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STUDY OF NON-ISOTHERMAL CRYSTALLIZATION PROCESS OF DIFFERENT POLYOLEFINS

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The non-isothermal crystallization behavior of Ziegler-Natta (ZN) and single site (SS) based ethylene/1-butene and ethylene/1-hexene copolymers (named as linear low density polyethylenes, LLDPE, in general) as well as high density polyethylene (HDPE) and their molar mass (MM) and compositional fractions has been studied by differential scanning calorimetry (DSC).

Whole unfractionated copolymers with different comonomer content C_{com} were studied by DSC at different scanning rates, namely 5, 10, 100 and 300°C/min. It was found that in ethylene/ α -olefins at all used scanning rates three peaks of crystallization (hightemperature crystallization peak (HTCP), low temperature crystallization peak (LTCP), and a small very-low temperature crystallization peak (VLTCP)) are observed on DSC endotherms and the character of dependences on the same molecular parameters is similar for all scanning rates. VLTCP is present at temperatures in between 60-75°C. The area of VLTCP increases with decreasing scanning rate and the shape of this peak broadens. The higher the scanning rate the better is the resolution of VLTCP: the peak becomes sharper and higher [1].

It was observed in non-isothermal DSC scans that for molar mass fractions with MM larger than 10 kg/mol VLTCP can be seen. Such peak is absent for the lowest MM fractions. The remarkable fact is the absence of melting peak in DSC endotherms directly corresponding to VLTCP.

It was found that the crystallinity as related to the area of the VLTCP is catalyst type dependent, and is higher for the SS catalyst compared to the ZN. Within the same type of catalyst (ZN) the VLTCP crystallinity is larger for LLDPE than for HDPE. Peak temperature of VLTCP linearly decreases with increasing comonomer content while the VLTCP crystallinity practically does not change with comonomer content.

For comparison with LLDPE fractions the commercial ZN catalysed HDPE was fractionated according to MM. Similar effect of MM was found: for fractions with lowest MM no VLTCP was observed, for fraction with MM higher than 10 kg/mol VLTCP can be seen and it increases in the same manner as for LLDPE fractions.

References

1. E. Tarasova, T. Poltimäe, A. Krumme, A. Lehtinen, A. Viikna, Macromol Symp 282 (2009) 175-184.