

Thermodynamics of dissolution temperatures in polyethylene wax/n-alkane mixtures*

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The treatment of folded-chain crystals as frozen-in inhomogeneous microphases has been proven to be an adequate model for interpreting crystallization in polyethylene wax with a broad chain-length distribution where a prominent fraction of chains of sufficient length undergo folded-chain crystallization. The thermodynamics of coexistence of folded-chain crystals with a multicomponent melt is developed. With the aid of this approach the liquidus ('dissolution temperature') of polyethylene wax (PE130)/n-alkane solutions is consistently described in terms of a quasi-binary model. For n-decane/PE130 solutions a mixing gap with an upper critical point lies just below the liquidus. The role of interchain entanglements is discussed.

(Keywords: thermodynamics; dissolution temperature; polyethylene wax; folded-chain crystals)

INTRODUCTION

It has been discussed elsewhere that folded-chain crystals (FCs) in polymers should be considered as microphases when longitudinal growth in the direction of the chain axis lattice cores is restricted¹⁻⁸. Every FC comprises chain segments and chains of different length, which are linked together in the microphase. Chains do not undergo lateral diffusion within FCs. Chain segments do not continuously exchange with those of the surrounding melt. Hence, the configuration of the chains of different length is clamped by FCs in the sense of Fischer's freezing model⁹.

FCs must be treated thermodynamically as frozen inhomogeneous microphases¹. Coexistence of these microphases with a multicomponent melt seems to be possible¹⁰. This suggestion is critically proven in this paper by studying the dissolution temperatures of polyethylene wax (PE130)/solvent mixtures. These temperatures will be described with the aid of thermodynamic relations, the derivation of which includes a clear definition of a folded-chain crystal as a 'growth-restricted and frozen mixed microphase'.

THERMODYNAMICS

The general situation

We consider a wax comprised of linear chains that are distributed in a broad chain-length distribution so as to cover the range of oligomers and polymers. A prominent fraction of long polymer chains undergo folded-chain crystallization while the complementary fraction of shorter chains form chain-extended mixed crystals. To seek a description of dissolution temperatures of PE130/solvent mixtures, we have to understand coexistence of FCs with a multicomponent solution.

* Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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Folded-chain crystals

The mean thickness of a folded-chain crystal is described by the fold height y_f , expressed as the number of repeat units, which in polyethylene is the number of CH_2 groups. Defect front layers come into existence as lattice-incompatible, 'quasi-permanent' conformational defects are segregated. The folded-chain lamella is, nevertheless, a cooperative unit. Including the defect layers, the folded-chain lamella represents an inhomogeneous microphase (Figure 1)^{1,11}. Owing to the presence of fold loops or entanglements, the structure in the defect layers is similar to the melt¹². The thickness of the front layers is adjusted to minimize the free energy in the whole FC. As proposed by Fischer⁸, 'surface melting' at constant fold height is therefore induced during heating. Skeletal units pass into the boundaries at the expense of the lattice core. When the internal state is characterized by the enthalpy $h^{(i)}$ and the entropy $s^{(i)}$, the condition of internal equilibrium reads:

$$(\partial h^{(i)}/\partial T)_{p,y_f} = T(\partial s^{(i)}/\partial T)_{p,y_f} \quad (1)$$

In this way, the thermal stability of folded-chain crystals is not affected. The melting temperature of a microphase of fold height y_f is therefore correctly defined by¹:

$$T_{mf} = T_m \left(1 - \frac{2\sigma_e + \alpha}{\Delta h_0 y_f} \right) \quad (2)$$

where T_m is the asymptotic melting temperature of a chain-extended crystal comprising chains of 'infinite length'; $2\sigma_e$ is the molar free surface energy in the longitudinal interlayers; α is related to the excess free energies of conformational defects located in the defect layers; and $\Delta h_0 = \Delta h(T_m)$ is the molar melting enthalpy per repeat unit at T_m . It is found that $2\sigma_e/\Delta h_0$ is constant since $2\sigma_e(T)$ seems to display the same dependence on temperature as the melting enthalpy.

According to Fischer's conformational freezing model⁹, the configuration of chains of different lengths should not be changed during folded-chain crystallization. Each

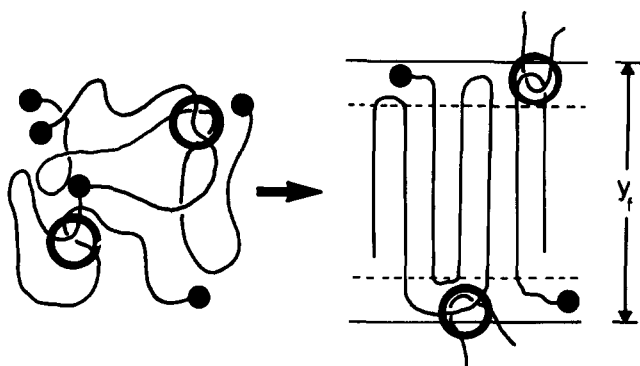


Figure 1 Two-dimensional sketch of a folded-chain lamella, its 'inhomogeneous structure' being due to the existence of longitudinal defect layers

folded-chain crystal include chain segments, and under some circumstances whole molecules are built in the same FC. For formulating coexistence of an FC with a multicomponent melt we assume that each FC represents a mixed microphase characterized by a well defined mean chain length y . This chain length should be identical with the mean chain length in that fraction which participates in folded-chain crystallization.

The dissolution temperatures of eutectoid oligomer-polymer

We are now ready to derive the thermodynamic equations of the liquidus of PE130/solvent mixtures. To that end, let us first recall the description of the maximum melting temperature in a eutectoid multicomponent system with extended-chain mixed crystals (MECs) only.

According to the thermodynamics of eutectoid oligomers or polymers, MECs are formed by segregating chains of different lengths in lamellar-shaped mixed microphases (Figure 2). The maximum disparity of chain lengths in a MEC was shown to be given by^{11,13}:

$$(3) \quad \Delta y = Ay \quad 0.2 \leq A \leq 0.3$$

where y is identical with the mean length of chains built into the MEC. A is a constant, which characterizes the limit of compatibility in solid solutions, covering the range as indicated. A broad thickness distribution of MECs is therefore formed in PE130. Because melting and crystallization run consecutively with regard to the thickness of MECs, the liquidus describes the melting of just the thickest MECs. In the case of a broad molecular-weight distribution the mass fraction of these MECs is so small that it is a good approximation to set the concentration in the melt equal to that in the uncrystallized solution. The liquidus temperature (being identical with the so-called 'dissolution temperature'), T_{my} , is then written as^{14,15}:

$$T_{my} = T_m \left(1 - \frac{2\sigma_e}{\Delta h_0 y^*} \right) / N_1 \quad y^* = (1 - A/3)y \quad (4)$$

with

$$N_1 = 1 + \frac{RT_m}{\Delta h y^*} \left(\ln \frac{2y}{\Delta y + 2} - \ln \frac{x_y^m}{x_y^c} - \ln \frac{y}{\langle y \rangle_{pl}} - 1 + \frac{y}{\langle y \rangle_{pl}} - \frac{1}{2}(y-1)\chi_{pp}(1-\phi^2) + y\chi_{pl}\phi^2 \right) \quad (5)$$

Here R is the gas constant; Δh is the molar melting enthalpy per repeat unit, which depends on temperature according to:

$$\Delta h = \Delta h_0 - \Delta C(T_m - T_{my}) \quad (6)$$

with ΔC being the difference of the molar heat capacities in the melt and in the crystal lattice respectively. The mole fraction of the chains of length y in the melt is defined by:

$$x_y^m = \frac{\Phi(y)}{2} (1 - x_1) \quad (7)$$

where $\Phi(y)$ gives the molar chain-length distribution in the oligomer-polymer system. It is assumed that at the coexistence temperature T_{my} , just half of the total number $\Phi(y)$ of chains of length y is built in MECs. Dilution by a solvent is described by the factor in the brackets on the right-hand side of equation (7), the mole fraction of the solvent, written as:

$$x_1 = n_1 / (n_p + n_1) \quad (8)$$

with n_1 as the mole number of solvent molecules; n_p gives the total number of oligomer and polymer chains:

$$\sum n_y = n_p \quad (9)$$

By introducing the volume fraction of the solvent molecules of size y_1 :

$$\phi = \frac{n_1 y_1}{n_p \langle y \rangle_p + n_1 y_1} \quad (10)$$

x_1 can be rewritten as:

$$x_1 = \phi \langle y \rangle_{pl} / y_1 \quad (11)$$

If the size parameter of the solvent molecules, y_1 , is related to the size of the repeat unit of the oligomer-polymer components (in PE130 the CH_2 unit), the mean size in the solution reads:

$$\langle y \rangle_{pl} = [(1 - \phi) / \langle y \rangle_p + \phi / y_1]^{-1} \quad (12)$$

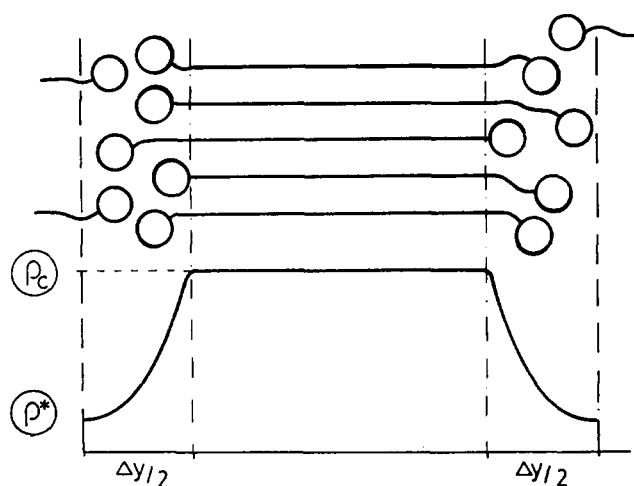


Figure 2 Model of an extended-chain mixed crystal characterized by the mean chain length y and a maximum disparity in chain length $\Delta y = Ay$ ($A = 0.3$). Chain ends are squeezed into longitudinal defect layers of mean thickness $\Delta y / 2$. The degree of order within these layers is reduced, substantially lowering the density²⁷ (ρ_c is the density in the crystal lattice, ρ^* the minimum density in the layers)

where the mean chain length in PE130 is defined by:

$$\langle y \rangle_p = \frac{\sum_{y_i}^{y_m} y \Phi(y)}{\sum_{y_i}^{y_m} \Phi(y)} \quad (13)$$

and y_i and y_m are the minimum and maximum chain lengths in the chain-length distribution of PE130. In (5) χ_{pp} and χ_{pl} are the Flory–Huggins parameters of the polymer–polymer and polymer–solvent interactions related to the CH_2 group.

The mole fraction of the chains of length y in the MEC of mean thickness y is equal to:

$$x_y^c = \Phi(y) \left/ \sum_{y' = y - \Delta y/2}^{y + \Delta y/2} \Phi(y') \right. \quad (14)$$

From the equations given, one recognizes that the solvent is *de facto* described in terms of a quasi-binary mixture.

Dissolution temperatures of folded-chain crystals in coexistence with a multicomponent melt

We now proceed to consider coexistence of FCs with a multicomponent melt. It is expected that the fraction of long chains which participate in folded-chain crystallization is segregated as a whole complex which undergoes crystallization without showing fractionation of chains of different lengths. The complementary fraction of shorter chains is fully squeezed out of the folded-chain regions. When the last FCs melt at the liquidus temperature, the above segregation will be reversed so as to recover the homogeneous solution. In these circumstances, the liquidus of the folded-chain crystals is obtained by replacing the ‘Thomson term’ $T_m(1 - 2\sigma_e/\Delta h_0 y)$ in equation (4) by $T_m[1 - (2\sigma_e + \alpha)/\Delta h_0 y_f]$ and by reformulating the mole fraction of the chains of length y within the FCs:

$$T_{mf} = T_m[1 - (2\sigma_e + \alpha)/\Delta h_0 y_f]/N_f \quad (15)$$

where

$$N_f = 1 + \frac{RT_m}{\Delta h_0 y} \left(\ln \frac{2y}{\Delta y_f + 2} - \ln \frac{x_y^m}{x_{yf}^c} - \ln \frac{y}{\langle y \rangle_{pl}} - 1 + \frac{y}{\langle y \rangle_{pl}} - (y-1)\chi_{pp}(1-\phi^2)/2 - y\chi_{pl}\phi^2 \right) \quad (16)$$

$$x_{yf}^c = \Phi(y) \left/ \sum_{y' = y - \Delta y/2}^{y + \Delta y/2} \Phi(y') \right. \quad (17)$$

Here Δy_f defines the width of the chain-length distribution which is considered to be built into the FC; y describes the mean chain length within that fraction of chains which participate in folded-chain crystallization.

RESULTS AND DISCUSSION

The chain-length distribution of PE130

The chain-length distribution of PE130 (Höchst Co.), having a mean chain length of $\langle y \rangle_p = 130 \text{ CH}_2$ units, was deduced from gel permeation chromatography and from a computer analysis of calorimetric measurements of a sample crystallized under high pressure^{4,16}. The results shown in Figure 3 agree within the limits of confidence. Gel permeation is known often not to be very exact in the range of long chains. The empirical distribution

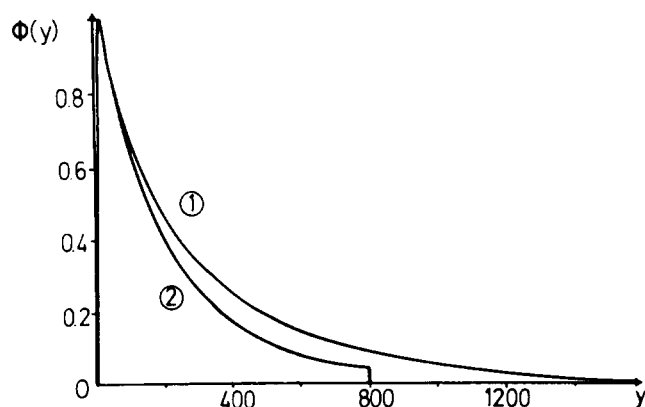


Figure 3 The chain-length distribution of PE130 deduced (1) by gel permeation chromatography and (2) from an analysis of d.s.c. melting curves of a high-pressure crystallized sample. The chain-length parameter is the number of skeleton C atoms. $\Phi(y)$ is the number distribution function given in arbitrary units

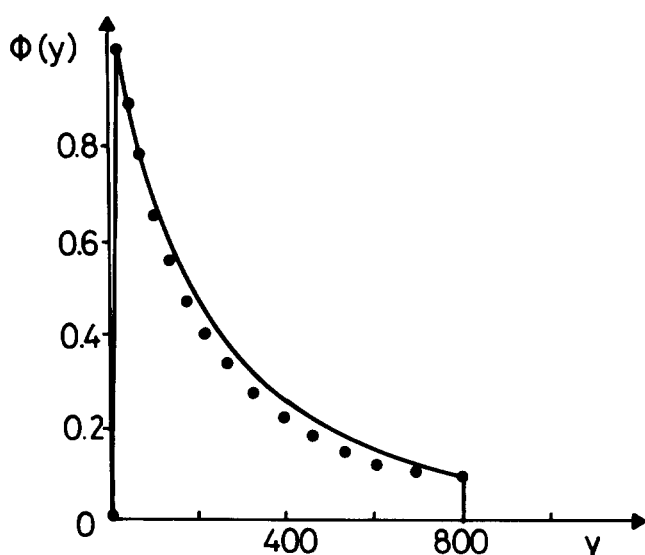


Figure 4 Chain-length distribution of PE130 according to gel permeation chromatography measurements (—) and its representation by the use of equation (18) (·····)

function:

$$\Phi(y) = \frac{A_1}{(A_2 + y)^n} \quad A_1 = 372, A_2 = 100, n = 1.2 \quad (18)$$

reproduces the experimental data fairly well (Figure 4).

The liquidus measured for solvents of different size, y_1 , are depicted in Figure 5. The full curves are calculated with the aid of equation (15) by introducing the parameters listed in Table 1. Extended-chain crystallization is limited to the range of chain lengths $y < y_f^* = 180 \text{ CH}_2$ units, so that chains in the range 180 CH_2 units $= y_f^* \leq y \leq y_{\max} = 800 \text{ CH}_2$ units only crystallize by chain folding. The disparity in chain lengths within FCs, Δy_f , thus covers a range of about 620 CH_2 units. In the calculations presented here, the parameter y_f^* was set to be always equal to $y_f = 180 \text{ CH}_2$ units.

Consequences

It is evident that folded-chain crystals with fold height $y_{f,\max}$ suffer a melting point depression which is uniquely related to the thermodynamic properties of the melt and the folded-chain crystals. The depression is reduced with

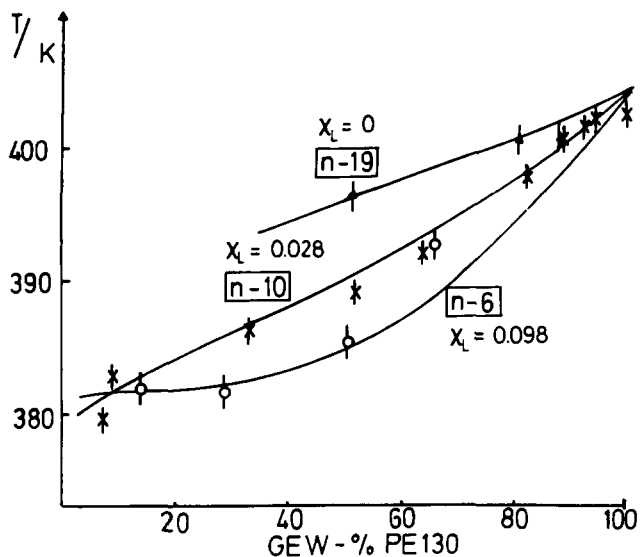


Figure 5 The dissolution temperatures ('liquidus') of PE130/n-alkane mixtures as a function of the weight fraction of the wax. The full curves are computed with the aid of equation (15) by using the parameters collected in Table 1. The size of the solvent molecules is indicated with each liquidus

Table 1 Parameters used in the calculation of the liquidus

$T_m = 415 \text{ K}$
$\Delta h_0 = 970 \text{ cal (mol CH}_2 \text{ unit)}^{-1}$
$\Delta C = 1.4 \text{ cal K}^{-1} \text{ (mol CH}_2 \text{ unit)}^{-1}$
$2\sigma_e/\Delta h_0 = 2.15$
$\langle y \rangle_p = 130 \text{ CH}_2 \text{ units}$
$A = 0.3$
$y_f = 180 \text{ CH}_2 \text{ units}$
$\Delta y_f = 620$
$2\sigma_e + \alpha = 5000 \text{ cal (mol CH}_2 \text{ unit)}^{-1}$
$y_{f,\max} = 350 \text{ CH}_2 \text{ units (maximum thickness of FCs that melt at the liquidus temperature)}$
$\chi_{pp} = 0.015$
$\chi_{pl}(\text{hexane}) = 0.098$
$\chi_{pl}(\text{decane}) = 0.028$
$\chi_{pl}(\text{nonadecane}) = 0$

growing mean size of the solvent molecules. The dependence of the size of the n-alkane solvent molecules follows exactly that predicted by the thermodynamics of the eutectoid multicomponent systems. This includes an assumption that the last FCs as 'frozen mixed microphases' should have approximately the same intrinsic properties.

To make a quantitative fit of the calculations to the data, one has to adjust the interaction parameter χ_{pl} . According to the data listed in Table 1 χ_{pl} increases with decreasing length of the n-alkanes. Decreasing compatibility is indicated with an enhanced sigmoidal bending of the liquidus (Figure 5). In highly diluted solutions the slope of the liquidus at the point of inflection becomes nearly zero.

It turns out that thermodynamic equilibrium in the multicomponent melt is rapidly adjusted so as to make our thermodynamic description so effective. The special properties of FCs are accounted for by introducing the fold-height parameter y_f and the excess parameter α . What is not straightforwardly understandable is that the calculations were successfully done by using an invariant fold-height parameter, $y_{f,\max}$. This leads to the curious consequence that kinetics of folded-chain crystallization should not be altered in highly diluted solutions. We shall come back to this problem later.

Critical phenomena

When the mixing gap lies above the liquidus one observes a strictly horizontal section in the liquidus which is limited by the two points where the bimodal and liquidus intersect (Figure 6)^{13,17,18}. Hence, from the liquidus observed for PE130/n-hexane solutions it is suggested that demixing should happen just below the liquidus (Figure 7).

To find the bimodal, we deduce the critical parameters of the quasi-bimodal solution. The critical volume fraction is given by¹⁹:

$$\phi^{cr} = [1 + (y_f/\langle y \rangle_p)^{1/2}]^{-1} \quad (19)$$

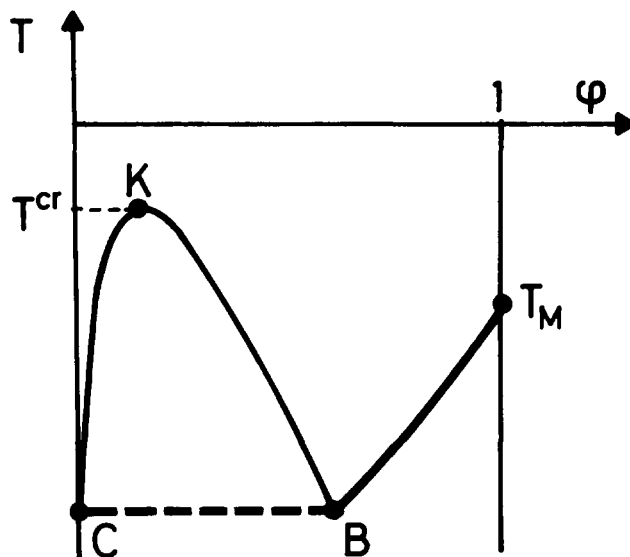


Figure 6 Sketch of an isobaric state diagram of a polymer solution with an upper critical point K at the temperature T^{cr} . According to the mixing gap in the melt the liquidus should show a horizontal section CB representing the tie line of the coexisting phases^{15,16}

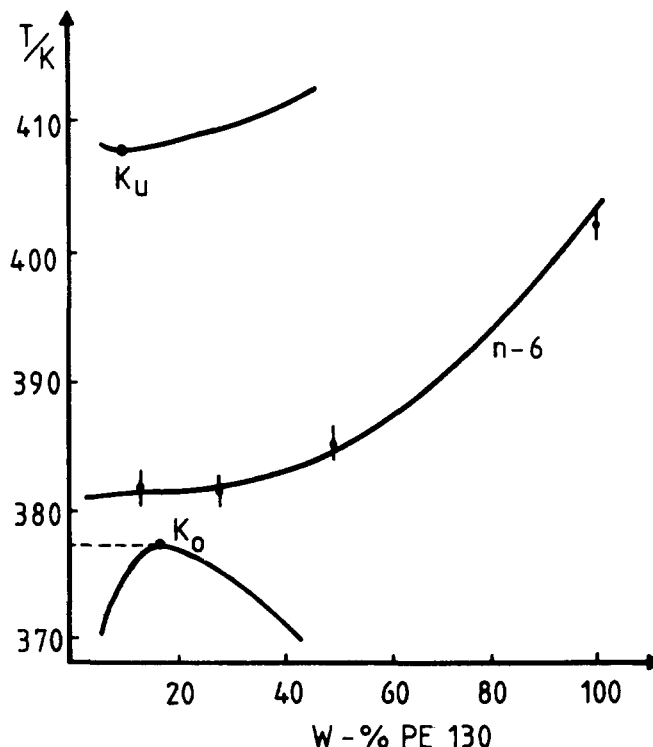


Figure 7 The isobaric state diagram of PE130/n-hexane mixtures showing mixing gaps with a lower (K_u) and an upper critical point K_o just below the liquidus (see also ref. 21)

while the critical temperature is given by:

$$T^{cr} = \frac{\chi_{pl}^h}{\chi_{pl}^{cr} + \chi_{pl}^s} \quad (20)$$

where χ^{cr} is the critical Huggins parameter; χ_{pl}^h and χ_{pl}^s are the enthalpy and entropy components of the Flory-Huggins parameter χ_{pl} defined according to:

$$\chi_{pl} = (\chi_{pl}^h)/T - \chi_{pl}^s \quad (21)$$

For PE130/hexane solutions the theta-temperature Θ is known²⁰:

$$\Theta = \chi_{pl}^h/\chi_{pl}^s = 406 \text{ K} \quad (22)$$

so that we are able to compute the critical interaction parameter χ_{pl}^{cr} :

$$\chi_{pl}^{cr} = (\chi_{pl}^h/T^{cr}) - \chi_{pl}^s \quad (23)$$

with the aid of the χ_{pl} deduced from the fit of the liquidus. For PE130/hexane solutions we deduce the critical parameters:

$$T^{cr} = 381 \text{ K} \quad \varphi^{cr} = 0.82 \quad \chi_{pl}^{cr} = 0.092 \quad (24)$$

Where the critical point K_u is located as shown in the isobaric state diagram drawn out in *Figure 7*. We find an upper critical point K_u just below the liquidus, the existence of which should lead to phase separation within the melt of the semicrystalline system. That this has an influence on the superstructure will be discussed in another paper¹⁰.

In the sketch in *Figure 7* we have additionally represented the lower critical solution temperatures as measured and discussed by Orwoll and Flory²¹. One has to keep in mind that under normal pressure conditions the boiling point of *n*-hexane is $T = 342 \text{ K}$. For this reason an extreme temperature and pressure dependence of the excess free enthalpy is expected, which leads to a change in sign in the excess enthalpy of mixing²¹. This explains why we might have mixing gaps with an upper and a lower critical point.

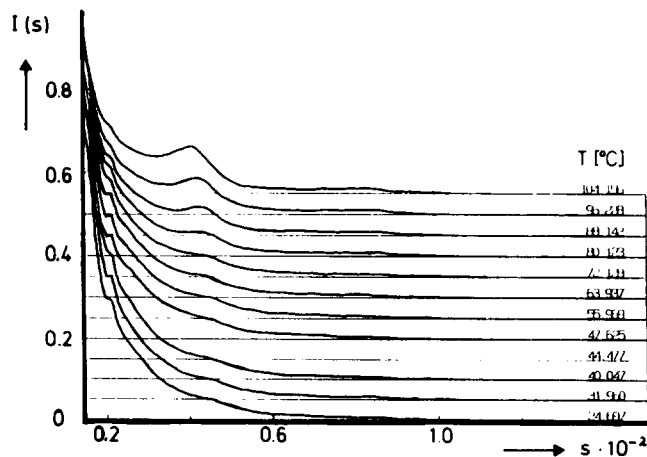
An interesting hypothesis

We come back to the discussion of the fold height of FCs formed below the liquidus in solutions. The liquidus was represented by calculations with an invariant fold height. This is in contradiction with synchrotron small-angle X-ray (SAXS) measurements, an example of which is shown in *Figure 8*. According to *Table 2* the long period decreases in PE130/*n*-decane mixtures when the concentration of the solvent is increased.

To discuss this effect, let us define the crystallization

Table 2 PE130/*n*-decane mixtures: $T_m = 415 \text{ K}$; $2\sigma_e = 2000 \text{ cal (mol surface unit)}^{-1}$; $\Delta h_0 = 970 \text{ cal (mol CH}_2 \text{ unit)}^{-1}$; $b = 1.3$; $y_i = 10 \text{ CH}_2 \text{ units}$, $y_f^* = 180 \text{ CH}_2 \text{ units}$, $y_m = 800 \text{ CH}_2 \text{ units}$; $\langle y \rangle_{pf} = 325 \text{ CH}_2 \text{ units}$; $\alpha_{seif} = \alpha_{inter} = 3200 \text{ cal (mol CH}_2 \text{ unit)}^{-1}$

φ (vol%)	0	0.33	0.66
T_k (K)	396 ± 12	384 ± 2	372 ± 3
T_{kf} (K)	398	384	376
L (Å)	300 ± 20	242 ± 15	177 ± 10
$\langle y \rangle_{pf}$ (CH ₂ units)	230 ± 15	190 ± 10	177 ± 10
$\langle y \rangle_{pl}$ (CH ₂ units)	385	26	15
$\alpha(\varphi)$ (cal (mol CH ₂ unit) ⁻¹)	6924–6100	5800–5000	4800–4200
α_{theo} (cal (mol CH ₂ unit) ⁻¹)	6400	5400	4350



concentration. By equation (27) it is guaranteed that the Thomson term itself has the defined and invariant value. If A_f is adjusted to $y_f^* = 180 \text{ CH}_2$ units ($A_f = 38.8$) by setting the molar interfacial free enthalpy and the molar melting enthalpy equal to $2\sigma_e = 2000 \text{ cal mol}^{-1}$ and $\Delta h_0 = 970 \text{ cal mol}^{-1}$ per CH_2 unit, we compute the $\alpha(\varphi)$ as listed in Table 2. Hence, we arrive at the result that the excess term in the defect front layers has to decrease in a well defined manner if the fold height decreases.

The role of entanglements

The question is why the fold height decreases in diluted PE130/*n*-alkane solutions. Suppose that the conditions of heterogeneous nucleation and growth are the same; the defect situation in the front layers of FCs should also depend on the concentration of entanglements in the melt^{1,23}. In solution, interpenetration of chains and therefore the density of interchain entanglements are reduced.

In the pure polymer the number of interchain entanglements per chain of length y should be proportional to:

$$\frac{\text{volume of a coil}}{\text{volume of a chain}} = \eta \frac{y^{3/2}}{y} = \eta y^{1/2} \quad (28)$$

where the parameter η is constant. In solution, this number is smaller. When the volume occupied by the solvent is accounted for, the reduction is described by:

$$y^* = y \left(1 + \frac{n_1 y_1}{n_y \langle y \rangle_{\text{pf}}} \right) = y \left(1 + \frac{x_1 y_1}{(1 - x_1) \langle y \rangle_{\text{pf}}} \right) \quad (29)$$

with x_1 given by equation (8). In (29) $\langle y \rangle_{\text{pf}}$ is the mean length in the fraction of chains in the PE130/*n*-decane solution that participate in folded-chain crystallization:

$$\langle y \rangle_{\text{pf}} = \sum_{y_i}^{y_m} \Phi(y') y' / \sum_{y_i}^{y_m} \Phi(y') \quad (30)$$

where y_m is the maximum length of chains. The excess term $\alpha(\varphi)$ has to include defects due to self-entangling of each chain (α_{self}). This is taken to be an invariant and additive effect, and we are led to:

$$\alpha(\varphi) = \alpha_{\text{self}} + \eta(\varphi) \alpha_{\text{inter}} \quad (31)$$

where with the aid of equations (28) and (29) $\eta(\varphi)$ is obtained as:

$$\eta(\varphi) = \frac{y^{1/2}}{1 + x_1 y_1 / (1 - x_1) \langle y \rangle_{\text{pf}}} \quad (32)$$

The value $\langle y \rangle_{\text{pf}} = 325 \text{ CH}_2$ units is derived from the known chain-length distribution as given in equation (18) by using $y_f^* = 180 \text{ CH}_2$ units and $y_m = 800 \text{ CH}_2$ units. The $\alpha(\varphi)$ data can be reproduced by defining $\alpha_{\text{self}} \equiv \alpha_{\text{inter}} = 3200 \text{ cal (mol CH}_2 \text{ unit)}^{-1}$ (Table 2). Inter- and intramolecular conformational defects should, in any case, be identical. It is because interchain penetration in solutions decreases that the final concentration of quasi-permanent conformational defects in the boundaries of folded-chain crystals becomes smaller.

As the total defect concentration in FCs is diminished, nucleation and growth of folded-chain lamellae of shorter thickness are possible. Under invariant kinetic circumstances, a minimum fold height is predicted, in the present case equal to $y_{f,\text{min}} = 134 \text{ CH}_2$ units. Such 'single-chain lamellae' should be formed in highly diluted solutions.

EXPERIMENTAL DETAILS

Samples

The polymer was PE130 (Höchst Co.); $\langle y \rangle_p = 130 \text{ CH}_2$ units. The chain-length distribution is depicted in Figure 1. As solvents we used: (a) *n*-hexane, purity better than 0.97 (Merk); (b) *n*-decane, purity better than 0.95 (Mer-Schuchhardt); (c) nonadecane, purity better than 0.99 (EGA-Chemie).

Wax and solvent were sealed in a glass tube. The samples were then homogenized by annealing for half an hour at a temperature lying 20 K above the melting point. Afterwards, the samples were cooled at the constant rate of 0.5 K min^{-1} . Isotropy of the crystallized samples was in any case proven by means of WAXS measurements.

High-pressure experiments

PE130 was heated in a high-pressure dilatometer (Abt-Angewandte Physik der Universität Ulm) up to 533 K, and the pressure was increased to 5 kbar. Afterwards, the sample was cooled down to room-temperature (cooling rate of about 10 K h^{-1}).

Calorimeter measurements

Caloric measurements were performed with a constant heating rate of 0.5 K min^{-1} either using an MCB micro-differential calorimeter (Barbari) or a d.t.a. device as designed by Müller, Martin and Kilian^{24,25}. The maximum melting temperatures (liquidus temperatures) were assumed to be given by the point of intersection of the rear flank of the melting curve with the c_p curve in the melt.

Gel permeation chromatography

The chain-length distribution of PE130 was deduced from gel permeation chromatographic measurements. The column was packed with beads of poly(styrene-divinylbenzene), the pore size of which varies from 5 to 10^5 nm . The apparatus was calibrated using a set of different polystyrene fractions, with the aid of the equation:

$$\log M = \log M_a + Kt \quad (33)$$

where M is the molecular weight, t is the time of elution and K the characteristic parameter of the column. The constant parameter M_a was determined by measuring the retention time of the oligomer $\text{C}_{28}\text{H}_{58}$. The g.p.c. measurements were carried out on solutions of 20–40 mg of PE130 in 6 ml tetrachlorobenzene prepared at $T = 393 \text{ K}$. To delete broadening effects, the g.p.c. data were deconvoluted with the detected g.p.c. function of the standard oligomer used.

Synchrotron SAXS measurements

SAXS measurements were carried out in the Hamburg Synchrotron Laboratory (HASILAB). While the sample, sealed in a cell with glimmer plate windows, was heated at a rate of 2 K min^{-1} (oven designed by Zietz and Heuer²⁶) SAXS patterns were measured every minute, in each case accumulating the scattered X-rays for 30 s.

CONCLUSIONS

The thermodynamic description of the liquidus of FCs in PE130/solvent solutions justifies the concept of

treating folded-chain lamellae as a cooperative unit. Each FC represents an inhomogeneous microphase, the fold height of which is kinetically fixed. Conformational defects being squeezed into front layers, the structure within FCs is regulated so as to minimize the free enthalpy of the whole FC.

In linear waxes bundles of interpenetrating molecules of lengths $y \geq y_f^*$ are separated during crystallization from chains $y < y_f^*$ which are too short to participate in folded-chain crystallization. The configuration of chains of different lengths $y \geq y_f^*$ is not substantially changed during crystallization. The folded-chain crystal assembly links a mixture of chains of different lengths in a crystal network. Mixing or demixing of chains is inhibited until the last FCs melt.

It is possible to elicit Flory–Huggins parameters from a description of the liquidus. PE130/hexane solutions exhibit a mixing gap with an upper critical point just below the liquidus.

What is an interesting matter is that the liquidus can be correctly calculated with a constant fold height. This opposes synchrotron SAXS results, according to which the fold height of solution-grown FCs falls to lower values. All the results are only consistent if one assumes that the defect energy and fold height are interrelated. Reduced thickness of the FCs in solution appears to be the consequence of having a reduced density of interchain entanglements.

In view of these results, it can be taken as verified that folded-chain crystals can be treated like thermodynamically well defined inhomogeneous microphases. The 'non-equilibrium' parameters like the fold height y_f or the defect energy parameter $\alpha(\varphi)$ can be defined as hidden variables. When a folded-chain crystal is formed, these hidden variables are fixed. It is therefore possible to derive the conditions of coexistence with a multi-component melt. But uniqueness is lost: within a given chain configuration, each folded-chain microphase with the same ratio α/y_f has the same melting point (see equation (27)).

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