Influence of Microstructure on Space Charges of Polypropylene

XIANG LI,1 QIANGGUO DU,1 JIE KANG,2 DEMIN TU2

1Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymer, Fudan University, 220 Handan Road, Shanghai 200433, China
2Department of Electrical Engineering, Xi’an Jiaotong University, Xi’an 710049, China

Received 8 August 2001; revised 5 October 2001; accepted 30 November 2001

ABSTRACT: The correlation of chemical structure, crystalline morphology, and space charge distribution under a dc electrical field was investigated with three kinds of poly(propylene) (PP) with a different chemical structure, that is, homogeneous PP and block copolymer and random copolymer of PP. The space charge distribution of the samples was prominently affected by their chemical sequence structure and crystalline microstructure. Among samples of different PPs, all isothermally crystallized at 140 °C, the sample of random coPP represents the most well proportional space charge distribution and the smallest number of space charges. The effect of thermal history on the space charge distribution was also investigated by the samples of block coPP. The sample thermally treated at 50 °C clearly represents a better proportional distribution than that at higher temperature of 140 and 100 °C. Subsequent experiments indicate that the better proportional distribution attributes to imperfect and fine sperulites with the fine distribution of the “amorphous” region. The imperfect and fine sperulites originate from the random incorporation of ethylene segments or units into PP chains or from the low annealing temperature, and play an important role in the formation of shallow traps and transportation of space charges. © 2002 John Wiley & Sons, Inc. J Polym Sci Part B: Polym Phys 40: 365–374, 2002; DOI 10.1002/polb.10100

Keywords: charge transport; poly(propylene) (PP); structure; morphology

INTRODUCTION

Polymers and polymer blends are frequently used for insulators in electrical engineering. The insulation characteristic of polymers lies in many localized states in energy band structure and local accumulation of space charges. It is, therefore, important to understand the mechanism of formation and accumulation of space charges in power cables and discuss the possibility of elimination. Polyethylene (PE) has been extensively used as an insulating material for power cables and communication cables because of its high resistivity and low tan δ. A few articles have been published on space charge distribution and electrical conduction in a PE system.1–4 Space charges have a close relationship with crystalline morphology in semicrystalline polymers like PE. Recently, the polypropylene (PP) system has attained a great amount of interest because of its potential value in the field of insulators.5,6 Usually three kinds of PP, from the point of chemical structure, are mainly used in the industrial field, that is, homogeneous PP, block PP, and random PP. The three polymers have different chemical structures and different crystalline morphologies.
and further show the difference in properties including mechanical and electrical properties. However, many previous studies have not correlated the space charge distribution of PP with the structure of polymer chains. Compared with the homoPP, the regularity of sequence structure in the block and random coPP is broken with the incorporation of ethylene units, and the effect of the breaking on the distribution and number of space charges is still unknown.

In this work, the relationship between space charges and the sequence structure of PE and the relationship between space charges and crystalline morphology were studied.

EXPERIMENTAL

Materials

Three kinds of commercial PPs (designated by A, B, and C, respectively) with different chemical structures were used (Table 1). $^{13}$C NMR and IR were used to determine their sequence structures. The 500-MHz quantitative $^{13}$C NMR spectra of the raw materials in this study are shown in Figure 1. $^{13}$C NMR spectra were measured from polymer samples dissolved in a solvent of $o$-dichlorobenzene-$d_4$. Sufficient 4,4-dimethy-1,4-silapentance sodium sulfonate was used to maintain a lock signal on a Bruker DMX500 NMR spectrometer at 130 °C. The chemical shift and corresponding component are assigned in Table 2. Greek letters are used to distinguish various methylene carbons and designate the location of the nearest methane carbons as suggested by Carman et al. Reference data from Ray and coworkers, an isotactic PP and an ethylene-propylene copolymer containing 3% ethylene, are also listed in Table 2. The constant difference, about 1.5 ppm, between the measured data and reference data is generated from different internal standards. The eth-

ethylene content was determined by the method of Paxson and Randall (see Table 1).

A Nicolet 510 Fourier transform infrared spectrophotometer was used to record IR spectra between 3100 and 650 cm$^{-1}$. IR spectra of the three kinds of PP are given in Figure 2 where there is little difference among them in the range from 720 to 730 cm$^{-1}$ [see Fig. 2(a)] and about 2850 cm$^{-1}$ [see Fig. 2(b)]. The results of IR analysis confirm

Figure 1. Quantitative $^{13}$C NMR spectra of the raw polypropylenes designated by A, B, and C.

<table>
<thead>
<tr>
<th>Table I. Polypropylene Samples Used in This Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
</tbody>
</table>

$^a$ Measured in this study.

$^b$ Measured from $^{13}$C NMR spectra.
that ethylene units in PP designated by C are distributed randomly along the PP chain, whereas those in PP designated by B are consecutive. Combined with the $^{13}$C NMR results, it was demonstrated that the raw PP A is the homopP, the raw PP B is the ethylene-propylene block copolymer, and the raw PP C is the ethylene-propylene random copolymer.

Sample Preparation and Heat Treatment

Some sheets of 0.5 mm were prepared on a hot press at 200 °C for 5 min, and then some isothermally crystallized at 140 °C for 24 h. Other sheets were quenched from 200 °C into ice water for 2 min and then annealed at the temperature of 100 or 50 °C for 24 h. All the sheets were used for the pulsed electroacoustic (PEA) experiments, wide-angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC). The corresponding films of 10 μm with the same thermal history were obtained on a hot stage and used for polarized light microscopy (PLM). During the processing of cable, polymer is usually extruded from a die, rapidly cooled in water, and then dried in hot air. Thus, in the experiments the preceding tested samples were prepared in simulated conditions. Table 3 summarizes the samples in this study, designated by pertinent information about the materials and the thermal treatment temperature.

Space Charge Measurement

Space charge distribution in samples was measured by the PEA method as shown in Figure 3.
The diameter of the copper electrode was 25 mm. Aluminum was deposited on two sides of the plate samples as the electrodes. Silicone oil was used as an acoustic coupling agent to make a good acoustic contact between the measured electrode and the sample’s surface. The principle of this method and details of measurement are described in the literature. The measurement result gives a curve of positive or negative space charge density ($\rho$) versus the vertical distance (depth) from the anode. In the following figures of space charge distribution, the distance between two vertical dotted lines is the depth of samples equal to the distance from anode to cathode; the average space charge density of a certain vertical section can be directly read from the ordinate value, and the number of space charges can be obtained from the absolute value of integral areas. In addition, the characteristic of the space charges is divided by the abscissa baseline, positive above and negative below.

**WAXD**

X-ray diffraction was performed on a Rigaku diffractometer with a Geiger counter, using Ni-filtered Cu Kα radiation operating at 40 kV and 100 mA. The data were collected in the 2θ range of 5–40°, in steps of 0.04° and a scanning rate of 4 s per point.

**DSC**

The melting and crystallization analysis of various PP samples was carried out on a DSC (PerkinElmer DSC-7) at a heating rate of 10 °C/min, calibrated against indium and zinc. All the crystallization processes were performed under nitrogen atmosphere and carried out on samples of about 12 mg.

**RESULTS AND DISCUSSION**

**Space Charge Distribution of Samples**

Space charge distribution in three kinds of PP samples, isothermally crystallized at 140 °C, is represented in Figures 4 and 5. Figure 4 illustrates the space charge distribution obtained while dc voltages were being applied at stresses of 5, 10, and 15 kV/mm; and Figure 5 indicates the space charge distribution obtained after the short circuit (discharging) for 1 s, 10 s, and 2 min. Figures 6 and 7 describe the space charge distribution for B samples, crystallized at 140 °C and annealed at 100 or 50 °C, under charging or discharging in the same conditions as Figures 4 and 5, respectively.

Under dc voltages in Figure 4, space charges in all the samples are mainly hetero. Most prominent negative space charges are observed near the anode, and a few positive space charges are found near the cathode. As the applied field increases, the negative space charges near the anode increase remarkably in the A140 and B140 samples. A negative space charge peak in A140 seems to separate from the interface charge peak at the cathode in high field strength, which is the

---

**Table III. Samples and Their Thermal History Used in This Study**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Used Here</th>
<th>Raw Polypropylene</th>
<th>Thermal History</th>
</tr>
</thead>
<tbody>
<tr>
<td>A140</td>
<td>A</td>
<td>Kept at 200 °C for 5 min and then thermally crystallized at 140 °C for 24 h</td>
<td></td>
</tr>
<tr>
<td>B140</td>
<td>B</td>
<td>Kept at 200 °C for 5 min and then thermally crystallized at 140 °C for 24 h</td>
<td></td>
</tr>
<tr>
<td>C140</td>
<td>C</td>
<td>Kept at 200 °C for 5 min and then thermally crystallized at 140 °C for 24 h</td>
<td></td>
</tr>
<tr>
<td>B100</td>
<td>B</td>
<td>Kept at 200°C for 5 min, quenched into ice water for 2 min, and then annealed at 100°C for 24 h</td>
<td></td>
</tr>
<tr>
<td>B50</td>
<td>B</td>
<td>Kept at 200°C for 5 min, quenched into ice water for 2 min, and then annealed at 50°C for 24 h</td>
<td></td>
</tr>
</tbody>
</table>
result of charge emission at the cathode. However, the samples of C140 (in Fig. 4), B100, and B50 (in Fig. 6) reveal a different behavior completely. There is almost no space charge near the cathode, and only a few negative space charges appear near the anode without prominent changes with increasing applied field strength. If the samples, isothermally crystallized or annealed at different temperatures, are considered, the number of space charges apparently decreases significantly on lowering the temperature (see Fig. 6). It is more interesting that nearly no space charge remained in the samples of B50 and C140 after discharging as short as 1 s, although a few negative space charges remained in other samples (see Figs. 5 and 7).

Both samples of C140 and B50 represent the well-proportioned distribution, which means a small number of space charges together with a constant space charge density. The A140 and B140 samples appear in a completely converse distribution—a large number of space charges together with variable space charge density. These results indicate that considerable shallow traps must exist in B50 and C140 so that the space charges formed during the charging step are not trapped in locality but disappear easily to electrodes upon removal of the voltage. Considerable deep traps may be contained in both samples of A140 and B140 and capture local space charges during the transportation process of space charges.

**WAXD**

The X-ray diffraction patterns of the samples are displayed in Figure 8. All the samples have five principal crystalline reflection peaks at 2θ of 14.1, 17.0, 18.4, 21.2, and 21.9° corresponding to 110, 040, 130, 111, and 131 lattice planes of the monoclinic α form of PP with no indication of β, the γ form. These results indicate that the preselected condition of crystallization or annealing did not change the crystal form. However, the sample of B100 displays a weak peak (designated with an arrow in Fig. 8) at about 23.5°, which corresponds to 200 lattice plane of PE and attributes of crystallizations of a long sequence of —(CH₂)ₙ— in block coPP. The B140 and B50 samples do not
display the peak because the temperature of heat treatment is too high or too low for the long sequence of ethylene to crystallize.

As suggested by Vittoria, the reciprocal of width at the half-height of the diffraction peak (1/β) located at about 14.1° was chosen as a reliable parameter to evaluate both the size and perfection degree of crystallites, and it increases with increasing size and/or perfection degree. Among the parameter (1/β) of three samples isothermally crystallized at 140 °C, value 1.59 of C140 is the smallest (see Table 4). Increasing the temperature of annealing or crystallization from 50 to 140 °C, the parameter (1/β) progressively increased from 1.67 to 2.00. The data of the crystal plane distance for the three major peaks summarized in Table 4 also suggest the same tendency. From the results of WAXD, both samples of C140 and B50 represent the worst perfection and the smallest size of crystallites. The corresponding samples, coincidentally, represent the best space charge distribution and the smallest number of space charges (see Figs. 4–7).

Melting Analysis

The shape of the melting curve obtained from DSC can be used for interpretation of lamella thickness, and the heat of fusion offers an alternative way of quantitatively assessing the proportions of the crystalline phases in the samples. Melting behaviors of the three samples A140, B140, and C140 are compared in Figure 9, and melting behaviors of the three samples B140, B100, and B50 are compared in Figure 10. The melting behavior of C140, in Figure 9, occurs at the lowest temperature and shows the broadest curve. The melting peak, in Figure 10, shifts to low temperature with a decrease in the thermal treatment temperature, where the melting behavior of B50 occurs at the lowest temperature with the broadest curve. The decrease of melting temperature, accompanied by the broadening of melting transition, indicates the imperfection of its crystalline structure, and the decreasing lamella thickness with a broad distribution of lamella thickness indicates consid-

Figure 6. Space charge distribution at the voltages of 10, 20, and 30 kV/mm for samples of B140, B100, and B50.

Figure 7. Space charge distribution after short circuit of 1 s, 10 s, and 2 min for samples of B140, B100, and B50.
erable crystalline defects. Using a melting enthalpy value of a perfect iPP of 165 J/g, Table 5 lists the crystallinity, melting temperature, and half-peak width of samples, where the effect of ethylene units is neglected because of its low content. In addition, the special structure of the raw PP B makes it possible that ethylene segments and propylene segments can crystallize, respectively, which has also been demonstrated from the melting characteristics of B100 by displaying two peaks, among which the peak at the 69.1 °C is assigned to the behavior of ethylene segments.

**Spherulite Morphology**

Insight into the crystalline morphology of samples is gained with the PLM measurement. In Figures 11 and 12 the samples show a completely different crystalline morphology from each other. In Figure 11, the A140 sample shows the biggest spherulites and the clearest interfaces, but the spherulites in B140 were clearly divided up and minced to some extent. The others, especially C140 (Fig. 11) and B50 (Fig. 12), display a crystalline morphology with the finest crystalline particles.

**Discussion**

From the preceding experiments and results, we easily found the distribution, and the number of hetero space charges was severely af-

---

**Table IV.** Characteristic Values $1/\beta$ and $D_{hkl}$ Determined by WAXD

<table>
<thead>
<tr>
<th>Samples</th>
<th>110</th>
<th>040</th>
<th>130</th>
<th>$1/\beta$ (degree$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A140</td>
<td>6.25</td>
<td>5.20</td>
<td>4.76</td>
<td>2.22</td>
</tr>
<tr>
<td>B140</td>
<td>6.26</td>
<td>5.21</td>
<td>4.76</td>
<td>2.00</td>
</tr>
<tr>
<td>C140</td>
<td>6.32</td>
<td>5.26</td>
<td>4.80</td>
<td>1.59</td>
</tr>
<tr>
<td>B100</td>
<td>6.66</td>
<td>5.20</td>
<td>4.76</td>
<td>1.67</td>
</tr>
<tr>
<td>B50</td>
<td>6.30</td>
<td>5.25</td>
<td>4.78</td>
<td>1.69</td>
</tr>
</tbody>
</table>

**Figure 8.** Wide-angle X-ray diffraction patterns for samples of A140, B140, C140, B100, and B50.

**Figure 9.** Melting characteristics of A140, B140, and C140 isothermally crystallized at 140 °C.

**Figure 10.** Melting characteristics of B140, B100, and B50.
affected by the chemical sequence structure and thermal history. Generally speaking, the hetero space charges originate mainly from the ionization of impurities. In the case of polymers, “impurity” is a broad term covering weak polar molecules, initiator residues, macromolecular end segments, metal ions, and so forth. The impurities and noncrystalline materials as well as the growth of lamellae are expelled out and localized at or near fold-surface areas of lamellae and the boundaries of spherulites. We also have had a basic idea that, depending on the dispersion of impurities and density fluctuation of them, the ratio of shallow traps to deep traps and the number of them play an important role during the transportation of space charges. Shallow traps act as hopping sites of space charges, extend the mean free path of space charges to enable the subsequent space charges to travel the whole materials freely, and finally reduce the space charge accumulation in partial localities. Deep traps play a reversed role in the transportation of space charges and decrease prominently in number because of the well-proportioned dispersion of impurities. Therefore, both samples of C140 and B50 can be deduced to contain many hopping sites or shallow traps. Both samples, coincidentally, represent such imperfect crystalline structure and fine crystalline morphology with a broad distribution of lamella thickness and small lamellae intrinsically originate from the difference of amorphous-chain conformation, caused by the incorporation of ethylene units into PP segments or the low annealing temperature.

CONCLUSIONS

The chemical sequence structure, together with heat treatment, plays an important role in the distribution and number of space charges in PPs under the dc electrical field.

Among the three kinds of PP samples crystallized at the same conditions, the random copolymer C represents the most well proportioned distribution and the smallest number of space charges. The most likely reason is that in the random copolymer the isolated ethylene units hold back

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
<th>Width of Half-Peak in DSC (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A140</td>
<td>113.8</td>
<td>174.8</td>
<td>12.8</td>
</tr>
<tr>
<td>B140</td>
<td>95.5</td>
<td>173.5</td>
<td>14.4</td>
</tr>
<tr>
<td>C140</td>
<td>73.5</td>
<td>150.7</td>
<td>24.8</td>
</tr>
<tr>
<td>B100</td>
<td>15.5</td>
<td>69.1</td>
<td></td>
</tr>
<tr>
<td>B50</td>
<td>63.9</td>
<td>169.4</td>
<td>14.5</td>
</tr>
</tbody>
</table>
Figure 11. Polarized light micrographs of A140, B140, and C140 isothermally crystallized at 140 °C.

Figure 12. Polarized light micrographs of B140, B100, and B50.
the crystallization of the propylene units, leading to imperfect and fine crystalline morphology, the broad distribution of lamella thickness, and considerable small lamellae that contribute to the formation of considerable shallow traps. Intrinsically, with the incorporation of ethylene units, whether in the form of segments or isolated units into PP segments, the regularity of the chemical sequence is broken randomly along the chains, and the breaking finally attributes to the fine crystalline morphology.

Likewise, the thermal history also has a prominent effect on the space charge distribution. The sample thermally treated at a relatively low temperature of 50 °C clearly represents the more even space charge distribution than that treated at higher temperatures of 140 and 100 °C.

This work was supported by the Key Laboratory of Molecular Engineering of Polymer of Fudan University, Ministry of Education, China. This work was also subsidized by the Special Funds for Major State Basic Research Projects (G1999064800). D. Tu thanks the Natural Science Fund Committee for financial support under project 59777001.

REFERENCES AND NOTES