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Interphase Thickness of Linear Polyethylene

L. MANDELKERN,* R. G. ALAMO, AND
M. A. KENNEDY

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306

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It was pointed out by Flory some years ago that for crystalline polymers the boundary between the ordered crystalline region and the disordered liquidlike region cannot be as sharp as in monomeric systems.[1,2] The continuity of a long-chain molecule imposes severe constraints on the transition between the perfect order of the crystalline region and the disorder of the isotropic, liquidlike state. A significant proportion of the flux of chains that emanate from the basal plane of the lamellar crystallite needs to be dissipated because of the severe conformational differences between the two states. This results in the return of some chains to the crystallite of origin but not necessarily in juxtaposition. Therefore, a diffuse boundary, or interphase, is formed. Recent theoretical calculations of model systems have given a more quantitative description of the interfacial structure.[3-8] The major factors that determine the structure and extent of the interphase are the free energy of making a fold or bend, the chain density at the crystallite surface, and the ratio of the cross-sectional area of a chain segment in the crystalline and liquidlike state. Kumar and Yoon estimated that for linear polyethylene the interfacial thickness should range from 10 to 30 Å.[8] A variety of experimental methods, such as broad-line proton[9] and high-resolution ^{13}C NMR,[10,11] electron microscopy,[12,13] small-angle neutron scattering,[14] dielectric relaxation,[15,16] and Raman spectroscopy,[17,18] have shown that a significant interfacial region exists in crystalline polymers. The difference in crystallinity levels between density and heat of fusion measurements is directly related to the interfacial content.[19] Therefore, a crystalline polymer is comprised of three major structured regions: the ordered crystalline region, the disordered, isotropic, interlamellar region, and the interfacial region. We report here the determination of the thickness of the interfacial region of linear polyethylene from analysis of the Raman internal and longitudinal acoustical (LAM) modes.

Experimental Section

Two series of linear polyethylene samples were used in this work. One was a set of molecular weight fractions and the other possessed most probable molecular weight distributions. The latter set were prepared following the method of Kaminsky et al.[20] using $(C_2H_5)_2ZrCl_2$ as catalyst. The highest molecular weight fraction, $M_\eta = 1.2 \times 10^6$, was prepared by the fractional crystallization from dilute solution of a high molecular weight whole polymer, $M_\eta = 8 \times 10^6$. The other fractions were obtained from the Societé National Elf Aquitaine and ranged in molecular weight from 1.05×10^4 to 9.11×10^5. All the samples were rapidly quenched into a saturated mixture of dry ice and 2-propanol. This crystallization process was deliberately adopted since it yields crystallites having a narrow thickness distribution.[21,22] Fraction 8.08×10^4 has been used in previous work and was crystallized at 118 °C for 2 and 20 min.[23] This crystallization procedure also resulted in a narrow crystal thickness distribution. Thus, in this report we are dealing with samples having narrow crystallite thickness distributions.

The crystallite core thickness was calculated from the analysis of the Raman LAM. The instrumentation and the method of analyzing the raw data have already been described in detail.[24,25] The crystalline content, α_c, the liquidlike fraction, α_a, and the interfacial content, α_b, were determined from the Raman internal modes using methods that have also been previously described.[18,26]

Results and Discussion

Since we are dealing with systems having narrow crystallite thickness distributions, we can identify the maximum value L_r in the LAM-determined ordered sequence distribution with the crystallite thickness $L_c = L_r \cos \theta$, where θ is the angle of inclination between the chain axis and the normal to the basal plane of the lamellar crystallite. Defining L_a as the thickness of the liquidlike region and L_b as the thickness of the interface that is associated with one of the crystallite basal planes, it follows that the crystalline fraction is given by

$$\alpha_c = \frac{L_c}{(L_a + 2L_b) + L_c} \qquad (1)$$

and the interfacial fraction by

$$\alpha_b = \frac{2L_b}{(L_a + 2L_b) + L_c} \qquad (2)$$

A corresponding relation will hold for α_a. The denominator in these equations represents the long period, as is conventionally obtained by either small-angle X-ray scattering or electron microscopy, and includes the statement that there are two interfaces per crystallite. Since α_a, α_c, α_b, and L_c are determined experimentally, the values of L_a and L_b can be calculated. The tilt angle θ has been taken to be 30°;[27] if a slightly higher tilt angle is used, the basic conclusions remain essentially unaltered.

The results for the linear polyethylene fractions crystallized by quenching to −78 °C are illustrated in Figure 1. The experimentally determined core crystallite thickness remains constant, at ~140 Å, as the molecular weight increases from 10^4 to 10^6. Concomitantly, over the same molecular weight range, the thickness of the disordered interlamellar layer increases from ~75 to 175 Å. These results are in accord with electron microscopy studies where it was found that for molecular weight fractions crystallized under similar conditions, the average crystallite thickness remained constant while the long period increased with chain length.[12] Similar results have recently been obtained by small-angle X-ray scattering.[28] The major interest of the present work is in the value of the interfacial thickness. L_b is found to be molecular weight dependent, and its values range from 14 Å at $M = 10^4$ to ~25 Å for $M = 10^6$. The interfacial thickness thus clearly makes a significant contribution to the total structure.

The same type of analysis can be made for the isothermally crystallized samples. The crystallization of fraction $M = 8.08 \times 10^4$ at 118 °C represents the lower temperature limit for isothermal crystallization, and crystallite thickening does not take place under these conditions. The ordered sequence length distribution, in this case, is centered at 237 Å and corresponds to a core crystallite thickness of 205 Å. From the values of α_c and α_b of 0.63 and 0.06, respectively, the interfacial thickness is found to be 10 Å. When the crystallization is allowed to take place for 20 min, the distribution of ordered sequence lengths is still relatively narrow but is now centered at 260 Å. From the α_c and α_b values of 0.65 and 0.10 the interfacial thickness is calculated to be 17 Å. The interfacial thicknesses of the isothermally crystallized fractions agree quite well with the quenched samples described in Figure 1. Thus an appreciable interfacial region also develops under isothermal crystallization conditions.

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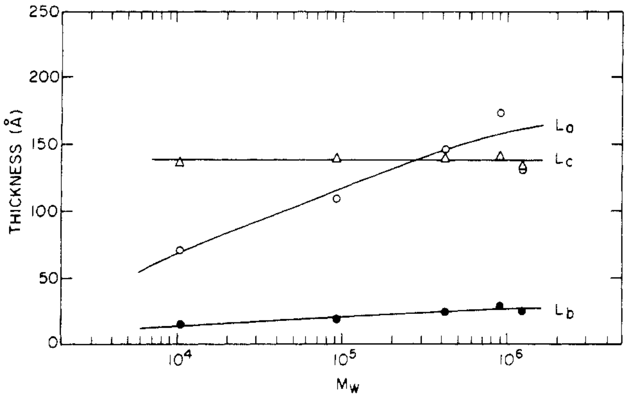

Figure 1. Plot of thickness values as a function of molecular weight for linear polyethylene fractions quenched to −78 °C: (△) crystallite core thickness L_c; (○) interlamellar thickness L_a; (●) interfacial thickness L_b.

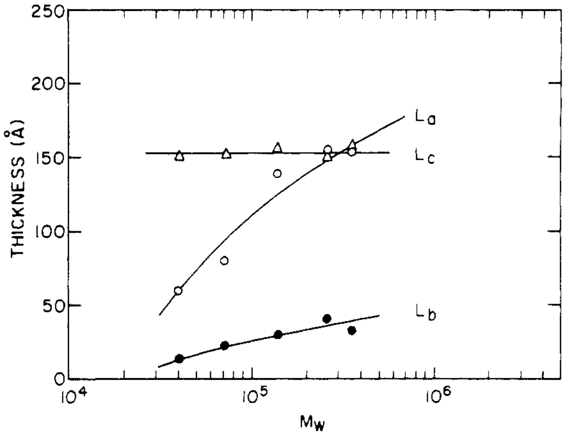

Figure 2. Plot of thickness values as a function of weight-average molecular weight for linear polyethylene samples having a most probable molecular weight distribution quenched to −78 °C: (△) crystallite core thickness L_c; (○) interlamellar thickness L_a; (●) interfacial thickness L_b.

The results for the quenched samples having most probable molecular weight distributions are given in Figure 2. The same general trend is found for the dependences of L_c, L_a, and L_b with molecular weight. The crystallite core thickness is invariant with molecular weight, while L_a and L_b monotonically increase with chain length. The interfacial thickness varied from 13 Å for $M_w = 4 \times 10^4$ to 33 Å for M_w = 351 000 and is again a significant part of the total structure. On close examination small differences can be found between the results of Figures 1 and 2. The core crystallite thickness of the samples having the most probable molecular weight distributions are ~10 Å greater than the fraction crystallized under comparable conditions. Although not directly pertinent to the present work, preliminary studies indicate that this difference can be attributed to altered crystallization kinetics.

The main conclusion from these results is that for crystallization from the pure melt there is a very significant molecular weight dependent interfacial region in linear polyethylene. The values of the interfacial thickness are in agreement with the theoretical expectations of 10–30 Å. Kinetic restraints to the crystallization process, which are known to be severe, have not been considered in these calculations, which are for an idealized, pseudoequilibrium structure.[19,29] Thus topological constraints such as entanglements as well as limited chain mobility have not been taken into account. These factors will become more severe as the molecular weight increases and this qualitatively explains the fact that L_b increases with chain length. The interfacial free energy associated with the basal plane of the mature lamellar crystallite increases with increasing chain length.[30] This result is consistent with the development of a thicker interfacial region. The theoretical considerations, as well as the experimental results reported here, require an irregularly structured interface for polyethylene which is incompatible with a set of regular folded chains.

Table I
Structural Parameters of Linear Polyethylene Fractions Crystallized from Dilute Solution

$M_w \times 10^{-4}$	T_c, °C	α_c	α_a	α_b	L_r	$L_c{}^{a,b}$	$L_b{}^b$	$L_a{}^b$
5.26	87	0.80	0.16	0.04	127	110	3	22
11.5	87	0.77	0.14	0.09	127	110	6	20
16.1	87	0.78	0.16	0.06	136	118	5	24
22.5	87	0.78	0.19	0.03	127	110	2	27
80.0	87	0.79	0.15	0.06	134	116	4	22
150.0	87	0.73	0.18	0.09	126	109	7	27
80.0	0	0.68	0.26	0.07	93	81	8	30

[a] Tilt angle taken as 30°. [b] Values in angstroms.

A similar analysis can be performed on crystals formed in dilute solutions, using data already existing in the literature.[26] The results are summarized in Table I. At a fixed crystallization temperature, T_c, the quantities L_c, L_a, and L_b are independent of molecular weight. The data in the last two columns of Table I contrast strongly with the results obtained for the bulk-crystallized fractions. L_b is ~5 Å, a value very similar to that deduced from a comparison of Raman LAM and small-angle X-ray scattering.[26] There is also a significant disordered overlayer, of ca. 20–25 Å, associated with these crystals.

The invariance of L_b with molecular weight and its reduced value relative to bulk-crystallized systems are striking features of crystals formed in dilute solution. The features can be explained by the reduced influence of topological restraints, as well as other kinetic factors, to the crystallization process in dilute systems. Molecular weight effects would also be expected to be minimal under these conditions. Consequently, the value of L_b is found to be close to that expected from the theoretical calculations for idealized systems.

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