

STUDIES OF INTERMOLECULAR HETEROGENEITY DISTRIBUTION IN ETHYLENE/1-HEXENE COPOLYMERS USING DSC METHOD*

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Abstract

The investigation of the intermolecular composition distribution of an ethylene/1-hexene copolymers using DSC method has been carried out. The known methods: step crystallization (SC) and successive self-nucleation/annealing (SSA) have been adapted for this purpose, and particularly, the optimal condition of the process have been chosen to enable the best fractional crystallization of the copolymer. The method has been applied for fractionation of two ethylene/1-hexene copolymers synthesized with supported vanadium and zirconocene catalysts and having similar concentrations of 1-hexene. Although metallocene catalysts are known from their more homogeneous structure of active sites in comparison to multi-site Ziegler–Natta catalysts, the copolymers obtained over both catalytic systems gave DSC curves resolved into several peaks but with different melting points. Using the Thomson–Gibbs equation, comparable average lamellar thickness of the separated peaks has been calculated. The amounts of copolymer fraction with defined lamellar thickness have been determined. It was obtained that the copolymer produced from the metallocene system contains a thinner and more homogeneous lamella thickness than that obtained with Ziegler–Natta vanadium catalyst supported on the same carrier.

Keywords: DSC method, ethylene/1-hexene copolymer, intermolecular heterogeneity

Introduction

Linear low-density polyethylene (LLDPE), typically produced by the copolymerization of ethylene with various α -olefin comonomers, is an important class of polymer products in the petrochemical industry because of their specific properties. The incorporation of α -olefin units during the polymerization reaction produces short branches along the chains. The versatility in physical properties of ethylene/ α -olefin copolymers depends not only on the type and amount of the α -olefin comonomer in the polymer but also on its distribution along the polymer chain [1]. The α -olefin incorporation into polymer chain influences comonomer sequence distribution along a polymer chain (intramolecular distribution of short chain branching) and distribution of comonomer among polymer macromolecules (intermolecular distribution of short

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chain branching). The short chain branching distribution, also referred as chemical composition distribution (CCD), has been shown to be a critical structural parameter with strong impact on product performance [2]. Various methods to characterize the CCD have been developed. The most widely used ones for the characterization of intermolecular heterogeneity are the fractionation procedures such as direct extraction by solvent/non-solvent mixtures and crystallization/dissolution fractionation (TREF) [3]. Recently, measurements of the comonomer distribution in branched polyethylene, especially in LLDPE, have mostly been performed using differential scanning calorimetry (DSC). This method is based on several steps of isothermal crystallization of a polymer on decreasing the temperature from the melt [1, 3–5]. The procedure enables the fractionation of copolymers according to their composition, which can be seen by the multiplication of the melting peaks on the curves.

The comonomer distribution in polyethylene depends on the type of catalyst as well as polymerization conditions. Homogeneous metallocene catalysts are known to be much more homogeneous than conventional Ziegler–Natta catalysts. It was the reason why copolymers obtained over metallocene catalysts are expected to provide unique chemical compositions and properties. However, homogeneous catalysts must be immobilized on a solid support for the use in gas-phase industrial processes. Therefore, many recent papers [6–14] have been dealing with the heterogenization metallocene systems.

In our research [15, 16] we studied the copolymerization process of ethylene with longer α -olefins over vanadium, titanium and zirconocene catalysts supported on $\text{MgCl}_2(\text{THF})_2$ and activated by organoaluminium compound. In the present study, the thermal behavior of ethylene/1-hexene copolymer prepared by supported zirconocene catalyst was investigated by DSC method. We have applied two known from literature [1, 3] procedures of fractional crystallization of the copolymer: step crystallization (SC) and successive self-nucleation/annealing (SSA). These procedures were adapted and particularly such conditions of the measurement were selected which provide the best fractionation and would be useful to qualitatively characterize the comonomer distribution in the copolymer studied. Moreover, ethylene/1-hexene copolymer synthesized over vanadium-based catalyst was investigated by selected procedure in order to make a comparative study of intermolecular heterogeneity of copolymers obtained over metallocene as well as Ziegler–Natta catalysts supported on the same magnesium support.

Experimental

The studies were carried out on ethylene/1-hexene copolymers obtained on $\text{MgCl}_2(\text{THF})_2/\text{MAO}/\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ [16] and $\text{MgCl}_2(\text{THF})_2/\text{VCl}_4/\text{Et}_2\text{AlCl}$ [15] systems.

1-Hexene content in the ethylene/1-hexene copolymer was estimated by FTIR method using the $A_{\text{CH}_3}^{1379}/A_{\text{CH}_2}^{1369}$ absorbance ratios, which were determined by the separation of analytical bands [17]. Molecular mass and molecular mass distribution of the copolymer were determined by gel permeation chromatography (GPC) with a Waters instrument, model 150-C. The operating conditions of GPC method were de-

scribed [18]. DSC measurements were performed using apparatus DSC-2010 TA Instruments.

Results and discussion

From the results of the melting temperature (T_m) measurement of the ethylene/1-hexene copolymer obtained on the supported zirconocene catalyst it was found that the increase of 1-hexene contribution is depicted by DSC peak widening, and in some cases by appearance of two melting peaks (Fig. 1). The similar observation we have obtained earlier for ethylene/1-hexene copolymers synthesised on Ziegler–Natta catalysts supported on the same carrier [19]. The broadening of these lines could be explained by the increase of the heterogeneity of the copolymers with the increase of the comonomer content [20]. The wide comonomer distribution is assigned to the heterogeneity of catalyst active species. It should be stressed however that copolymers obtained on homogeneous single-site metallocene catalysts show same thermal behaviour [21].

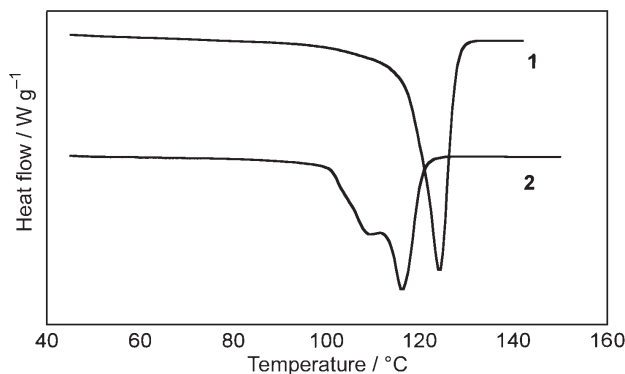


Fig. 1 Comparison of the melting curves obtained for ethylene/1-hexene copolymers; 1-hexene content in the copolymer: 1 – 2.3 mol% and 2 – 4.9 mol%

Two fractionation techniques (SC and SSA) allowed segregation during thermal cycles in DSC analysis were also used in order to better characterize the heterogeneity in comonomer unit distribution in the copolymer studied.

In SC method, polymer after melting is fractionally crystallized on decreasing temperature. The essence of this method is exemplified in Fig. 2. The influence of temperature differences on the stages of isothermal crystallization was investigated. The results obtained are shown in Fig. 3. As can be seen, this method enables splitting of the DSC curve into several single peaks; however, the number of programmed crystallization stages has a considerable effect on the curve shape. Based on the results presented one can find that the smaller temperature intervals between crystallization stages, the better segregation of fraction.

Slightly different procedure was applied in the SSA method described by Müller *et al.* [1]. In this procedure polymer undergoes multiple alternate melting and crystallization processes on decreasing temperature. The essence of the method and the con-

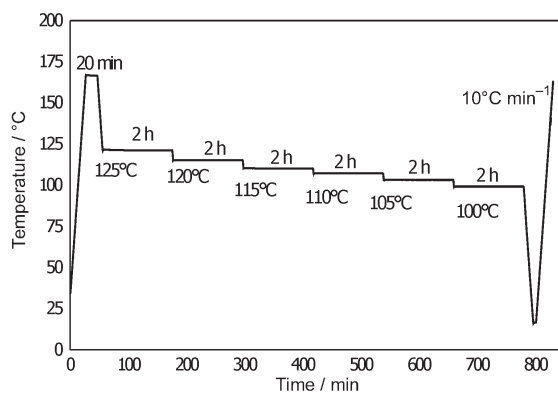


Fig. 2 Scheme of analysis procedure applied in SC method

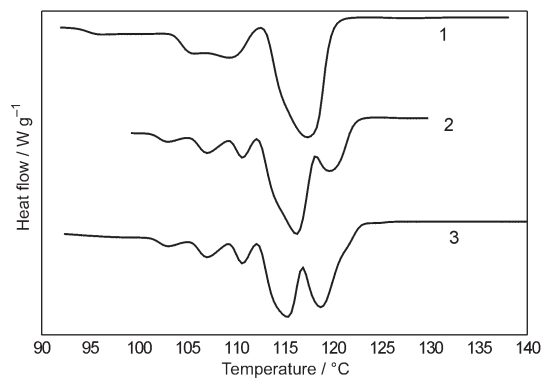


Fig. 3 Influence of the number of temperature stages on the melting curve shape; 1 – 125, 115, 105, 95°C; 2 – 125, 120, 115, 110, 105, 100°C; 3 – 125, 123, 121, 118, 114, 111, 107, 103°C

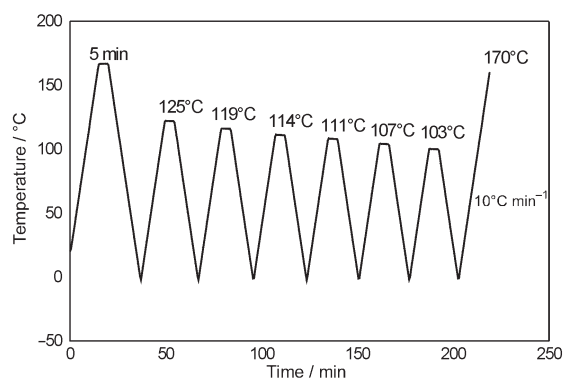


Fig. 4 Scheme of analysis procedure applied in SSA method

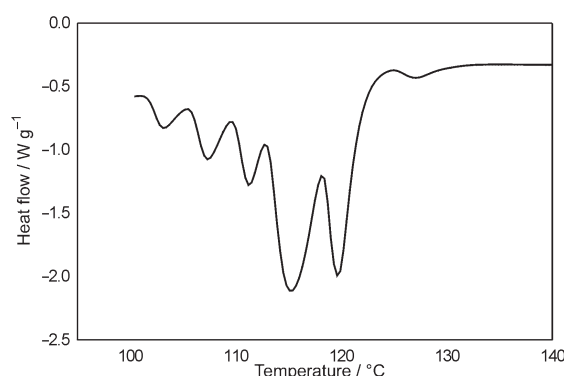


Fig. 5 The melting curve using SSA method for analysis ethylene/1-hexene copolymer

dition applied are presented in Fig. 4 and the results are presented in Fig. 5. The application of the procedure of multiple crystallization also enables copolymer fractionation. Although, in paper [1] authors informed that SSA provides better fractionation than other techniques based on step crystallization, we found that the curve shape is almost identical to that obtained using the former method under optimal conditions (Fig. 3, curve 3). Therefore, both procedures step crystallization (SC) and successive self-nucleation/annealing (SSA) enable the determination of copolymer macromolecule composition contribution resulting in an endotherm with several peaks. However, each method has some advantages and disadvantages. The former is time-consuming, a single analysis can last more than several hours. The latter is considerably shorter however a very large amount of liquid nitrogen is used.

For comparison the SSA procedure was also applied to characterize the copolymer obtained over vanadium catalysts. As can be seen in Fig. 6, annealing for both studied copolymers took place from about 128 to 103°C. It should be stressed that metallocene copolymer alike to its counterpart obtained with vanadium catalysts

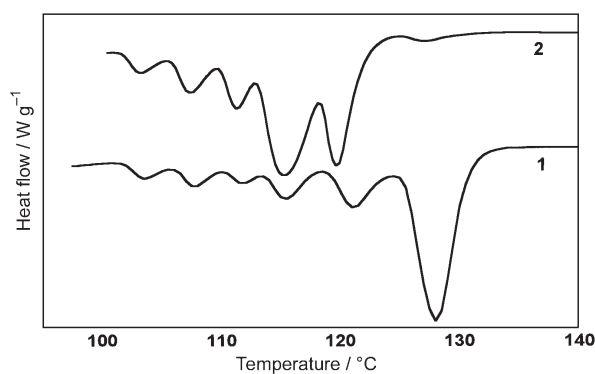


Fig. 6 Comparison of the melting curves of ethylene/1-hexene copolymers obtained with vanadium (curve 1) and zirconocene (curve 2) catalysts using SSA method for analysis

showed six peaks on DSC curves. In works [5, 22] were also noticed that copolymers although expected to be almost homogeneous, gave a curve resolved into several peaks which meant that the investigated material comprised families of macromolecules or blocks of monomer units. It can be noticed, however, that the curves of the ethylene/1-hexene copolymers, produced from both studied catalysts, are considerably different. They differ in the position of melting peaks and magnitude but the number of peaks on their DSC curves is the same. The differences can be attributed to a diversity in macromolecules size, molecular mass distribution and comonomer content in the copolymer. It should be noticed that copolymers obtained over both catalysts have similar content of 1-hexene (about 4.5 mol%) but different molecular mass and molecular mass distribution ($\overline{M}_w=27.8 \cdot 10^3 \text{ g mol}^{-1}$ and $45.9 \cdot 10^3 \text{ g mol}^{-1}$; $\overline{M}_w/\overline{M}_n=3.01$ and 8.35 for the copolymers obtained over zirconocene and vanadium catalysts, respectively). It should be stressed that despite of significant diversification of molecular mass distribution of the studied copolymers, the number of peaks on their DSC curves is the same. Therefore, it can be concluded that the fractionation of the copolymers is according to their composition, but not macromolecule dimension. Simanke *et al.* [23] have also reported that the influence of molecular mass and molecular mass distribution can be neglected as a reason for the broadening of the endothermic DSC lines. Besides, the results presented in another work [24] reveal that the copolymer composition distribution does not depend on the molecular mass distribution of the catalyst used.

Table 1 Melting point, lamellar thickness and share of different fraction in ethylene/1-hexene copolymers obtained with vanadium and zirconocene catalysts

Catalyst precursor	Peak no.	Melting point/ $^{\circ}\text{C}$	Lamella thickness, $l_c/\text{\AA}$	Share of fraction/%
VCl_4	1	103.41	53.11	3.4
	2	107.65	59.79	4.4
	3	111.72	67.91	2.1
	4	115.44	77.77	8.2
	5	121.09	99.45	12.3
	6	128.09	151.96	69.6
Cp_2ZrCl_2	1	103.09	52.66	5.8
	2	107.29	59.16	10.3
	3	111.21	66.85	9.4
	4	115.13	76.85	47.1
	5	119.75	93.28	24.9
	6	127.07	141.10	2.5

Accordingly, for instance, Hosoda [25], the melting temperature is closely related to the lamella crystal thickness, which significantly depends on the amount and

distribution of the α -olefin units in the macromolecular chain. So, the shape of the DSC endothermic curve with multiple peaks represents a mixture of lamellae of different thickness in ethylene/ α -olefin copolymers. Each peak of endotherm curve corresponds to poly(ethylene) lamellae with different thickness. The thicknesses for the separated peaks obtained by SSA fractionation were calculated using known Thomson and Gibbs equation combined melting temperature with lamella thickness [25]. Table 1 presents results obtained. Additionally, the amount of crystalline material comprising lamellae of a specific size was calculated based on relatively area of the DSC peaks, in order to explain the differences comonomer distribution of the copolymers studied. As can be noticed from the data presented in Table 1 both copolymers contain mixture of lamellae of thickness from about 52 to 152 Å but with different distribution. It can be seen that fractions 4 and 5 (l_c about 76 to 93 Å) prevail for the copolymer produced from the metallocene catalyst. On the contrary, the fraction of the highest thickness of the lamellae (l_c about 151 Å) predominates for the copolymer produced from the vanadium system. The lamella crystal thickness significantly depends on the methylene stem length. Because homogeneous comonomer distribution reduces the crystallizable methylene sequence and as a consequence, this leads to a thinner and homogeneous lamella thickness [6], therefore the results indicate that the copolymer produced from the metallocene system has higher homogeneity than the one obtained over Ziegler–Natta vanadium catalyst supported on the same carrier.

Conclusions

Two DSC methods were applied for the investigation of intermolecular composition distribution i.e. step crystallization and successive self-nucleation/annealing. The results obtained showed that both methods enable the determination of copolymer macromolecule composition contribution and it should be noticed that the shape of curves obtained with SC as well SSA methods (made in defined conditions) were almost identical. It was also demonstrated that the DSC endotherm of analysed copolymer obtained over supported zirconocene catalyst differs from this obtained for copolymer synthesized with vanadium-based counterpart. The copolymers produced from the metallocene system contains a thinner and more homogeneous lamella thickness than that obtained with Ziegler–Natta catalyst.

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