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CRYSTALLIZATION AND MELTING OF LLDPE IN RELATION TO MOLECULAR STRUCTURE

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The heterogeneous character of the distribution of comonomer elements (1) in* LLDPE is a remarkable phenomenon. This heterogeneity can be deduced, for instance, from the crystallization and melting behaviour. Differential scanning calorimetry (DSC) shows crystallization and melting to cover large temperature ranges, and DSC curves - see Fig. 1 - often show several peaks (2,3,4). This suggests that an LLDPE sample is not uniform in composition as regards the number, shape and degree of perfection of its crystallites. A possible molecular cause of the non-uniformity in crystallization behaviour might be a heterogeneous distribution of comonomer elements, leading to a multi-peak ethylene sequence length distribution.

A look at model ethylene copolymers with homogeneous distribution of comonomer elements (see f.i. 5,6,7) might, by the contrasting picture it presents, provide some enlightenment on this point. Homogeneity should here be understood to indicate that the comonomer distribution in the copolymer molecule and the related single-peak sequence length distribution can be described by one set of reactivity ratios, there being moreover, no difference between individual molecules. Such copolymers produce a single-peak DSC curve (Fig. 1), the shape of which is dependent on the ethylene sequence length distribution. Also LDPE, the sequence length distribution of which is primarily determined by the distribution of short chain branching, gives a single-peak DSC curve.

Another question which comes up in this connection and which will also be discussed, is whether the heterogeneity observed exists within individual molecules (is intra-molecular) and/or between different molecules (inter-molecular) (1,8). Unequivocal information on this point can only be obtained by means of fractionation experiments. This is a far from simple matter, since the complexity of LLDPE necessitates cross-fractionation. An ideal, but difficult, method is first to separate by molecular size and next to separate the resulting fractions according to ethylene sequence length. Such a fractionation carried out on a preparative scale (9) not only answers the above question, it also enables a detailed investigation into differences in molecular structure

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between, for instance, butene-1 and octene-1 LLDPEs, which, in turn, throws light upon differences in crystallization and melting behaviour.

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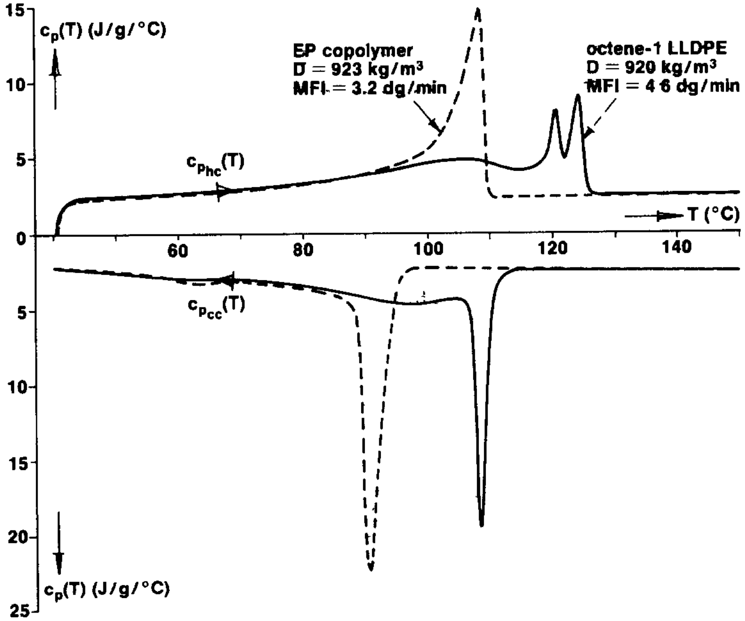

Fig. 1 DSC-2 continuous heat capacity curves for cooling ($c_{p_{cc}}$) at 5 K/min from 200 °C to 40 °C and subsequent heating ($c_{p_{hc}}$) at 5 K/min. Isothermal stays of 5 min, sample weights 4.870 mg (EP) and 4.976 mg (LLDPE)