

Note

CRYSTALLIZATION SEGREGATION DSC STUDIES OF PP/PE COPOLYMERS

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Abstract The structural analysis of two PP/PE copolymer samples, 1 and 2, was conducted by using ^{13}C -NMR, GPC and crystallization segregation DSC (CSDSC) techniques. A pure polypropylene sample was also used for comparison. It was found that the two copolymer samples are very close in composition (the ethylene mol content is 4.3% and 4.5%, respectively), stereoregularity (96% and 97%) and molecular weight ($M_w = 7.0 \times 10^4$ and 7.3×10^4 ; $M_w/M_n = 5.0$ and 6.1, respectively). While the CSDSC thermograms of the two samples are quite different from each other. Sample 1 shows a higher average melting temperature and a broader distribution of its thermogram. These phenomena were explained as an indication of a less uniform distribution of ethylene units along the PP chains for sample 1. It was noted that CSDSC is a very sensitive and convenient technique for structural studies of copolymers.

Keywords PP/PE copolymer, Sequence distribution, Crystallization segregation DSC, ^{13}C -NMR

INTRODUCTION

Polyolefins are the most popular polymeric resources commercially available in countries all over the world due to their large scale production, low price, good processability and properties. Copolymerization is now widely used to improve or modify the characteristics of polyolefins. One of the important examples is linear low-density polyethylenes (LLDPEs), which are copolymers of ethylene with other α -olefins such as propylene, 1-butene, 1-hexene and 1-octene. The purpose is to modify the crystallization and melting behavior and the molecular packing of polyethylenes for meeting the different application requirements.

For these copolymers the composition and the sequence distribution of the comonomers in molecular chains are the important structural characteristics which may significantly influence the morphology and properties of the final products. Usually NMR techniques are used for determining the short-range sequence distribution of two monomer units along the main chain of copolymers. For random copolymers with low content of the second monomer, like LLDPEs, knowledge about the distance between two units of the second monomer or the length of PE segments separated by second monomer units and its distribution is necessary in studies of structure-property relationships.

A practical method for this purpose is the so-called crystallization segregation DSC technique (CSDSC). The principle of this technique is the crystallization segregation of polymer segments of different length and the DSC detection of the melting behavior of the segregated samples. This technique is quite convenient in that the two processes, the crystallization and the DSC detection, can be conducted using the same DSC instrument. After properly designing the slow cooling program for crystallization segregation a thermogram of high resolution reflecting the heterogeneity of samples in segment length can be obtained. It has been demonstrated in studies of various PEs^[1-10] that CSDSC technique is a sensitive and convenient method for characterizing the segment length distribution of polyethylene copolymers and is of great interest in structure-property relationship studies of

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crystalline copolymers. In this work the CSDSC method was used for the characterization of polypropylene copolymers with low content of ethylene units.

EXPERIMENTAL

Two experimental samples, 1 and 2, of polypropylene/polyethylene copolymers supplied by the Shanghai Petrochemical Company were used in this work. Their melting index was 0.27 and 0.22 g/10 min, respectively (230°C, 2.16 kg). A commercially available polypropylene sample T300 was also used for comparison.

CSDSC measurements were performed using a Perkin Elmer DSC-4 apparatus in a nitrogen atmosphere. Indium (m.p. 156.6°C) was used for temperature calibration. The samples were first heated rapidly to a temperature well above their melting temperature, usually around 180°C–200°C, after that the temperature was programmed to the first annealing temperature. A successive annealing at decreasing temperatures was performed until no thermal effect of crystallization was detected. After that the samples were cooled down to room temperature, and then CSDSC thermograms were recorded in a heating process at a rate of 5 K/min. The interval of two successive annealing temperatures was 8 K and the time length of each annealing step was 12 h.

The ^{13}C -NMR spectra were recorded at 125°C on a 75.48 MHz Bruker DMX-300 NMR spectrometer. In all measurements the pulse width was 6.5 μs and the repetition time was 2 s between pulses. The number of accumulation scans was 2000–3000. The solvent used was *o*-dichlorobenzene- d_4 and the concentration was around 15% (W/V). The molecular weight and polydispersity of the samples were measured at 135°C by using a gel permeation chromatograph, Waters PL-GPC220, equipped with 3MIXED-B columns. The columns were calibrated with polystyrene standards and 1,2,4-trichlorobenzene was used as the eluent solvent. The flow rate was 1.0 mL/min.

RESULTS AND DISCUSSION

The comonomer content of these polypropylene copolymers was determined by ^{13}C -NMR measurements according to the methine resonances^[11, 12]. It was found that they are copolymers of very close composition, the mol contents of ethylene units are 4.3% and 4.5% for samples 1 and 2, respectively (Table 1). The data for stereoregularity of the samples are also listed in Table 1. Sequence distribution analysis based on ^{13}C -NMR measurements indicates that no sequences of two or more successive ethylene units were detected. It implies a quite random nature of the copolymerization. The weight average molecular weight M_w and molecular weight distribution index of the samples determined from GPC measurements are also given in Table 1.

Table 1. Composition and molecular weight of the samples

Sample	Ethylene content (mol%)	Isotacticity (%)	$M_w \times 10^{-4}$	M_w/M_n
1	4.3	96	7.0	5.0
2	4.5	97	7.3	6.1

The CSDSC thermograms of the samples are given in Fig. 1. Multiple melting behavior was observed for both PP/PE copolymers and also the homo-polypropylene sample. The peak positions of these thermograms are listed in Table 2. The average melting temperature T_{mAV} and the root-mean-square deviation of melting temperature $(\Delta T_{\text{m}}^2)^{1/2}$ can be determined from experimental curves (Fig. 2) and are defined as follows^[10]:

$$T_{\text{mAV}} = \Sigma \Delta H_i T_{\text{mi}} / \Sigma \Delta H_i \quad (1)$$

$$(\Delta T_{\text{m}}^2)^{1/2} = [\Sigma \Delta H_i (T_{\text{mi}} - T_{\text{mAV}})^2 / \Sigma \Delta H_i]^{1/2} \quad (2)$$

The average melting temperature corresponds to the average segment length incorporated in crystallites and the root-mean-square deviation $(\Delta T_{\text{m}}^2)^{1/2}$ gives information about the width of the segment length distribution. The values of the two parameters for the samples were calculated from the curves given in Fig. 1, and the results are given in Table 3.

The content of ethylene units in the two copolymer samples is very low, around 4.4 mol%, but their T_{mAV}

values are obviously lower than that of the pure polypropylene. This may imply that the ethylene units are randomly distributed in the main chains as indicated by NMR studies and seriously reduce the average polypropylene segment length of the copolymers.

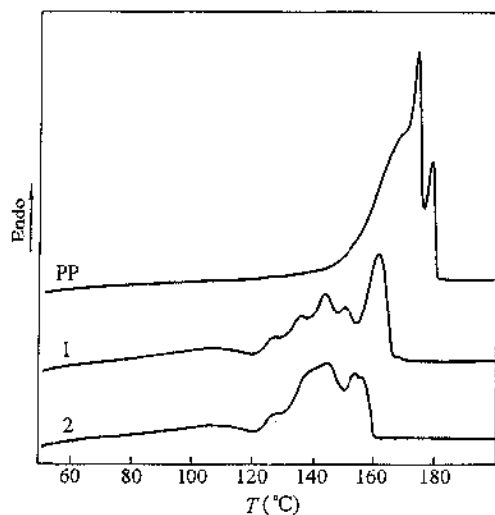


Fig. 1 CSDSC thermograms for polypropylene and copolymer samples 1 and 2

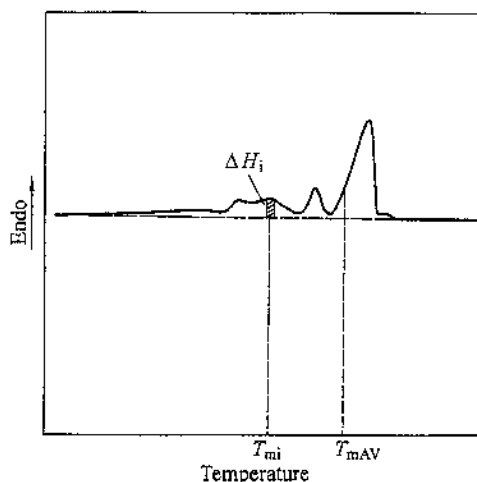


Fig. 2 Scheme for calculating T_{mAV} and $(\Delta T_m^2 AV)^{1/2}$

Table 2. Peak temperatures of CSDSC thermograms (°C)

Sample	T_{m1}	T_{m2}	T_{m3}	T_{m4}	T_{m5}	T_{m6}	T_{m7}	T_{m8}	T_{m9}	T_{m10}
PP	177.6	172.9*	167.9							
1			166.5	160.7*		149.6	142.9	134.0	126.0	107.0
2					154.6	152.7	143.7*	137.1	126.1	107.1

* The highest peak

Table 3. T_{mAV} and $(\Delta T_m^2 AV)^{1/2}$ values of samples

Sample	T_{mAV} (°C)	$T_{mAV}(PP) - T_{mAV}$ (K)	$(\Delta T_m^2 AV)^{1/2}$ (K)
PP	165.9	0	9.32
1	143.0	22.9	18.2
2	138.1	27.8	16.2

Figure 1 indicates that the CSDSC curve of pure polypropylene is grouped in a high temperature range with main peaks at 177.6 °C, 172.9 °C and 167.9 °C, respectively, while the CSDSC thermograms of the two copolymers significantly shift to lower temperatures without obvious melting phenomenon in the peak temperature range of polypropylene. It seems that samples 1 and 2 consist of only PP/PE copolymer molecules, or, at least, the amount and molecular weight of pure polypropylene molecules are quite low, so that they do not result in any obvious thermal effect in the temperature range above 165 °C.

In addition to the decrease of the average melting temperature, the introduction of ethylene units also results in a broadening of the CSDSC curves for PP/PE copolymers. The $(\Delta T_m^2 AV)^{1/2}$ values of the two copolymers are about twice as high as the value for pure polypropylene. It corresponds to a broad distribution of PP segment length in the copolymers.

Although samples 1 and 2 are quite similar in composition, stereoregularity, molecular weight and its distribution, their CSDSC curves still show some important differences. Sample 1 have obviously higher values of T_{mAV} and $(\Delta T_m^2 AV)^{1/2}$ than sample 2. In CSDSC studies of polyethylenes^[10] it was found that the T_{mAV} values of copolymers may decrease with increasing the comonomer content. However the small difference of the two PP/PE samples in composition will not account for their T_{mAV} difference. Therefore the different CSDSC results

of the two PP/PE copolymers are mainly attributed to their different sequence distribution. It implies that for sample 1 the ethylene units are less uniformly distributed along the polypropylene chains. As a result a large fraction of long PP segments appears in sample 1, and the crystallization of these segments contributes the most strong melting peak at a temperature as high as 160.7°C and a very small peak at even higher temperatures, while for sample 2 no detectable thermal effect was observed in this temperature range. It is clear then the T_{mAV} and $(\Delta T_{mAV}^2)^{1/2}$ for sample 1 should be higher than those for sample 2.

All these results for PP/PE copolymers indicate that CSDSC is a very sensitive and convenient technique for structural studies of copolymers, especially when it is used in combination with other methods of structure analysis.

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