THE NUCLEATION IN OLIGOMER MELTS*

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Impulse NMR has been used to study the crystallization conditions of oligo-ethylene- and oligo-butylene adipates as a function of the melt temperature at constant crystallization temperature. Residual crystal structures have been found in the melts above the melting temperature; these act as nuclei in the subsequent crystallization. The Avrami equation describing the crystallization kinetics from the melt has been modified on the basis of this result; in addition to the classical and homogeneous nucleation there is one in which the crystal nuclei are the residual crystal structures already existing in the melt.

Structural irregularities which can play the part of crystallization centres in a subsequent crystallization were found to exist in the melts of polymers above their melting temperature (T_m) [1–3]. The melts of some low molecular weight (mol.wt.) compounds [4] and of oligomers [5] are also assumed to contain some pseudocrystal structures, but their effects on subsequent crystallization had not been examined.

The purpose of this study was to find the effect of structural irregularity in oligomer melts on the crystallization kinetics, and especially on the type of nucleation.

EXPERIMENTAL

The study objects were oligo-ethylene adipate with $\bar{M}_n = 1800$ ($T_m = 52°C$) and oligo-butylene adipate with $\bar{M}_n = 1700$ ($T_m = 51°C$); these are subsequently labelled EA and BA respectively. There is qualitative agreement of results for the two substances, and the results will therefore be examined in detail only on the EA sample.

The parameter characterizing crystallization was taken to be the dynamic crystallinity P_c which is determined by the relative amplitude of the descending component of transverse nuclear magnetism which is characterized by the shortest spin-spin relaxation time T_2 when the sample is exposed to a sequence of radio frequency impulses [6]. The P_c determinations as a function of crystallization time t_c were made on an impulse-coherent NMR spectrometer [7]. While crystallizing in the spectrometer counter (cell) at $T_c = 25 \pm 0{\cdot}1°C$ (for EA) or $40{\cdot}2 \pm 0{\cdot}1°C$ (for BA). The melting took place in a U-8 oven at various temperatures $T_m = 53$–$100°C$. The melts were kept at the T_m for periods ranging from 10 min to 5 hr.

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