Molecular fractionation in melt-crystallized polyethylene: 2. Effect of solvent extraction on the structure as studied by differential scanning calorimetry and gel permeation chromatography

U. W. Gedde, S. Eklund and J.-F. Jansson
Department of Polymer Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

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The effect of solvent treatment (extraction) on melt-crystallized polyethylene is considered in this second paper in a series on molecular fractionation (segregation) in polyethylene. Polyethylenes with a variety of thermal histories were treated with *p*-xylene at different temperatures and the changes in the samples were followed by differential scanning calorimetry and gel permeation chromatography. Information is obtained concerning the general dissolution behaviour of the polycrystalline samples including the selectivity of the extraction of the segregated species, how crystallinity varies within the structures and the molecular structure of the segregated component.

Keywords Melt-crystallized polyethylene; molecular fractionation; solvent treatment; dissolution; morphology; molecular structure

INTRODUCTION

This paper, the second in a series on molecular fractionation (segregation) in melt-crystallized polyethylene (PE), presents data obtained by differential scanning calorimetry (d.s.c.) and gel permeation chromatography (g.p.c.) showing the effect of solvent (*p*-xylene) extraction on a number of PE samples having different thermal histories. Part 1[1] presented d.s.c. data relating the melting behaviour of polyethylenes with different thermal histories to molecular fractionation. Together with the data in this paper and with the results of a subsequent paper[2] concerned with microscopy of solvent-treated samples, information is obtained concerning the molecular fractionation occurring in melt-crystallized PE, including the kinetics, the molecular architecture of the rejected species and the topology of the domains of the segregated material.

Investigating linear polyethylenes (LPE) from the melt isothermally crystallized at T_c, Mehta and Wunderlich[3] showed some years ago that the segregated component (the fraction of the sample which is not crystallizable at T_c) could be selectively separated from the material by solvent extraction using *p*-xylene as solvent. The efficiency of the separation, was checked by d.s.c. At optimum conditions of extraction, the almost complete disappearance of the low temperature (LT) melting peak together with the almost unchanged high temperature (HT) melting peak was taken as evidence for the high selectivity of the extraction. Mehta and Wunderlich[3] showed also that the dissolved component is low molecular weight material. Later, both Dlugosz *et al.*[4] and Winram *et al.*[5] prepared samples for microscopy by the *p*-xylene treatment. Evidence was obtained that the segregated material was selectively removed from the samples by the solvent treatment.

EXPERIMENTAL

Materials

The polyethylenes studied, characterized in *Table 1* of ref. 1 were treated (for the details, see ref. 1) as follows:

(1) Isothermal crystallization (IC) (from the melt) at 393.2, 398.2 and 401.2K. The residence times at the respective temperatures were 327.5, 312.5 and 332 h, which was long enough to ensure the establishment of an equilibrium fraction of segregated component. The samples were subsequently quenched in water (280K).

(2) Annealing (A) at 393.2, 398.2 and 401.2K of systems originally crystallized at a cooling rate of $\simeq 1\,\mathrm{K\,min^{-1}}$. The times of isothermal treatment were 327.5, 350 and 332 h, respectively. After the isothermal period the samples were cooled as in the IC case.

Extraction procedure

Pieces cut from the PE samples, $\simeq$0.2 mm thick, 4–5 mm wide and weighing 5 ± 1 mg, were treated with *p*-xylene, 15 ml solvent for each sample, resulting in a maximum concentration of dissolved PE of 0.03% (wt/wt), for 48 h at different temperatures ranging from 350 to 383K.

For the particular sample geometry used, a dissolution equilibrium is reached after approximately 10 h treatment. From studies of samples of 2215 and 2912A-treated at 401.2K having varying thicknesses ranging from 0.08 and 1 mm, a thickness independent dissolution was established in contrast to what has been found for samples of a thickness of the same order of magnitude as the spherulite size[6]. The extractions were carried out in closed glass tubes, with a nitrogen atmosphere, placed in a constant temperature bath. The temperature varied in a periodic manner ±0.15K. The 5 mg samples, placed in

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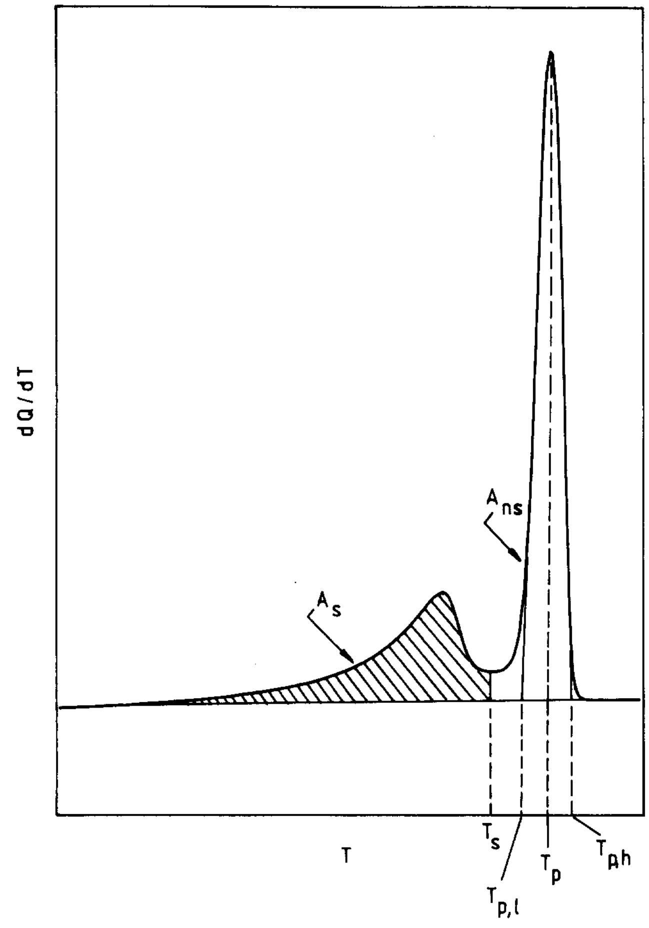

Figure 1 **Melting endotherm of PE sample including definitions of relevant quantities**

metal gaskets in the solvent-containing glass tubes, were agitated periodically during the extractions. After extraction, the samples were washed with fresh solvent at the extraction temperature and finally dried to constant weight.

D.s.c.

D.s.c. (instrument: Perkin-Elmer DSC-2) scans were run between 300K and 450K on the samples both before and after solvent treatment. The heating rate used was 10K min^{-1}. Further experimental details are given in ref. 1.

G.p.c.

The molecular weight distributions (MWD) of the segregated and non-segregated components were obtained by g.p.c. analysis. About 20–50 mg of material rich of segregated component were isolated from each sample as follows:

Pieces, each 0.2 mm thick and totally weighing 50–500 mg were treated with 30 ml *p*-xylene for 48 h at the 'optimum' temperature (at which a maximum part of the segregated component is dissolved while the non-segregated component is left unaffected). The concentration of dissolved PE varied for the different samples between 0.2 and 1.5% (wt/wt). It was shown that this relatively high concentration did not give different results (in terms of percentage of dissolved material, etc.) than those obtained for the 5 mg samples.

After the isothermal stage, the solution was separated from the undissolved, solid residues, an excess of methanol was added to the stirred solution allowing the dissolved polymer to precipitate, and for $\simeq$15 h this system was kept at 273K to ensure complete precipitation. After centrifugation, the PE crystals were separated from the solution by decanting and the precipitate was dried *in vacuo* to constant weight. The samples were finally analysed by g.p.c.

Analysis of d.s.c. data

Figure 1 gives the concepts used in the analysis of the melting endotherms.

The mass fractions of segregated and non-segregated component are defined, respectively, as:

$$W'_s = A_s/(A_s + A_{ns}) \qquad (1)$$

$$W'_{ns} = A_{ns}/(A_s + A_{ns}) \qquad (2)$$

Owing to the difference in crystallinity between the two components[1], the values estimated according to equations (1) and (2) are not absolutely correct. However, these data may still be used to determine the selectivity of the extractions.

The relative reductions of the respective components by extraction were calculated as follows:

$$\Delta W'_s/W'_s = (W'_s - W'_{s,e}(1-\Delta m))/W'_s \qquad (3)$$

$$\Delta W'_{ns}/W'_{ns} = (W'_{ns} - W'_{ns,e}(1-\Delta m))/W'_{ns} \qquad (4)$$

where W'_s and $W'_{s,e}$ are the fractions of the segregated component before and after extraction, respectively, W'_{ns} and $W'_{ns,e}$ are by analogy the fractions of non-segregated component before and after extraction, respectively, and Δm is the fraction of the sample dissolved by the solvent treatment. The multiplication of $W'_{s,e}$ and $W'_{ns,e}$ by the factor $(1-\Delta m)$ corrects for the weight reduction by the extraction. Thus, $W'_{s,e}(1-\Delta m)$ is the undissolved part of the segregated component which would be in the system before extraction.

The temperatures characterizing the HT peak shown in *Figure 1*, T_p, $T_{p,l}$ and $T_{p,h}$ were corrected for superheating and the inadequate experimental conditions as described in ref. 1 to obtain T_{htp}, $T_{htp,l}$ and $T_{htp,h}$, respectively.

RESULTS AND DISCUSSION

The dissolution of crystals in polycrystalline samples

The temperature for complete dissolution (T_d) of a sample was estimated on the basis of the plot of weight reduction (Δm) *versus* extraction temperature (T_e), with an accuracy of a few tenths of a K. *Figure 2* summarizes all the data obtained.

It has been shown in earlier reports, e.g. by Huseby and Bair[7], that the dissolution point of a polymer crystal is related to the thickness of the crystal (L) as follows:

$$T_d = T_d^0 \times (1 - \sigma_e/(\Delta H \times L)) \qquad (5)$$

where T_d^0 is the dissolution point of an infinitely thick crystal, σ_e is the free energy of the fold surface and ΔH is the heat of fusion of the crystal. Combination of equation (5) with the well-known Thomson–Gibbs equation gives:

$$T_d = (T_d^0/T_m^0)T_m \qquad (6)$$

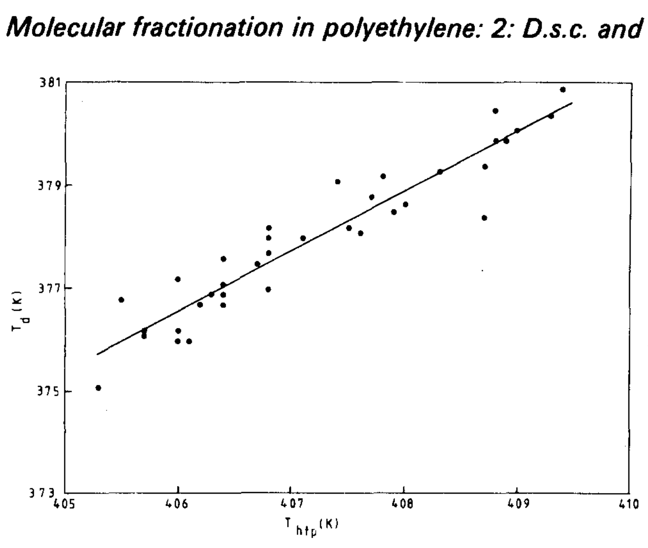

Figure 2 Dissolution point (T_d) as a function of the melting peak temperature (T_{htp})

The factor T_m^0 refers to the equilibrium melting point, for PE amounting to 414.6K[8]. Equation (6) is the equation of a line between the points (0.0) and (T_m^0, T_d^0) in a plot similar to *Figure 2*. By extrapolating the T_m *versus* T_d plot to $T_m = T_m^0$ an estimation of T_d^0 is made possible. However, the extrapolation of the T_{htp} *versus* T_d plot would result in an incorrect T_d^0. The peak temperature T_{htp} should instead be replaced by the temperature of the last trace of melting, $T_{htp,h}$. On an average the latter amounts to $T_{htp}+2.2$ (± 0.5). A value of 382 ± 1K for T_d^0 is the result of the extrapolation. This is in agreement with some of the data earlier reported[7,9,10] but deviates clearly from data of other papers[11,12].

It is next of interest to establish whether all the crystals of the polycrystalline samples dissolve according to equation (6). *Figures 3* and *4* show graphs relating the melting behaviour to the dissolution characteristics.

The IC-treated sample 7022 seems to dissolve almost according to equation (6), whereas the dissolution of the IC-treated 2215 sample deviates considerably from the expected behaviour, particularly for crystals of low melting point. Because of the thermodynamic character of equation (6), neglecting kinetic factors, it is reasonable to explain the low dissolution of sample 2215 at the lower temperatures by the impediment to the transport of the dissolved material out of the sample into the main liquid phase. As is shown later in this paper, the average molecular weight of the segregated component is higher for sample 2215 than for sample 7022. The coils of the dissolved molecules are larger in sample 2215 and the resistance to their diffusion out of the sample is consequently larger. In addition, the crystals of the segregated component of sample 2215 should be more interconnected, i.e. have a higher concentration of interlamellar tie chains than the corresponding crystals of sample 7022 owing to this difference in molecular structure. The long-range motion of the dissolved molecules should be more of a co-operative process in sample 2215, thus requiring the dissolution of more than one crystal, which in turn reduces the probability of transport occurring.

The effect of solvent treatment on the crystallinity

The crystallinity of the samples is altered significantly by the solvent treatments, as illustrated in *Figure 5*. There are two processes which account for the clock-shaped W_c–T_e curve. The region of increasing W_c with increasing T_e is due to the preferential dissolution of the segregated component which according to the previous paper[1] is of a lower crystallinity than the other parts of the structure. The rectilinear W_c–W_s' plot shown in *Figure 5* supports this view.

The sharp decrease in W_c with T_e at the higher T_e is not correlated with changes in W_s'. In this T_e range the crystals melting in the HT peak gradually dissolve. The decrease in W_c may be assigned to the occurrence of a dissolution–recrystallization process. The data indicate that the recrystallized material is of a lower crystallinity than the material prior to dissolution.

Selectivity of solvent treatment

The primary aim of the solvent treatments was to obtain information concerning the structure in terms of the segregated and non-segregated components. The melting endotherms of the solvent-treated samples were compared with the melting endotherms of the samples before the treatments and the relative reductions of the

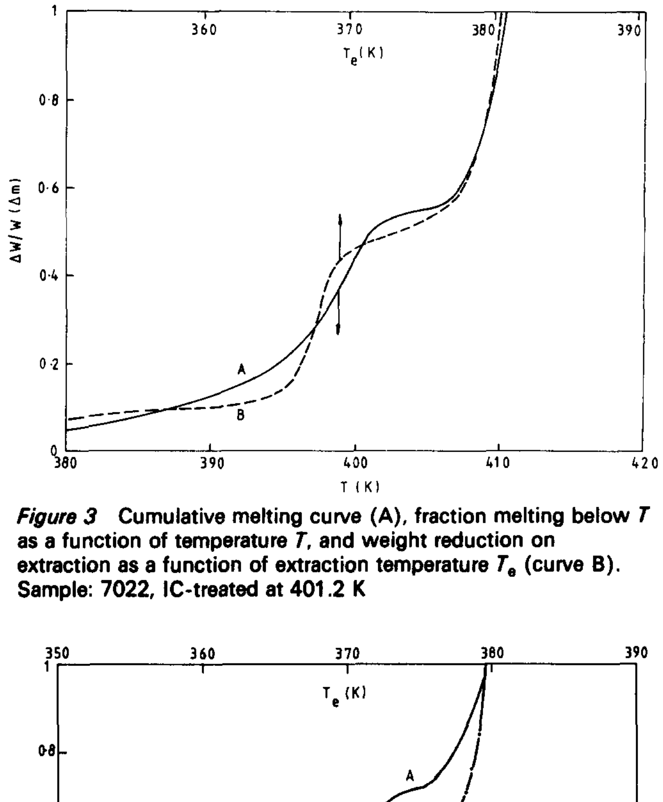

Figure 3 Cumulative melting curve (A), fraction melting below *T* as a function of temperature *T*, and weight reduction on extraction as a function of extraction temperature T_e (curve B). Sample: 7022, IC-treated at 401.2 K

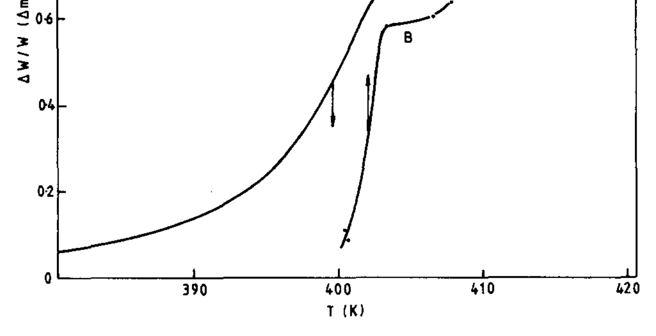

Figure 4 Cumulative melting curve (A), fraction melting below *T* as a function of temperature *T*, and weight reduction on extraction as a function of extraction temperature T_e (curve B). Sample: 2215, IC-treated at 401.2 K

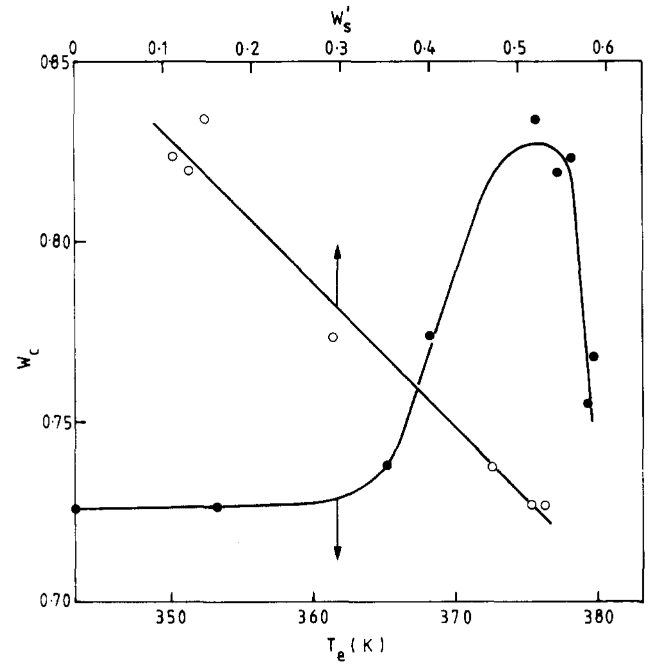

Figure 5 Crystallinity (W_c) of solvent-treated samples (7022, IC-treated at 401.2 K) plotted *versus* the temperature of extraction (T_e) and *versus* the mass fraction of segregated component (W_s'). Data points at T_e's above the maximum of the W_c–T_e plot are excluded from the W_c–W_s' plot

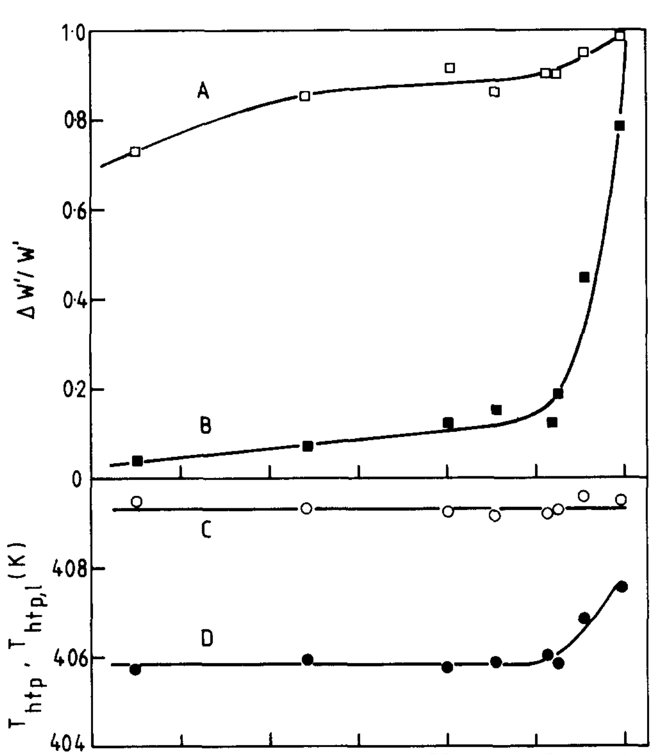

Figure 6 (a) Relative reduction of the mass fraction of segregated component ($\Delta W_s'/W_s'$, curve A) and non-segregated component ($\Delta W_{ns}'/W_{ns}'$, curve B) of solvent-treated samples of 7022, IC–401.2 K plotted *versus* the temperature of extraction T_e. (b) Melting temperatures T_{htp} (curve C) and $T_{htp,1}$ (curve D) of solvent-treated samples of 7022, IC–401.2 K plotted *versus* the temperature of extraction T_e

two melting (LT and HT) peaks were calculated according to equations (3) and (4). The upper graphs of *Figure 6* show these quantities plotted *versus* T_c.

As illustrated in *Figure 6*, extraction is never completely selective, i.e. there are no extraction temperatures at which $\Delta W_s'/W_s' = 1$ and $\Delta W_{ns}'/W_{ns}' = 0$ simultaneously. The maximum selectivity in the extraction is obtained at a temperature 4–5K below the temperature of complete dissolution of the sample. The corresponding values of $\Delta W_s'/W_s'$ vary systematically with the molecular structure, as will be shown later. The region of rapid increase of $\Delta W_{ns}'/W_{ns}'$ associated with the dissolution of crystals melting in the HT peak is of the order of 2–3K. According to *Figure 6*, T_{htp} is constant and $dT_{htp,l}/dT_c$ is approximately equal to 1 in the T_c range between 378.2 and 379.9K. Hence, the dissolution of the crystals dissolving in this range is in agreement with equation (6). However, at temperatures $>$379.9K, the behaviour is different. The dissolution point range for these crystals appears to be considerably narrower than their melting point range. This observation can be explained by the absence of an interconnecting network of these crystals at these high temperatures of extraction. The crystals can be dispersed, therefore, (as undissolved crystals) in the main liquid phase.

Figure 7 shows how the LT peak of one of the samples is influenced by the solvent treatment. The quantity $W_i(1-\Delta m)$, the weight fraction of the sample melting within a certain temperature range (corrected for the weight reduction of the sample by the solvent treatment) is plotted *versus* the temperature of extraction T_c.

Three regions can be distinguished in each curve. At low T_c values, no dissolution occurs and $W_i(1-\Delta m)$ is constant. At slightly higher T_c values, $W_i(1-\Delta m)$ decreases. A progressively larger fraction of the crystals dissolves. At even higher T_c values there is a region of only weakly decreasing $W_i(1-\Delta m)$. The temperature range width of the region of strong $W_i(1-\Delta m)$ decrease is in reasonable agreement with melting point range for the

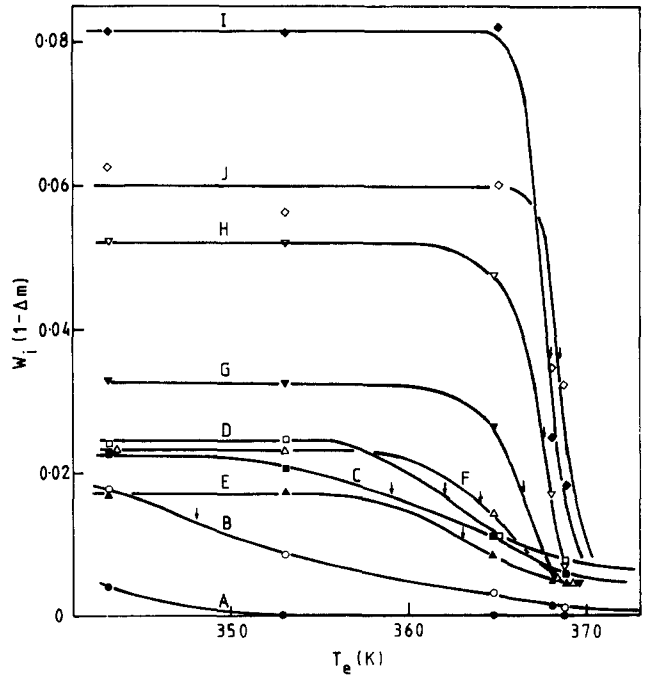

Figure 7 The development of the LT peak (sample: 7022, IC–401.2 K) as a function of the temperature of extraction T_e. The quantity $W_i(1-\Delta m)$, explained in the text, is plotted *versus* T_e. Melting point range: A, 360–370; B, 370–380; C, 380–386; D, 386–390; E, 390–392; F, 392–394; G, 394–396; H, 396–398; I, 398–400; J, 400–402 (K). The arrows indicate the inflection points of the curves

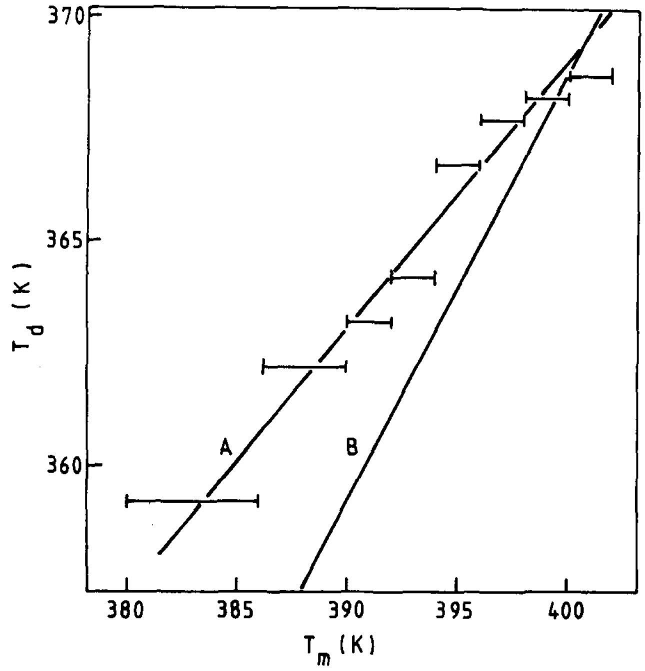

Figure 8 Dissolution point T_d, determined according to the text from the data of *Figure 7* plotted *versus* the melting point of the crystals (curve A). Curve B is based on the data presented in the foregoing section according to equation (6)

crystals concerned. *Figure 8* shows the relation between T_d and T_m, the former obtained as the temperature of the inflection point of the $W_i(1-\Delta m)-T_e$ curve and how these data compare with the T_d-T_m data presented earlier. There is relatively good agreement between the two sets of data at the higher temperature regions of the graph. However, crystals of low melting point appear to dissolve at slightly higher temperatures than expected, which indicates that kinetic factors to some extent determine the dissolution/migration of the crystals/molecules involved. In addition, the data of *Figure 8* are consistent with the data presented in *Figure 3*.

Figure 9 shows the optimum selectivity of extraction for the investigated samples expressed in $(\Delta W_s'/W_s')_{opt}$ as a function of W_s'.

The following conclusions can be drawn from the data of *Figure 9*:

(1) The optimum selectivity of extraction increases with increasing W_s' which is most apparent in the B plot. It is reasonable to assume that topological effects, i.e. how the segregated component is dispersed in the structure, should be of importance for the dissolution and transport of the segregated species. A certain amount of the segregated material must be more or less surrounded by regions of non-dissolvable (at the actual T_e) non-segregated material and is, therefore, to some extent hindered from dissolving or being transported out of the sample. The fraction of the segregated material which is surrounded in this way should increase with decreasing W_s', which may serve as an explanation for the $(\Delta W_s'/W_s')_{opt}-W_s'$ data obtained. However, as discussed later, other explanations are also feasible.

(2) The optimum selectivity of extraction is, at the same W_s', generally higher for 6375 than for the other materials, between which only smaller differences are observed. This difference in behaviour can be assigned to different possible causes:

(a) An interplay between the topological hindrance described in item 1 and the size of the coils of dissolved molecules. The coils expand approximately linearly with the square root of the molecular weight. Material 6375 has the lowest degree of chain branching of the studied materials and as shown by g.p.c. (see later) the segregated material is of a lower molecular weight for 6375 than for the other materials. The smaller coils of the segregated molecules of 6375 migrate more easily through the microchannel system than for the other materials.

(b) Another possible reason for the inefficiency in the extraction of the segregated component is the occurrence of molecular contiguity between crystals melting in the LT peak with those melting in the HT peak. This contact is accomplished by interlamellar tie chains. The extraction cannot be selective if molecular connections exist between the LT and HT crystals. The dissolution and transport of such segregated material require the simultaneous dissolution of the connected HT crystals. The increasing molecular weight[13], the lowering of crystallization temperature, and the increasing inhomogenity of the distribution of chain branches along the molecules all enhance the formation of such interlamellar tie chains. According to Mandelkern[14] this effect is particularly important for species of extremely high molecular weight, for which chain entanglements play a vital role in the crystallization. A considerable part of the high-temperature isothermal crystallization is hindered by the presence of the entangelements in favour of the post-isothermal crystallization at lower temperatures[14]. The increase in the contiguity of the crystals accompanying the reduction of crystallization temperature may be an important factor, as an alternative to that suggested in (1), which contributes to the observed increase in $(\Delta W_s'/W_s')_{opt}$ with increasing W_s'.

By taking into consideration the surface melting of the HT crystals (a detailed presentation of this is given in item

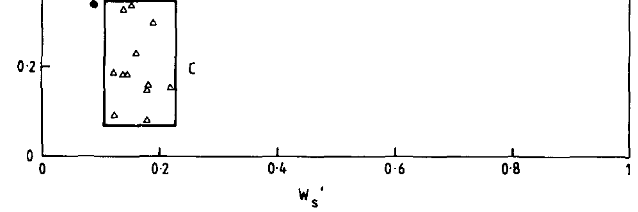

Figure 9 Optimum selectivity of the extractions expressed in $\Delta W_s'/W_s'$ plotted *versus* W_s'. A, Samples of 6375, with (□, ---) and without (■, ———) the correction for the surface melting of the crystals melting in the HT peak; B, samples of 7022, 7006, 2912 and 2215, with (○, ---) and without (●, ———) the correction for the surface melting of the crystals melting in the HT peak; C, samples of 7022, 7006, 2912, 2215 and 6375, first solvent-treated at optimum conditions, then melted and recrystallized or reannealed as before. The data shown relate to samples heat-treated at 398.2 and 401.2 K

(3)), the quantity of segregated component remaining undissolved after optimum solvent treatment was calculated for the different materials and the results, presented as an average for the samples of all the heat-treatments, were as follows: 6375—0.008; 7022—0.053; 2912—0.066; 7006—0.068; 2215—0.090. It seems that the amount increases with increasing degree of chain branching of the materials (compare with the data of *Table 1* of ref. 1), A great deal of this undissolved material can be due to the existence of chain-branch-rich sections of otherwise linear molecules. The linear sections crystallize first at a low degree of supercooling in HT crystals, whereas the chain-branch-rich sections crystallize at lower temperatures forming LT crystals which are connected by interlamellar tie chains to the HT crystals. Hence, the existence of the inhomogeneous molecules may provide an explanation, in addition to the two previously suggested, for the $(\Delta W'_s/W'_s)_{opt}-W'_s$ dependence presented in *Figure 9*.

(3) The surface melting of the crystals melting in the HT peak is considered in the analysis using the data by Bares and Wunderlich[15]. A corrected selectivity measure $(\Delta W'_s/W'_s)_{corr}$ was calculated as follows:

$$(\Delta W'_s/W'_s)=1-(1.02W'_{s,e}-0.02)(1-\Delta m)/$$

$$(1.02W'_s-0.02) \qquad (7)$$

Arguments against this simple treatment have been provided by Mandelkern[16], who rationalized a collection of data in a three-component model in which an interfacial component, with a molecular mobility and location between the liquid-like amorphous regions and the crystalline lamellae, plays a vital role. Subsequently, n.m.r. data[17] has supported the view that the relative size of the interfacial regions changes with molecular weight. Hence, the existence of a remaining LT peak after optimum solvent treatment can in principle to some extent be assigned to a larger enthalpy of the surface melting than is expected from the data of Bares and Wunderlich[15].

(4) The samples which were solvent-treated at optimum conditions, melted and recrystallized or re-annealed isothermally as originally, showed the lowest degree of optimum selectivity of extraction of all the samples (group C in *Figure 9*). A comparison between the melting endotherms of these samples and those obtained after the first optimum solvent treatment showed that both W'_s and W_c were almost similar for the two groups of samples, which can be considered as evidence that the remaining LT peak material of the optimum solvent-treated samples cannot be assigned to dissolved and internally recrystallized molecules which originally belong to the HT crystals. The occurrence of a selective extraction, most significant for the samples recrystallized or re-annealed at 398.2 and 401.2K, supports the idea of surrounded segregated material suggested in (1).

The samples of 3140 could not be selectively extracted. Both segregated and non-segregated species were removed in large quantities from the samples. This sharp difference in dissolution behaviour in relation to the other materials is most probably assigned to the large-scale of the segregation expected to occur in 3140. Material 3140 is a 50/50 blend of linear and branched PE and it is possible that these components are segregated into different spherulites. The data indicate that aggregates of undissolved crystals of the LPE component, evidently not connected with other similar structures, are dispersed into the main liquid phase.

G.p.c.

The problems in determining the molecular weight distribution (MWD) of the segregated and the non-segregated components arise from the fact that extraction is never completely selective. The extracted (dissolved) fraction, in all cases obtained at selective conditions of extraction, includes both segregated and non-segregated species as shown in *Table 1*.

These circumstances make almost impossible a rigorous analysis of the MWD of the extracted (dissolved) fraction (denoted MWD_e) in MWD_s (segregated component) and MWD_{ns} (non-segregated component). *Figure 10* shows the MWD_e's for samples of 6375 and 7006.

From the data of *Figure 10* and *Tables 1* and *2* several conclusions can be made:

Table 1 Features of the extracted fraction of IC samples

Material	Cryst. temp. (K)	$W_{ns,e}$[a]	$W_{ns,e}$ (mean)[b]
7022	393.2	0.36	0.37
7006	393.2	0.41	
2912	393.2	0.35	
2215	393.2	0.37	
6375	393.2	–	
7022	398.2	0.21	0.14
7006	398.2	0.13	
2912	398.2	0.11	
2215	398.2	0.10	
6375	398.2	0.15	
7022	401.2	0.08	0.09
7006	401.2	0.11	
2912	401.2	0.18	
2215	401.2	0.10	
6375	401.2	0.00	

[a] Concentration of non-segregated component in the extracted fraction of the samples. Calculated from d.s.c. data

[b] Mean value for all the materials treated at a certain temperature

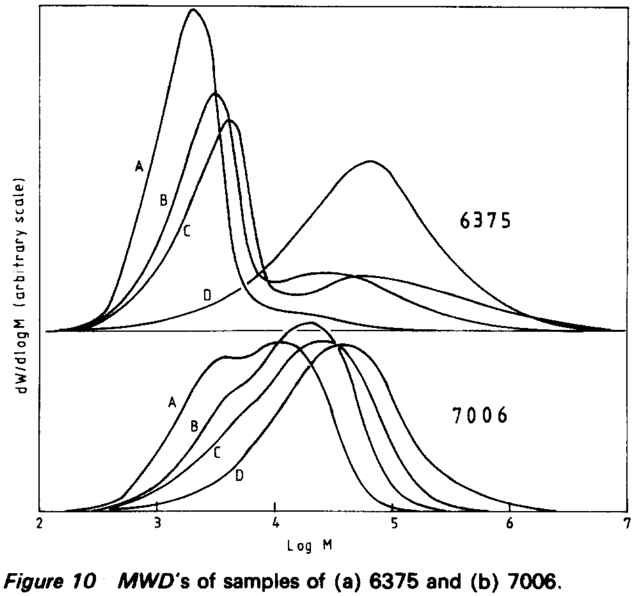

Figure 10 *MWD*'s of samples of (a) 6375 and (b) 7006. A, MWD_e of IC–393.2 K sample; B, MWD_e of IC–398.2 K sample; C, MWD_e of IC–401.2 K sample; D, *MWD* of whole material, denoted MWD_{6375} and MWD_{7006}, respectively

Table 2 Features of *MWD*$_e$ of IC samples

Material	Cryst. temp. (K)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	Rel. peak size[a]	Log M_l[b]	Log M_h[c]
7022	393.2	2.3	7.0	1.08	3.5	3.9
7006	393.2	2.8	9.6	0.91	3.5	4.1
2215	393.2	2.2	44.3	2.8	3.4	4.1
6375	393.2	1.2	4.0	18.00	3.3	4.0
7022	398.2	3.7	12.8	0.84	3.8	4.15
7006	398.2	5.1	17.1	0.66	3.7	4.3
2912	398.2	4.0	22.7	0.66	3.7	4.3
2215	398.2	4.1	52.4	0.87	3.6	4.6
6375	398.2	2.1	30.6	4.11	3.5	4.4
7022	401.2	5.9	27.1	0.83	3.9	4.4
7006	401.2	6.2	27.0	0.56	3.85	4.4
2912	401.2	5.5	30.4	0.55	3.8	4.5
6375	401.2	2.6	100.7	3.71	3.6	4.8

[a] Height of low molecular weight peak/height of high molecular weight peak
[b] Molecular weight at low molecular weight peak maximum
[c] Molecular weight at high molecular weight peak maximum

(1) The extracted fractions (curves A, B and C) are generally low molecular weight material with reference to the MWD of the whole sample. With increasing T_c, the MWD$_e$'s are shifted to higher values.

(2) For all samples, a pronounced bimodal MWD$_e$ appears, as illustrated in *Figure 10*.

(3) *Figure 10* shows that the relative size of the high molecular weight peak increases with increasing T_c of the samples, whereas according to *Table 1* the relative amount of co-dissolved non-segregated material decreases with increasing T_c. Thus, the high molecular weight peak can only to a minor extent be assigned to the presence of co-dissolved non-segregated material. The major part of this peak especially at the higher T_c's is due to the occurrence of such material in the segregated component.

(4) For the samples of 6375 the low molecular weight peak dominates, whereas for the samples of 7006 the heights of the two peaks are of the same order of magnitude. The data shown in *Table 1* of ref. 1 and *Table 2* indicate that the relative size of the high molecular weight peak, also reflected in M_{low}, M_n and M_w, increases with increasing degree of chain branching. This supports the view that the low molecular weight peak is due to segregated species of a low degree of chain branching, indicating the occurrence of a molecular weight segregation, whereas the high molecular weight peak can be assigned to segregated species of a higher degree of chain branching, indicating the occurrence of a chain branch segregation. These two simultaneously occurring segregation processes involving effects of both molecular weight and chain branching are in agreement with general ideas concerning the crystallizability of molecules: chain ends and chain branches are both irregularities of the molecular structure and cannot be included in the crystals without an increase of free energy.

The IC samples of 6375 were highly selectively extracted (see *Figure 9*). The highly-resolved low molecular weight peak in the MWD$_e$'s assigned to the molecular weight segregation, therefore, provides a suitable basis for determinations of M_{crit}. *Figure 11* shows such data with reference to data from the literature[3].

The following comments may be made with reference to *Figure 11*:

(1) The data obtained (curves A, C and D) are in reasonable agreement with the literature data (curve B), particularly for $T_c \leqslant 398.2$K.

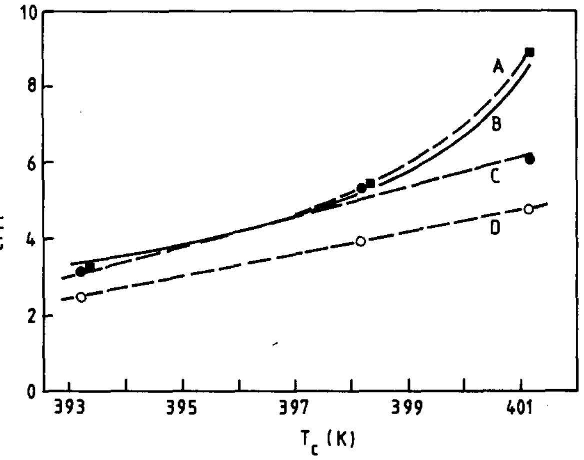

Figure 11 Critical molecular weight of material left uncrystallized at T_c (M_{crit}) plotted *versus* T_c. A, Molecular weight corresponding to a low molecular weight tail of W_s, estimated from MWD_{6375}. The quantity W_s was determined from d.s.c. data; B, according to data by Mehta and Wunderlich[3]; C, chosen such that 90% of the molecules of $MWD_{e,1}$ (*MWD* of the low molecular weight peak) are lower in molecular weight; D, 80% of $MWD_{e,1}$, otherwise analogous with C

(2) The deviation between curves A and C at 401.2K illustrates the relevance of chain branch segregation at the higher T_c's. This is consistent with the occurrence of a more developed high molecular weight peak in MWD$_e$ at this T_c (see *Figure 10*). At lower T_c's, curves A and C approach each other indicating a dominance of molecular weight segregation at these temperatures.

(3) For the other materials, not shown in *Figure 11*, the A curves are shifted upwards significantly with reference to curve B. This can be taken as a manifestation of the occurrence of a higher degree of chain branch segregation within these materials.

Figure 12 shows both experimental and calculated MWD's of different fractions of 6375. The MWD$_e$'s are shifted, as expected, to lower molecular weights compared with the MWD$_{solid}$'s. The calculated values of MWD$_{solid}$ are not anomalous, which demonstrates the consistency of the g.p.c. measurements of MWD$_{6375}$ and MWD$_e$. However, if a pure molecular weight segregation is assumed, the calculated MWD$_{ns}$ goes through negative values at low molecular weights for both samples IC-

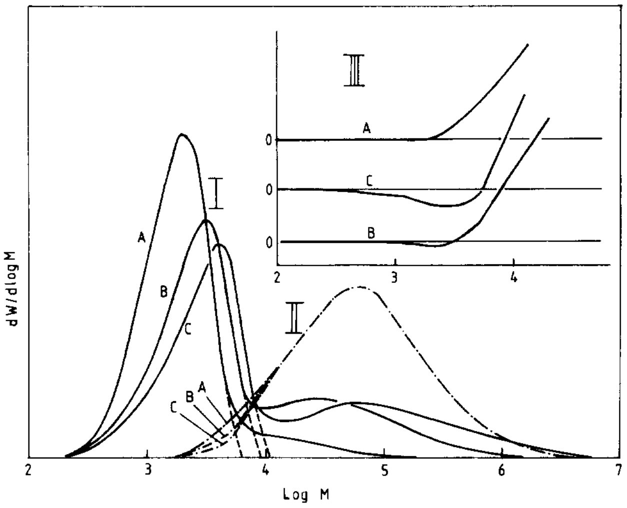

Figure 12 *MWD*'s of different fractions of 6375. A, IC–393.2 K; B, IC–398.2 K; C, IC–401.2 K; I, –: *MWD*'s of extracted (dissolved) fractions (MWD_e). The connected broken lines show the high molecular weight tail of the low molecular weight peak ($MWD_{e,1}$). II, –·–·–: *MWD*'s of solid residues left behind after extraction (MWD_{solid}). They are calculated according to:

$$MWD_{solid} = MWD_{6375} - \Delta m \times MWD_e \quad (8)$$

III, Low molecular weight tail of the *MWD*'s of the non-segregated component (MWD_{ns}) assuming pure molecular weight segregation. Calculated according to:

$$MWD_{ns} = MWD_{6375} - W_s \cdot MWD_{e,1} \quad (9)$$

The zero lines adjacent to the curves indicate the occurrence of negative d*W*/dlog *M* values in some molecular weight ranges

398.2K and IC-401.2K. For all the other materials, not shown in *Figure 12*, the same observation was made. The occurrence of these anomalous data can be assigned to the fact that in addition to the molecular weight segregation a significant amount of chain branch segregation occurs at both 398.2 and 401.2K. At $T_c = 393.2$K, however, there is no evidence for any chain branch segregation in 6375.

In a previous paper[1] d.s.c. data were presented showing most significant differences in W_s' between samples IC- or A-treated at the same temperature. However, a comparison of the MWD$_e$'s of these samples reveals no obvious differences between the two groups of samples. The minor differences observed between them can either be assigned to different MWD of the segregated component or to differences in the sampling (selectivity of extraction).

CONCLUSIONS

According to thermodynamic principles, the dissolution of a crystal should follow an equation: $T_d = (T_d^0/T_m^0)T_m$, where T_d is the dissolution point, T_m is the melting point, and T_d^0 and T_m^0 are the dissolution and melting points, respectively, of an infinite crystal. The deviations from the expected behaviour in melt-crystallized samples, i.e. in polycrystalline samples of wide melting point distributions, were very different for different samples and appeared primarily for the crystals of low melting points. This behaviour can be assigned to kinetic factors and to the existence of interlamellar tie chains connecting crystals of different T_d. There are also indications, i.e. the appearance of a non-selective extraction of the samples of 3140 (50/50 blend of linear and branched PE) and the narrowing of the dissolution temperature range (compared with the melting point range) for the crystals of high melting points, that aggregates of undissolved crystals, evidently not connected with other similar structures, are dispersed into the main liquid phase. The observations for the samples of 3140 indicate the occurrence of large-scale segregation between the linear and branched species in these samples, e.g. in different spherulites.

Evidence is provided for the occurrence of preferential dissolution of regions of the structure of lower crystallinity. These findings are in accordance with the idea, which has been presented earlier[1], that the segregated component has a lower crystallinity than the non-segregated component.

No solvent treatment was found to provide a complete selective extraction of the segregated component. The optimum selectivity was found to be related to different factors, e.g. W_s', the molecular structure. These findings can be due to different causes:

(1) topological effects, i.e. how the segregated component is dispersed in the structure;

(2) the occurrence of surface melting of the crystals melting in the HT peak; and

(3) the occurrence of molecular connections (interlamellar tie chains) between crystals melting in the LT peak with those melting in the HT peak. The increasing molecular weight, the lowering of crystallization temperature, and the increasing inhomogeneity of the distribution of chain branches along the molecules enhance the formation of tie chains and reduce the possibility of selective extraction. In particular, the complicated molecular structure, i.e. the possibility of the occurrence of chain-branch-rich sections of otherwise linear molecules can be of major importance.

The extracted (dissolved) fractions of the samples were found to be of low molecular weight and to have a bimodal MWD. There is experimental support for the assignment of the low molecular weight peak to almost linear chains, indicating the occurrence of molecular weight segregation, and of the high molecular weight peak to molecules of a higher degree of chain branching, indicating the occurrence of a chain branch segregation. Data were obtained for the critical molecular weight associated with molecular weight segregation. These data were in good agreement with data earlier reported by Mehta and Wunderlich[3] for samples of low T_c's ($\leqslant$398.2K), but were slightly lower at the higher T_c's.

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REFERENCES

1 Gedde, U. W. and Jansson, J.-F. *Polymer* 1983, **24**, 1521
2 Gedde, U. W. and Jansson, J.-F. *Polymer* 1983 submitted
3 Mehta, A. and Wunderlich, B. *Coll. Polym. Sci.* 1975, **253**, 193
4 Dlugosz, J., Fraser, G. V., Grubb, D., Keller, A., Odell, J. A. and Goggin, P. L. *Polymer* 1976, **17**, 471
5 Winram, M. M., Grubb, D. T. and Keller, A. *J. Mat. Sci.* 1978, **13**, 791

6 Winram, M. M. *MSc Thesis*, University of Bristol, 1976
7 Huseby, T. W. and Bair, H. E. *J. Appl. Phys.* 1968, **11**, 4969
8 Wunderlich, B. 'Macromolecular Physics', vol 3, Academic Press, New York, 1980
9 Nakajima, A. *et al. Kolloid Z.Z. Polym.* 1968, **222**, 124
10 Cormier, C. M. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1966, **4**, 666
11 Jackson, J. F., Mandelkern, L. and Long, O. C. *Macromolecules* 1968, **1**, 218
12 Pennings, A. J., van der Mark, J. M. M. A. and Kiel, A. M. *Kolloid Z.Z. Polym.* 1970, **237**, 336
13 Vadimsky, R. G., Keith, H. D. and Padden Jr., F. J. *J. Polym. Sci., Polym. Phys. Edn.* 1969, **7**, 1367
14 Mandelkern, L. Presentation at the 14th Europhysics Conference on Macromolecular Physics, Vilafranca del Penedes, Spain, September, 1982
15 Bares, V. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 397
16 Mandelkern, L. *J. Polym. Sci., Polym. Symp.* 1973, **43**, 1
17 Kitamaru, R., Horii, F. and Hyon, S-H. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 821