Study on Thermal Behavior of Impact Polypropylene Copolymer and Its Fractions

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ABSTRACT: An impact polypropylene copolymer (IPC) was fractionated into three fractions using *n*-octane as solvent by means of temperature-gradient extraction fractionation. The glass transitions, melting, and crystallization behavior of these three fractions were studied by modulated differential scanning calorimeter (MDSC) and wide-angle X-ray diffraction (WAXD). In addition, successive self-nucleation and annealing (SSA) technique was adopted to further examine the heterogeneity and the structure of its fractions. The results reveal that the 50°C fraction (F_{50}) mainly consists of ethylene-propylene random copolymer and the molecular chains may contain a few of short but crystallizable propylene and/or ethylene unit sequences; moreover, the lamellae thicknesses of the resulting crystals are extremely low. Furthermore, 100°C fraction (F_{100}) mainly consist of some branched polyethylene and various ethylene-propylene block copolymers in which some ethylene and propylene units also randomly arrange in certain segments, and some polypropylene segments can form crystals with various lamellae thickness. An obvious thermal fractionation effect for F_{100} samples after being treated by SSA process is ascribed to the irregular and nonuniform arrangement of ethylene and propylene segments. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1560–1566, 2011

Key words: impact polypropylene copolymer (IPC); successive self-nucleation and annealing (SSA); fractionation

INTRODUCTION

Due to providing an ideal combination of good mechanical performance, heat resistance, fabrication flexibility and low cost, isotactic polypropylene (*i*PP) is widely used in many aspects. However, poor impact property, especially in low temperatures, is one of the main shortages of *i*PP. In the past several decades, many efforts have been made to improve the impact strength of *i*PP through physical or chemical approaches, among which the copolymerization of propylene with ethylene is thought of as one of the most effective methods.

In general, impact polypropylene copolymer (IPC) is produced by two-step continuous polymerizations, i.e., the homopolymerization of propylene and the following copolymerization of propylene and ethylene.[1,2] It is noted that IPC is a multiphase system, and consists of ethylene-propylene random copolymer (EPR), a series of ethylene-propylene block copolymers, with different sequence lengths (E*b*P) and propylene homopolymer (HPP).[3–8] The rubbery phase consisting of ethylene-propylene copolymer is dispersed in the homopolymer matrix in the second stage,[9,10] and the copolymer phase facilitates enhancing the impact strength of the product.

It is known that fractionation is an essential approach to study the heterogeneity of polymeric materials composed of multicomponents. Even some works concerning composition analysis of IPC through solvent fractionation and thermal fractionation have been reported,[1,11–13] some details involving the structure and composition of the IPC are still not clear and need to be probed due to the extremely complex compositions. It has been known that the IPC consists of three components, EPR, E*b*P, and HPP. However, among the previous works concerning the fractionation of IPC with temperature-gradient extraction fractionation method, few are related to the direct fractionation of IPC in three parts. In contrast, the major part of IPC is often fractionated with fixed temperature intervals (10°C, for example).[1,12,13] As a result, the composition and thermal behavior for the components of IPC are just indirectly reflected by those of the fractions. In addition,

the studies on the thermal behaviors for the fractions or components of IPC has been mainly focused on the melting and crystallization of the crystallizable part of the polymer, and some low temperature behaviors such as glass transitions for the components of IPC has been rarely reported.

SP179 is a commercial IPC with high impact toughness and wide applications. In the present article, we fractionate SP179 into three fractions, corresponding to the three components of the IPC, and study the thermal behaviors of the fractions in a wide range of temperature by using modulated differential scanning calorimeter (MDSC).

EXPERIMENTAL

Materials

The commercial IPC (SP179) was made by SINOPEC Qilu Petrochemical, China. The molecular weight and relevant parameters of the IPC were listed in Table I. In addition, the commercial isotactic polypropylene T300 was made by SINOPEC Shanghai Petrochemical, and two kinds of low density polyethylene (LDPE, QLT17, and LD100BW) were made by SINOPEC Qilu Petrochemical, China and SINOPEC Beijing Yanshan Petrochemical, China, respectively.

Fractionation of the IPC

The IPC was fractionated through temperature-gradient extraction fractionation by using n-octane as the solvent to successively extract the sample at different controlled temperatures. First, 25 g origin IPC pellets were completely dissolved in n-octane at 125°C, and the solution was subsequently cooled down to 50°C to hold for 72 h and the fraction was collected. The sample was named as 50°C fraction (F_{50}). Then, the remained sample was extracted at 100°C for 72 h and the correspondingly collected fraction was named 100°C fraction (F_{100}). After above two-step extraction, the remainder was 125°C fraction (F_{125}). The weight ratio and the molecular weight of the fractions were listed in Table I.

Thermal analyses

The thermal behavior was examined by using a Q100 MDSC (TA Instrument Corporation) with nitrogen as purge gas. The low temperature thermal behavior was measured in modulation mode. Firstly, the samples were heated to 200°C and held at the same temperature for 5 min to eliminate the heat history, and then quenched to −90°C. Subsequently, the samples were heated from −90°C to 50°C at 3°C/min with an amplitude of 1°C and a period of 60 sec. The glass transition temperature (T_g) was

TABLE I
Molecular Weight and Fraction Amount for IPC and its Fractions

Sample	$M_n \times 10^4$	$M_w \times 10^4$	PD
IPC	4.39	17.4	3.96
F_{50}	8.45	22.7	2.68
F_{100}	1.60	18.0	11.25
F_{125}	4.60	15.1	3.28

determined by the software of MDSC. The high temperature thermal behavior was measured in standard mode: the samples were heated to 200°C and held at the same temperature for 5 min to eliminate the heat history. Then, the samples were cooled down to 30°C at a cooling rate of 10°C/min. Finally, the samples were heated from 30 to 200°C at 10°C/min.

Successive self-nucleating and annealing (SSA)[14] was performed as follows: the samples were first preheated at 200°C for 5 min and then cooled down to 30°C at a cooling rate of 10°C/min, and held at the same temperature for 1 min. Subsequently, the SSA process was started: The sample was heated to the first self-seeding temperature (T_s) with 10°C/min and hold for 10 min, and cooled down to 30°C with the same scanning rate. The first self-nucleating circle was then finished. The process of the following circles was the same with that of the first circle, only the T_s for every circle was 5°C lower than that for last circle. It is noted that the first T_s in SSA course should be the temperature at which almost all the polymer crystals have melt and only leave small crystal fragments that can act as self-nuclei.[11,15] Hence, the self-nucleation experiments have been done to determine the melting domains of PP component for IPC, F_{125} and F_{100}.[16] Accordingly, 169°C was chosen as the first T_s for both SP179 and F_{125}, and 153°C for the F_{100} in this study. For the SP179, the temperature range of the thermal fractionation was from 84 to 169°C. Similarly, for F_{125}, the temperature range was from 139 to 169°C; for F_{100}, the temperature range was from 88 to 153°C. After the fractionation process, the melting traces were recorded at a heating rate of 10°C/min.

Wide angle x-ray diffraction

Wide-angle X-ray diffraction (WAXD) patterns were obtained using a D/Max-2550/PC X-ray diffractometer (Rigaku Corporation, Japan) with a copper target and a Ni filter. The voltage and current adopted for the test were 40 kV and 30 mA, respectively. The d-spacing of the sample was scanned at 2°/min. The diffracted X-ray intensity (I) was recorded automatically in ach interval of 0.01°.

RESULTS AND DISCUSSION

It is noted that compared with the conventional DSC, the advantage of MDSC is that it can divide the total heat flow into two parts: one is the capacity component which is generally referred to as the reversible heat flow, and the other is the kinetic component which is referred to as the nonreversible heat flow. Because the T_g is only determined by the reversible heat flow, for some materials, the T_g which is difficult to be reflected in conventional DSC can be detected by MDSC due to the elimination of the interference of the kinetic component. Figure 1(a) gives the reversible heat flow of IPC sample. It can be found that there appear two T_gs. The higher T_g should be attributed to the propylene homopolymer, and the other, to EPR, according to the previous reports.[17–19] Even it has been reported that IPC contains ethylene-propylene block copolymer as a third component,[19] the T_g of this block copolymer is difficult to be determined. The reasons for these results are involved in two factors: one is that the T_g of the block copolymer is the same with that of the EPR or propylene homopolymer, hence the transition of the block copolymer is covered by that of other components; the other is that the content of the block copolymer in IPC is too low. Figure 1(b) gives the melting trace of IPC sample. It can be found that two melting peaks exist at different temperatures. The melting peak at about 163°C should be attributed to the melting of propylene homopolymer, and the melting peak at bout 116°C results from the melting of polyethylene crystal. These results indicate that IPC contains some polyethylene homopolymer or ethylene-propylene copolymer in which the ethylene segments could crystallize independently. Figure 1(c) shows the melting trace of SP179 subjected to an eighteen steps SSA treatment with decrease of the 5°C per step from 169°C to 84°C. The appearance of a series of melting peaks in the curve indicates that thermal fractionation has occurred during the SSA treatment and each peak should correspond to the melting of a particular lamellar population and the highest temperature peak represents the melting of propylene crystal with the lowest defects concentration. These melting peaks could be divided into two parts, one of which is the higher temperature part where the melting peaks labeled as 1 to 5, representing the melting trace of polypropylene crystals; and the other, the lower temperature part in which the melting peaks labeled as 1' to 8', being the melting trace of polyethylene crystals. Moreover, no melting peaks appearance in the temperature range from 125°C to 150°C, indicating that there is no tendency of cocrystallization for PE and iPP in IPC because they have different crystal structures.[20] It is known that the fractionation effect of
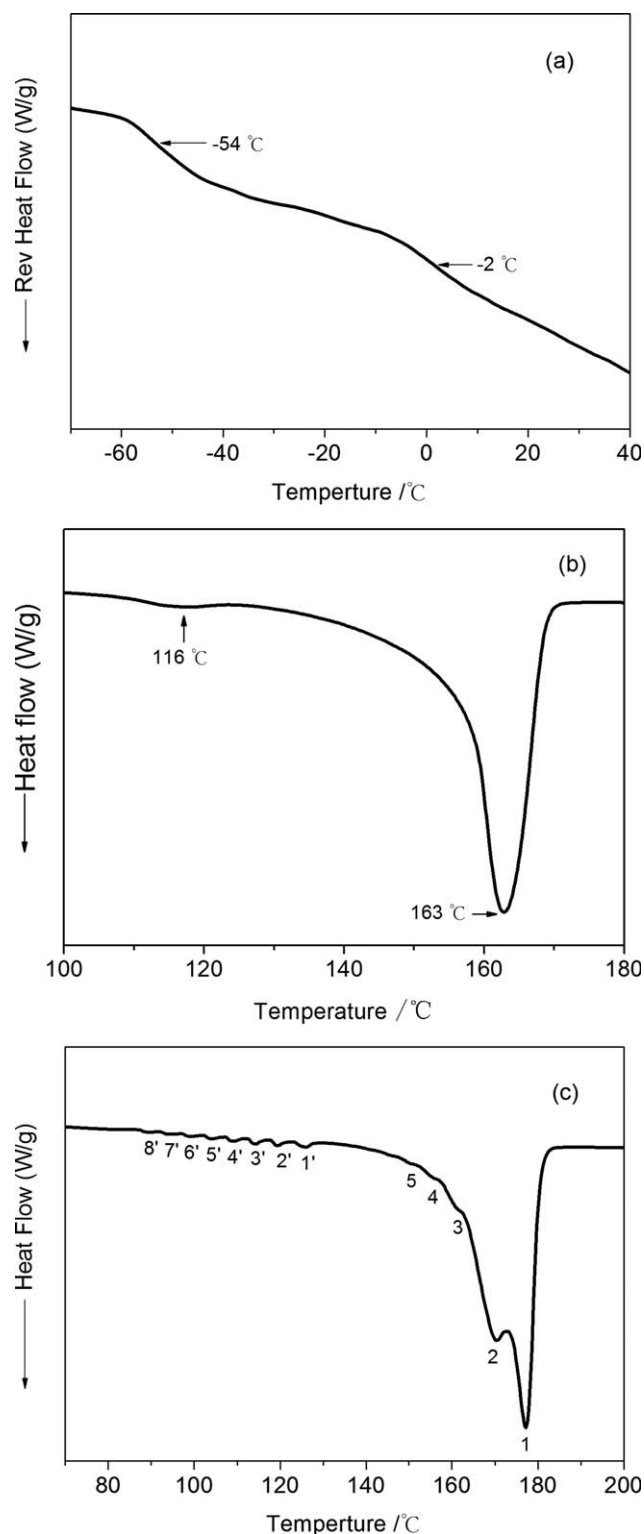

Figure 1 DSC reversible heat flow (a), heat flow (b) and heat flow after being treated by SSA (c) for IPC.

the SSA procedure mainly depends on the defect contents of the polymer chains, and isslightly influenced by the molecular weight distribution.[21] The lamellae thickness of the crystals has a wide distribution because the polymer chains are heterogeneous.
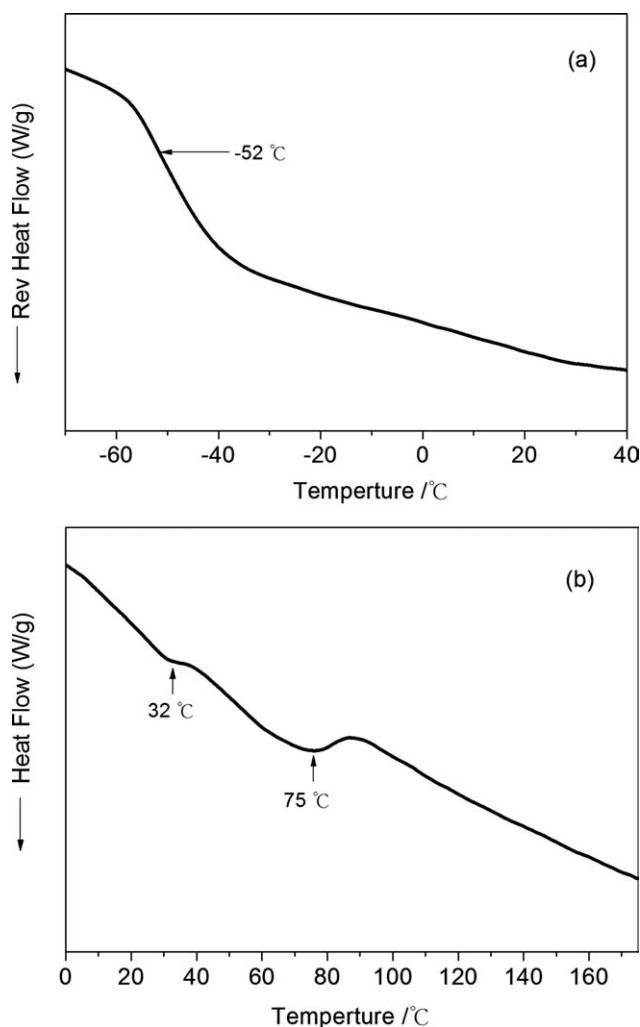
Figure 2 DSC reversible heat flow (a) and heat flow (b) for F_{50}.

For polypropylene component, the chain defect may result from the ethylene units which enter the polypropylene sequence since polypropylene catalyzed by Ziegler-Natta catalyst has a high isotacticity and a negligible branching content. On the other hand, for polyethylene component, the chain defect may result from the branched structure. The later analysis of the fractions of IPC sample will give more detailed information about the SSA fractionation results.

Figure 2(a) presents the reversible heat flow curve of F_{50}. An obvious glass transition peak corresponding to the T_g of EPR component can be seen and the T_g obtained by software is about −52°C. However, the glass transition of PP component could hardly be observed from this curve, revealing that the F_{50} contains no propylene homopolymer. Figure 2(b) gives the melting trace of F_{50}. There are two tiny peaks at about 32 and 75°C, respectively, and theses peaks should be attributed to the melting of PE or PP crystals with low lamellae thickness. Hence, it is believed that the F_{50} mainly consist of EPR and a

very small amount of PE or PP segments which can form crystals with thin lamellae.

Figure 3(a) presents the reversible heat flow curve of F_{125}. Only one glass transition at about 1°C can be
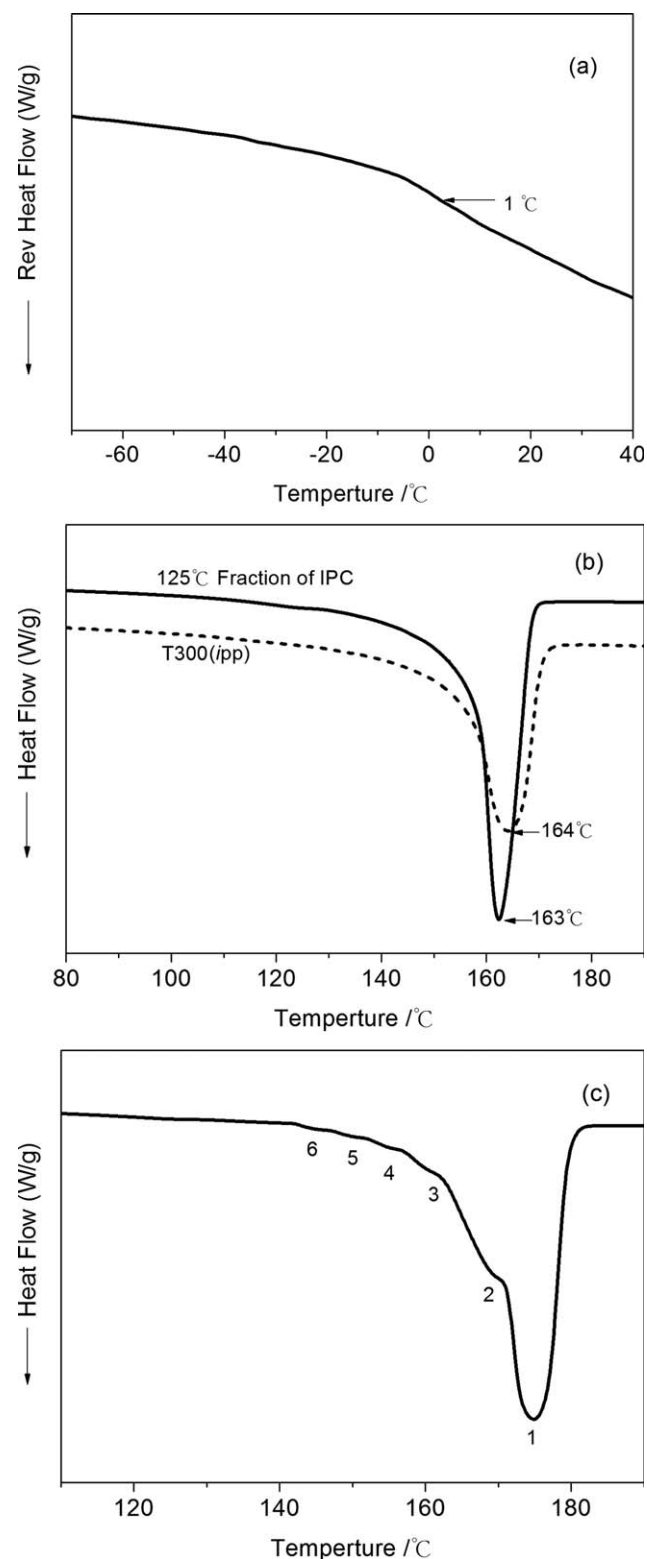

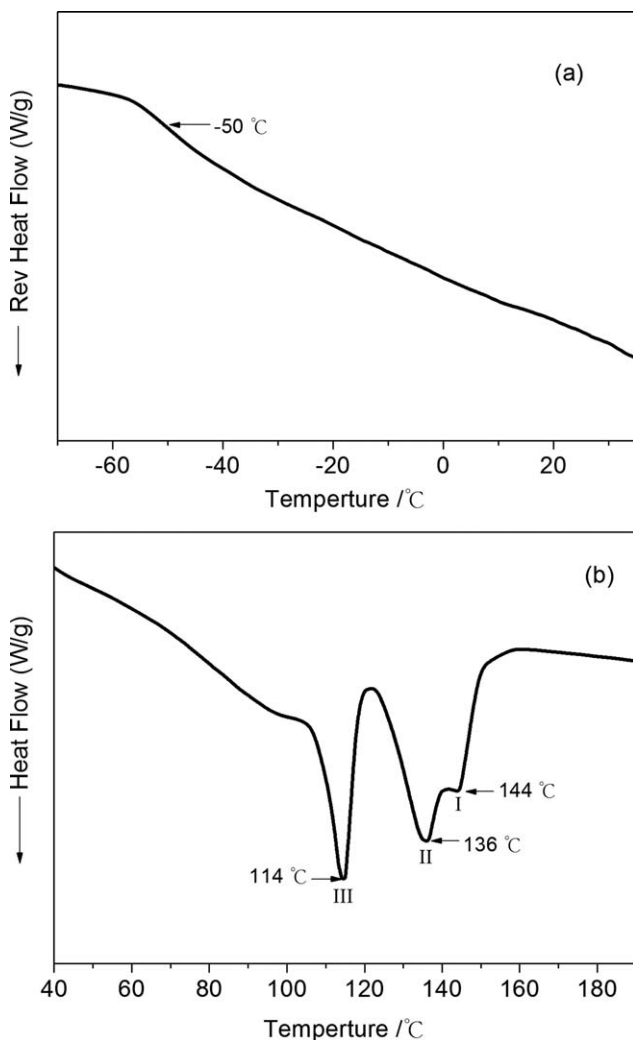**Figure 3** DSC reversible heat flow (a), heat flow (b) and heat flow after being treated by SSA (c) for F_{125}.

Figure 4 DSC reversible heat flow (a) and heat flow (b) for F_{100}.

observed in the curve and it should be attributed to the T_g of PP component. Figure 3(b) shows the melting trace of F_{125}. An obvious melting peak appears at about 162°C and this melting peak is ascribed to the melting of polypropylene crystal as compared with the melting trace of a commercial isotactic polypropylene T_{300}. Based on above results, the main component of this fraction is believed to be isotactic polypropylene. Figure 3(c) shows the melting curve of the F_{125} after being subjected to a seven-step SSA treatment with the following T_s temperatures for self-nucleation and/or annealing: 169, 164, 159, 154, 149, 144, and 139°C, respectively. The melting trace indicates that the effect of thermal fractionation of SSA on this fraction is limited, and meanwhile confirms the above deduction that the fraction only contains isotactic polypropylene, since the foundation of thermal fractionation of SSA is the compositional heterogeneity and neat isotactic polypropylene has a very low heterogeneities content.

Figure 4(a) gives the reversible heat flow curve of the F_{100}. Only a single glass transition peak can be observed at about −50°C, corresponding to the T_g of EPR segments. As compared with that of F_{50}, the glass transition peak of F_{100} is much weaker, indicating that this fraction only contains a small amount of EPR. In addition, EPR should exist as the short segments in the molecular chains of F_{100}, otherwise these chains should be extracted at 50°C and become a part of F_{50}. Concerning that the main content of F_{100} is ethylene-propylene block copolymer which may act as a compatibilizer for the PP and EPR components for IPC1, 13, 19, the results of analysis here imply that the F_{100} and F_{50} are probably compatible since they commonly contain the EPR segment. Figure 4(b) shows the melting trace of F_{100}. Three melting peaks, labeled as I, II and III, appear at 144, 136, and 114°C, respectively. Peak I and II should represent the melting of polypropylene crystals with low lamellae thickness, on the basis of the fact that the temperatures of these peaks are higher than T_m of HDPE but lower than T_m of iPP. Moreover, the existence of these two peaks located in a wide temperature range implies that F_{100} contains block polypropylene segments with different lengths and can form the crystals with different lamellae thickness. Since Peak III locates in the temperature range of melting point of polyethylene crystal or polypropylene crystal formed by chains with low perfections, it is also difficult to learn the adscription of this peak only from DSC curve. To understand it more carefully, the components responsible for the melting peak III will be further discussed in next section.

Figure 5 shows the WAXD patterns of F_{100}. Both diffraction characteristic of PP and PE exist, indicating that this fraction indeed contains polypropylene and polyethylene crystals. The result supports the above assumption that the fraction consists of crystallizable polypropylene and polyethylene segments.
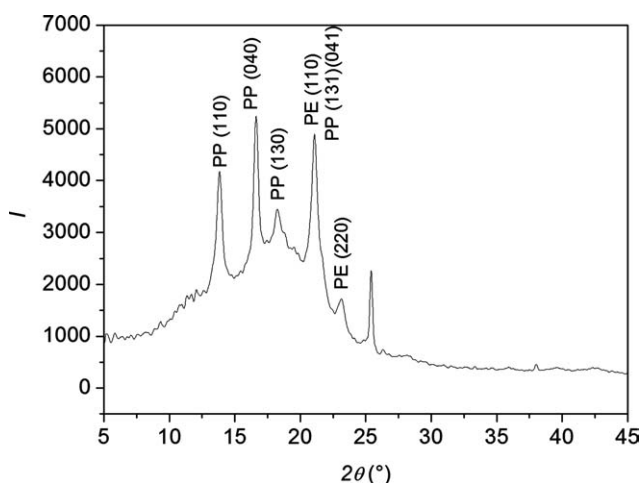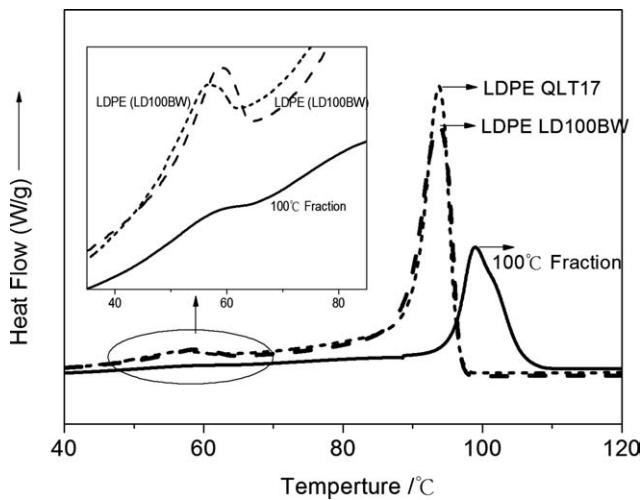

Figure 5 WAXD patterns of F_{100}.

Figure 6 Cooling traces of F_{100} and two LDPEs.

Figure 7 DSC heat flow of F_{100} after being treated by SSA.

Because IPC SP179 contains a certain amount of polyethylene crystals with melting point of about 115°C as shown in Figure 1(b), and the melting traces of F_{50} and F_{100} exhibit no melting peaks at this temperature range, the Peak III in the Figure 4(b) is probably attributed to the melting peak of crystals formed by polyethylene with some branch content.

Figure 6 presents the cooling traces of the F_{100} and two LDPEs at a cooling rate of 10°C/min. Even the melting trace of F_{100} demonstrates three melting peaks at a heating rate of 10°C/min, only two crystallization peaks appear in the cooling trace due to the nucleation effect of the polypropylene. The peak at 99°C in the cooling curve of F_{100} should result from crystallization of polypropylene and polyethylene segments, while the peaks around 94°C in the cooling traces of the two LDPE samples are ascribed to the crystallization of the polyethylene chains. A crystallization peak corresponding to the characteristic crystallization peak of branched polyethylene can be observed at 55°C for all the three curves. This result also supports the above conclusions that the F_{100} contains crystallizable branched polyethylene segments and these branched segments result in the significant SSA fractionation effects for polyethylene component of IPC as shown in Figure 1(c).

Figure 7 presents the melting trace of the F_{100} after being subjected to a fourteen steps SSA treatment with decrease of the 5°C per step from 153 to 88°C. Like the melting trace of IPC after the SSA treatment, these 15 peaks can also be divided into two parts: one is the high temperature part consisting of peak 1 to 7, responsible for the melting peaks of polypropylene crystals, and the other, is low temperature part consisting of peak 8 to 15, the melting peaks of polyethylene crystals. For the polypropylene component, the peaks in higher temperatures represent the melting of the polypropylene crystals
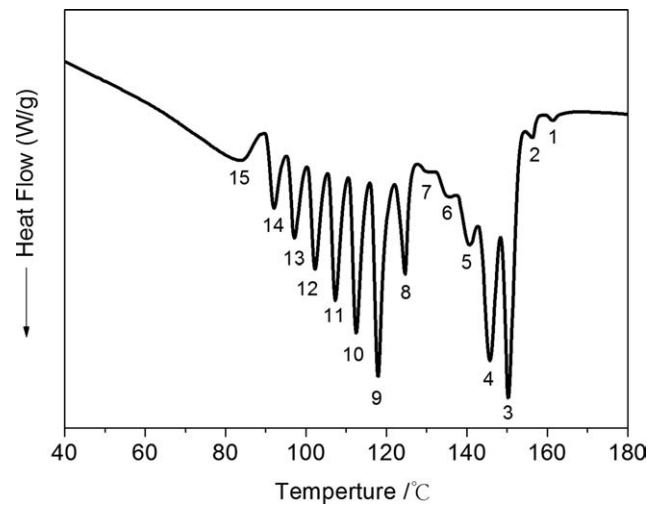
formed by chains with fewer defects. Since the polypropylene component has a high isotacticity and a negligible branching content and the SSA technique can hardly effectively fractionate polymer through the different molecular weight distribution, the peaks reflecting the melting of crystals with different lamellae thickness should result from the crystallization of propylene segments with different structures. The obvious thermal fractionation effect of the fraction and multipeaks of the curve indicates the complex of the components for the fraction which is the consequence of the irregular arrangement of ethylene and propylene segments for this fraction.
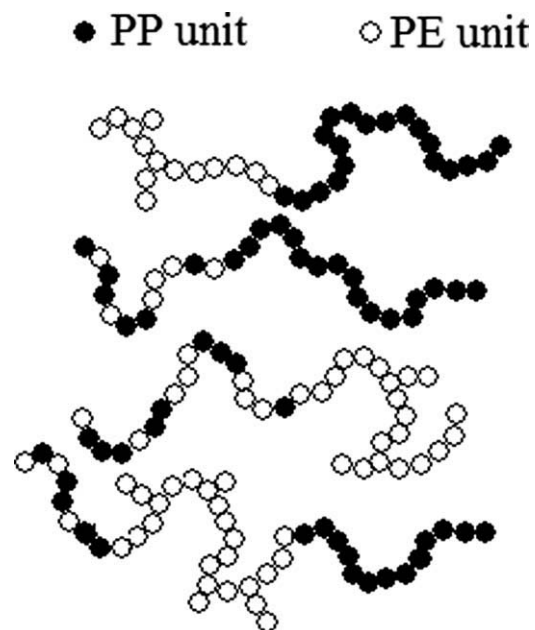

Figure 8 Schematic diagram of probable chain structure of F_{100}.

On the basis of the above analysis, we believe that the main components of F_{100} are some branched polyethylene and various ethylene-propylene block copolymers. In these block copolymers some polypropylene segments can form crystals with various lamellae thickness, and some ethylene and propylene units randomly arrange in certain segments. Accordingly, Figure 8 presents the reasonable macromolecular structure of F_{100}.

CONCLUSION

The IPC could be fractionated into three fractions using n-octane as solvent, and the heterogeneity of the structure of IPC and its fractions were investigated through the thermal fractionation technique (SSA). The thermal behaviors such as glass transition, melting and cooling process of IPC and its fractioned samples were examined. Results show that the F_{50} mainly consists of EPR copolymer, and the molecular chains may also contain a few of short but crystallizable propylene and/or ethylene unit sequences, however the lamellae thickness of the crystals are extremely low. The F_{100} mainly consist of some branched polyethylene and various ethylene-propylene block copolymers. Moreover, in these block copolymers some polypropylene segments can form crystals with various lamellae thickness, and some ethylene and propylene units randomly arrange in certain segments. In addition, the obvious thermal fractionation effect detected by SSA process also indicates that the arrangement of ethylene and propylene segments for this fraction is rather irregular and nonuniform. The main component of F_{125} is assigned to propylene homopolymer whose molecular chains exhibit a low defects concentration and high tacticity.

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