

Molecular Structure, Melting Behavior, and Crystallinity of 1-Octene-Based Very Low Density Polyethylenes (VLDPEs) as Studied by Fractionation and Heat Capacity Measurements with DSC

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Synopsis

Heat capacity measurements with DSC on 1-octene-based very low density polyethylenes (VLDPEs), with densities from 888 to 907 kg/m³, show crystallization between 120 and -60°C and melting between -60 and 130°C. Under the assumption that hardly any octene groups are present in the crystal lattice, the experimental heat capacity values were compared with reference values for purely amorphous and purely crystalline linear polyethylene on the basis of a two-phase model. The enthalpy-based weight crystallinity data as a function of temperature show that the crystallinities at -60°C are about 40% higher than those at room temperature, which vary from 25 to 40% and are in good agreement with volume-based weight crystallinities. The crystallization and melting curves show several peaks. Fractionations by the crystallization/dissolution method and the direct extraction method show that this is due to intermolecular heterogeneity of comonomer incorporation and that VLDPE is a reactor blend of molecules ranging from the uncrystallizable and poorly crystallizable type to the HDPE type.

INTRODUCTION

The current trend toward development of high performance plastics has a large impact on day-to-day laboratory practice. Research on relationships between polymerization, molecular structure, processing, morphology, and properties increasingly requires an integral approach at each stage, involving a variety of analytical methods.

This publication concerns fractionation and DSC results from such research. Fractionation techniques have long been known and, until recently, were usually avoided because they are very laborious. Their widespread reintroduction is necessitated by the complexity of the new materials studied. The resolution and stability of DSC are taxed to the utmost by some new semicrystalline materials, on account of the intrinsically small heat effects of the physical processes to be studied or because the processes cover a wide temperature range. Further, flexibility of measuring procedures is important, a requirement that is mainly a software problem. In many cases, in-house software development is necessary.

Examples of polymeric materials with small heat effects are certain blends, liquid crystalline polymers, and EPDM rubbers. The very low density polyethylenes reported here, which are known as VLDPEs or ULDPEs (ultra-

low density polyethylene),¹⁻³ are examples of materials whose crystallization and melting ranges are very wide.

During the past few years, there have been interesting developments in the molecular structure of ethylene-based polymers, for example ultra-high molecular weight polyethylenes (UHMWPE) and the ethylene co- and terpolymers with low densities. On the basis of their molecular structure, the ethylene copolymers can be divided into heterogeneous and homogeneous copolymers.

A typical example of a heterogeneous ethylene copolymer is linear low density polyethylene (LLDPE), in which, besides ethylene, a 1-alkene, in particular 1-butene or 1-octene, has been incorporated into the chain. LLDPEs are available in densities from about 915 kg/m³. The heterogeneity is intermolecular in nature.⁴⁻⁷

There are several examples of homogeneous ethylene copolymers.^{4,8} Such copolymers have not only been prepared as model samples over a wide density range⁹⁻¹¹; they are also commercially available in the form of amorphous to low-crystalline EPDM rubbers and some types of TAFMERS¹² with densities from 888 to 898 kg/m³. These copolymers are both intra- and intermolecularly homogeneous.

The commercially available VLDPEs¹³⁻¹⁸ have densities below 915 kg/m³, while some of the examples reported here concern materials with a density below 890 kg/m³. With the aid of DSC, the crystallization and melting behavior of this new type of polyethylene was investigated, and, by combining the DSC measurements with fractionation experiments, insight was obtained into the molecular structure in terms of comonomer incorporation. A morphology study on some of the samples reported here has been published very recently.³

EXPERIMENTAL

Samples and Measuring Techniques

Polymerization was carried out in solution, using the catalyst components SEAC (sesquiethylaluminium chloride), EBM (ethylbutyl magnesium), and TBT (tetrabutoxytitanium), with 1-octene as comonomer.

The melt flow index (MFI) of the polymer (dg/min) was determined according to ASTM D 1238, cond. E. The density D (23°C) (kg/m³) of compression-molded test specimens of the polymer was determined according to ASTM D 1505. The mole percentage of 1-octene, X_8 (%), was derived from the number of CH₃ groups per 1000C which was determined by infrared measurement.

For the DSC measurements, use was made of a measuring assembly comprising a Perkin-Elmer calorimeter, type DSC-2, arranged on-line with a Tektronix 4052 computer, a Hewlett-Packard 3495A scanner-multiplexer, and a Hewlett-Packard 3455A digital volt meter (5½–6½ digit). To ensure calorimeter stability, the block surrounding the DSC unit was thermostatted at –120°C with the aid of liquid nitrogen controlled by a Cryoson TRL 5 unit. The sample weights were determined to the nearest 1 μg with a Mettler ME 22/36 electronic microbalance.

Fractionation Methods

In the crystallization/dissolution fractionation procedure, 5 g of the sample were dissolved, during stirring, in 1.5 L of xylene at 120°C, for 4 h, after which stirring was stopped and the material was crystallized from the solution by cooling to room temperature at a rate slower than 1°C/min. Next, the fractions were drained off, first at room temperature (K-1) and then, after heating with stirring, at 68 (K-2), 91 (K-3), and finally 110°C (K-4). The yields ranged from 0.3 to 3 g. As antioxidant, DBPC was used.

In the direct extraction procedure, starting from 4.21 g of the sample, fractions were obtained at 109°C (D-1–D-9) by variation of the volumetric ratios in xylene/ethylene glycol monoethyl ether mixtures from 120/180 to 300/0 mL/mL. As antioxidant, DBPC was used. The yields ranged from 250 to 600 mg.

DSC Procedure

Since orienting measurements had shown that the crystallization and melting processes covered wide temperature ranges, it was deemed necessary to carry out the measurements according to the "continuous" method.¹⁹ The classical, stepwise method with relatively small temperature increments is hardly feasible because the crystallization and melting processes proceed as a function of time at any temperature, which means that there is no temperature at which the situation is stable. This in turn means that no stable isotherms are to be expected before or after a temperature increment, which makes truly quantitative measurement impossible.

Therefore, the measurements—under dry nitrogen—were carried out, after rapid heating to 180°C, by cooling in one run from 180 to –70°C and then heating in one run from –70 to 180°C, always at a rate of 10°C/min, holding the sample isothermally at –70 and 180°C for 5 min.

The procedure is that of a genuine c_p measuring method, that is, first the empty pan together with the lid is measured, and then the same pan and lid assembly with the sample in it is measured in exactly the same way. Every 0.2°C, the temperature and the corresponding measuring value are recorded. The values for the empty pan and lid are subtracted from the values for the pan and lid with sample at each temperature and the result is divided by the sample weight and the scan rate, resulting in the $c_p(T)$ of the sample.

In the first instance, the temperature and enthalpy calibrations were performed with indium and lead at the same scan rate. Later, the temperature calibration in cooling was improved via a calibration with 4,4-azoxyanisole. About this substance it is known that the temperature corresponding to the transition between isotropic and anisotropic melt is virtually independent of whether the transition occurs during cooling or heating. The enthalpy calibration was checked by measurements on sapphire (Al_2O_3), in cooling and heating via the continuous method. The $c_p(T)$ values thus obtained for the heating curve were compared with literature values and were found to agree with these values within a few percent over the whole temperature range of 250°C. This also confirms that the continuous measuring method—especially in heating—can be considered to be quantitative, as demonstrated in earlier publications.^{9,19}

RESULTS AND DISCUSSION

Crystallization and Melting

Figure 1 shows the results of specific (per g polymer) heat capacity measurements of VLDPE7 and a homogeneous ethylene/1-octene copolymer with virtually the same mole percentages of 1-octene. The sample weights were 10.005 mg (VLDPE) and 9.259 mg (EO).

The terminology used here is that of Ref. 19. In each measurement, a sample was heated to 180°C and maintained at that temperature for 5 min, after which it was cooled at a rate of 10°C/min. The corresponding curve is indicated by $c_{p_{cc}}(T)$ (cc stands for cooling curve), the (positive) c_p value having been plotted in downward direction. Crystallization for the VLDPE takes place between about 120°C and the lowest measuring temperature of -60°C. As can be seen in Figure 1, and as appears from torsion damping measurements, the sample is in a glassy state at -70°C, which state is sufficiently stable, for the purposes of DSC measurements, to make it possible to hold the sample isothermally for some time. Peaks are observable at about 70 and 109°C. The EO copolymer has a single-peak curve, with a peak temperature of about 70°C. After having been held isothermally for 5 min at -70°C, each sample was heated at a rate of 10°C/min, resulting in the DSC curves indicated by $c_{p_{hc}}(T)$ (hc stands for heating curve), with the (positive) c_p value being plotted in upward direction. In the case of the VLDPE, melting takes place from the lowest measuring temperature onward until the remarkably high temperature of about 130°C. Peaks are observable at about 91, 121, and 125°C. The EO copolymer again has a single-peak curve, with a peak temperature of about 76°C.

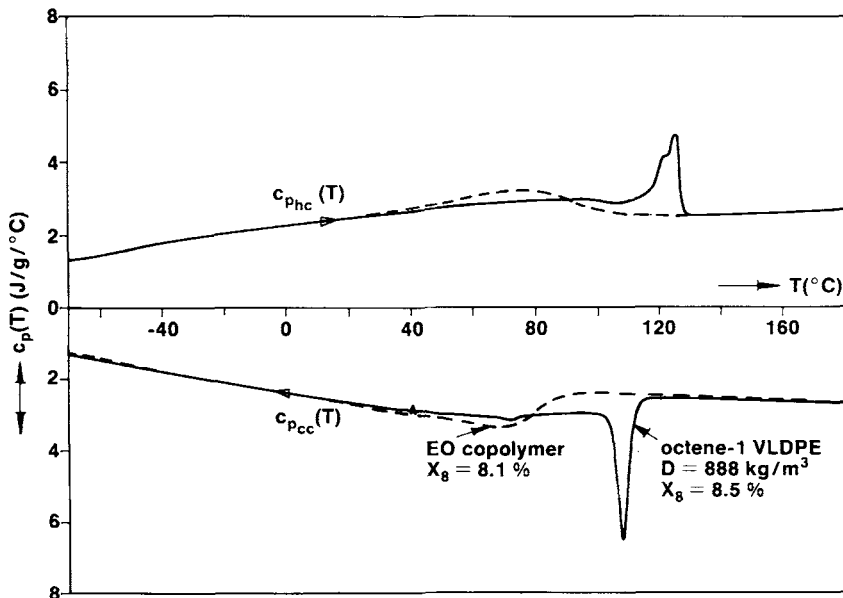


Fig. 1. DSC-2 continuous specific heat capacity curves for cooling ($c_{p_{cc}}$) and subsequent heating ($c_{p_{hc}}$) for a homogeneous ethylene copolymer and VLDPE7.

It should be noted that low-temperature peaks are more difficult to characterize in terms of peak temperatures, because the phenomena represented by such peaks cover wide temperature ranges. It is clear that in the case of VLDPE the crystallization process starts at much higher temperatures than in the case of the EO copolymer and that, accordingly, the melting process ends at higher temperatures.

On the basis of previous research,⁵ it can be concluded from the DSC curves, especially the occurrence of more than one peak, that VLDPE is a heterogeneous copolymer. DSC peaks that differ strongly with regard to the position on the temperature axis are considered to indicate differences in comonomer incorporation in the chains.

According to this line of thought, the several peaks in the heating curve relate to crystals of different thermodynamic stability,^{3,20-22} causing differences in melting point. For these copolymers, the crystallization and melting behavior is to a large extent determined by molecular structure, a particularly dominant factor being the crystallizable ethylene sequences in the chains. It is to be expected that, considering the length of the comonomer 1-octene, the majority of the octene groups will be excluded from the crystal lattice²³⁻²⁶ and will effectively hinder crystal growth in the chain direction,²⁷ with a minority possibly causing hindrance also in transverse direction²⁸ or giving rise to defect structures^{29,30} during crystal growth in that direction. Further, it is known that, under the conditions described here, the octene groups show no side chain crystallization.²³ This means that the manner in which the comonomer is incorporated into the chain and, in direct relation to this, the number, nature, and arrangement of the ethylene sequences are the relevant molecular structure parameters to be determined.

In the case of homogeneity of comonomer incorporation one can make the simplifying assumption that it suffices to determine the—single peak—ethylene sequence length distribution³¹ and correlate this distribution to the crystal dimension distribution and the melting point distribution via a crystallization model.⁷ The chain structure and the ethylene sequence length distribution can in this case be derived from the reactivity ratios—calculated from ¹³C NMR data with the help of a polymerization model—and the monomer/comonomer concentration ratio during polymerization.

In the case of heterogeneous comonomer incorporation, the heterogeneity can be intra- and/or intermolecular in nature, that is, there can be differences in comonomer incorporation within a chain and/or between chains. Fractionation techniques can reveal this⁴⁻⁷ (cf. the introductions of Refs. 5 and 32). A multiplex ethylene sequence length distribution could then be viewed as a superposition of several single-peak distributions, caused by the catalyst itself^{32,33} and/or the polymerization conditions. Obviously, in a crystallization model not only interactions between ethylene sequences within one particular sequence length distribution should be taken into account, but also interactions between sequences belonging to different distributions.

Moreover, in view of the wide temperature range covered by the crystallization and melting processes in the polymers under review here, the crystallization model should also account for a possible transition from folded chain crystallization at relatively high temperatures to fringe micelle crystallization at relatively low temperatures.

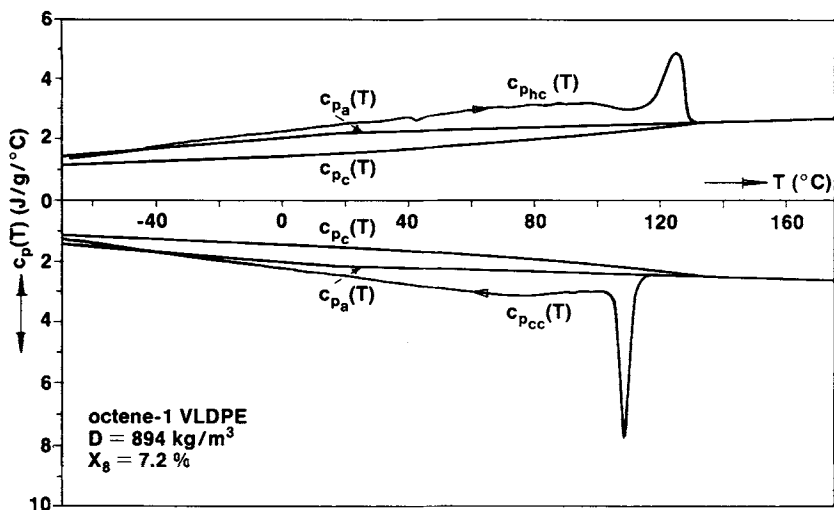


Fig. 2. Cooling curves ($c_{p_{cc}}$) and heating curves ($c_{p_{hc}}$) as in Figure 1 for VLDPE5. Reference curves for purely amorphous polyethylene (c_{p_a}) and purely crystalline polyethylene (c_{p_c}).

With these extremely wide crystallization and melting ranges, the material can be said to be in a stable condition only at the highest and the lowest measuring temperatures. This becomes especially clear from a comparison of the experimental c_p curves with the reference curves $c_{p_a}(T)$ and $c_{p_c}(T)$ for purely amorphous (subscript a) and purely crystalline (subscript c) polyethylene, respectively, as determined in Ref. 34 under the assumption of the two-phase model.

Figure 2 shows such a comparison for VLDPE5. The sample weight was 8.704 mg. In the melt, $c_p(T)$ is in close agreement with $c_{p_a}(T)$ while only at the lowest temperatures the $c_p(T)$ curve lies between the $c_{p_c}(T)$ curve and the $c_{p_a}(T)$ curve, indicating that there is virtually no crystallization or melting.

Enthalpy-Based and Volume-Based Crystallinity

The above findings with regard to the extremely wide temperature ranges are also confirmed by a special representation of the measuring results as applied in Ref. 19 on the basis of Ref. 34. In Figure 3, the $h_{hc}(T)$ curve (hc again stands for heating curve) of the VLDPE from Figure 2 is included. This curve was obtained via numerical integration of the $c_{p_{hc}}$ values and calibration at (141.4°C, 779 J/g). In addition, the reference curves $h_a(T)$ and $h_c(T)$ are given, which were, of course, obtained via integration of $c_{p_a}(T)$ and $c_{p_c}(T)$, respectively. For details see Refs. 19 and 34.

With the help of these data, the value $W^c(T)$ can be calculated for any temperature, according to the definition

$$W^c(T) = \frac{h_a(T) - h(T)}{h_a(T) - h_c(T)} \times 100\%$$

This quantity is hence related to the enthalpy of the sample and to the

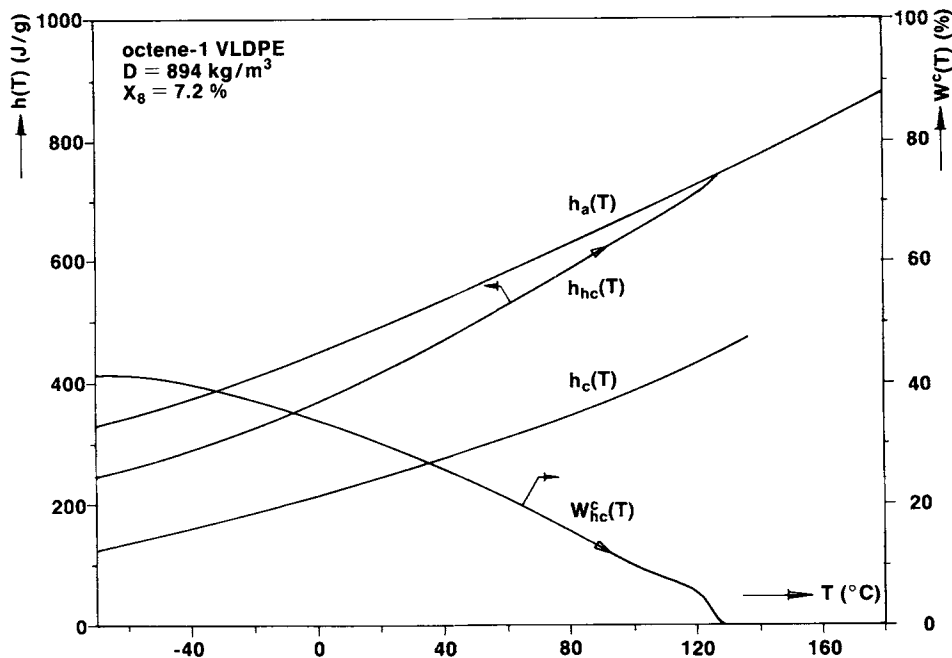


Fig. 3. Specific enthalpy heating curve (h_{hc}) for the VLDPE of Figure 2, the reference curves for purely amorphous polyethylene (h_a) and purely crystalline polyethylene (h_c), and the enthalpy-based weight crystallinity heating curve (W_{hc}^c).

enthalpy extremes (based on the two-phase model) of linear polyethylene, and is a sensitive measure of the degree to which these extremes have been realized.

There are good reasons to assume that the two-phase model is applicable to the polymers under review, which means that the quantity $W^c(T)$ may be identified with the enthalpy-based weight crystallinity. After all, under the plausible assumption that the majority of the octene groups are excluded from the crystal, as discussed before, we may assume that the crystalline phase is well defined. Further, we may assume that interface phenomena, such as orientation and consequent lowering of the entropy or changes in the gauche/trans ratio or better packing and hence a lowered enthalpy, hardly give rise to a specific heat capacity different from $c_{p_d}(T)$.

The only other scientifically valid and practical method of determining the crystallinity of ethylene polymers via DSC curves, viz. by extrapolation from the melt using the $\Delta h(T)_M$ approximation,¹⁹ is inadequate here, for extrapolation from the melt along an approximately straight line is possible down to 17°C but not lower, on account of the discontinuity in $c_{p_d}(T)$ at that temperature.³⁴

The $W_{hc}^c(T)$ curve, the numerical values of which are indicated on the right-hand axis, shows a continuous decrease in $W^c(T)$ from -60°C . A particularly striking fact is that the value of W_{hc}^c at 23°C , which is about 29%, is considerably lower than the value at -60°C , which is about 41%. This illustrates once more that the melting process is already in progress from -60°C onwards and that, conversely, such samples will continue to crystallize

when cooled from room temperature. For this particular sample, too, the melting process is not finished until about 130°C.

The densities of the samples measured at room temperature enable comparison of the quantities $W_{hc}^c(23^\circ\text{C})$, the enthalpy-based weight crystallinity determined from the heating curve, and $W^c(23^\circ\text{C})$, with $W^c(23^\circ\text{C})$ being defined as

$$W^c(23^\circ\text{C}) = \frac{v_a(23^\circ\text{C}) - v(23^\circ\text{C})}{v_a(23^\circ\text{C}) - v_c(23^\circ\text{C})} \times 100\%$$

where $v_a(23^\circ\text{C}) = 0.00117 \text{ m}^3/\text{kg}$ and $v_c(23^\circ\text{C}) = 0.001 \text{ m}^3/\text{kg}$, while $v(23^\circ\text{C}) = 1/D(23^\circ\text{C}) \text{ m}^3/\text{kg}$. Again, if the two-phase model applies to the samples discussed here, this $W^c(23^\circ\text{C})$ may be identified with the volume-based weight crystallinity.

Although the enthalpy-based and volume-based weight crystallinities may be expected to be related, they are not necessarily numerically equal, because the measuring techniques used interact with parts of the material examined in different ways. In particular, the presence of an interfacial layer will affect the volume-based weight crystallinity. Further, thermal histories in density measurement and DSC measurement differ, e.g., on account of the different cooling rates in the compression-molding procedure and the DSC cooling procedure.

The volume-based and enthalpy-based crystallinities of a few relevant VLDPEs listed in Table I do not differ much, taking into account the measuring error of a few percent in $W_{hc}^c(23^\circ\text{C})$ and $W^c(23^\circ\text{C})$. This can be due to absence of the effects mentioned, but the effects may also cancel one another. In any case, this comparison, too, demonstrates the usefulness of the method and technique used here, which enable crystallinity determination across a wide temperature range instead of a single point measurement at room temperature. Besides additional sample data, Table I also includes an octene-1 LLDPE.

In Figure 4, the enthalpy-based weight crystallinities as a function of temperature are compared for VLDPE7 (10.005 mg) and for the LLDPE

TABLE I
Sample Data and Comparison of Enthalpy-Based
and Volume-Based Weight Crystallinities for
some VLDPEs and an LLDPE

Sample code	$D(23^\circ\text{C})$ (kg/m^3)	MFI (dg/min)	X_g (%)	$W_{hc}^c(23^\circ\text{C})$ (%) enthalpy	$W^c(23^\circ\text{C})$ (%) volume
LLDPE	919	0.9	3.2	51	48
VLDPE1	907	4.5	4.9	41	40
VLDPE2	903	2.5	5.7	40	37
VLDPE3	901	5.5	6.0	38	35
VLDPE4	898	4.3	6.6	36	33
VLDPE5	894	4.4	7.2	29	31
VLDPE6	891	5.2	7.9	28	28
VLDPE7	888	6.9	8.5	25	26

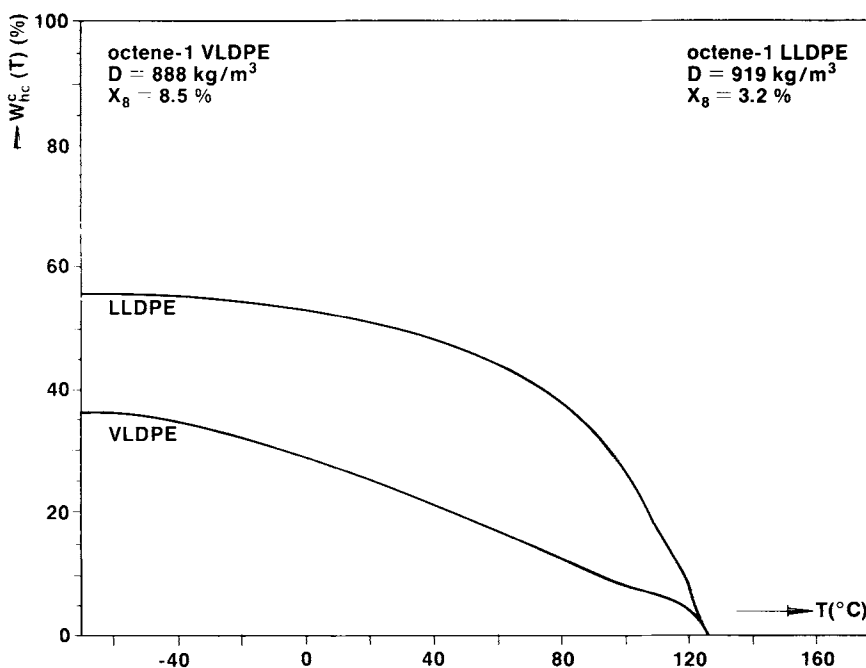


Fig. 4. Enthalpy-based weight crystallinity heating curves as in Figure 3 for VLDPE7 and an LLDPE.

(8.729 mg). This LLDPE, too, is heterogeneous according to DSC- c_p curves. The figure shows that the crystallinity of the LLDPE strongly changes above room temperature, whereas in the VLDPE strong changes already occur above -60°C . At room temperature, the crystallinity of the LLDPE is about twice as high as that of the VLDPE. The final melting points of the two materials hardly differ.

Molecular Heterogeneity

As mentioned before, the multiple peaks of the DSC-specific heat capacity curves are reason to assume that the VLDPEs are molecularly heterogeneous. Fractionation techniques are excellently suited for further verification of this assumption.⁴⁻⁷

If the heterogeneity is intermolecular in nature, a crystallization/dissolution fractionation is a suitable method of research. By this method, VLDPE7 was divided into four fractions, K-1-K-4 (see Fig. 8 for further data).

Figure 5 includes the specific heat capacity curves of the fractions obtained from the DSC heating curves, plotted for the mole percentages of 1-octene in question. For clarity of representation, the curves have been plotted up to 160°C , although the measurements were carried out up to 180°C . Unlike the curve for the whole sample (see Fig. 1), the curves for the fractions are virtually single-peaked. In the case of the first fraction obtained, K-1, for example, the final melting temperature is about 90°C and high-melting material is absent, whereas in the last-obtained fraction, K-4, with a final melting temperature of more than 130°C , the low temperature peak is absent.

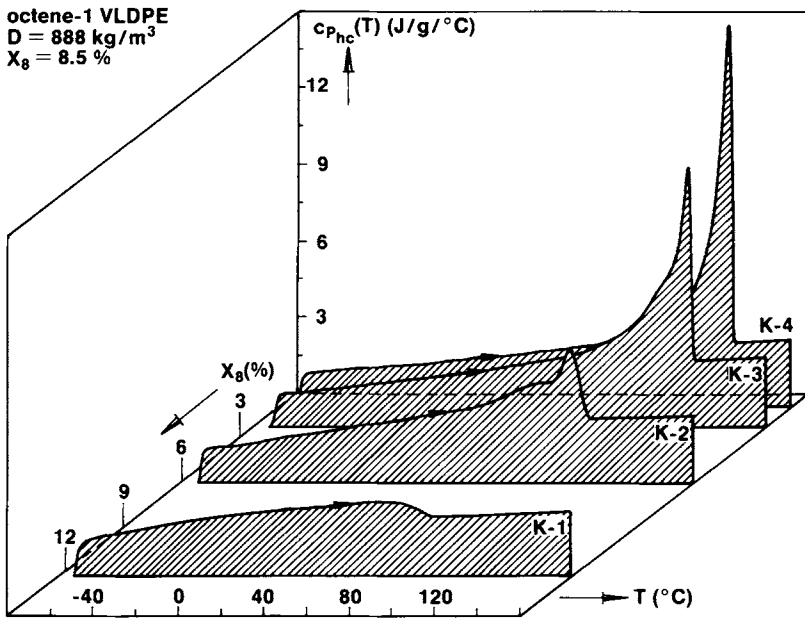


Fig. 5. Specific heat capacity heating curves ($c_{p,nc}$) as a function of the mole percentage of octene for fractions of VLDPE7 obtained by the crystallization/dissolution method.

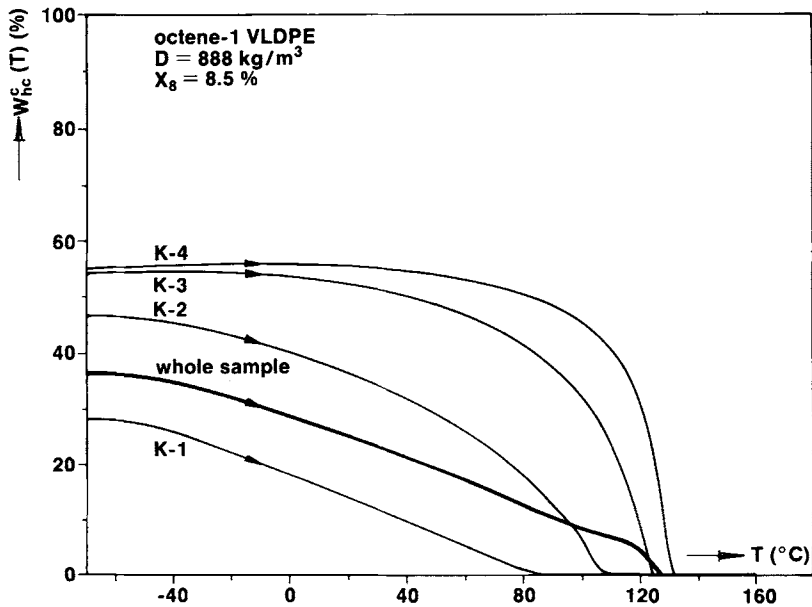


Fig. 6. Enthalpy-based weight crystallinity curves for VLDPE7 and fractions of it (see Fig. 5) obtained by the crystallization/dissolution method.

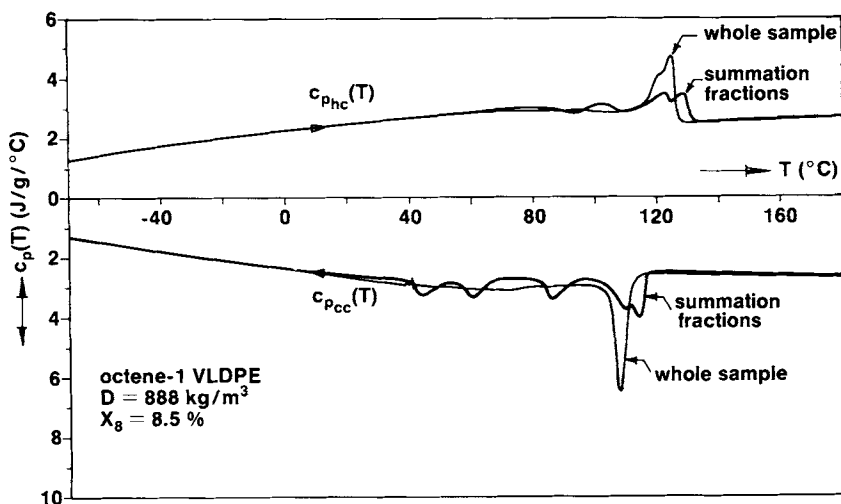


Fig. 7. Cooling curves ($c_{p,cc}$) and heating curves ($c_{p,hc}$) for VLDPE7 and, via summation, for fractions of it obtained by the crystallization/dissolution method (see Fig. 5).

This implies that the heterogeneity is at least in part of an intermolecular nature. Since, in addition, the first fraction represents no less than 66 wt % of the material (see also Fig. 8), it follows that VLDPE is in large part, if not wholly, intermolecularly heterogeneous. This means that VLDPE should be regarded as a blend of ethylene copolymer molecules with widely different comonomer incorporation percentages, the blend having been obtained by polymerization. In fact, the whole range of molecules, from HDPE-like molecules to very low crystalline/amorphous material, seems to be present. The demonstration of intermolecular heterogeneity also in the material melting at low temperatures requires further work, in particular low temperature fractionation of this portion of the material, which, especially in terms of weight, is an important portion.

The enthalpy-based weight crystallinity curves in Figure 6 for VLDPE7 and its fractions once more clearly illustrate that the fractions differ greatly in melting behavior and crystallinity. At room temperature, one quarter of the material (in terms of weight) is crystalline. At that temperature, more than 60% of the material (K-1) has a weight crystallinity of less than 20%, and more than 30% of the material (K-2 plus K-3 and K-4) has a weight crystallinity of, on average, about 45%.

Figure 7 shows the specific heat capacity curves in cooling, $c_{p,cc}(T)$, and heating, $c_{p,hc}(T)$, for VLDPE7 and for its fractions via summation after correction for the fraction weights.

The crystallization curve of the fraction with the lowest comonomer incorporation percentage (K-4) starts at a higher temperature than that of the whole sample. The corresponding melting curve has a single peak, and melting also ends at a higher temperature than in the case of the whole sample. This increase in crystallization and melting temperature is not surprising, given the fact that the whole sample should be regarded as a blend. After all, in the converse situation, the least branched component will in a blend show a lower

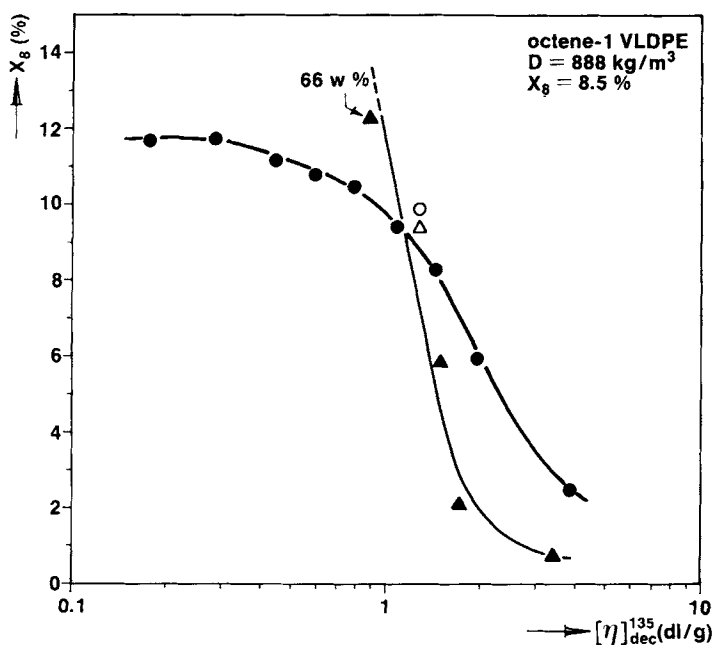


Fig. 8. Mole percentages of comonomer and intrinsic viscosities for fractions of VLDPE7 obtained by the direct extraction method (●) and the crystallization/dissolution method (▲); (○, △) summed fractions.

crystallization and melting temperature than in isolation. The crystallization curve of the fraction with the highest comonomer incorporation percentage (K-1) shows two clear peaks; the corresponding melting curve has a single peak. Further, it can be seen that the individual fractions crystallize and melt more pronouncedly, which is linked to changes in the nucleation of and the interaction between the molecule segments. The total areas under the curves, and hence the crystallinities, do not differ significantly.

Figure 8 shows the relationship between intrinsic viscosity and comonomer content for the fractions K-1–K-4. On account of the limited amount of data currently available, this relationship cannot be exactly indicated for 66 wt % of the material, with an average comonomer content of about 12%. Low temperature fractionation would be required to get a clearer picture. The figure shows that, besides variation in comonomer content, a strongly deviant value of the intrinsic viscosity (molar mass) is found for the fraction with the lowest comonomer content, K-4, on the analogy of the findings in the case of LLDPE. This may have a molecular cause, but there is also the possibility that the crystallization/dissolution procedure followed not only gives the expected separation according to comonomer content but also a certain fractionation according to molar mass.

Besides fractionation by the crystallization/dissolution method, a fractionation by the direct extraction method³⁵ was also performed. The latter method is known to yield good separation according to molar mass.^{5,6,36} Indeed, this time the material is also found to be strongly fractionated according to intrinsic viscosity (see Fig. 8) and hence according to molar mass.

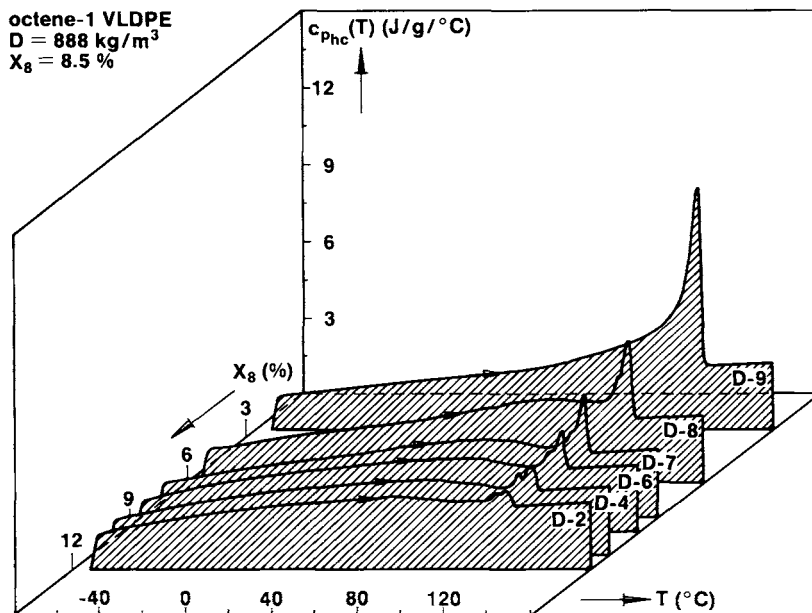


Fig. 9. Specific heat capacity heating curves ($c_{p_{hc}}$) as a function of the mole percentage of octene for VLDPE7 and for a number of fractions of it obtained by the direct extraction method.

After all, in the absence of long chain branching there is an unambiguous relationship between intrinsic viscosity, comonomer content, and molar mass.³⁷ Further, it can be seen that, above an intrinsic viscosity of about 1 dL/g, the comonomer incorporation percentage strongly decreases with increasing viscosity. In the case of fractions obtained by the direct extraction method, such a decrease was previously seen in LLDPE types, where, incidentally, there were differences associated with the several polymerization routes. Here, too,

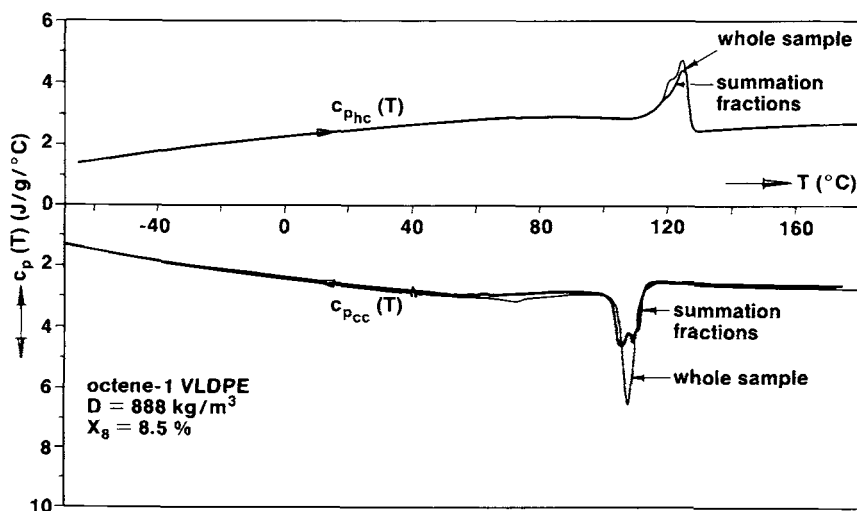


Fig. 10. Cooling curves ($c_{p_{cc}}$) and heating curves ($c_{p_{hc}}$) for VLDPE7 and, via summation, for fractions of it obtained by the direct extraction method (see Fig. 9).

it cannot be excluded that, apart from the observed fractionation according to molar mass, the direct extraction method also gives a separation according to comonomer content.

Unlike the crystallization/dissolution method, the direct extraction method yields a well-balanced distribution of the weights over the fractions: 6.3% for D-1, 8.0% for D-2, 9.6% for D-3, and between 10.8% and 15.4% for the remaining fractions. In other words, a higher comonomer content presents no problems in direct extraction fractionation.

In Figure 9, specific heat capacity curves have been plotted as a function of the comonomer percentage for a number of direct extraction fractions. There is a clear difference with the results of crystallization/dissolution fractionation (Fig. 5); even in the fraction with the highest comonomer content, D-2, high-melting material is still present. Therefore, it is not surprising that summation of the specific heat capacity curves for the fractions results in cooling and heating curves that differ much less from those of the whole sample (see Fig. 10) than in the case of crystallization/dissolution fractionation.

CONCLUSION

The VLDPEs under review here crystallize and melt across extremely wide temperature ranges, viz. between 120 and -60°C and between -60 and 130°C , respectively. This implies that for DSC measurements the isotherms are best taken below -60°C and above 130°C . Absolute heat capacity measurements, which, for the samples concerned, were performed in continuous runs across 250°C , have been found to be very useful. In combination with reference curves for purely amorphous and purely crystalline linear polyethylene, they yield quantitative insight into the crystallization and melting processes. Integration of the c_p curves yields the enthalpy curves. Under the assumption of a two-phase model, comparison of these curves with reference curves for purely amorphous and purely crystalline linear polyethylene gave useful enthalpy-based weight crystallinity curves as a function of the temperature. The enthalpy-based weight crystallinities at room temperature are in good agreement with the values for the volume-based weight crystallinities, which means that any crystalline-amorphous interfacial layer effects are negligible or that the several effects cancel one another. In the application of the two-phase model it is assumed that hardly any octene groups are present in the crystal lattice.

The DSC curves have several peaks. The peak temperatures of the most important peaks differ so much that these peaks must be linked to mutually different crystal types. A direct extraction of a VLDPE gave fractions with widely different molar mass, while the DSC curves of the fractions show the same multiplicity of peaks as in the case of the whole sample. Via a crystallization/dissolution fractionation of the same VLDPE, fractions with widely different comonomer contents were obtained, while peak multiplicity of the DSC curves was clearly less or even absent. This means that the multiple peaks of the DSC curves are related to differences in crystallization behavior of molecules with different comonomer contents, which in turn means that the heterogeneity of comonomer incorporation in VLDPE is mainly intermolecu-

lar in nature. Molecules with the same length are found to differ in comonomer content. In summary, VLDPE can be regarded as a reactor blend of ethylene copolymer molecules ranging from the uncrystallizable and poorly crystallizable type up to and including the HDPE type.

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