of ψ along the path CDE in Figure 2.

2. Thermal Annealing. Annealing involves heating polymers to temperatures below the melting point, which reduces the strain energy to a lower energy state and leads to a more stable crystal structure. Annealing follows the path ABC for $\lambda < 1$ or EDC for $\lambda > 1$, which results in lamellar thickening or fribrillar shortening. The lowest attainable energy equilibrium point C is dependent on the time and temperature of annealing which is discussed in a later part of the paper.

3. Pressure Effect. At constant temperature, the strain energy increases with an increase of pressure, which is represented by BA in Figure 2. The aspect and thickness ratios of lamellae decrease with an increase of pressure.

All the corresponding variations of the lateral dimension follow in Figure 1. The interpretation of these phenomena by eq 17 seems consistent with experimental observations summarized in ref 1.

The volume of a crystal, $V = a^2 l$, can also be written as a function of ψ according to eq 16 and 17

$$V = V_0/(1 + \psi) \tag{19}$$

where $V_0 = 64\gamma^2\gamma_e/(\Delta g_0)^3$. Equation 19 shows that the volume of polymer crystals increases during annealing and decreases during stretching, as expected from observations.

The structural reorganization of ultraoriented high-density polyethylene fibers has been extensively studied as a means of achieving more desirable tensile properties.[12] Consider polyethylene with the properties[16] $\gamma_e = 80$ erg/cm^2, $\gamma = 10$ erg/cm^2, $T_m^\circ = 145$ °C, and $\Delta h_f^\circ = 67$ cal/cm^3 and assume $T = 130$ °C. Figure 3 shows the relative aspect ratio λ, volume ratio V/V_0, and melting temperature T_m of the polyethylene fibers plotted vs. the normalized strain energy $w/\Delta h_f^\circ$. The melting point elevation in the strained state is described by the equation[8,10]

$$T_m = \frac{T_m^\circ}{1 - (T_m^\circ/T)(w/\Delta h_f^\circ)} \tag{20}$$

The melting point is increased in the same way as λ. When

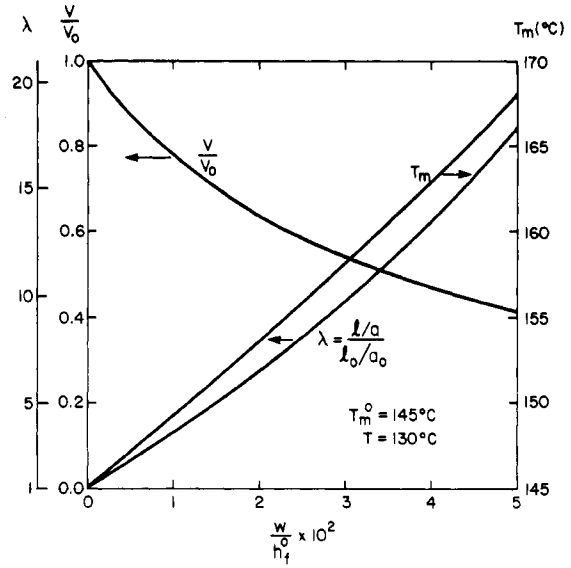

Figure 3. Plots of λ, V/V_0, and T_m vs. w/h_f° for a polyethylene crystal.

the aspect ratio of an extended polyethylene crystal is increased[12] from $\rho_0 = 8$ to $\rho = 25$ (i.e., $\lambda = 3.1$), Figure 3 shows that a strain energy of 0.5 cal/cm^3 is required, which also results in a 17% reduction of crystal volume and 3 °C rise in melting point.

Elastic moduli of semicrystalline polymers depend on the volume fraction and aspect ratio of oriented chain fibers.[17,18] The high tensile modulus of ultradrawn polyethylene is due to the high values of ρ.[12,17] Similarly, annealing drawn linear polyethylene results in a decrease in modulus caused by the reduction of ρ[2,17] We have shown that the tensile modulus is a strong function of ρ for $\rho > 1$ and is only slightly affected by ρ for $\rho < 1$.[18] The tensile modulus for $\rho < 1$ is mainly a function of volume fraction. This explains the contradiction[2] between the effects of annealing on drawn fibers and unoriented crystalline polymers which shows a modulus increase with annealing as a result of an increase of crystal volume during stress relief.

Annealing Kinetics

A change in crystal shape is the major effect of annealing polymer crystals and this has been discussed without including any time dependence. The nonequilibrium behavior of lamellar thickening during annealing was studied by Sanchez, Colson, and Eby as an irreversible process driven by the surface free energy under the assumption of constant crystal volume.[5] The purpose here is to see whether the general relationship between strain energy and crystal shape, eq 17, can adequately be applied to explain the same nonequilibrium behavior. The thermodynamic force will be the strain energy gradient rather than the surface free energy.

Consider the rate of thickness variation of a crystal which can be expressed by the following phenomenological equation for an irreversible process:[5,19]

$$a^2\left(\frac{dl}{dt}\right) = -k\left(\frac{\partial(wV)}{\partial l}\right) \tag{21}$$

where t is time and k is a proportionality constant. When the strain energy and crystal volume equations, eq 17 and 19, are substituted into eq 21, we obtain

$$\frac{\partial\lambda}{\partial t} = \frac{12}{\tau}\frac{1-\lambda}{(1+\lambda)^2}\left(\frac{1+2\lambda}{3}\right)^{3/2} \tag{22}$$

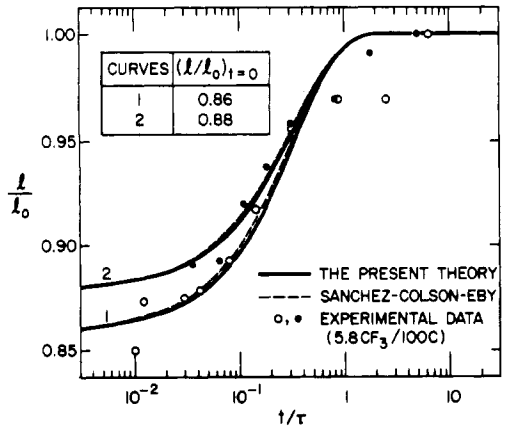

Figure 4. Comparison of the present theory with experimental data and the existing theory which is based on a surface free energy consideration.

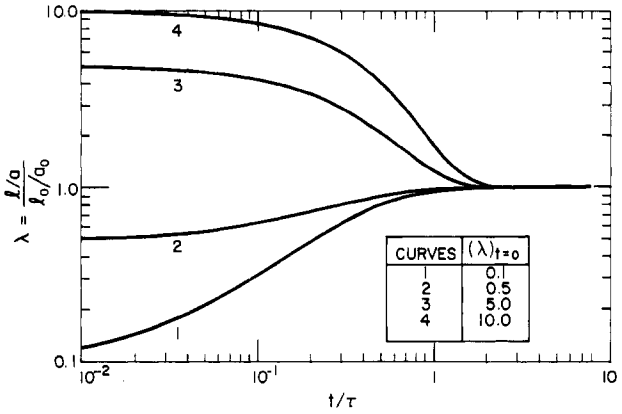

Figure 5. Change in relative aspect ratio as a function of reduced time.

where λ is defined by eq 14 and $\tau = l_0^2/\gamma_e k$. The parameter τ is considered to be an effective relaxation time related to a molecular mechanism by[5]

$$\tau = \tau_1 \exp[\nu \Delta h_f^\circ (T_m^\circ - T)/RTT_m^\circ] \quad (23)$$

where τ_1 is a weak function of temperature, R is the gas constant, and ν is the number of chain units required for cooperative chain backbone motion through the crystal. Assuming τ is independent of λ and letting

$$\eta = [(1 + 2\lambda)/3]^{1/2} \quad (24)$$

we can integrate eq 22 and obtain

$$(t - t_1)/\tau = f(\eta) - f(\eta_1) \quad (25)$$

with

$$f(\eta) = -\frac{3}{8}\eta - \frac{1}{24\eta} + \frac{1}{3} \ln \left|\frac{1 + \eta}{1 - \eta}\right| \quad (26)$$

The above equations are expressed in terms of the relative aspect ratio, which may easily be related to the thickness ratio by eq 18.

A comparison of eq 25 with the theory of Sanchez, Colson, and Eby and experimental data of lamellar thickening in random copolymers of tetrafluoroethylene and hexafluoropropylene, with about 5.8 CF_3 units per 100 carbon atoms in the backbone,[5] are shown in Figure 4. This confirms that the strain energy gradient is a thermodynamic force capable of driving the thickness phenomenon from a state of high to one of low strain energy during annealing (see Figure 2). Figure 5 illustrates the changes in relative aspect ratios, calculated from eq 25, from the initial ratios of 0.1, 0.5, 5, and 10 to the equilibrium value $\lambda = 1$. The thinning of needlelike crystals and the thickening of lamellar crystals are both moving in the direction of lower strain energy states.

Conclusions

The major effect of strain energy on macromolecular crystals is to change the crystal shape. Recognizing polymer crystallization as a nonequilibrium process with the postulate of local equilibrium, the present analysis provides a unified understanding of the effects of such familiar phenomena as stretching, annealing, and pressure in terms of a single thermodynamic driving force—the strain energy. The specific conclusions are as follows:

1. A general relationship between the minimum strain energy and the equilibrium crystal shape under strained conditions is derived assuming that the strain energy per unit volume is not a constant but a function of crystal shape.
2. The thickening of lamellae and extended fibers during annealing and stretching, respectively, and the thinning of a lamellar crystal under pressure are well-documented observations which are adequately explained by the state of strain energies involved in these processes.
3. The strain energy of ultraoriented high-density polyethylene fiber is estimated. The effects of orientation and annealing on the tensile modulus and structural reorganization of drawn linear polyethylene are discussed.
4. The strain energy gradient is treated as a thermodynamic force in analyzing nonequilibrium annealing behavior of polymer crystals. The prediction of the theory is in good agreement with experimental data of lamellar thickening and the theory of Sanchez, Colson, and Eby, who considered the surface free energy as the driving force.
5. The theory can also be applied to predict the irreversible thinning phenomena of needlelike drawn crystals.

References and Notes

(1) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1976; Vol. 2.
(2) Schultz, J. M. "Polymer Materials Science"; Prentice-Hall: Englewood Cliffs, N.J., 1974.
(3) Hoffman, J. D. *SPE Trans.* **1964**, *4*, 315.
(4) Price, F. P. In "Nucleation"; Zettlemoyer, A. C., Ed.; Marcel Dekker: New York, 1969.
(5) Sanchez, I. C.; Colson, J. P.; Eby, R. K. *J. Appl. Phys.* **1973**, *44*, 4332.
(6) Sanchez, I. C.; Peterlin, A.; Eby, R. K.; McCrackin, F. L. *J. Appl. Phys.* **1974**, *45*, 4216.
(7) Lindenmeyer, P. H. *Polym. Eng. Sci.* **1979**, *19*, 386.
(8) Flory, P. J. *J. Chem. Phys.* **1947**, *15*, 397.
(9) DiMarzio, E. A.; Guttman, C. M.; Hoffman, J. D. *Macromolecules* **1980**, *13*, 1194.
(10) Yamamoto, M.; White, J. L. *J. Polym. Sci., Part A-2* **1971**, *9*, 1399.
(11) Wu, W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1671.
(12) Mead, W. T.; Porter, R. S. *J. Appl. Phys.* **1976**, *47*, 4278.
(13) Turnbull, D.; Fisher, J. C. *J. Chem. Phys.* **1949**, *17*, 71.
(14) Ward, I. M. "Mechanical Properties of Solid Polymers"; Wiley: New York, 1971.
(15) Yeh, G. S. Y.; Hong, K. Z. *Polym. Eng. Sci.* **1979**, *19*, 395.
(16) Geil, P. H. "Polymer Single Crystals"; Interscience: New York, 1963.
(17) Chow, T. S. *Polymer* **1979**, *20*, 1576.
(18) Chow, T. S. *J. Mater. Sci.* **1980**, *15*, 1873.
(19) deGroot, S. R.; Mazur, P. "Non-equilibrium Thermodynamics"; North-Holland Publishing Co.: Amsterdam, 1963.