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Studies of ethylene/1-hexene copolymerization over zirconocene catalyst supported on MAO-modified $MgCl_2(THF)_2$. The effect of copolymerization conditions on the intermolecular heterogeneity of copolymers

RAPID COMMUNICATION

Summary — Composition of catalytic system and copolymerization reaction conditions influence on heterogeneity of ethylene/1-hexene copolymers obtained over $MgCl_2(THF)_2/MAO/Cp_2ZrCl_2/MAO$ catalyst was studied. One of the DSC techniques, *i.e.* successive self-nucleation/annealing (*SSA*) method allowing separation of the polymer into fractions with differing chemical composition in result of alternating crystallization and melting cycles was applied. It was found that the intermolecular heterogeneity exists inside all studied samples irrespective of the reaction conditions (temperature and time) and the catalyst composition (Al/Zr molar ratio). It was also confirmed that catalyst composition has a considerably greater impact on heterogeneity of the copolymers as compared with copolymerization conditions, which — apart from the first period of the reaction — do not exert significant influence on this parameter of copolymer structure.

Key words: ethylene/1-hexene copolymers, zirconocene catalyst, SSA method, intermolecular heterogeneity, lamella thickness.

Copolymerization of ethylene with higher 1-olefins (as 1-butene, 1-hexene, 1-octene, *etc.*) leads to linear low-density polyethylene (PE-LLD) containing short chain branches of identical size derived from comonomers. It is well known that short chain branching (*SCB*) and also long chain branching (*LCB*) represent the key to achieving control of polyethylene properties such as melting temperature, density, processability, optical clarity, stiffness, strength, toughness, stress crack resistance and blend compatibility [1]. Thus, properties of olefin copolymers, apart from molecular weight and molecular weight distribution (*MWD*), are influenced by a type of comonomer, comonomer content and monomer sequence distribution. Besides *MWD* determination, in the case of copolymers, it is necessary to measure chemical composition distribution (*CCD*) also denoted as short chain branching distribution, to have a more complete understanding of active site types and polymer properties [2]. Note that two kinds of *CCD* heterogeneity exist, *i.e.* intra- and intermolecular heterogeneity. The former concept implies that *SCB* distribution is not uniform within one polymer chain, while all the molecules posses the same *SCB* distribution. In the second case, *SCB* distribution is not uniform among the molecules, however, each molecule possesses a uniform *SCB* distribution along its backbone [3—5].

Characterization of intermolecular compositional heterogeneity of copolymers is usually carried out by different fractionation methods. The most widely used for this purpose methods are the temperature rising elution fractionation (TREF) [6, 7], crystallization analysis fractionation (CRYSTAF) [8] and methods based on differential scanning colorimetry (DSC) [9—11]. It was demonstrated [12] that these three analytical methods yield comparable results with respect to the comonomer distribution of PE-LLD.

The intermolecular heterogeneity is studied with utilization two basic procedures of fractional crystallization of the copolymer using DSC methods [9—11]: step crystallization (SC) and successive self-nucleation ever, properties such as: melting point, degree of crystallinity, molecular weight and bulk density are just slightly influenced by copolymerization time. It was concluded that the changes of properties are generated by changes of the amount comonomer incorporated.

As shown in Fig. 2 incorporation of 1-hexene into the polymer chain causes both shifting and broadening of the peak on the DSC thermogram. This effect is stronger for copolymer with higher comonomer content and can be caused by the increase of heterogeneity of the polymer macromolecules. In order to confirm this hypothesis we decided to apply fractional crystallization of studied copolymers.

Previously [16] it was found that type of catalyst has an important effect on the intermolecular heterogeneity of copolymer composition. Therefore, it was interesting to extend the investigation on the composition of a catalytic system expressed by molar ratio of precatalyst/cocatalyst. The exemplary DSC thermograms of copolymers obtained at various Al/Zr molar ratios in the $MgCl_2(THF)_2/MAO/Cp_2ZrCl_2/MAO$ catalyst and using SSA procedure are shown in Fig. 3. Thus, DSC thermogram of the copolymer obtained after applying this method is resolved into several endotherms (1—5) that represent the melting process of molecules with different *SCB* distribution.

the more branched ones. Therefore, each melting peak represents the melting of the crystal formed from molecules having the same or at least very similar *SCB* content [3, 11].

Lamella thicknesses of different lamella can be calculated from Thomson—Gibbs equation [5]:

$$T_m = T_m^0 \cdot \left(1 - \frac{2\delta_e}{\Delta H \cdot l_c}\right) \tag{1}$$

where: T_m — *observed melting point (K),* T_m^0 — *equilibrium melting point of an infinite polyethylene crystal (414.5 K),* δ_E — *surface energy of a polyethylene crystal (70 ·* 10^{-3}*, J/m*$^{-2}$*),* ΔH — *enthalpy of fusion per unit volume (288 ·* 10^6*, J/m*^{3}*),* l_c — *thickness of the lamella with melting point* T_m *(m).*

As each melting endotherm is proportional to the amount of crystals comprising lamella of a specific size, the relative quantity of lamella of different thicknesses (l_c) was calculated based on area of the thermogram peaks (Fig. 4). Values of melting points of copolymer fraction obtained correspond to lamella thicknesses of about 58 to 122 Å. In all investigated samples the increase of Al/Zr catalytic system molar ratio causes an increase in fraction content of smaller lamella thicknesses and a decrease in content of the thickest lamella; even leading to the disappearance of the copolymer fraction with the lowest content of 1-hexene.

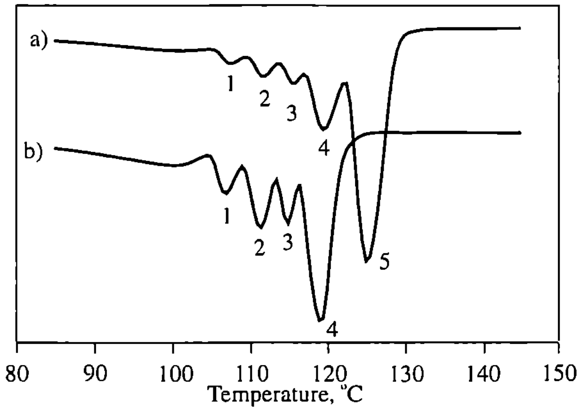

Fig. 3. The influence of Al/Zr molar ratio in catalytic system on copolymer intermolecular heterogeneity; Al/Zr molar ratio: a) 2000, b) 6000; for explanation 1—5 see text

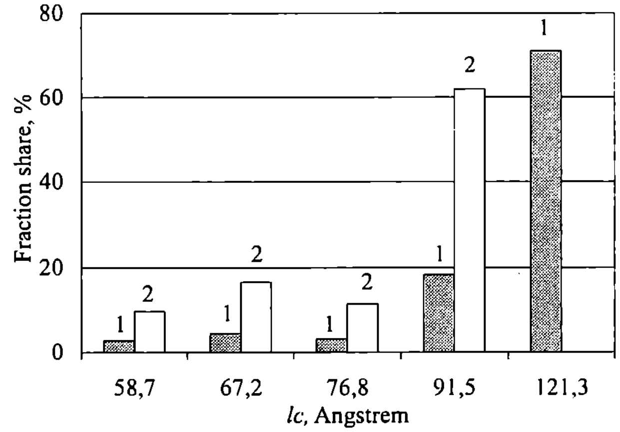

Fig. 4. The influence of Al/Zr molar ratio in catalytic system on the share of fraction with different lamella thickness; Al/Zr molar ratio: 1 — 3000, 2 — 7000

Presented results indicate that composition of the catalytic system has great influence on copolymers heterogeneity. As shown, they differ in number of peaks, their position and magnitude. The higher Al/Zr molar ratio is, the higher content of comonomer incorporated and the more homogeneous the copolymer is.

It is known that the amount and distribution of comonomer incorporated (*SCB* distribution) affects lamella thickness; the less branched molecules containing thicker lamellae crystallize at higher temperature than

As shown in Figs. 5 and 6, the number of endothermic peaks was nearly the same independently of both polymerization temperature (from 20 to 70°C) and polymerization time (from 20 to 75 minutes). Moreover, only slight differences in location and value of peaks were confirmed for copolymers obtained at different polymerization temperatures (Fig. 5). Copolymers obtained at different polymerization times (Fig. 6) show bigger differences in both locations of the peaks, as well as their values, especially for the copolymer obtained at

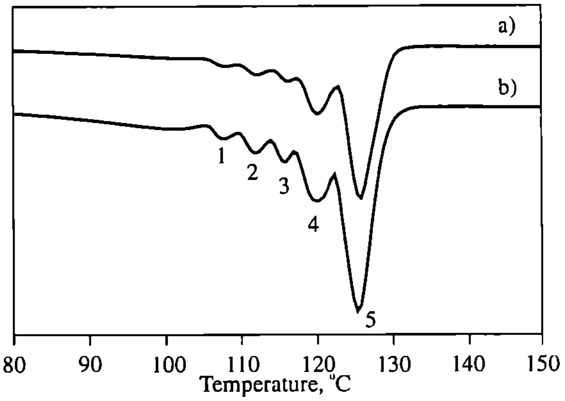

Fig. 5. The influence of copolymerization temperature on copolymer intermolecular heterogeneity; copolymerization temperature: a) 20°C, b) 70°C (for explanation 1—5 see text)

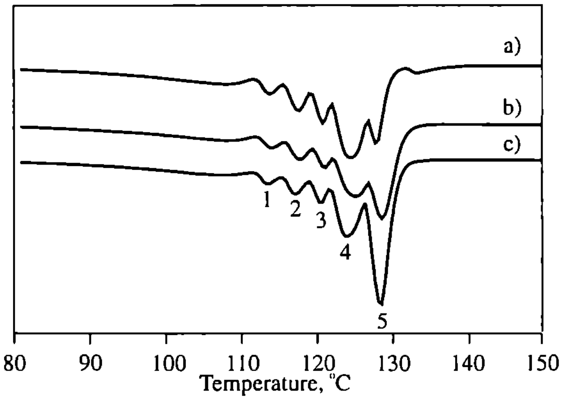

Fig. 6. The influence of copolymerization time on copolymer intermolecular heterogeneity. Copolymerization time: a) 20 min, b) 50 min, c) 75 min (for explanation 1—5 see text)

shorter polymerization time. Note that copolymers obtained at different polymerization times have almost the same amount 1-hexene incorporated (from 5.0 to 5.9%) and that copolymers obtained at different temperature have much more diversified composition (comonomer content from 2.6 to 4.8%). It can be concluded that polymerization conditions, apart from polymerization conducted at shortest time frames, do not have great influence on heterogeneity of the copolymer composition.

In summary, it can be concluded that intermolecular heterogeneity exists inside all studied samples independently of reaction conditions and catalyst composition. The investigated copolymers were obtained over zirconocene catalyst. This type of catalytic system is called a single-site catalyst due to its ability of producing polymers with very narrow molecular weight distribution. However, chemical composition distribution even in case of the copolymers obtained over this type of catalysts is not uniform. Previously, it was found [16] that heterogeneity of copolymers composition greatly depends on transition metal precatalyst used in catalytic system. Now, it was additionally shown that other changes in catalyst composition such as precatalyst/cocatalyst molar ratio have the significant impact on comonomer incorporation and heterogeneity of copolymers. It was also confirmed that polymerization conditions such as temperature and reaction time do not exert significant influence upon copolymer structure.

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