Table II

Relative Concentration of Triads

| Sample no. | Polym cond MF, mol % | Conv, % | Relative concentration of triads $V$, % III | IIF | FII | FIF | IFI |
|---|---|---|---|---|---|---|---|
| A | 6.5 | 10 | 11.6 | 18.0 | 18.0 | 17.2 | 35.2 |
| B | 13 | 10 | 3.8 | 16.2 | 16.0 | 24.0 | 40.0 |
| C | 14 | 13 | 2.6 | 13.3 | 12.9 | 29.0 | 42.3 |
| D | 15 | 32 | 27.0 | 12.4 | 12.4 | 17.9 | 30.3 |
| E | 19 | 20 | 2.0 | 8.3 | 8.6 | 36.3 | 44.8 |
| F | 21 | 32 | 8.5 | 12.1 | 12.0 | 27.6 | 39.7 |
| G[a] | 19 | 13 | 7.8 | 10.3 | 9.9 | 30.9 | 41.1 |

[a] Sample G was polymerized at 0°, while others were polymerized at 25°.

composition ratios determined from an elemental analysis and from nmr data according to eq 21. Agreement is fairly good except for the sample A, in which isobutylene content estimated from nmr data is lower than that from elemental analysis. Probably this disagreement results from the terminal group effect, which cannot be negligible in the copolymer A. The copolymer A is greaselike, and its molecular weight is not so high because it was polymerized from a monomer mixture with an extremely high isobutylene concentration. In the proton spectrum of copolymer A the resonances appearing at 9.0 ppm and at higher fields, which are assigned to the terminal methyl groups, are stronger in intensity than in the spectra of the other copolymers.

Table III

Verification of Copolymer Equations

| Sample no. | $V_{\mathrm{IIFI}}/V_{\mathrm{FIFI}}$ | $V_{\mathrm{IIF}}/V_{\mathrm{FIF}}$ | $m_{\mathrm{I}}{}^{a}/m_{\mathrm{F}}$ | $m_{\mathrm{I}}{}^{b}/m_{\mathrm{F}}$ | $r_{\mathrm{IFI}}$ |
|---|---|---|---|---|---|
| A | 1.05 | 1.05 | 1.84 | 5.66 | 0.07 |
| B | 0.60 | 0.67 | 1.50 | 1.64 | 0.10 |
| C | 0.46 | 0.46 |  | 1.38 | 0.07 |
| D | 0.67 | 0.69 | 2.30 | 2.23 | 0.12 |
| E |  | 0.19 | 1.23 | 1.30 | 0.05 |
| F |  | 0.44 | 1.52 | 1.63 | 0.11 |
| G | 0.31 | 0.33 | 1.43 | 1.56 | 0.08 |

[a] Calculated from nmr data according to eq 21. [b] Determined from elemental analysis.

In Table III are given $r_{\mathrm{IFI}}$ values estimated from nmr data using eq 17. In principle it is possible to calculate values of $r_{\mathrm{III}}$ and $r_{\mathrm{FII}}$ from these data in accordance with eq 16, and the comparison of these values with $r_{\mathrm{IFI}}$ may lead to the order of the Markoff process by which the copolymerization reaction is expressed. It was, however, difficult to evaluate $r_{\mathrm{III}}$ and $r_{\mathrm{FII}}$ from the ratio $V_{\mathrm{III}}/V_{\mathrm{IIF}}$. One of the reasons is in the difficulty of the precise determination of $V_{\mathrm{III}}$, because trace amounts of isobutylene homopolymer may be included in the copolymer. Since a large amount of polyisobutylene is detected in the crude copolymer obtained at −78° as described previously, it may be suspected that a homopolymerization of isobutylene takes place simultaneously to some extent at 25° *via* a cationic mechanism. Further work is now in progress.

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# Thermodynamic Study of Fold Surfaces of Polyethylene Single Crystals

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ABSTRACT: Calorimetric data obtained on single crystals of polyethylene are analyzed to derive information on the nature of fold surfaces. From the magnitudes of surface enthalpy and entropy, it is estimated that a fold, on the average, would consist of 20 or more segments and thus a substantial layer of disorder exists at the surface of single crystals. The surface free energy value was determined by two methods: from the customary plot of melting temperature *vs.* reciprocal lamellar thickness and from the free energy of formation of crystals calculated from the observed values of specific heat. The results of these two methods agree well. The surface enthalpy value was determined from the plot of heat of fusion *vs.* reciprocal lamellar thickness. The assumptions underlying these procedures have been analyzed and the conditions for proper evaluation of thermodynamic quantities are stated and followed. In particular, some of the crystals were cross-linked lightly in order to suppress lamellar thickening during measurements.

## I. Introduction

The nature of the surfaces of folded-chain single crystals of polyethylene and other polymers has been the subject of intensive study in recent years. Despite many efforts, there still remain important questions. One of the main points of argument is concerned with the size of the folds, *i.e.*, the average number of segments that are participating in a fold. In this work we present new evidence on polyethylene single crystals, indicating that a fold would consist of 20 or more $CH_2$ units on the average. In other words, there appears to exist a substantial layer of disorder on the crystal surfaces amounting to an average depth of at least ten $CH_2$ units. This is obviously in conflict with the picture of arrays of tight, regular folds which have been favored by many during the past decade.

The evidence we present is obtained from calorimetric studies on polyethylene single crystals prepared under a variety of conditions. We examined melting points and apparent heats of fusion as a function of the lamellar thickness. In addition, specific heats have been measured through a range of temperatures on one of the samples. From analysis of these calorimetric data we determine the values of surface free energy and its enthalpy and entropy components. The magnitudes of surface enthalpy and entropy are surprisingly large. By comparing these with the enthalpy and entropy of fusion we are led to an estimate of the lower limit to the average number of segments in a fold.

## II. Thermodynamic Equations

The free-energy difference per segment between the crystal and the supercooled liquid is

$$\Delta F(T,\zeta) = F(T,\zeta) - F_a(T) \qquad (1)$$

where subscript a refers to amorphous liquid, and $\zeta$ is the average number of segments in a section of the polymer chain running between the two lamellar surfaces. If we designate the quantity pertaining to a large extended chain crystal by a superscript zero, as in $F^0(T) \equiv F(T, \infty)$, we then have

$$\Delta F(T,\zeta) = [F(T,\zeta) - F^0(T)] + \Delta F^0(T) \qquad (2)$$

Here $\Delta F^0(T)$, the free energy of formation of long extended chain crystals from melt, can be estimated approximately by expressions such as

$$\Delta F^0(T) = -\Delta H_u \frac{T_m^0 - T}{T_m^0} \qquad (3)$$

where $\Delta H_u = -\Delta H^0(T_m^0)$ is the heat of fusion per segment. The first term in (2), $F(T,\zeta) - F^0(T)$, represents the free-energy excess arising from the fact that the lamellar thickness is finite rather than infinite. The excess arises mostly from the perturbation at the fold surface, but may partly be contributed from internal defects or lattice distortions. As long as these latter effects originate from the propagation of strain from the fold surface, their contribution to the excess free energy would still be proportional to the surface area. We therefore write

$$F(T,\zeta) - F^0(T) \equiv 2\sigma_e(T)/\zeta \qquad (4)$$

where $\sigma_e(T)$ is the surface free energy per fold in the broader sense, including the small contributions from the surface-induced lattice defects, etc. (Note: A "fold" is here defined as the sequence of $CH_2$ units with both ends terminating at the crystalline lattice surface, and would thus occupy the area of two lattice sites.)

Experimentally, the free energy of formation of crystals from supercooled liquid, $\Delta F(T,\zeta)$, can be determined from the observed values of specific heat[1] (per segment) $C_p(T,\zeta)$ by

$$\Delta F(T,\zeta) = -\int_T^{T_R} [C_p(T',\zeta) - C_{p,a}(T')](1 - T/T')\mathrm{d}T' \qquad (5)$$

where $C_{p,a}(T)$ is the specific heat of supercooled liquid and $T_R$ is a reference temperature above the melting point. Obviously, for the calculation of $\Delta F(T,\zeta)$ by (5), the specific heat has to be determined under the experimental condition whereby $\zeta$ remains constant. Once $\Delta F(T,\zeta)$ is determined, the surface free energy $\sigma_e$ can be calculated from (2) and (4). The more usual,[2,3] alternate way of obtaining $\sigma_e$ is based on the fact that $\Delta F(T,\zeta)$ vanishes at the melting point $T_m^\zeta$, leading to

$$T_m^\zeta = T_m^0 - \frac{T_m^0 2\sigma_e(T_m^\zeta)}{\Delta H_u \zeta} \qquad (6)$$

We show later in the text that the values of $\sigma_e$ obtained by these two methods agree with each other satisfactorily.

Although the enthalpy $q_e$ and entropy component $s_e$ of $\sigma_e$ can, in principle, be calculated from the temperature dependence of $\sigma_e$, the experimental accuracy normally attainable does not warrant such a procedure. Instead, we have to look for a way of determining the surface enthalpy $q_e$ directly. For the average enthalpy difference per segment, $\Delta H(T,\zeta)$, between the crystal and the supercooled liquid, one can write equations paralleling those given for $\Delta F(T,\zeta)$. Thus

$$\Delta H(T,\zeta) = H(T,\zeta) - H_a(T) = [H(T,\zeta) - H^0(T)] + \Delta H^0(T) \qquad (7)$$

where

$$\Delta H^0(T) \equiv H^0(T) - H_a(T) \qquad (8)$$

The first term in (7), $H(T,\zeta) - H^0(T)$, is the excess of enthalpy per segment belonging to a crystal of finite thickness over the value for an extended-chain perfect crystal. In analogy to the reasoning given for the free energy excess one can write

$$2q_e(T)/\zeta = H(T,\zeta) - H^0(T) \qquad (9)$$

where $q_e(T)$ is the surface enthalpy per fold. When the temperature variation of enthalpies can be neglected, eq 7, 8, and 9 can be combined to the simplified expression[4]

$$\Delta Q = \Delta H_u - 2q_e/\zeta \qquad (10)$$

where $\Delta Q$ is the heat of fusion commonly measured with differential scanning calorimetry. The surface enthalpy $q_e$ is then given by the slope of the plot of $\Delta Q$ against $1/\zeta$.

## III. Experimental Section

Polyethylene single crystals (Marlex 6000, Type 50) used in this work can be divided into three groups according to the method of their preparation. Those in the first group were crystallized at 70, 77, 85, 90, and 95° from dilute xylene solution[5] (with a self-nucleation technique[6] at 95°). Those in the second group were crystallized at 84, 95, 100, and 105°

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(3) T. W. Huseby and H. E. Bair, *J. Appl. Phys.*, **39**, 4969 (1968).

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(5) H. E. Bair, T. W. Huseby, and R. Salovey, "Analytical Calorimetry," Plenum Press, New York, N. Y., 1968, p 31.

(6) D. J. Blundell, A. Keller, and A. J. Kovacs, *J. Polym. Sci., Part B*, **4**, 481 (1966).

Table I
Summary of Thermodynamic Data

| Sample no. | $T_c$, °C | Solvent | $l$, Å | $T_m$, °C | $\Delta Q$, cal/g |
|---|---|---|---|---|---|
| 1 | 70 | Xylene | 104 | 120.8 | 50.0 |
| 2 | 77 | Xylene | 111 | 121.3 | 50.0 |
| 3 | 85 | Xylene | 126 | 125.2 | 54.0 |
| 4 | 90 | Xylene | 145 | 127.4 | 59.0 |
| 5 | 95 | Xylene | 178 | 131.0 | 56.0 |
| 6 | (85)[a] | Xylene | 289 | 136.5 | 61.2 |
| 7 | 84 | Hexadecane | 111 | 120.7 | 45.0 |
| 8 | 95 | Hexadecane | 125 | 122.9 | 51.0 |
| 9 | 100 | Hexadecane | 130 | 125.7 | 52.6 |
| 10 | 105 | Hexadecane | 154 | 128.5 | 53.8 |

[a] Sample no. 6, crystallized at 85°, was subsequently annealed at 126 ± 1° for 190 hr.

from dilute hexadecane solution.[7] A crystal sample for the third group was obtained by first crystallizing at 85° from dilute xylene solution and then annealing at 126 ± 1° for 190 hr. The lamellar thickness $l$ (in ångströms) was determined from the spacing of the diffraction peak in the low angle X-ray photographs, and is listed in Table I.

The experimental details for the measurement of melting temperatures[5] and heats of fusion[7] are described elsewhere. For one sample (crystallized at 105° from hexadecane solution), the specific heat was measured much more carefully from 100° to above $T_m$. The calorimeter was calibrated for this purpose with a sapphire crystal standard supplied by the National Bureau of Standards. The thermodynamic analysis given in the previous section was based on the premise that the lamellar thickness $\zeta$ is an independent variable specifying the system. In accordance with such an analysis, our measurements were all performed under conditions in which $\zeta$ was kept constant during the run. For crystals with $l$ larger than 150 Å (samples 5, 6, and 10) the rate of lamellar thickening was slow enough not to require any special device during the calorimetric run with a 10°/min heating rate. Crystals with $l$ smaller than 150 Å were lightly cross-linked with electron irradiation. It was demonstrated previously[5] that such light cross-linking was sufficient to suppress the lamellar reorganization completely that would otherwise have occurred extensively during the run at a heating rate of 10°/min. The evidence presented there[5] well supports the contention that such cross-linking affects, if ever, the thermodynamic values obtained to an extent which is entirely within the experimental error.

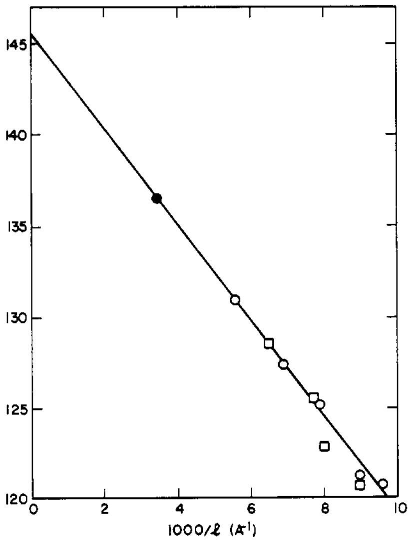

Figure 1. Melting temperatures of polyethylene single crystals as a function of reciprocal lamellar thickness: ○, crystals prepared from dilute xylene solution (●, subsequently annealed for 190 hr at 126°); □, crystals prepared from dilute hexadecane solution.

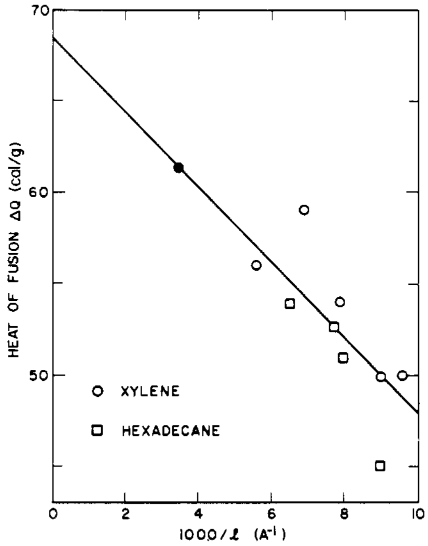

Figure 2. Apparent heat of fusion $\Delta Q$ of polyethylene single crystals as a function of reciprocal lamellar thickness. *Cf.* Figure 1 for the symbols.

## IV. Results and Discussion

In Figure 1 the melting points are plotted against the reciprocal of the crystal thickness $l$ observed with low-angle X-ray. Similarly, in Figure 2 the heats of fusion are plotted against $1/l$. Good linear relations are obtained in both instances. The intercept in Figure 1 coincides well with the theoretical melting point $T_m^0$ of 145° estimated by Flory and Vrij[8] and Broadhurst.[9] Similar y, the heat of fusion extrapolates at $1/l = 0$ to a value of 68 ± 1 cal/g which agrees well with the value of 960 cal/mol (or 68.6 cal/g) for $\Delta H_u$ obtained by polymer–diluent mixture studies.[10] From the slopes of the plots, we obtain the value of 4.7 ± 0.3 kcal/mol of folds (89 ± 5 erg/cm$^2$) for the surface free energy $\sigma_e$, and the value of 22.1 ± 2.0 kcal/mol of folds (420 ± 40 erg/cm$^2$) for the surface enthalpy $q_e$. From these two, the value of surface entropy $s_e$ is calculated to be 39 ± 5 eu/mol of fold (0.83 ± 0.10 erg/cm$^2$ deg) at $T = 400°$K.

We note here that the linear relations in Figures 1 and 2 are obtained with all the crystals differing in the method of preparation and thermal history. The heat of fusion data reported by Mandelkern and others,[4] which were obtained with solution crystallized samples of polyethylene fractions, would fall also on the straight line drawn in Figure 2. (There is another set of heat of fusion data available in the literature, *i.e.*, those given

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(7) H. E. Bair, R. Salovey, and T. W. Huseby, *Bull. Amer. Phys. Soc.*, **14**, 364 (1969).

(8) P. J. Flory and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).

(9) M. G. Broadhurst, *J. Res. Nat. Bur. Stand., Sect. A*, **70**, 481 (1966).

(10) L. Mandelkern, *Rubber Chem. Technol.*, **32**, 1392 (1959).

by Fischer and Hinrichsen.[11] For some reason, their data do not seem to correlate well with each other among themselves. We have not, therefore, attempted to make any useful comparison of their data with ours, although, if plotted in Figure 2, theirs would lie, in general, above the straight line shown.) Especially noteworthy here is the point (solid circle) in Figure 2 which was obtained with annealed crystals. This indicates that although the prolonged annealing increased the thickness from 126 to 289 Å, the structure of the fold surface remained essentially unchanged. If smoothing of fold surfaces occurred by annealing, the value of heat of fusion of annealed crystals would have been higher than expected and risen above the straight line drawn in Figure 2. From consideration of kinetics of crystallization, Lauritzen and Passaglia[12] earlier postulated that the roughness of the fold surface increases as the crystallization temperature is lowered. From this, Hoffman, *et al.*,[13] concluded that the effective surface free energy of such crystals would be much larger than the value one obtains from the melting point data because of the possible smoothing of the rough surfaces during heating prior to melting. Our data noted above, however, do not support such a contention.

The values of the specific heat determined for the crystals grown at 105° from dilute hexadecane solution are plotted in Figure 3. The melting is surprisingly sharp for polymer crystals: about 90% of the melting occurs within a 3-deg interval. From the values of $C_p$, as given in Figure 3 (and the values of $C_{p,a}$ for the supercooled liquid in the literature[1]), we calculated the free energy of formation of crystals, $\Delta F(T,\zeta)$, according to eq 5, and the result is shown in Figure 4. Except in the melting range encompassing a few degrees just below $T_m$, the plot of $\Delta F(T,\zeta)$ *vs.* $T$ follows a straight line very closely. Also shown in Figure 4 are the values of $\Delta F^0(T)$ calculated from eq 3. The difference between $\Delta F(T,\zeta)$ and $\Delta F^0(T)$, multiplied by $\zeta$ (which for this sample is equal to 121), gives the value of $\sigma_e$. The value of $\sigma_e$, thus determined, remains approximately constant at 5.2 kcal/mol through the temperature range studied up to a few degrees below $T_m$. With the onset of major melting a gradual reduction in $\sigma_e$ is noted, until at $T_m$ the value has decreased to 4.7 kcal/mol. This latter value is the one that is usually determined from the plot of $T_m^\zeta$ *vs.* $1/\zeta$. The larger value of 5.2 cal/mol is more appropriate to crystals prevailing before the onset of major melting; however, the difference is not very much larger than the experimental error, and would not justify a fine distinction between them. Again, the approximate constancy of $\sigma_e$ observed below $T_m$ is in apparent contradiction to the large surface entropy $s_e$ previously deduced. However, the value of 39 eu/mol for $s_e$ can be accommodated by a change in the slope of $\Delta F(T,\zeta)$ *vs.* $T$ in Figure 4 by about 10%, which is probably still within the experimental error. Finally, the decrease in $\sigma_e$ near $T_m$ probably reflects the gradual thickening of the disordered surface layer which we have shown[14] to occur from theoretical consideration of a random walk model of the folds.

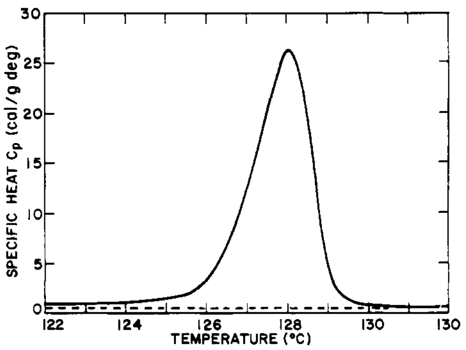

Figure 3. The solid line gives the specific heat observed for polyethylene single crystals prepared at 105° from dilute hexadecane solution plotted as a function of temperature. The broken line represents the specific heat of supercooled melt of polyethylene.

The magnitudes of surface enthalpy and entropy obtained above are unexpectedly large and can be reconciled only by assuming that a large number of segments, of the order of 20 on an average, are involved in a fold. We here attempt to estimate the size of fold first by analyzing the value of 22.1 kcal/mol for $q_e$. We take the value of heat of fusion $\Delta H_u$ = 0.96 kcal/mol of segments as the reference point. One can consider the value of $\Delta H_u$ as consisting of two parts, one associated with conformational change of the molecule on melting and the other associated with the increase in interatomic distances accompanying volume expansion. Since about 40% of the carbon bonds are *gauche* in the liquid state,[15] and all are *trans* in the crystal, the enthalpy difference due to the conformational change amounts to about 0.2 kcal/mol of $CH_2$ if the energy difference between the two rotational states is taken as 0.5 kcal/mol. The rest of the heat of fusion, *i.e.*, 0.76 kcal/mol, would then be considered as arising from the

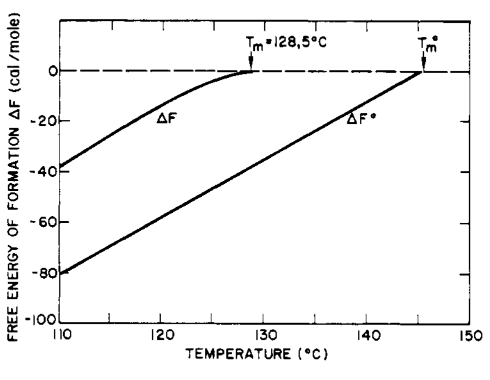

Figure 4. The upper solid line plots the free energy of formation from supercooled melt, $\Delta F(T, \zeta)$, of polyethylene single crystals prepared at 105° from dilute hexadecane solution ($\zeta$ = 121), calculated from the specific heat data shown in Figure 3. The lower solid line is the free energy of formation $\Delta F^0(T)$ of a large extended-chain crystal, calculated from eq 3. The difference between $\Delta F$ and $\Delta F^0$, multiplied by $\zeta$, gives the surface free energy $\sigma_e$.

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(15) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience Publishers, New York, N. Y., 1969.

decrease in intermolecular interaction. The quantity of interest is now the average gain in enthalpy per segment, $\Delta H_f$, when a segment is transferred from the interior of a crystal to a fold. We will estimate the upper limit to $\Delta H_f$. Since the proportion of *gauche* bonds in the fold would be in general larger than in liquid, we assign 0.5 kcal/mol as the maximum possible contribution to $\Delta H_f$ arising from the conformational change. Second, we would expect the packing of segments in the fold retains remnants of order carried over from the interior of the crystal, or in other words, the specific volume available per segment of the fold would be somewhat smaller than that in liquid. Still, we assign 0.76 kcal/mol as the maximum possible contribution to $\Delta H_f$ from the volume expansion on going from the lattice to the surface. The upper limit to $\Delta H_f$ is thus estimated to be 1.26 kcal/mol of segments. Dividing the value of $q_e$ with $\Delta H_f$, we find then that the lower limit to the average number of segments per fold is 18 segments.

Next we consider the observed value of the surface entropy $s_e$. In order to estimate the upper limit to the entropy excess $\Delta S_f$ per segment of a fold over that of the interior segment, we again compare it with the entropy of fusion $\Delta S_u$. Starkweather and Boyd[16] have shown that, of the value of 2.3 eu/mol observed for $\Delta S_u$, 0.5 eu/mol is associated with the increase in volume on melting and the remaining 1.8 eu/mol with the increased degree of conformational freedom available to polymer molecules in liquid. As stated above, we expect that the volume available to a segment of a fold would be smaller than that for an amorphous segment. We will nevertheless assign 0.5 eu/mol as the upper limit to the component of $\Delta S_f$ contributed by the increase in specific volume. The conformational degrees of freedom available to segments in the fold is again much smaller than that in liquid because[14] the two ends of the fold are fixed and the space occupied by crystalline lattices is not available for access. Thus, 1.8 eu/mol would be a generous upper limit to the conformational component of $\Delta S_f$. We thus estimate the upper limit to $\Delta S_f$ to be 2.3 eu/mol of segments and by dividing the value of surface entropy $s_e$ with it we find a fold to consist of at least 17 $CH_2$ segments.

The analysis of surface enthalpy and entropy both lead to the conclusion that a fold consists of around 20 segments in the least. The upper limits to $\Delta H_f$ and $\Delta S_f$ we estimated are, we believe, very generous, so that the number of segments per fold could actually be considerably larger than 20. Such a conclusion is in agreement with those derived by Fischer and Schmidt[17] on the basis of density measurement and by Peterlin and Meinel[18] from the results of nitric acid digestion of single crystals. The number of 20 or more segments we estimate is the average value. Earlier, from consideration of a random flight on lattices as a model for the fold, we calculated[14] that the distribution of fold sizes has to be very broad. In conjunction with the above result, we would then visualize the fold surface to be made up of a large number of fairly short, tight folds which are interspersed with a much smaller number of long, winding folds; the proportions of long and short folds are such that on the average the disordered layers at both surfaces of single crystals are about ten segments or more deep. We note that a picture very similar to the above had been proposed by Flory[19] some time ago and by Peterlin[20] more recently.

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# Surface Activity of Polystyrene–Polysiloxane–Polystyrene ABA Block Copolymers

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ABSTRACT: The surface activity of a series of ABA polystyrene–polysiloxane–polystyrene block copolymers of different compositions has been investigated by measuring the surface tension of their solutions in styrene and their effect on the critical surface tension of wetting of polystyrene. The results suggest a model for the copolymer in the solvent surface where the cross-sectional area of the copolymer is determined by the packing together of distorted A segments.

Although the last few years have seen a renewal of interest in the surface tensions of liquid polymers and of polymer solutions, very little is known about block copolymers in this context. This is surprising, for the solution properties of block copolymers are also receiving considerable attention, and many of the results are consistent with the different polymer subchains occupying different domains of the polymer–solvent mixture. For copolymers whose different subchains have different surface energy contributions this should result in a concentration of the more surface active segments in the surface. Such behavior is evident with poly(ethylene oxide)–poly(propylene oxide) block copolymers,[1,2] and with poly(alkylene

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