Chain folding in melt crystallized polyethylene?

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Introduction

The folded chain morphology of polyethylene single crystals formed during crystallization from dilute solution occupies a unique place in polymer crystallization theories[1], particularly since this structure is widely ascribed to the lamellae observed in melt crystallization from the quiescent melt. However, there is much controversy about the exact chain configuration at the surface of the lamellae, and the structure of the amorphous interlamellar regions. Flory and Yoon[2] have recently argued that the overall topology of the chains in the liquid state cannot be extensively altered during rapid crystallizations, and the single crystal model of tight adjacent reentry folds, as envisaged for the single crystal, cannot be entertained for melt crystallization. Evidence is similarly absent for slowly crystallized samples[3].

Painter *et al.*[4], using Fourier transform i.r. spectroscopy, have come to similar conclusions that regular adjacent re-entry chain folding is not present to any substantial extent in melt crystallized polyethylene. By comparison with a cyclic hydrocarbon the *gauche–gauche* configuration of the $-CH_2-$ groups in the fold was assigned to the 1348 cm^{-1} band, and while this band was also observed in solution grown crystal held in suspension to prevent distortion, it was absent from the spectra of melt crystallized material and also of melted and recrystallized single crystals.

Using the cyclic hydrocarbons as models for adjacent re-entry folded crystals, as suggested from the similarity in the i.r. spectroscopic assignment, we have come to similar conclusions concerning the chain morphology of the lamellae from their relative thermodynamic stability.

Models of chain folding and the thermodynamics of melting. Two extreme models suggest themselves for the polyethylene lamellae involving (i) an extended chain, with correspondingly no adjacent re-entry of the chain, and (ii) regular folding and adjacent re-entry (see *Figure 1*). These can be applied respectively to the n-alkanes and the cyclic-alkanes. In the first case, crystallographic evidence can be cited for the totally extended chain with the methyl terminal units on the lateral surface[5], and in the second for tight folds and adjacent re-entry[6]. However, differences exist in the thermodynamic parameters of melting of the two models which have their derivation in the lateral surface free energy, σ_e, and the dependence of the lamellar thickness degree of polymerization n[7].

According to Broadhurst[8], the heat of fusion of the orthorhombic n-alkanes of degree of polymerization, n, at the equilibrium melting point, T_m°, is

$$\Delta H_n = n\Delta h + \Delta h_e + n\Delta C_p \Delta T \qquad (1)$$

in which $\Delta T = (T_m^\circ - T_m)$, T_m the observed melting point of the alkane, Δh and Δh_e the heats of fusion of the monomer unit and the two terminal units, i.e. $-H$, and ΔC_p the heat capacity change between solid and liquid per monomer unit. This applies accurately to polyethylene oligomers[9]. The corresponding relationship for the entropy of fusion is,

$$\Delta S_n = n\Delta s + 2R\ln(n) + n\Delta C_p \Delta T + \Delta s_e \qquad (1a)$$

including an additional term corresponding to the entropy of mixing the terminal units with the repeat units on melting, $2R\ln(n)$.

Equating, $T_m^\circ = (\Delta h/\Delta s)$, $T_m = (\Delta H_n/\Delta S_n)$ and

$$\Delta G_e = \Delta h_e - T_m^\circ \Delta s_e = 2\sigma_e$$

then

$$T_m = T_m^\circ\{1 - 2RT_m^\circ \ln(n)/n\Delta h - 2\sigma^e/n\Delta h - \text{etc.}\} \qquad (2)$$

Evidence has been given that σ_e should be less than Δh for the alkanes and the final terms contribute little to the reduction of T_m°[9]. *Hence,*

$$T_m = T_m^\circ\{1 - 2RT_m^\circ \ln(n)/n\Delta h\} \qquad (2a)$$

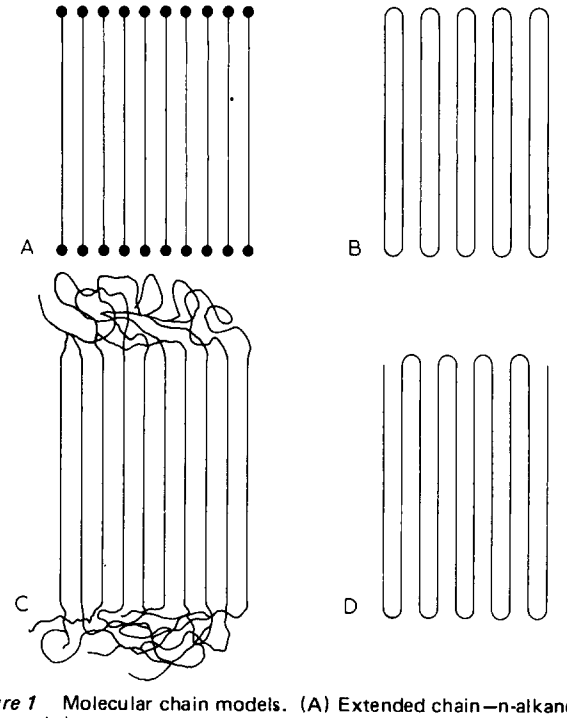

Figure 1 Molecular chain models. (A) Extended chain—n-alkane crystals; (B) regular chain folding—cyclic alkane crystals; (C) switchboard model—polyethylene lamellae; (D) regular adjacent re-entry—polyethylene single crystals

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Table 1 Thermodynamic parameters of melting

		n-Alkanes	Polyethylene	Cyclic-Alkane	Single crystal
Equation 1	Δh (kJ)(CH_2 Mol)$^{-1}$	4.2 ± 0.1	4.1 ± 0.1	–	4.25 ± 0.20
	Δh_e (kJ)(CH_2 Mol)$^{-1}$	19.0 ± 5.0	21.0 ± 5.0	–	96.0 ± 25
	T_m^0 (K)	435 ± 20	420 ± 20	–	–
Equation 2a	Δh (kJ)(CH_2 Mol)$^{-1}$	4.1 ± 0.1	4.1 ± 0.1	5.8 ± 0.8	6.5 ± 0.9
	T_m^0 (K)	419 ± 1	419 ± 1	425 ∓ 6	421 ± 3

Results and discussion

Application of equation 2a to the melting point-degree of polymerization dependence of the n- and cyclic alkanes indicated that they exhibited separate dependences (see *Figure 2*). In applying the equation to cyclic alkanes, and subsequently to the lamellar crystals, allowance was made for the stem thickness degree of polymerization, n, such that in the cyclic alkanes the thickness was taken to be half the molecular length. No allowance was made for the $-CH_2-$ units involved in the fold, but addition of such a correction would have increased the separation between the two melting point dependences rather than produced coincidence. As has been reported earlier[10], the dependence of the melting point of chain extended polyethylene exactly parallels that of the orthorhombic n-alkanes, and identical values of T_m^0 and Δh were obtained from the intercept and slope to plots of T_m against $\ln(n)/n$, see *Figure 2* and *Table 1*.

In the analysis, the melting points of monodisperse low molecular weight polyethylenes, which crystallized from the melt as extended chain lamellae and with melting points which were independent of the crystallization temperature, and of high pressure melt crystallized chain extended lamellae, were both included[9,10]. Each exactly paralleled the dependence exhibited by the orthorhombic hydrocarbons. The analysis was also applied to the melting characteristics of solution grown single crystals, using the stem length degree of polymerization as measured by LXAS. However, it has been well established that during melting single crystals begin to thicken rapidly and the observed melting points increase with decreasing rate of heating through the melting range. Fast rates of heating, in general, are not sufficient to eliminate lamellar thickening[11], and, perhaps more importantly, fast rates lead to greater uncertainties in the measurement of the melting point. Bair *et al.*[12] observed that lightly irradiated single crystals did not thicken during melting, and melting occurred over a narrow temperature range of 3K. Only the data listed by Bair *et al.*[12] for the lightly irradiated single crystals were analysed by equation 2a, since their data were consistently different from that listed by others for single crystals prepared under identical conditions. The data were observed to fit the projected dependence of the melting points of the cyclic hydrocarbons, rather than that of the linear hydrocarbons. For similar stem thicknesses the melting points of the single crystals were substantially greater than those of the extended chain lamellae, and accordingly a clear distinction could be made between regular folded chain and extended chain crystals. Accordingly, this procedure was applied to the melting points listed[13-15] for melt crystallized polyethylene to determine the chain conformation at the surface of the crystalline-amorphous boundary.

The melting points for which stem thicknesses were

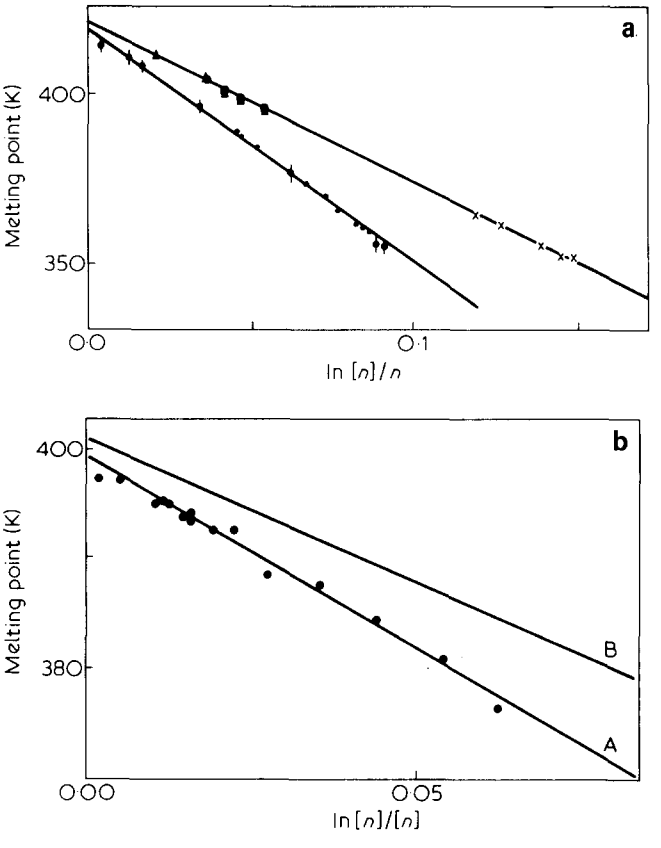

Figure 2 Melting point dependence on stem degree of polymerization, n. (a) n-Alkane, (●); polyethylene, (●); cyclic-Alkanes (X); polyethylene single crystals, (▲). (b) Melt crystallized polyethylene, (●); A–A n-alkanes; B–B cyclic-alkanes

available were included in the analysis, provided there was evidence that lamellar thickening was absent. This limited the data available to those melt crystallized lamellae prepared at low degrees of super-cooling and hence slow crystallization—conditions conducive to the production of the more regular crystalline structures. All the samples, so chosen, exhibited the same dependence as the extended chain model (see *Figure 2b*) and evidently were different from the regular folded chain.

The two different melting point dependences were also reflected in the molar heats of fusion, corrected to the standard temperature T_m^0, i.e. $\{\Delta h_n - n\Delta C_p \Delta T\}$. The molar heat of fusion of the single crystals, taking the molecular weight of the stem, increased linearly with the degree of polymerization, n, as required by equation (1), but while closely paralleling that observed for linear hydrocarbons, the intercept at $n=0$, corresponding to the molar heat of mixing of the surface layer Δh_e, was substantially lower (see *Table 1*). Accordingly, although the heat of fusion per

repeat unit was substantially the same in both cases, within the standard deviation, i.e. 4.2 ± 0.5 kJ mol^{-1}, end group effects and surface free energy were different. These alone account for the thermodynamic stability of the lamellar crystals.

Conclusion

The conclusion must be drawn from these melting studies that little or no chain folding with regular adjacent re-entry of the chain, as observed in the crystal structure of polyethylene single crystals and cyclic hydrocarbons, can be present in the lamellae produced in slow melt crystallization of polyethylene. Differences in the thermodynamic stability of the lamellar crystals arise from the lateral surface free energy and the stem length.

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Kerr effect relaxation measurements on glassy amorphous poly(methyl methacrylate)*

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Introduction

Optically and structurally isotropic materials can become birefringent under the influence of an electric field (Kerr effect). Between the steady state value of the birefringence Δn_0 and the intensity of the electric field E_0 the relation

$$\Delta n_0 = B \cdot \lambda \cdot E_0^2 \qquad (1)$$

almost always holds, where λ is the wavelength of the used light and B is the so-called Kerr constant. Theoretically it can be shown relatively easily, that B contains information on molecular electrical parameters such as dipole moments and anisotropies of electric, optical and hyperpolarizabilities[1]. Furthermore, in a system of coupled molecules the Kerr constant gives hints to orientation correlations. Therefore, for polymers information on chain conformation and interactions between the chains can be obtained[2].

The term 'static Kerr effect measurements' is used, only if the steady state value of the birefringence is considered. This value, however, will be obtained only after a certain time following a sudden application of the electric field (*Figure 1*). For 'dynamic Kerr effect measurements', the corresponding time function $\Delta n_R(t)$ as well as the function $\Delta n_D(t)$ which describes the decay of the birefringence after switching off the field are additional sources of information. The relaxation depends on the character of the reorientation process (e.g. rotational diffusion or large angle jumps) and the magnitude of the mobility of the molecules[3]. In the case of polymers, conclusions are possible on the conformational and reorientational dynamics of the chain as a whole and its subunits. The curves $\Delta n_D(t)$ and $\Delta n_R(t)$ can be calculated for different models of molecular rearrangement.

Based on these considerations and theoretical calculations many successful investigations on reorientational dynamics and molecular electrical parameters were car-

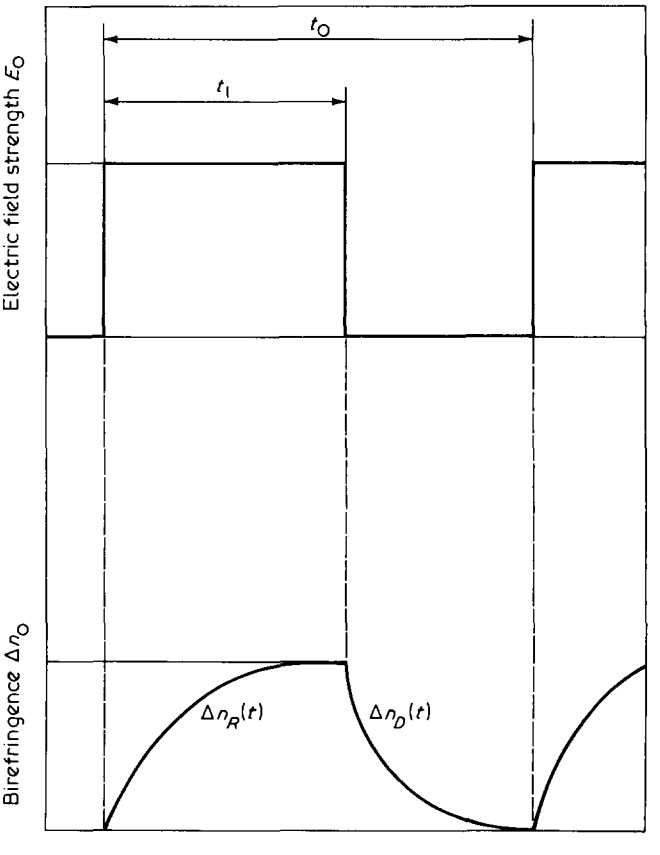

Figure 1 Schematic diagram of electric field and birefringence transients

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