Thermodynamics of the melting of pseudoeutectic linear copolymers systems

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(Received 8 September 1976; revised 5 January 1977)

The melting process of random copolymers of ethylene (short-chain branched copolymers) has been determined experimentally for a variety of systems. A thermodynamic description can be accomplished by considering the crystallizable sequences in the chains (*c*-sequences) as components of a polydispersed multicomponent system. Lamella-shaped extended *c*-sequence mixed crystals occur which represent solid solutions having a limited solubility. Thus, local fractionation by appropriate surrounding of parts of the chains is needed for crystallization. The total fusion process of the random copolymers of ethylene can be quantitatively described by means of the theory developed, fitting a single set of a few parameters.

INTRODUCTION

For an individual molecule to be capable of undergoing crystallization, it must possess a high degree of chemical and structural regularity among its chain elements. The introduction into a polymer chain of units that differ chemically or structurally from the predominant chain-repeating elements imposes restrictions on crystallization and influences the melting process[1,2,18]. Only those units that occur in large quantities are capable of crystallization. In the following discussion these units will be designated as 'crystallizable units' (*c*-units), the other chain units as 'non-crystallizing units' (*nc*-units).

For linear copolymers composed of two chemically or structurally different chain units, we have a distribution of length for the crystallizable sequences (*c*-sequences). Thus surroundings of appropriate parts of the chains in microdimensions only are needed to establish lamellar-shaped crystallites. The size distribution of these crystallites should be related to the length distribution of the *c*-sequences[1,2,18]. The crystallization process is therefore controlled by local crystallization due to fractionation of the *c*-sequences, exhibiting a microstructure with a characteristic alternation of crystallized and non-crystallized regions.

If the counits are distributed randomly, the *c*-sequences are very short and cannot be involved in crystallization. The maximum crystallinity w^c_{max} is therefore typified by relatively small values compared to block copolymers (*Figure 1*). There should exist a critical value x^*_{nc} of the *nc*-units above which no crystallization will occur. In this case the essential question we are interested in is how to relate the properties of the crystallized copolymer system to the chemical structure of the chains by applying the formalism of classical thermodynamics.

From the fact that suitable methods of controlled copolymerization should be known, we have been induced to investigate copolymers of ethylene with randomly distributed counits (calling them 'pes-copolymers').

THEORY

A theory of equilibrium crystallization of copolymers has been given by Flory[1]. He stated the significance of the eutectic *nc*-units that are excluded from the crystalline phase. Thus the crystalline phase comprises crystallites of varying length. Taking into account the surface-free energy of the crystallites, crystallization and melting cover a broad temperature range. The width of the melting range increases with increasing concentration of the *nc*-units. A definite depression of the maximum melting temperature is anticipated to be dependent on the heat of fusion and the composition of the random-type copolymers. In spite of lack of complete agreement between theory and experiment, the calculations in *Figure 2* display substantial characteristics of measured fusion curves.

The length of the copolymer molecules is decisive in the formation of crystal networks. This special aspect has been taken into account by Krigbaum and coworkers[5,6]. However, a consideration of the broad distribution of sequence lengths in a random copolymer with its concomitant effect on the longitudinal crystallite sizes (the thicknesses of the lamellar-shaped crystallites) is not included in this theory.

In this paper, we present a thermodynamic theory of the melting of random copolymers, proceeding from considerations given elsewhere[2]. The *c*-sequences of different length are considered as the components of the systems in spite of their being linked together. Ignoring crystallization by *c*-sequence-folding, which can be neglected for sequences of the appropriate length, crystals containing extended *c*-sequences of various lengths appear to be the thermodynamically most stable configuration of the system[7]. Accepting

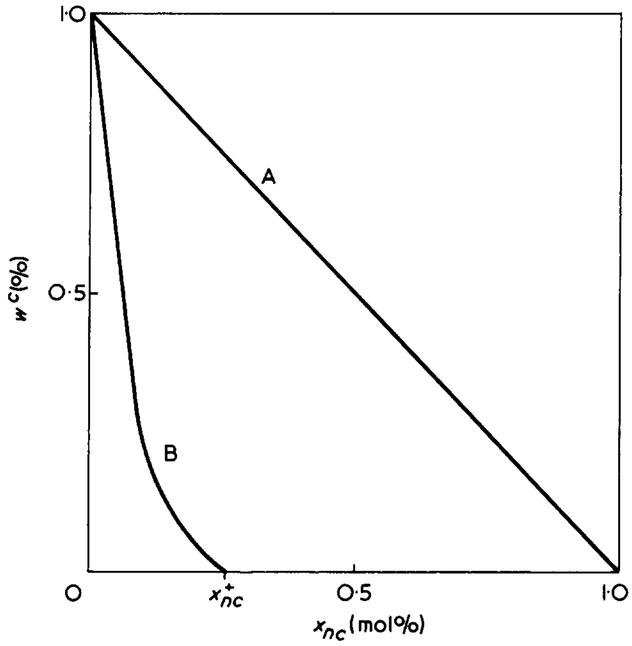

Figure 1 Schematic diagram of the fraction of crystalline units w^c as a function of composition (mole fraction of *nc*-units x_{nc}) for: A, block copolymers containing crystallizable sequences of a uniform length which is large enough for participating in crystallization; B, random-type copolymer

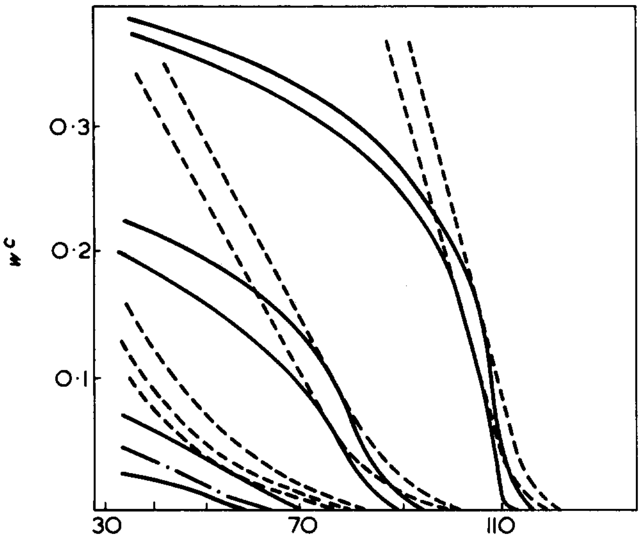

Figure 2 The degree of crystallinity[13] (calculated from specific volume data) as a function of temperature for the copolymer with n-propyl and ethyl substituents. ———, n-propyl; ——— . ———, ethyl; — — — — — — — —, theoretical

only a limited solubility in the solid state for *c*-sequences of different lengths, the thickness distribution of the extended *c*-sequence mixed crystals (ESMC) is controlled by fractionating processes of the *c*-sequences.

BASIC CONCEPT OF THE ESMC MODEL

To avoid dealing with the molecular weight distribution, the chains are assumed to be sufficiently long. Thus the copolymer system can theoretically be composed of the *nc*-units and the large number of *c*-sequences of different lengths as the elements of a multicomponent system[2].

With the mole numbers n_c and n_{nc} of the *c*- and the *nc*-units respectively, the mole fraction of the *nc*-units is given by:

$$x_{nc} = n_{nc}/(n_c + n_{nc}) \tag{1}$$

obeying the standardization condition:

$$x_c + x_{nc} = 1 \tag{2}$$

For randomly distributed counits the mole fraction of the *c*-sequences composed of y *c*-units can be computed from:

$$x_y = x_{nc}^2 \times x_c^{y-1} \tag{3}$$

with

$$\sum_{y=1}^{\infty} x_y = x_{nc} \tag{4}$$

The crystallizing copolymer system is related to the behaviour of an oligomer multicomponent system exhibiting extended-chain crystals[19]. Because of the extraordinary width of the sequence length distribution (*Figure 3*), fractionating of *c*-sequence during crystallization is an underlying principle that governs the crystallization of pes-copolymers. During crystallization, lamellar-shaped extended *c*-sequence mixed crystals (ESMC) appear, the solubility of which is determined by the limits of the intrinsic stability of the solid solution.

An appropriate model of an extended *c*-sequence mixed crystal is shown in *Figure 4*. We now need to consider the definition of a phase. We have defined the *c*-sequences to be the components of the system. From *Figure 4* we realize that not all the *c*-units which are members of a crystallized *c*-sequence can be placed in ideal lattice positions. Thus we have to modify the classical phase concept by accepting a defined number of defects located in the end surface layers of these ESMC crystals.

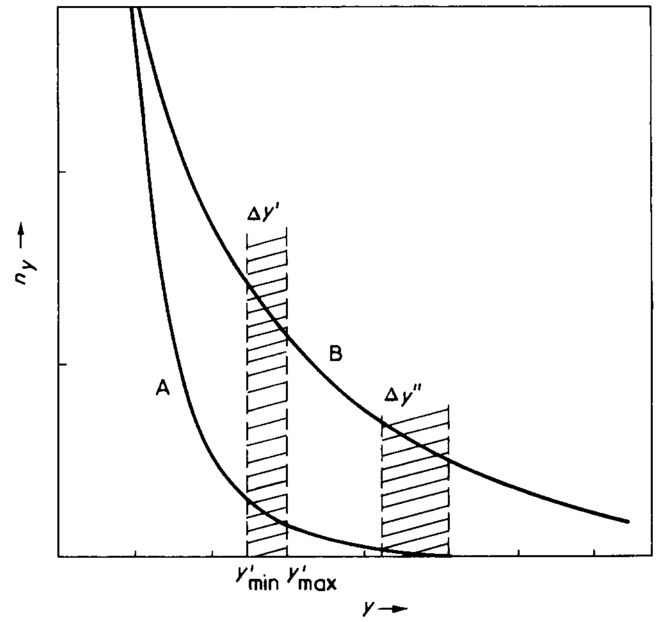

Figure 3 Mole number of *c*-sequences of different lengths, n_y, for x_{nc}(A) > x_{nc} (B). The solubility within the crystals is represented by the hatched area. $M' = \Delta y'$; $M'' = \Delta y''$

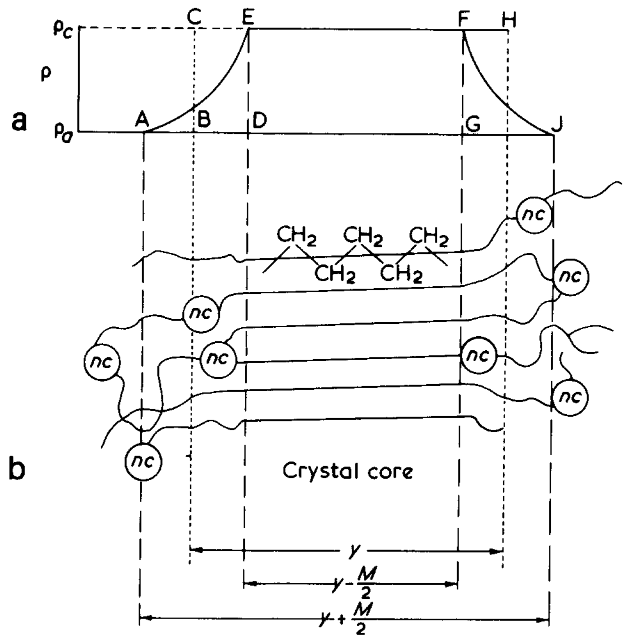

Figure 4 Schematic diagram of a model of an ESCM. The *nc*-units for each chain are represented as being excluded from the well-ordered crystal core of thickness $y - M/2$. The parameters $M = \Delta y$ defines the maximum difference in chain lengths within the ESCM. A plot of density function is shown in (a); ρ_c and ρ_a are the average density in the crystal core and the amorphous regions respectively

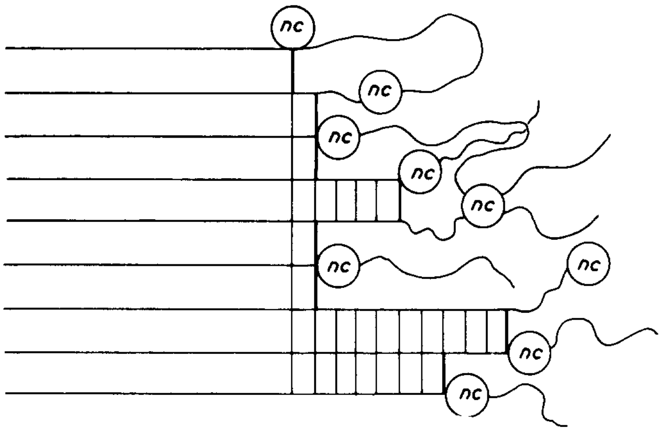

Figure 5 Schematic diagram of the molecular arrangement in the longitudinal surface layers of an ESCM. According to the simplified two-phase concept the boundary between the crystal and melt phases should be defined by the solid line

Considering the crystalline lamellae as well as the amorphous layers as microphases, the conditions for microphase equilibrium in crystallized pes-copolymer systems are expressed by the equivalence of the chemical potentials of the *c*-sequence *y* in each of the co-existing microphases, i.e.

$$\mu_y^{c\alpha} = \mu_y^{c\beta} = \ldots = \mu_y^{c\mathcal{H}} = \mu_y^{m} \qquad (5)$$

where α, β and $\mathcal{H}$ are designated ESMCs of different average longitudinal thickness, and *c* and *m* defines the crystalline and melt phase respectively.

This theoretical approach is based on the following assumptions.

(1) *nc*-units and *c*-units have no common crystal lattice, i.e. they represent eutectic counits;

(2) The *c*-sequences are components in the multicomponent system in spite of being linked together;

(3) The microphases (lamellar-shaped crystals and amorphous layers) are assumed to be thermodynamically autonomous phases;

(4) Microphases with the same properties are thermodynamically equivalent;

(5) Each *c*-sequence should belong entirely to a certain microphase in spite of having no perfect internal order when included in an extended *c*-sequence mixed crystal;

(6) Crystallization results in extended chain crystals; *c*-sequence folding in the crystals is not considered.

THERMODYNAMICS FOR AN EXTENDED C-SEQUENCE MIXED CRYSTAL (ESMC)

The extended *c*-sequence mixed crystal shown in *Figure 4* contains *c*-sequences whose lengths cover the range:

$$y'_{\max} = y + M/2 \geqslant y \geqslant y - M/2 = y'_{\min} \qquad (6)$$

The parameter *M* determines the solubility in the solid state. It is assumed that each *c*-sequence within this range should occur with the same probability.

We compute the number of lateral crystal contacts in the boundary layers, i.e. those *c*-units that can be regarded as incorporated into the crystalline phase, by employing the assumption that the two units with crystalline properties have both to be *c*-units belonging to adjacent *c*-sequences in the ESMC. Any other contacts are assumed to have similar properties to those in the liquid state (*Figure 5*).

In the layers of crystals in which the centres of the *c*-sequences within the ESMC are fixed in a crystallographic symmetry plane (see *Figure 6a*), *M*/2 crystal contacts should

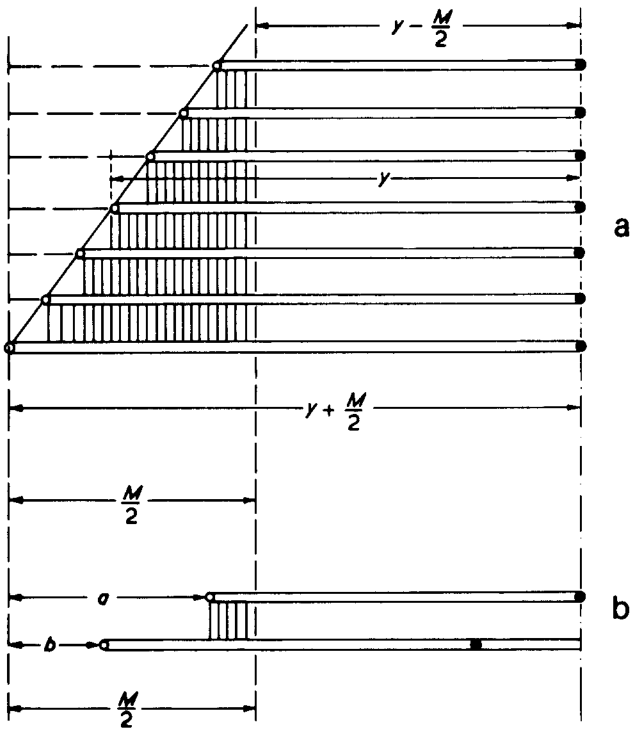

Figure 6 Schematic diagram of the *c*-sequences in an ESCM (a) with the centres of the *c*-sequences placed in the same crystallographic position. The centres are indicated by the solid circles. In (b) an example of nematically shifted *c*-sequences of the same length is given to explain the signs used in the text

occur. Making allowance for random shifts of the *c*-sequences in the longitudinal direction of the chain axes, with the restriction that the *nc*-units do not enter the crystallographic crystal core, we compute the number of crystal contacts in the longitudinal layers of the ESMCs:

$$z = \sum_{a=1}^{M/2} \left\{ a(M/2 - a) + \sum_{b=1}^{a} b \right\} = M(M+1)(M+2)/24 \qquad (7)$$

The meaning of the parameters *a* and *b* is illustrated in *Figure 6b*. Since the total number of contacts in the longitudinal layers belonging to crystallized *c*-sequences is equal to:

$$z_{\text{tot}} = M^3/8 \qquad (8)$$

we find for the fraction δ of the crystal contacts of all crystallizable *c*-units of the *c*-sequences in the longitudinal layers:

$$\delta = z/z_{\text{tot}} = (M+1)(M+2)/3M^2 \cong 1/3 \qquad (9)$$

In the longitudinal layers of thickness $M/2$, in a first approximation, only 1/3 of the *c*-units are found to be placed into crystallographic positions.

Introducing the parameter *M*, we compute for the partial molar enthalpy of the *c*-sequence of the length *y* in the ESMC:

$$h_y^c \cong (y - M/3)h_0^c + \frac{M}{3}h_0^m + 2\sigma_e \qquad (10)$$

where h_0^m and h_0^c are the molar enthalpies of the *c*-unit in the melt and crystal phase respectively, and σ_e is the longitudinal molar interfacial enthalpy of a unit (see *Figure 5*).

The most simple approach for the partial molar entropy of the *c*-sequence *y* in the ESMC is given by:

$$s_y^c = s_{iy}^c + s_{ky}^c + s_{\text{mix}y}^c \qquad (11)$$

where s_{iy}^c is the partial molar entropy of oscillations of the *c*-sequence *y*, postulating an invariant conformation of the centres of oscillation of the chain units; s_{ky}^c is the conformational entropy of the *c*-sequence *y* without consideration of the oscillation of the units; and $s_{\text{mix}y}^c$ is the partial molar entropy of mixing *c*-sequences *y* in the ESMCs with different core thicknesses.

The partial entropy of oscillation of a *c*-sequence *y* in an ESMC can be constructed on the same plan as developed above:

$$s_{iy}^c \cong (y - M/3)\, s_0^c + (M/3)\, s_0^m \qquad (12)$$

where s_0^m and s_0^c are the entropies of oscillation of the *c*-units in a *c*-sequence at constant configuration of the oscillation centre in the melt and the crystal phase respectively.

In this approach, the entropy of conformation in the ESMC is represented by random translational shifts of the *c*-sequences in the direction of the *c*-sequence axes:

$$s_{ky}^c = R\ln(M/2 + 1) \qquad (13)$$

The entropy of mixing of the extended *c*-sequences of different lengths, assumed to behave like rigid rods, can easily be computed from the number of the various distinguishable configurations in the ESMC:

$$s_{\text{mix}y}^c = -R\ln x_y^c \qquad (14)$$

Equation (14) determines the entropy of mixing for an ideal mixture (or ideal solution)[9]. The mole fraction of the *c*-sequences *y* in the ESMC is defined by:

$$x_y^c = n_y^c \Big/ \sum_{\text{ESMC}} n_\eta^c \qquad (15)$$

where n_y^c and n_η^c are the mole numbers of the *c*-sequences of the length *y* and η in the ESMC respectively.

Using the preceding equations, the chemical potential of the *c*-sequences, containing *y* *c*-units in the ESMC, can therefore be written:

$$\mu_y^c = \left(y - \frac{M}{3}\right)h_0^c + \frac{M}{3}h_0^m + 2\sigma_e + g_y^{cexh} - T\cdot\left\{\left(y - \frac{M}{3}\right)s_0^c + \frac{M}{3}\, s_0^m + R\left[\ln[(M+2)/2] - \ln x_y^c\right] + g_y^{cexs}\right\} \qquad (16)$$

The partial molar free enthalpy:

$$g_y^{cex} = g_y^{cexh} - Tg_y^{cexs} \qquad (17)$$

does duty for all actual effects not covered by the above of ESMC having energetic (g_y^{cexh}) or entropic origin (g_y^{cexs}).

COPOLYMER MELT

Besides the *c* sequences of different lengths the presence of low molecular weight solvent molecules is admitted for further applications of the theory. If there is no heat of mixing, the partial molar enthalpy of *c*-sequences of the length *y* in the liquid mixture may be written as:

$$h_y^m = yh_0^m \qquad (18)$$

employing the molar enthalpy of the *c*-unit h_0^m. The partial molar entropy of oscillation for a *c*-sequence *y* can be represented by the expression:

$$s_{iy}^m = ys_{i0}^m \qquad (19)$$

with the contribution of a single *c*-unit s_{i0}^m.

To compute the mixing entropy of the *c*-sequences in the melt we have to consider the fact that, for any surrounding of a single *c*-sequence in the melt, a certain number of neighbouring *c*-sequences must be cooperatively affected. Though it is not known how the cooperative effects of the surroundings occur in detail, we can nevertheless make an estimate of a representative length y_{eff}. Looking upon a *c*-sequence with *y* units, we are led to define:

$$y_{\text{eff}} = N\langle y_p\rangle + y \qquad (20)$$

where N adjacent *c*-sequences should take part in the cooperative exchanges. The quantity $\langle y_p \rangle$ is the average length of the *c*-sequences of a pes-copolymer system:

$$\langle y_p \rangle = \sum_{melt} (y x_y^m) \tag{21}$$

with the molar fraction of the *c*-sequences of the length y:

$$x_y^m = n_y^m \Big/ \sum n_\eta^m \tag{22}$$

The intuitive significance of y_{eff} is more easily demonstrated by:

$$q = y_{\text{eff}} / [(N+1)\cdot\langle y_p \rangle] = (N\langle y_p \rangle + y)/[(N+1)\langle y_p \rangle] \tag{23}$$

With increasing N, q tends rapidly towards the value 1, indicating that differences in length of the *c*-sequences are best not taken into account when the mixing entropy in the pes-copolymer melt is computed. Thus, the molar entropy of mixing may be written:

$$s_{\text{mix}}^m = -\mathrm{R}\cdot\left\{ \sum n_\eta^m \cdot \ln(\phi_\eta^m) + n_L \ln \phi_L^m \right\} \tag{24}$$

where n_η^m and n_L^m are the mole numbers of *c*-sequences containing η *c*-units and of the solvent molecules respectively, and ϕ_L^m and ϕ_η^m are the volume fraction of the solvent and the 'solute':

$$\phi_L^m = y_L n_L^m \Big/ \left(y_L n_L^m + \langle y_p \rangle \sum n_\eta^m \right) \tag{25}$$

$$\phi_\eta^m = \langle y_p \rangle n_\eta^m \Big/ \left(\langle y_p \rangle \cdot \sum n_v^m + y_L n_L^m \right) \tag{26}$$

Here we have assumed that the species of the *c*-sequences should have equal size $\langle y_p \rangle$. Calculating the partial molar entropy of mixing of the *c*-sequences y we derive from equation (26):

$$s_{\text{mix}y}^m = \partial s_{\text{mix}}^m / \partial n_y^m = -R\{\ln x_y^{m'} + \ln f_y\} \tag{27}$$

where the prime attached to the mole fraction:

$$x_y^{m'} = n_y^m / (\Sigma n_\eta^m + n_L^m) \tag{28}$$

is intended to indicate that solvent species are included therein. The activity coefficient f_y:

$$f_y = \frac{\langle y_p \rangle}{\langle y_m \rangle} \exp\{y(1/\langle y_p \rangle - 1/\langle y_m \rangle)\} \tag{29}$$

depends on the differences in average chain length only with:

$$\langle y_m \rangle = \Sigma \eta x_\eta^{m'} + y_L x_L^{m'} \tag{30}$$

representing the size of the components in the melt, averaged over all species. The molar fractions of the 'solute' and the solvent are:

$$x_y^{m'} = n_y^m / (\Sigma n_\eta^m + n_L^m) \tag{31}$$

$$x_L^{m'} = n_L^m / (\Sigma n_\eta^m + n_L^m) \tag{32}$$

For a pes-copolymer melt without solvent molecules we compute from equation (29):

$$\lim_{n_L^m \to 0} f_y = 1 \tag{33}$$

indicating that the partial molar entropy of mixing of the *c*-sequence in the pes-copolymer melt is identical with that of an ideal mixture.

For the athermic partial molar conformational entropy we use the relation[9]:

$$s_{c0,y}^m = R[\ln(y) + (y-1)\ln(z-1)/\gamma)] \tag{34}$$

where z is the lattice coordination number, and γ is Euler's constant.

Incorporating the partial molar excess term g_y^{mex} into the theory, the partial molar free enthalpy (the chemical potential of the *c*-sequences) in the melt is equal to:

$$\mu_y^m = y h_0^m - T\left\{ y \cdot s_0^m + R[\ln y + (y-1)\ln\left(\frac{z-1}{\gamma}\right) - \ln(x_y^{m'} \cdot f_y) \right\} + g_y^{mex} \tag{35}$$

MOLE FRACTIONS

For an application of equation (5) sufficiently detailed knowledge on the crystallized system is not available; therefore appropriate approximations must be made. Thus, the mole numbers of the *c*-sequences y included in an ESMC, n_y^c are assumed to be proportional to the total number of these *c*-sequences present in the system (denoted n_y^0).

$$n_y^c = \alpha \cdot n_y^0;\ 0 < \alpha < 1 \tag{36}$$

From the isobaric diagram of a binary n-alkane mixture, a justification for the above approximation can be made. What is important in this case is the limited temperature interval which is covered even in binary systems containing components with such a difference in size that the splitting up of the liquidus and the solidus is maximum (see *Figure 7*). Hence the splitting existent in the actual systems is omitted when we employ equation (36). Because of the width of the temperature interval in which melting of pes-copolymers usually occurs (see *Figure 2*), the physical significance of the approximation postulated should be limited accordingly.

A serious problem is concerned with the determination of the parameter of solubility M of *c*-sequences in the ESMC.

$$M = y_{\max} - y_{\min} \tag{37}$$

Without considering the theoretical determination of M at present we derive for the mole fraction of the *c*-sequences containing y^* units in the ESMC, employing equation (36):

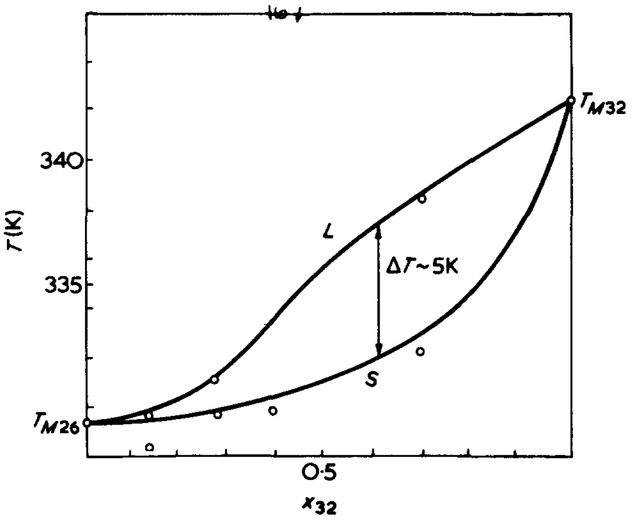

Figure 7 Plot of the isobaric state diagram of the binary oligomer system containing n-alkanes with $y = 26$ and $y' = 32$. x_{32} denotes the molar fraction of the $y = 32$ component, and T_{My} the melting temperatures of the single component systems y

$$x_{y*}^c = \alpha n_{y*}^0 \Big/ \left(\sum_{\eta = y - M/2}^{y + M/2} \alpha n_\eta^0 \right) = x_{nc} x_c^{y* - y} / (x_c^{-M/2} - x_c^{M/2}) \tag{38}$$

Focusing our considerations on the c-sequences $\langle y_c \rangle \equiv y$, we derive from equation (38):

$$x_y^c = x_{nc} / (x_c^{-M/2} - x_c^{M/2}) \tag{39}$$

Looking upon the ESMC of average thickness y as the thermodynamically stable crystal of minimum thickness at constant T and P, the fraction ϵ of the c-sequences y is 'crystallized':

$$\epsilon = \sum_{\eta = y}^{y + M/2} x_c^\eta \Big/ \sum_{\eta = y - M/2}^{y + M/2} x_c^\eta = (1 - x_c^{M/2}) / (x_c^{-M/2} - x_c^{M/2}) \tag{40}$$

Those c-sequences incorporated into ESMCs of average thickness $y < y' < y + M/2$ must be taken into consideration when we compute the molar fraction of the c-sequences of the length y in the melt:

$$x_y^m = x_{nc} x_c^y (1 - \epsilon) / (1 - x_c^y) \tag{41}$$

The factor $1/1 - x_c^y)$ is needed because the mole number of all the c-sequences in the melt is accordingly reduced by crystallization.

EXCESS TERMS

To determine the dependence of the molar excess-free enthalpy in the melt, g^{mex}, on the concentration of the components, we may use the generalized van Laar expression[13]:

$$\frac{g^{mex}}{RT} = (\Sigma_{\mu\upsilon} \chi_{\mu\upsilon}^m \phi_\mu \phi_\upsilon)(\Sigma n_\eta^m \eta + n_L^m y_L) \tag{42}$$

where $\chi_{\mu\upsilon}^m$ are the interaction parameters which characterize the free enthalpy of interaction between the components μ and υ in the melt. It is best to write the interaction parameter of the c-sequences in the form:

$$\chi_{\mu\upsilon}^m = (\chi_h^m / T + \chi_s^m)_{\mu,\upsilon} \tag{43}$$

where χ_s^m and χ_h^m are the interaction parameters taking into the account excess entropy and excess enthalpy.

In order to render the expression for the total excess free energy of polymer–polymer contacts in a suitable form, it appears reasonable to define the interaction parameter, averaged over all segments of the c-sequences:

$$\langle (\chi_h^m)_{\mu\upsilon} \rangle = \chi_h^m \tag{44}$$

$$\langle (\chi_s^m)_{\mu\upsilon} \rangle = \chi_s^m \tag{45}$$

Following the calculations in Appendix I we obtain for the partial molar excess enthalpy in the melt the approximation equation:

$$g_y^{mex} / RT = -y \left\{ \left(\frac{\chi_n^m}{T} + \chi_s^m \right) \left((1 - (\phi_L^m)^2 \right) \Big/ 2 + \chi_L (\phi_L^m)^2 \right\} \tag{46}$$

MOLAR DEGREE OF CRYSTALLINITY

The theory makes it possible to estimate the fraction of the c-units that are crystalline at temperatures less than T_M. This estimate is obtained by totalling all the c-sequences involved in crystallites, taking into account defects in the longitudinal surface layers of the ESMCs.

From studies on crystallization of binary oligomer n-paraffin systems[7] it follows that the solubility parameter M should obey the empirical equation:

$$M = A \cdot \langle y_c \rangle \tag{47}$$

where $\langle y_c \rangle$ is the average chain length in the binary solid solution. For the solubility parameter M of a polymer in which only one type of unit is capable of crystallizing, we are lead to an adequately generalized empirical relation:

$$M = A \cdot y + B; \quad A, B > 0 \tag{48}$$

The parameter B takes into account characteristic deviations from the crystallization fractionating experienced in binary oligomer systems.

Thus, from equations (3) and (9) we obtain for the molar degree of crystallinity w^c:

$$w^c = \sum_{\eta = y(T)_{\min}} x_{nc}^2 [\eta + M(\delta - 1/2)] \, x_c^{\eta - 1} \tag{49}$$

With equation (48), equation (49) can then be expressed by:

$$w^c = (1 - A/3)(x_{nc}^2 / x_c) \sum_{\eta = y_{\min}}^{\infty} (\eta - y_k) x_c^\eta \tag{50}$$

with

$$y_k = (B/3 - 1/2)/(1 - A/3) \tag{51}$$

This finally leads to the molar degree of crystallinity:

$$w^c = (1 - A/3)\, x_c^{y(T)_{\min}-1}\ \{[y_{\min}(T) - y_k]\cdot x_{nc} + x_c\} \tag{52}$$

Since $A > 0$ and $y_k > 0$ for a random copolymer with one crystallizing unit, equation (52) involves the general relation:

$$w^c < x_c \tag{53}$$

expressing the fact that in such copolymer systems perfect order can never be established.

y–T DEPENDENCE

$y(T)_{\min}$ represents the limiting size above which the crystallites can exist at equilibrium. ESMCs below this size are not stable at the temperature T_{My}. Utilizing equations (5), (16) and (35) as well assuming $g_y^{c\,ex} = 0$ and employing $y(T)_{\min} \equiv y$, T_{My} can be computed from:

$$T_{My} = T_M{}^*\{1 - [2\sigma_e - \chi_h^m\cdot(y-1)\cdot(1 - \phi_L^{m2})/2]/C_1\}/C_2$$

$$C_1 = (1 - A/3)\,(y - y_k)\cdot\Delta h$$

$$C_2 = 1 + (RT/C_1)\{\ln(y/[AY/2 + B/2 + 1]) - \ln([z-1]/\gamma) - \ln(x_y^m f_y/x_y^c) - \chi_s^m(y-1)\,(1 - \phi_L^{m^2})/2 - y\chi_L\cdot\phi_L^{m^2}\} \tag{54}$$

where $\Delta h = h_0^m - h_0^c$ is the molar melting enthalpy of the c-unit, and $\Delta s = s_0^m - s_0^c$ is the molar melting entropy of the c-unit.

$$T_M^* = \underset{y\to\infty}{\text{limit}}\, T_{My} = \Delta h/\{\Delta S + R\cdot\ln[(z-1)/\gamma]/(1 - A/3)\}$$

The functions x_y^m and f_y, related to the non-crystallized phase in the partially crystallized system, are not explicitly expressed. They can be computed utilizing equations (21), (29), (30), (43) and (41).

The temperature dependence of the molar melting enthalpy can be represented by [7,20,21]:

$$\Delta h = \Delta h(T_M) - \Delta c_p(T_M - T) \tag{55}$$

where T_M, defining the hypothetical melting temperature of a polymer single-component system consisting of chains of 'infinite length', can be expressed as:

$$T_M = \Delta h/(\Delta S + R\ln([z-1]/\gamma)) \tag{56}$$

By calculating the melting temperatures of n-paraffin homologues good agreement with the experimental data was found when the temperature dependence of the longitudinal interfacial energy was expressed in the form[21]:

$$\sigma_e(T) = \sigma_e(T_M)\cdot\Delta h(T)/\Delta h(T_M) \tag{57}$$

EXPERIMENTAL

*Preparation of random ethylene/α-olefine copolymers**

Polyethylene molecules with statistically distributed olefin side chains have been synthesized according to a method by Richardson, Flory and Jackson[3]. Two different diazoalkanes were polymerized in etherial solution at 0°C using BF_3 as catalyst. Assuming equal reactivity of both the diazoalkanes, as was found to be valid[3], this yields a polymer consisting of comonomer units in the same molar ratio as the starting reaction mixture.

Diazomethane was synthesized according to a standard procedure by alkaline hydrolysis of N-nitroso-toluyl-4 sulphomethylamide and after distillation was stored as an ethereal solution at −18°C. Higher diazoalkanes, that should yield different side groups in the copolymer, were synthesized by alkaline hydrolysis of the corresponding N-nitrosoureas. The concentration of diazoalkanes in ethereal solution was determined by back-titration of the surplus of a known amount of benzoic acid after esterification of the diazoalkanes[15].

To produce polymethylene with a known molar ratio of methyl side chains, i.e. a polyethylene with a distinct number of methyl side groups, appropriate molar amounts of diazomethane were polymerized at 0°C for 24 h with BF_3 as catalyst. The resulting precipitate was filtered off, washed with diethyl ether, reprecipitated twice from toluene, and vacuum dried at 70°C. Following this procedure, copolymers with statistically distributed methyl and propyl sidechains at molar fractions between 0.01 and 0.12 were synthesized.

Calorific measurements

We used a d.t.a. apparatus developed by Martin, Müller and Kilian[14], employing a linear heating rate of 0.5°C/min. By annealing the samples at temperatures of 50°C above the maximum melting temperature defined by the fusion of the last detectable fractions of crystals, a definite state of equilibrium in the copolymer melt should be realized. After cooling down at a rate of 0.05°C/min, the melting experiments revealed nevertheless the same d.t.a. curves when the annealing temperature and the annealing time of the samples were varied, indicating the dominant influence of the chemical chain structure on the crystallization of 'quasi-eutectical' copolymers. This was very favourable for the investigation of the chlorinated samples which undergo thermal degradation at temperatures above 90°–100°C.

Figure 8 shows a representative d.t.a. diagram. By separating the background, the degree of crystallinity w^c can be evaluated using the relation:

$$w_{\exp}^c = \int_{T_{\min}}^{T} \Delta c_p(T')\mathrm{d}T'/\Delta h^*(T) \tag{58}$$

$$\Delta h^*(T) = \Delta h(T_M) - \Delta c_p\cdot\Delta T - 2\sigma_e/\langle y_c\rangle \tag{59}$$

By extrapolation of the sharp high temperature deflection of the $c_p(T)$ curve in *Figure 8*, we obtain the intersection point A with the background, assigning to it the temperature T_M'. The theoretically desired maximum melting tem-

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* We are greatly indebted to Professor Vollmert (University of Karlsruhe) for advice when performing the copolymerization processes.

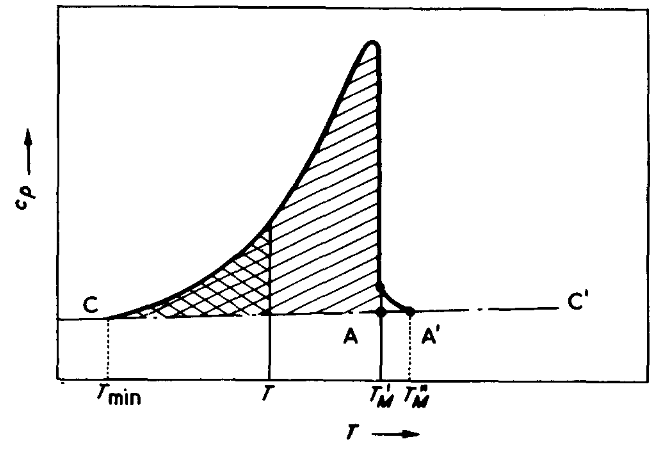

Figure 8 Schematic diagram of a thermogram. T_{min} denotes the beginning of melting. The difference $T_M \approx T_M'' - T_M'$ marks the limit of accuracy of the maximum melting temperature determined from thermogram

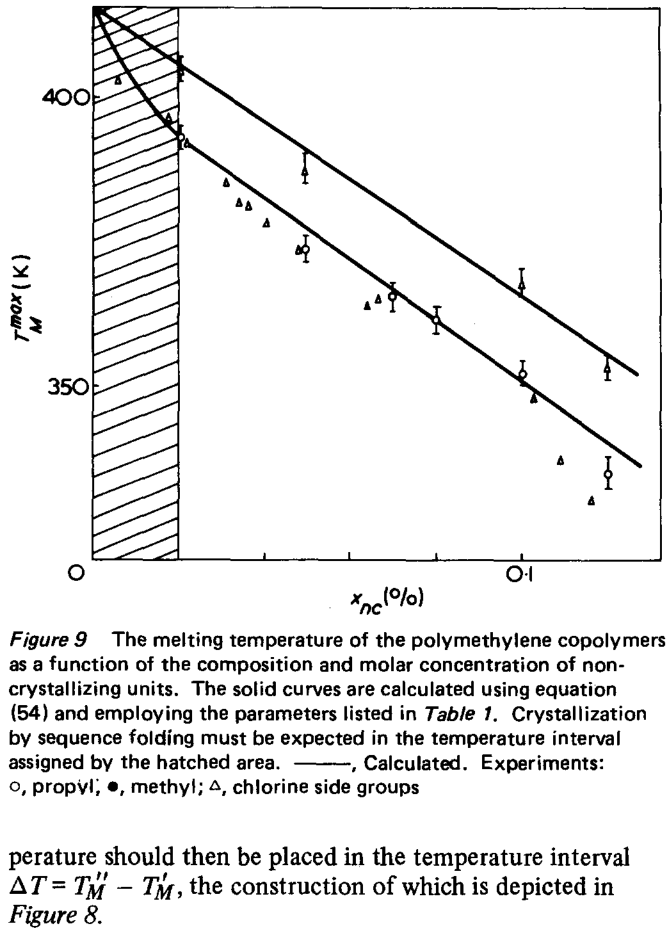

Figure 9 The melting temperature of the polymethylene copolymers as a function of the composition and molar concentration of non-crystallizing units. The solid curves are calculated using equation (54) and employing the parameters listed in *Table 1*. Crystallization by sequence folding must be expected in the temperature interval assigned by the hatched area. ——, Calculated. Experiments: ○, propyl; ●, methyl; △, chlorine side groups

perature should then be placed in the temperature interval $\Delta T = T_M'' - T_M'$, the construction of which is depicted in *Figure 8*.

EXPERIMENTAL RESULTS AND DISCUSSION

When raising the concentration of the *nc*-units a considerable steady decrease of the maximum melting temperatures is observed (see *Figure 9*) as predicted from the eutectical character of the investigated crystallizing pes-copolymers of ethylene. CH_3– and Cl– branched polymethylenes yield essentially the same results. However, as far as the maximum melting temperatures are concerned, the copolymers containing *n*-propyl side groups exhibit distinct higher values.

Using a single set of parameters T_M, Δh, σ_e, ΔC, A, B, and χ_h^m, listed in *Table 1*, for all copolymers, there is a need for fitting χ_s^m only to compute the entire set of experimental curves. For systems with a relatively large concentration x_{nc}, no well ordered crystal core (see *Figure 4*) can be composed in our general model when the average thickness of the ESMCs takes the value $y = y_m$. When this occurs it was necessary to compute the solubility parameter M^{++} for all $y < y_m$ in the following manner:

$$M^{++} = M/2 + y \tag{60}$$

The solubility of the solid solutions in ESMCs with $y < y_m$ will apparently be reduced.

According to this theoretical description systematic deviations of the melting point depression, observed for pes-copolymers with side-groups of different size, should be attributed to different properties of the liquid microphases only.

The solid solutions, represented by the extended sequence mixed crystals which coexist with the melt at the maximum melting temperature, appear to have internal properties which will primarily be determined by the distribution of *c*-sequences involved. The different physical properties of the *nc*-units (different size as well as different interaction forces) show only a minor effect. Hence, the microstructure of pes-copolymers at their melting point can generally be expected to be characterized by the chemical chain structure, irrespective of the nature of the short chain-branches introduced.

Maximum degree of crystallinity

If the chain structure of pes-copolymers is so important, it should be possible to compute other properties of crystallized systems, employing the same formalism without any changes of the parameters used hitherto. Indeed, the degree of crystallinity at room temperature can be calculated for the pes-copolymers without any variation of the parameters listed in *Table 1*, using equation (52) (*Figure 10*).

The calculations of the maximum melting temperatures are not very sensitive for a proper choice of the parameter *B* owing to the analytical form of equation (48). The influence of *A* is increased for larger average thickness of ESMC. It appears to be advantageous, therefore, to adjust *B* by fitting the degree of crystallinity at room temperature. Adjusting *B* for one sample (CH_3-short-chain branched pes-copolymers with $x_{nc} = 0.05$) and using this constant value, it was possible to evaluate w^c for all the other pes-copolymers, achieving very good agreement with the experimental data.

This quantitative calculation of the degree of crystallinity at room temperature supports the validity of the theoreti-

Table 1 The parameters for the calculation of the melting of short branched linear copolymers of ethylene. $A = 0.15$; $B = 46$; $\chi_h^m = 0$

Branching	χ_s^m
Cl–	0.06
CH_3–	0.06
n-propylene	–0.02

T_M = 415K
$\Delta h(T_M)$ = 970 cal/mol CH_2
Δc_p = 1.2 cal/mol CH_2 degree
$\sigma_e(T_M)$ = 2050 cal/mol unit
$w^c(T_M y_{max})$ = 0.001
For $z = 4 \rightarrow T_M^* = 414.06$K

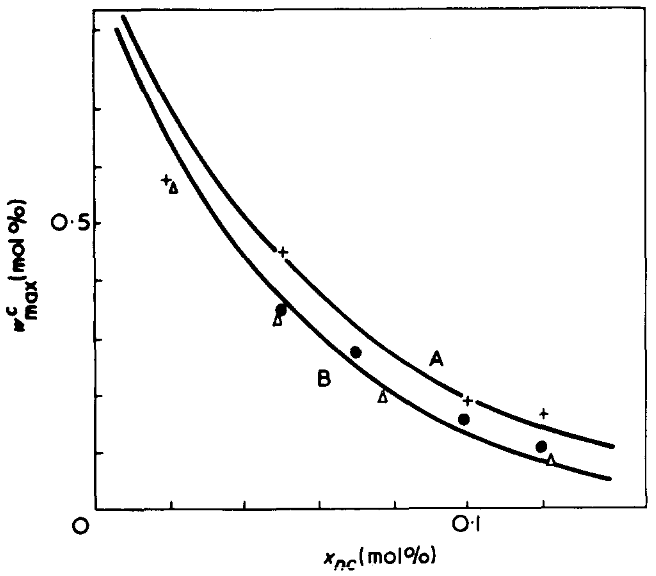

Figure 10 Plot of the molar degree of crystallinity at room temperature as a function of the composition for the random copolymers (+, n-propyl; ●, methyl; △, chlorine). A and B are calculated for room temperature employing the parameter listed in *Table 2*

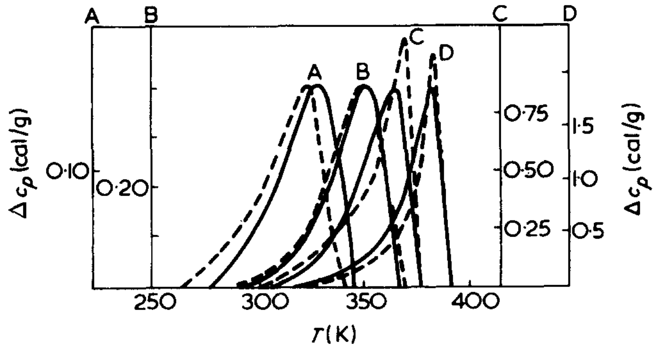

Figure 11 Plot of experimental Δc_p against the temperature for Cl-branched polyethylene (——). – – – –, are calculated using the parameters in *Table 2* and having the following concentrations: A, x_{nc} = 0.112; B, x_{nc} = 0.077; C, x_{nc} = 0.048; D, x_{nc} = 0.021. The Δc_p scales are indicated for each of these curves

cally postulated principle of local and defined crystallization fractionation of the *c*-sequences even for higher levels of crystallinity.

Melting process

Theoretical melting curves $\Delta w^c/\Delta T$ demonstrating the variation in the degree of crystallinity with temperature can be computed using equations (51), (52) and (54)–(57) with the same set of parameters as before (see *Table 1*). Representative plots including the experimental data are given in *Figures 11–13* for pes-copolymers. Satisfactory quantitative agreement between theory and experiment, independent of the concentration of the *nc*-units and the type of the *nc*-units, is achieved.

The unique features of the fusion of copolymers outlined above are primarily consequences of the broad distribution of *c*-sequence lengths in a random copolymer, that effect the longitudinal crystallite sizes. At a given temperature, only those *c*-sequences whose lengths exceed $y(T)_{\min}$ can participate in the crystallization process, $y_{\min}(T)$ being a defined function of the temperature. As the temperature is varied, both the composition and sequence distribution of the amorphous phase change. These factors, as well as the limited solubility of the *c*-sequences in the ESMCs in turn, govern the fractions of *c*-sequences that can participate in the crystallization. The major conclusions of our theoretical approach, related to the chemical chain structure of linear pes-copolymers, are, in fact, fully substantiated by a complete set of experiments.

The extended-c-sequence mixed crystal

A simple model of an extended-c-sequence-mixed crystal is shown in *Figure 4*. The randomness associated with the free mixing of the c-sequences of various lengths in the ESMC offers the apparent advantage of higher entropy and consequently of higher thermodynamic stability of the crystal. On the other hand, its formation requires that a large number of defects in the longitudinal surface layers participate. To estimate this effect we define the following ratio as a relative solubility parameter:

$$s = (M/2)/y \qquad (61)$$

From the data listed in *Table 2* it is apparent that the necessity of local crystallization fractionation of the *c*-sequences in pes-copolymers of ethylene is substantially reduced when the average thickness of the ESMCs diminished.

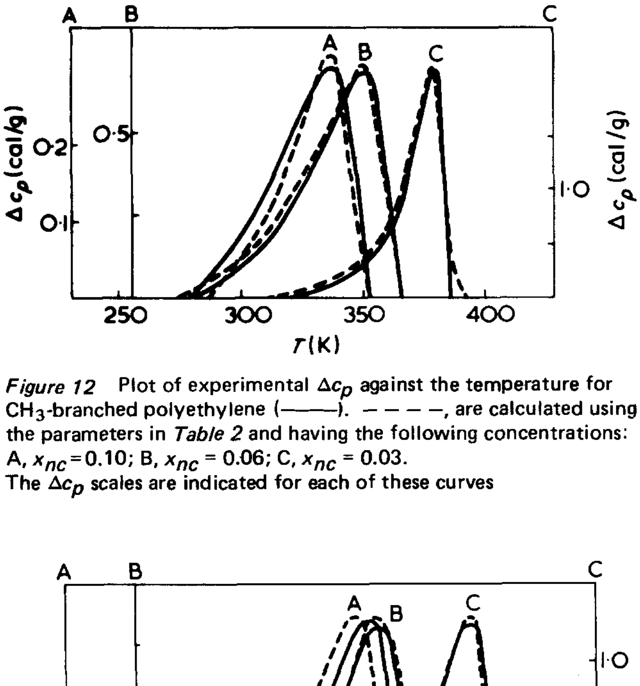

Figure 12 Plot of experimental Δc_p against the temperature for CH_3-branched polyethylene (——). – – – –, are calculated using the parameters in *Table 2* and having the following concentrations: A, x_{nc}=0.10; B, x_{nc} = 0.06; C, x_{nc} = 0.03. The Δc_p scales are indicated for each of these curves

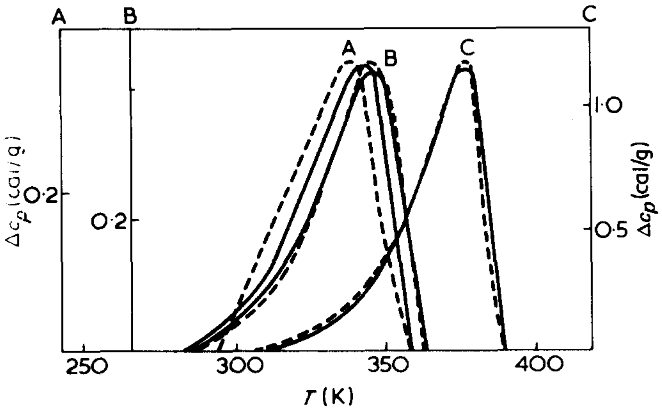

Figure 13 Plot of experimental Δc_p against the temperature for propyl-branched polyethylene (——). – – – –, are calculated using the parameters in *Table 2* and having the following concentrations: A, x_{nc} = 0.12; B, x_{nc} = 0.10; C, x_{nc} = 0.05

Table 2 The solubility of *c*-sequences of various length in ESCMs with $A = 0.15$, $B = 46$

y (periodic *c*-units)	s
500	0.12
100	0.31
60	0.46
40	0.65
y where $y - M/2 < 23$	1.0

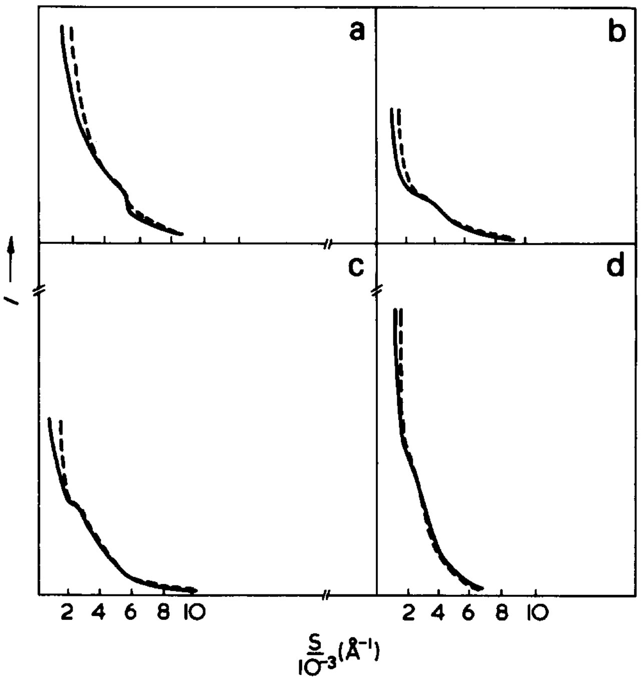

Figure 14 SAXS curves of n-propylene-branched pes-copolymers for some discrete temperatures. — — — — are calculated employing the same parameters as used in this paper according to ref 8. *N* denotes the average number of crystal lamellae within a microstructure cluster. (a) $T = 25°$C, $N = 1.5$; (b) $T = 65°$C, $N = 1.9$; (c) $T = 75°$C, $N = 1.8$; (d) $T = 85°$C, $N = 1.5$

CONCLUSIONS

Since $T_M, A, \Delta h_0$ and ΔC are determined independently, taking $\chi_h^m = 0$, there are only the parameters $\sigma_e(T_M)$, B and χ_s^m available to describe the experiments. The best fit between theoretical and observed maximum melting temperatures was accomplished with the set listed in *Table 1*. In spite of correlations between these parameters, allowance is not given for substantial modifications of the parameters involved. With the value of 46 assigned to the quantity B there is a definite dependence of the solubility parameter M on y [equation (50)]. This empirical result can be justified by appropriate considerations dealing with the problem of the stability of lamellar-shaped mixed crystals as multicomponent microphases[22].

The interfacial free energy $\sigma_e(T_M)$ of 2050 cal/mol is in contradication to the much larger values which must have been postulated when using the theory of Flory *et al.*[1,13]. However, this discrepancy should not be discussed in detail because of the lack of complete agreement between this theory and experiments in the lower temperature range.

The unique description of the fusion of copolymers outlined above is consistent with a quantitative synthesis of SAXS-curves for the same copolymers within the same temperature range employing the same single set of structural parameters[8]. Only a single additional parameter of the linear theory of para-crystalline structures[7], which characterizes the thickness of the crystal lamellae cluster, is needed. This parameter can be computed from properties of the structure model and is consistent with corresponding light-scattering experiments on electron micrographs of stained copolymer samples[23,24]. Some representative examples of SAXS, calculated and observed, are plotted in *Figure 14*.

NOMENCLATURE

pes-copolymers	pseudo-eutectic copolymers with randomly distributed counits,
c-units	crystallizable counits,
nc-units	non-crystallizable counits,
x_c	mole fraction of crystallizable units,
x_{nc}	mole fraction of non-crystallizable units,
y	length of crystallizable sequences (number of periodic *c*-units),
x_y^α	mole fraction of *c*-sequences of length y in the microphase α,
$\mu_y^{c\alpha}$	chemical potential of the chains y in the crystal phase α and the melt respectively,
$M \equiv \Delta y = y_{\max} - y_{\min}$	solubility parameter in the solid state defining the maximum difference in chain lengths built into an ESMC,
ESMC	extended-sequence mixed crystal,
h_y^c, h_y^m	molar enthalpy of *c*-sequences of length y in the crystals and the melt respectively,
h_0^c, h_0^m	molar enthalpy of the *c*-units in the crystal and the melt-phase respectively,
σ_e	molar interfacial enthalpy,
s_y^c	molar entropy of *c*-sequences y in the ESMC,
s_{ty}^c	partial molar entropy of oscillations of extended sequence y in the ESMC,
s_{ky}^c	conformational entropy,
$s_{\mathrm{mix},y}^c$	partial molar entropy of mixing,
s_0^c, s_0^m	partial molar entropy of oscillation of the units in crystals and the melt respectively,
$g_y^{\alpha ex}$	excess free enthalpy in the microphase α for the c-sequences y, respectively,
$g_y^{\alpha exh}, g_y^{\alpha exs}$	corresponding enthalpy and entropy excess functions respectively,
f_y	activity coefficient of the *c*-sequence of length y,
$\langle y_m \rangle$	average particle size in the liquid polymer–solvent mixture,
s_{c0y}^m	partial molar conformational entropy of *c*-sequences of length y,
z	coordination number of the lattice,
γ	Euler's constant,
G^{mex}	molar excess free enthalpy in the melt,

χ_h^m, χ_s^m	average interaction parameter of energetic and entropic origin respectively,
w_0^c	relative fraction of crystallized *c*-sequences,
$y(T)_{\min}$	average size of the crystal of smallest thickness at *T*,
$\langle y_p \rangle$	average length of *c*-sequences in the non-crystallized copolymer system,
$s_{iy}^m, s_{\mathrm{mix}y}^m$	partial molar entropy of oscillation and of mixing in the melt for the *c*-sequences of length *y*,
$\phi_y^\alpha, \phi_L^\alpha$	volume fractions of the *c*-sequences and the molecules of size *L* in the α phase respectively,
h_y^α, h_L^α	molar number of the *c*-sequences *y* length *y* and the solvent molecules of size *L* in the α phase respectively,
$\langle y_c \rangle$	average chain length in the ESMC,
w^c	molar degree of crystallinity,
y_k	defect parameter,
T_{My}	melting temperature of ESMCs of thickness *y*,
T_M	melting temperature of the ESMC of 'infinite thickness',
Δh, Δs	molar melting heat and entropy respectively,
$\Delta g_y^{ex}, \Delta h_y^{ex}, \Delta S_y^{ex}$	partial molar excess quantity difference at the melting point for *c*-sequences of length *y*
$\Delta c_p(T')$	heat capacity of melting.

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APPENDIX I

$$\frac{g^{mex}}{RT} = (\chi_h^m/T + \chi_s^m)\,(\Sigma\phi_\mu^m\phi_\upsilon^m)n^m/2 + \chi_L\phi_L^m(\Sigma\phi_\mu^m)n^m \qquad \text{(A1)}$$

where χ_L is the averaged excess interaction parameter for polymer–solvent units.

n^m is the number of all units present in the liquid mixture:

$$n^m = \Sigma n_\eta^m \cdot \eta + n_L^m y_L \qquad \text{(A2)}$$

Differentation of equation (49) with respect to n_y^m yields, for the partial molar excess contribution of the *c*-sequences of the length *y*:

$$(\partial g^{mex}/\partial n_y^m)/RT = g_y^{mex}/RT = (\chi_n^m/T + \chi_s^m)\cdot\{2\cdot(1 - \phi_p^m - \phi_L^m)$$
$$+ y\cdot\phi_L^m(1 - \phi_L^m)/2 - \Sigma\phi_\upsilon^m(1 - \phi_\mu^m)\} + \chi_L\cdot y\cdot\phi_L^{m^2} \qquad \text{(A3)}$$

with

$$\phi_p^m = \sum_{\text{Polymer}} \phi_\upsilon^m;\ \phi_p^m + \phi_L^m = 1 \qquad \text{(A4)}$$

Because of the condition $\phi_y^m \ll 1$ for copolymer systems with a random-type *c*-sequence length distribution, we obtain from equation (51) the more simple approximate expression

$$g_y^{m\,ex}/RT \cong -y\{(\chi_h^m/T + \chi_s^m)\,(1 - \phi_L^{m^2})/2 + \chi_L\phi_L^{m^2}\} \qquad \text{(A5)}$$

APPENDIX II

Taking *y* for the average thickness of thinnest *c*-sequence mixed crystal, the volume fraction of the solvent in the partially crystallized system will be equal to

$$\phi_L^m = y_L n_L^m/(y_L n_L^m + \sum_{\eta=1}^{y-1} \eta n_\eta^0) = \phi_L^{m0}/(1 + w_0^c[\phi_L^{m0} - 1]) \qquad \text{(B1)}$$

where ϕ_L^{m0} marks the volume fraction of uncrystallized solvent in the system.

$$\phi_L^{m0} = y_L n_L^m / (y_L n_L^m + \sum_{\eta=1}^{\infty} \eta \cdot n_\eta^{\circ}) \qquad \text{(B2)}$$

The fraction of the c-sequences with the length $\eta \geqslant y_{\min}$ can be computed from

$$w_0^c = \sum_{\eta=y_{\min}}^{\infty} \phi_\eta^0 = x_c^y \min (y_{\min} \cdot x_c + x_{nc}) \qquad \text{(B3)}$$

with

$$\phi_\eta^0 = \eta \cdot n_\eta^0 / \sum_{\epsilon=1}^{\infty} \epsilon \cdot n_\epsilon^0 \qquad \text{(B4)}$$

The molar fraction of the solvent in the partially crystallized system can be cast in the form

$$x_L^m = \phi_L^m \langle y_m \rangle / y \qquad (35)$$

with $\langle y_m \rangle$ defined by equation (32)