

Crystallization and Melting Behavior of Polyethylene Fractions Obtained by Various Fractionation Methods*

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SUMMARY

A high density polyethylene (HDPE) and a low density polyethylene (LDPE) were fractionated by means of preparative GPC, analytical GPC, direct extraction, and a crystallization/dissolution method, to enable determination of the chain branching distribution over the molar mass distribution.

The non-isothermal crystallization and melting behaviour of the HDPE and LDPE fractions and of a series of linear polyethylene (LPE) fractions was studied using DSC with a scanning rate of 5 K/min. After an initial increase, the crystallization temperature of the LPE fractions started to decrease at $M \approx 20$ kg/mol, to remain at a constant value from $M \approx 60$ kg/mol. This is illustrative of the crystallization being hindered by entanglements. With LDPE fractions showing a constant degree of short chain branching an analogous, but greater, decrease was observed in a corresponding range of molecular dimensions. The differences found for the HDPE fractions as compared with the LPE reference values are due mainly to short chain branching.

INTRODUCTION

Among the many factors determining crystallization from the melt of polyethylenes - and, in conjunction therewith, morphology and properties -, molar mass and chain branching of the macromolecules hold important places. Fractionation techniques effecting a separation unequivocally based on these structural parameters are therefore of great importance. In the following it will be shown in how far some of the currently available techniques do effect separations answering to this description.

The crystallization and melting behaviour of the fractions obtained was studied under non-isothermal conditions, so that the results have particular relevance to industrial practice. Differential scanning calorimetry (DSC) is a technique that is especially suitable and is therefore widely applied. As DSC results are quite often used as a basis for pronouncements on the presence of short chain branching (SCB) in a sample, and even on the distribution of SCB over individual molecules, this subject will receive special attention.

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EXPERIMENTAL

Fractionation methods

The fractionation methods on which attention is focussed here are analytical and preparative gel permeation chromatography (GPC), direct extraction (1), and a crystallization/dissolution method.

High-temperature preparative GPC was performed at the National Physical Laboratory using a Waters Anaprep apparatus, with TCB at 135 °C. Yields per fraction varied between 30 mg and 3 g.

High-temperature analytical GPC fractionation was carried out with a Waters GPC-200, using TCB at 140 °C. The GPC fractions, having weights varying between c. 10 µg and 1 mg, were precipitated on a filter placed upside down in a DSC pan to promote contact between sample and pan bottom. A pan with an unloaded filter was used for reference purposes.

Direct extraction experiments were performed by Chemische Werke Hüls AG in the Federal Republic of Germany, with p-xylene/ethyleneglycol/monoethylether mixtures at 119 °C; the fractions obtained varied in weight from c. 80 mg to 0.8 g.

In the crystallization/dissolution fractionation procedure the sample was dissolved at 134 °C in p-xylene and then crystallized on a net fastened to a stirrer, by cooling to 50 °C at the rate of 8 K/h. Following this, fractions were drained off at various solution temperatures, the yields being from c. 0.1 g to 2 g.

Measuring technique

For the DSC measurements use was made of Perkin-Elmer DSC-2's connected on-line to Tektronix 4051 and Hewlett-Packard 9836 systems. Samples were measured between 50 °C and 150 °C or between 40 °C and 200 °C, using a scanning rate of 5 K/min and 5-min isothermal waits. Sample weight was kept at 0.8 ± 0.025 mg, to minimize thermal lag and deformation of the DSC curve whilst yet allowing the heats of transition to be determined quantitatively. For the calibration use was made of indium, tin and lead, and weighing was done with a Mettler ME 22/36 electronic microbalance. Dry nitrogen was used as purging gas.

Samples

Linear polyethylene (LPE) fractions were obtained from Société Nationale Elf d'Aquitaine Production and the U.S. Dept. of Comm. Nat. Bureau of Standards, as well as by in-house cross-fractionations. The M_w/M_n and M_z/M_w values were around 1.5. Results of measurements on $C_{58}H_{118}$ and literature values (2) for $C_{64}H_{130}$ to $C_{140}H_{282}$ were added.

Hizex 7000 F, an HDPE, was fractionated using the direct extraction method (M_w/M_n and M_z/M_w values around 2), analytical GPC (M_w/M_n and M_z/M_w around 1.1) and the crystallization/dissolution method.

Stamylan 1520 S, an LDPE, was fractionated by both preparative GPC (M_w^*/M_n^* and M_z^*/M_w^* values around 2 - with * indicating that the GPC values are influenced by long chain branching, so that the apparent molar mass, M^* , which is related to the molecular dimensions in solution, is smaller than the true molar mass, M) and analytical GPC (M_w^*/M_n^* and M_z^*/M_w^* around 1.1).

RESULTS AND DISCUSSION

Linear polyethylene

The crystallization study was started with linear polyethylene, which was taken as the reference system for the other polyethylenes. An investigation was made into the influence of molar mass on the crystallization and melting behaviour, using polyethylene fractions from various sources. The literature data on these polyethylenes are based mainly on isothermal crystallization experiments. This type of experiment offers certain advantages, for instance in theoretical interpretations. However, in view of the relevance to day-to-day practice a choice was made here for crystallization and melting at a constant scanning rate, the rates used being $S_c = 5 \text{ K/min}$ and $S_h = 5 \text{ K/min}$, respectively.

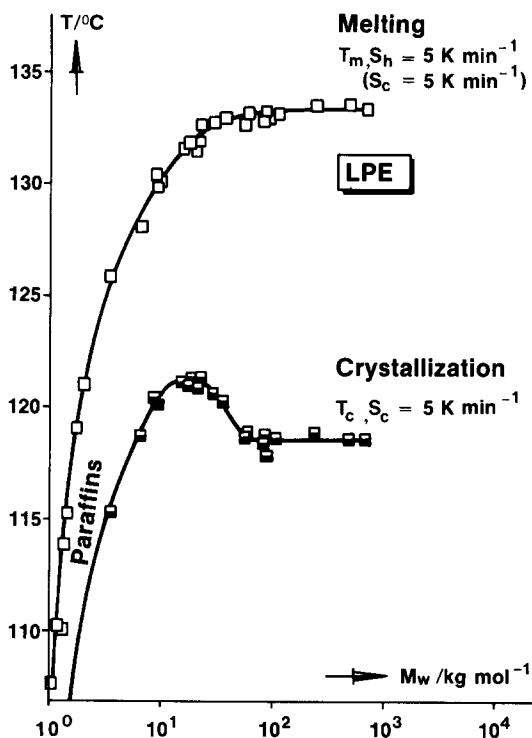


Fig. 1. Crystallization and melting peak temperatures for linear polyethylene (LPE) fractions and paraffins, as functions of M_w .

Fig. 1 shows crystallization and melting peak temperatures as functions of the mass-average molar mass. T_m shows a variation which at first sight appears quite normal; it is described by

$$T_m = 133.4 - 27.1/M_w \text{ (}^\circ\text{C)}, \quad M_w \text{ in kg/mol.}$$

A more interesting variation is shown by the crystallization peak temperature. After an initial, and expected, increase T_c decreases again from $M \approx 20$ kg/mol, to become more or less constant (118.6 °C) at $M_w \approx 60$ kg/mol. It is clear that from a given molar mass upwards crystallization is considerably hampered. This is also illustrated by the fact that the supercooling - i.e. the temperature difference between the theoretical crystal \rightleftharpoons melt transition temperature and T_c - increases with M_w by a factor 1.6, in the range from $M_w = 3$ kg/mol to $M_w = 700$ kg/mol. It should also be noted here that over the same range the difference between the transition temperature and T_m increases by a factor 2, which shows that T_m , too, reflects the impediment to crystallization, albeit less conspicuously than T_c .

Quantitative comparison with isothermal experiments is difficult, so that the discussion will be restricted to a qualitative interpretation. It is known that the isothermal crystallization rate as a function of M shows a maximum, which shifts from $M_\eta \approx 100$ kg/mol when the supercooling is only slight, to $M_\eta \approx 10$ kg/mol, when it is strong (3). In DSC experiments in which S_c was varied an analogous tendency was found for the maximum in T_c noted here, which makes a correspondence plausible.

The cause of the decrease of T_c between $M_w \approx 20$ kg/mol and $M_w \approx 60$ kg/mol finds an obvious explanation in an increase in the influence of entanglements. How complex the situation actually is will become clear if it is remembered that at the lowest M value there is a transition from extended chain crystallization to folded chain crystallization according to Regime I (4). At higher M the supercooling increases at constant cooling rate, as a result of the influence of entanglements becoming stronger, so that multiple nucleation can occur (Regime II) (4). This leads to fixation of chain parts at various crystal locations, thus also enabling the formation of intercrystalline links. At $M_w \approx 60$ kg/mol the situation has evidently become so extreme that chain parts will crystallize individually, so that T_c is no longer dependent on M , and crystallization according to Regime III (5) occurs. As M increases along the $T_c(M)$ curve, the morphology must change from d rods, through g rods and a-type spherulites to b-type spherulites (6).

It is intriguing that the specific $T_c(M)$ variation does not have a parallel in $T_m(M)$. This illustrates that in DSC studies the use of melting curves only can lead to a serious narrowing of the scope of information. Originally we assumed that reorganization phenomena disturbed the $T_c - T_m$ correlation only during heating. Calculations based on recent work (7) suggest, however, that - depending on crystallization temperature and cooling rate - also during cooling considerable thickening of lamellae can occur. Should this indeed be the case, not only the $T_c \rightleftharpoons T_m$ correlations, but also the correlations of T_c and T_m with the results of morphology studies at room temperature would become questionable.

HDPE and LDPE

In the case of HDPE and LDPE the influence of molar mass on crystallization and melting behaviour is expected to be accompanied by an influence of chain branching. A possibility to study short chain branching (SCB) and the related sequence length distribution independently of molecular dimensions is offered by GPC fractionation.

Stamylan 1520 S, an LDPE containing about 20 CH₃/1000 C, was fractionated by means of analytical and preparative GPC. Owing to the presence in this product of about one long chain branch (LCB) per 1000 C, molecular dimensions are so influenced that molecules with molar mass M have the same elution volume as linear molecules with molar mass M^* (with $M^* < M$). The GPC values will therefore be distinguished by means of a superscript asterisk, for instance M_w^* . SCB does not affect the molecular dimensions to any appreciable extent and can therefore be studied independently. As can be seen in Figs. 2 and 3, the T_c and T_m results obtained by means of these two methods correspond.

Hizex 7000 F, a HDPE with c. 4 CH₃/1000 C and containing butene-1 as comonomer, was fractionated according to molar mass by analytical GPC. Analysis of fractions obtained by direct extraction showed that this method likewise had made the separation according to molar mass, so that it provides an interesting possibility for preparative HDPE fractionation. From Figs. 2 and 3 it is seen that the results of the two methods show good correspondence.

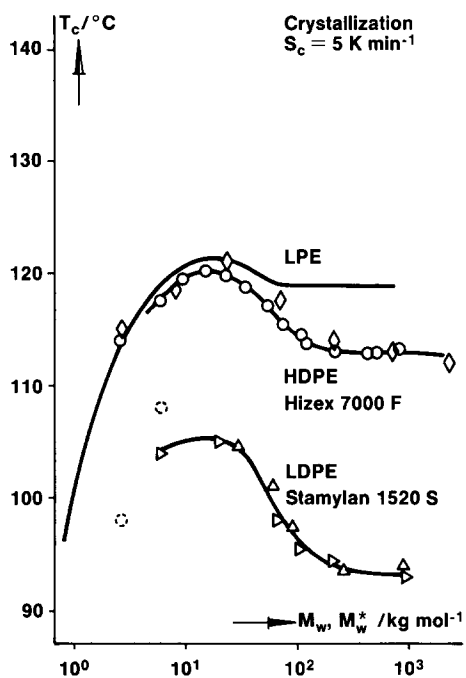


Fig. 2. Crystallization peak temperatures for Hizex 7000 F fractions (\circ : direct extraction; \diamond : analytical GPC) and Stamylan 1520 S fractions (\triangle : preparative GPC; \triangleright : analytical GPC), and the LPE reference curve according to Fig. 1.

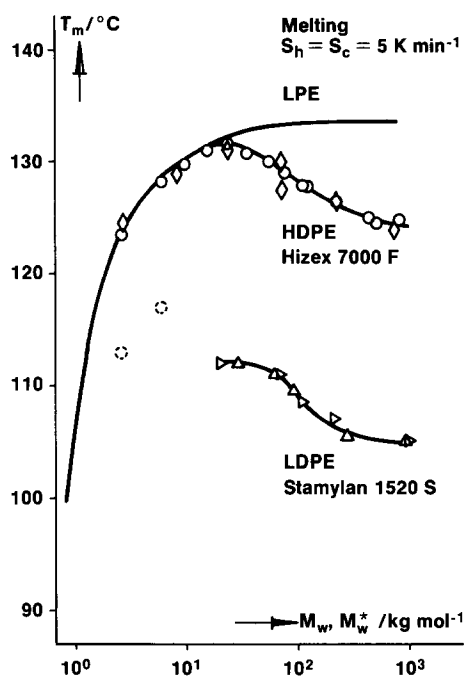


Fig. 3. Melting peak temperatures (rest as for Fig. 2). A smaller peak in the DSC curve is indicated by \circ (cf. Fig. 2).

It follows from the foregoing that a separation by analytical GPC followed by DSC analysis of the fractions can give reliable information on crystallization and melting behaviour, and, more generally, that it is possible to obtain information on GPC fractions by thermal analysis. It is, further, noteworthy that differences in polydispersity, in processing route, etc., due to the use of different fractionation techniques, do not affect the results. Also, the correspondence of the T_c values indicates that the content in seed nuclei of the fractions shows no appreciable differences from one method to another.

If one had no knowledge of the $T_c(M)$ variation for linear polyethylene fractions, one would be inclined to ascribe the sharp drop of T_c (12 °C!) with M_w^* in Fig. 2 for Stamydan 1520 S to an increase in the degree of SCB. IR and NMR analyses show, however, that the degree of SCB rather decreases slightly. This is in accordance with earlier investigations (8 - 13), which, strangely enough, have hardly attracted attention.

For Hizex 7000 F there is a simpler interpretation of Fig. 2, as in this case the T_c values are reasonably close to the T_c values of the linear polyethylene fractions, so that it may be assumed that the influence of entanglements may be roughly estimated from that observed in linear polyethylene (LPE). The difference $T_{c,LPE} - T_{c,HDPE}$ is then attributed mainly to the influence of SCB, in accordance with the IR data, on the assumption that there are no differences in nucleation density between the LPE and HDPE fractions.

It is interesting to note that the polyethylene types here considered show a T_c decrease at about the same values of M^* and M for LDPE and LPE/HDPE, respectively. This suggests that it is not so much molar mass (degree of polymerization, extended chain length) as molecular dimensions in the melt that play a role in the crystallization process. For, actually M^* and M , being GPC values, are determinative of the molecular dimensions in solution, which, in turn, are related to the molecular dimensions in the melt.

For Stamydan 1520 S Fig. 3 shows a substantial decrease (7 °C) with M^* also for T_m . Evidently, in this type of LDPE the decrease of T_c with M^* is so great that reorganization is unable to prevent the decrease from being clearly reflected in T_m (M^*). In complete analogy to the interpretation given in respect of T_c we assume also in this case that the low melting temperatures of the Hizex 7000 F fractions as compared with the LPE fractions are mainly attributable to SCB.

The results discussed here clearly illustrate once more that overall quantities such as $CH_2/1000$ C, density, heat of fusion, and also T_c and T_m , determined on a starting product do not necessarily point to one definite molecular structure of this product. Samples showing the same values of the overall quantities may, for instance, differ in SCB distribution. This alone makes evaluation of the shape of the DSC curve a necessary refinement, which, however, very readily introduces problems of interpretation. An evaluation as applied here actually does not provide much more than superficial information. To mention one point: important differences between the fractions as regards the shape of the DSC curve no doubt point to differences in SCB distribution.

CONSEQUENCES FOR SOME RELATIONSHIPS

In view of what goes before, one cannot expect simple relationships to exist between crystallization parameters like T_C and T_m on the one hand and SCB and M on the other. For instance, the difference $T_{C,LPE} - T_{C,HDPE}$ can be ascribed to SCB in a qualitative sense, but the quantification of this difference requires accounting for the value of M and in some cases for the influence of seed nuclei, the fact that the PE was dissolved during fractionation, the processing route, etc. In addition, a differentiation in crystallization behaviour may be expected also in dependence on nature, length and distribution of the branches.

FRACTIONATION TECHNIQUES

As observed before, direct extraction resulted for Hizex 7000 F in a fractionation according to M , whereas for both Hizex 7000 F and Stamylian 1520 S the GPC methods resulted in a fractionation according to M and M^* , respectively. In a fractionation by the crystallization/dissolution method, the separation is expected to be influenced by M and SCB (14 - 17), with the degree of this influencing being dependent on the specific way in which the fractionation is performed.

If the relationship between dissolution temperature and M may be assumed to be analogous to that between T_m and M , an interesting situation arises for Hizex 7000 F. For, the line representing a fraction drained off at a given temperature might then intersect the $T_{diss.}(M)$ curve in the $T_{diss.}$ vs. M graph at both low and high M . For such fractions DSC curves with one peak but bimodal GPC curves are expected.

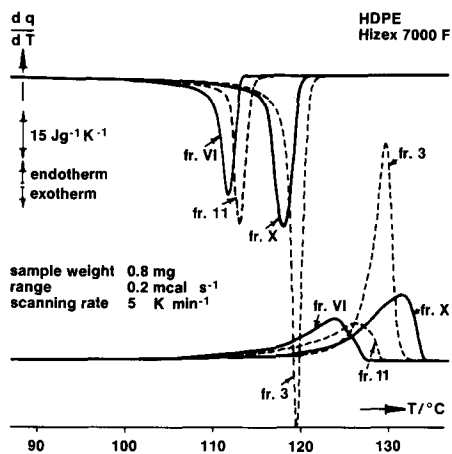


Fig. 4. DSC cooling and heating curves for Hizex 7000 F fractions; fr. 3 and fr. 11: direct extraction; fr. VI and fr. X: crystallization/dissolution fractionation.

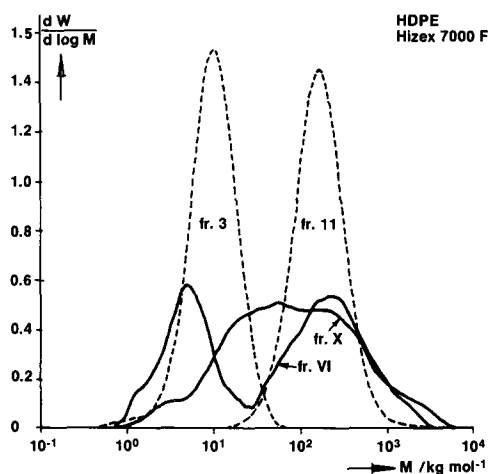


Fig. 5. Normalized GPC curves for the Hizex 7000 F fractions given in Fig. 4.

Fig. 4 shows DSC curves for two fractions obtained by the direct extraction method and for crystallization/dissolution fractions obtained after dissolution between 85 °C and 87.5 °C and between 95 °C and 100 °C. In accordance with expectation, the DSC curves show a single peak.

Fig. 5 gives the corresponding GPC curves. The direct-extraction fractions (fr. 3 and fr. 11) are unimodal, with M_n , M_w and M_z having values of 7.4, 12, 17 and 130, 210 and 440 kg/mol, respectively. Dissolution in the crystallization fractionation process at temperatures between 85 °C and 87.5 °C (fr. VI) does, indeed, result in a bimodal GPC curve, with M_n , M_w and M_z being 9, 210 and 820 kg/mol, respectively. Also a fraction obtained after dissolution at a temperature between 90 °C and 92.5 °C still shows a bimodal curve. However, if dissolution takes place between 95 °C and 100 °C (fr. X in Fig. 5), the curve is unimodal but broad (M_n , M_w , M_z being, respectively, 21, 280, 1380 kg/mol), which could correspond to the maximum in the $T_m(M)$ curve.

From the picture outlined above it follows that in the case of the Hizex 7000 F sample the crystallization/dissolution method used here does not unequivocally lead to a separation according to a molecular parameter; it is therefore useful here as a possibility for cross-fractionation according to SCB following a fractionation according to M.

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