Structure and Properties of Impact Copolymer Polypropylene. I. Chain Structure

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ABSTRACT: In this work, impact copolymer polypropylene (ICPP) was fractionated into 4 fractions. ICPP and the 4 fractions were studied using Fourier transform infrared and ^{13}C nuclear magnetic resonance analysis. The results demonstrate that fraction A is ethylene–propylene rubber, fraction B is ethylene–propylene (EP) segmented copolymer, fraction C is ethylene–propylene block copolymer, and fraction D is polypropylene with a few ethylene monomers in the chain. The differences in properties between different impact copolymer polypropylenes should be due to their fractions' differences in composition and chain sequence structure. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 93–101, 1999

Key words: impact copolymer polypropylene; fraction; chain structure; composition

INTRODUCTION

Toughened polypropylene (PP) is an important member of the PP family. The incentive to prepare it lies in the poor low-temperature impact properties of PP homopolymer. An obvious way to alleviate this drawback is to create a mixed system containing an elastomer compatible with the homopolymer. As is well known, it is an effective way to prepare the toughened product *in-situ* by polymerizing propylene first and then copolymerizing propylene with ethylene to form the elastomeric part of the product.[1–5]

The chain structure of the toughened PP, the *in-situ* prepared copolymer PP, has been studied by several authors.[6–12] Parson and Randall measured the ethylene content of random EP copolymers with low ethylene content using the nuclear magnetic resonance (NMR) technique and calibrated an infrared (IR) method with it as standard.[6] Cheng and Lee determined the assignments of ^{13}C-NMR spectra of impact copolymer PP.[9] Hayashi et al. carried out the hexadic sequence determination of impact copolymer polypropylene through ^{13}C-NMR.[10] However, the experimental results in these works only characterized the average chain sequence structure in *in-situ* prepared impact copolymer polypropylene.

In this work the *in-situ* prepared impact copolymer polypropylene (ICPP) samples were separated into 4 fractions. Using Fourier transform IR (FTIR) and ^{13}C-NMR, the chain sequence structure of each fraction has been determined. The results show that the 4 fractions' chain structures are quite different. The separation of the sample into fractions is necessary for precise characterization of the chain sequence structure of *in-situ* prepared impact copolymer PP.

Table I   The Molecular Weight and the Ethylene Monomer Content of Impact Copolymer Polypropylene

ICPP	Weight-Average Molecular Weight $\bar{M}_w \times 10^{-5}$	Number-Average Molecular Weight $\bar{M}_n \times 10^{-5}$	Molecular Weight Distribution	Ethylene Monomer Content (Wt %)
CPPB	1.73	0.44	3.93	9.13
CPPJ	2.37	0.39	6.02	9.43

EXPERIMENTAL

Samples

Two commercial *in-situ* prepared impact copolymer PPs were used in this work. They were purchased from Olefin Chemical Industries Co. Ltd. and Showa Denko K. K. in Japan (this impact copolymer polypropylene is identified as CPPJ in our work) and Belgium Neste Chemicals N. V. (This impact copolymer polypropylene is called CPPB in our work). Their molecular parameters and mechanical characteristics are measured and shown in Tables I and II.

Measurements

^{13}C-NMR spectra were recorded at 125°C on JEOL FX-90Q spectrometer operated at 22.45 MHz. The samples were prepared as 10% (w/v) solution in 1,2,4-trichloro benzene + benzene-d6 (90/10 V/V). Benzene-d6 provided the signal for the ^{1}H-NMR internal lock. In all measurements, broadband noise decoupling was used to remove [13]C—[1]H couplings. The pulse angle was 40°, and the pulse repetition time was 5 s. More than 10,000 field intensity desorption (FID) were stored in 8-K data points using the spectra's width of 4500 Hz for each sample. Double precision accumulation was employed. Hexamethyl–disiloxane (HMDS) was used as an internal reference (20.3 downfield from the resonance of tetramethylsilane (TMS)).

The Nicolet 170SX FTIR spectrometer was used to measure the spectra of all samples with a resolution of 2 cm^{-1} and 32 scanning times for each sample. The film of sample was cast from xylene solution ($\sim$ 1 wt %) on the plates of KBr at a temperature of 125°C. The residue of solvent was removed in a vacuum oven. The films were sufficiently thin to obey the Beer–Lambert Law.

Gel permeation chromatography (Waters 150C) was used to measure molecular weight and its distribution with solvent *o*-dichlorobenzene for each PP sample at 135°C. The sample for the calibration curve was standard polystyrene (PS). The standard mechanical properties were measured by a SHIMAZU DCS 5000 universal testing machine (according to ASTM D638; crosshead speed was at 50 mm/min, at room temperature) and an Izod impact tester in Qilu Petrochemical Co. in China (According to ASTM D256; impact rate was 3.35 m/s).

RESULTS AND DISCUSSION

Apparent Chain Sequence Structure of *In-Situ* Prepared Impact Copolymer Polypropylene

IR spectral fingerprints of CPPJ and CPPB samples are shown in Figure 1. As indicated in some

Table II   The Mechanical Properties of Impact Copolymer Polypropylene

ICPP	Melting Index (MI) g/10 min	Yielding Strength (10^5 Pa)	Notched Izod Impact Strength (J/m)	
			25°C	−20°C
CPPB	40	225	52	35
CPPJ	15	251	116	52

Figure 1 IR Spectra of (A) CPPJ and (B) CPPB.

works,[13,14] the absorptions at 998 and 841 cm^{-1} are due to methyl rocking modes and are associated with the threefold helix of isotatic PP, which is the characteristic structure of PP crystal. The band at 972 cm^{-1} is associated with methyl rocking vibrations of amorphous PP. The band at 720 cm^{-1} is due to —$(CH_2)_n$— ($n \geq 5$) rocking vibrations. The doublet at 720–740 cm^{-1} indicates the presence of a crystalline polyethylene (PE) block. When PE crystallinity is small, the band at 730 cm^{-1} of the doublet will be reduced to a shoulder of the band at 720 cm^{-1}. In Figure 1, evidently, PP in CPPJ and CPPB crystallizes, and the absorption of PP amorphous band is very weak. At the same time, the peaks at 720 cm^{-1}

Figure 2 ^{13}C-NMR spectrum of CPPJ.

are small. This means that the methylene sequence —$(CH_2)_n$—($n \geq 5$) content is low in these samples, particularly in CPPJ. In CPPJ, the polyethylene chain units almost did not participate in any crystallization, as shown in previous works.[5,12]

^{13}C-NMR spectra were measured, and the ^{13}C-NMR spectrum of CPPJ is shown in Figure 2. The nomenclature assigning the peaks for various car-

Figure 3 IR spectra (1350–650 cm^{-1}) of the fractions of (A) CPPJ and (B) CPPB: (a) fraction A; (b) fraction B; (c) fraction C; (d) fraction D.

Figure 4 ^{13}C-NMR spectra of fraction As of (A) CPPJ and (B) CPPB.

bons of ICPP follows the method suggested by Carman and Wilkes.[7] A methylene carbons is identified by the letter S and a pair of Greek letters that indicate its distance in both directions from the nearest tertiary carbons. For example, $S_{\alpha\gamma}$ is a methylene carbon, which is α to 1 tertiary carbon and γ to the other on the other side. The letter δ indicates that the distance of a methylene carbon to a tertiary carbon is 4 carbons or more. A methyl carbon is labeled by the letter P, and a tertiary carbon is labeled by the letter T and a couple of Greek letters like those labeling meth-

ylene carbon. The carbon nomenclature and the peak assignments are shown in Figure 2 and Figures 4–6. Using the intensity of the peaks of corresponding methylene carbon, we can calculate P %, E %, and the dyad sequence distribution. From the peaks of primary and tertiary carbons, the information about triad distribution with center P (PPP, PPE, and EPE) can be obtained. The data about triad distribution with center E (EEE, EEP, and PEP) are calculated from the peaks of methylene carbons. The distribution of all triads was normalized. All the results

Figure 5 ^{13}C-NMR spectra of fraction Bs of (A) CPPJ and (B) CPPB.

are shown in Table III. It can be seen that the ethylene content is similar in these 2 samples. But the distribution of ethylene sequence in the triads with center E is more homogeneous for CPPJ than for CPPB. It should be noticed that the content of EEE triad in CPPJ sample is low, which means that the content of long ethylene sequence in the sample is low.

The Method of Separating *In-Situ* Prepared Impact Copolymer Polypropylene Into Fractions

Besomles et al.[15] performed the fractionation of an ethylene–propylene block copolymer with a nominal 15% content of ethylene by weight near the lower critical solution temperature. Several solvents were used in fractionation, but in each fractionating procedure, only 1 solvent was used, and the several fractionating procedures are independent of each other. Furthermore, because the phase separation occurs above the boiling points of the solvent (132–210°C), the glass or steel container, in which a solution is placed, has to withstand the vapor pressure of the solvent up to its critical pressure. Kakugo et al.[16] studied the copolymer composition distribution and monomer sequence distribution of EP copolymers polymerized using various het-

Figure 6 ^{13}C-NMR spectra of fraction Cs of (A) CPPJ and (B) CPPB.

erogeneous catalysts. Although different fractions of EP copolymer were obtained, the investigation was not emphasized on interpreting the difference of the chain structure between different fractions.

In this work, 3 solvents, xylene, benzene, and heptane, were used for fractionation. The typical fractionating procedure is as follows.

The sample of ICPP was dissolved in xylene at 130°C, then the solution was gradually cooled to room temperature. While cooling, the ICPP were separated from the solution little by little until equilibrium is reached. So the system was sepa-

rated into 2 phases: the concentrated phase and the dilute phase. Xylene in both the concentrated phase and the dilute phase was evaporated. The solute from the dilute phase is the first fraction of ICPP and is named fraction A. The precipitate from the concentrated phase by removing residual solvent under vacuum is quiet loose, which makes the next extraction easier. The loose precipitate of the concentrated phase was extracted by boiling benzene for about 70 h. From the benzene solution, the second fraction (fraction B) was obtained. After being extracted by boiling benzene, the remained precipitate was dried under

Table III   The Content of the Propylene, Ethylene Monomer, and Triad Sequence Distributions of Impact Copolymer Polypropylene

Mark	P	E	PPP	PPE	EPE	PEP	PEE	EEE
CPPB	0.869	0.131	0.807	0.046	0.016	0.010	0.035	0.086
CPPJ	0.865	0.135	0.764	0.068	0.033	0.017	0.042	0.076

Table IV The Content of the 4 Fractions in Impact Copolymer Polypropylene

ICPP	Fraction A	Fraction B	Fraction C	Fraction D
CPPB	10.8	13.5	2.2	73.5
CPPJ	7.5	12.0	3.0	77.5

vacuum. Then extracted by boiling heptane, it was separated into 2 fractions, the fraction dissolved in heptane (fraction C) and the fraction insoluble in heptane (fraction D). The 4 fractions were weighted, respectively, and the data are in Table IV. Clearly, fraction D is the main component of ICPP.

FTIR and ^{13}C-NMR Analysis of Fractions

The IR spectra $(1350-650 \text{ cm}^{-1})$ of the 4 fractions of CPPJ and CPPB are shown in Figure 3. The spectra show several structural characteristics of the 4 fractions of CPPJ and CPPB as follows.

1. The spectra of fraction A of both ICPPS do not exhibit the crystalline bands of PP, which are obvious in ICPPs' IR spectra. A single band at 720 cm^{-1} occurs in these spectra and is stronger than that of ICPP. Such results indicate that in fraction A of ICPP, both PP segments and PE segments do not crystallize, and fraction A appears to be EP rubber. The band at 720 cm^{-1} is weaker in the IR spectrum of CPPJ's fraction A than in the IR spectrum of CPPB's fraction A. This means that the content of long ethylene sequences in CPPJ's fraction A is lower than that in CPPB's fraction A.

2. The spectra of both fraction Bs exhibit the crystalline bands of polypropylene, which are relatively weaker than that of ICPP. This means that the propylene sequences of fraction B have become long enough to crystallize. The band at 720 cm^{-1} becomes stronger. Simultaneously, the shoulder at 730 cm^{-1} also becomes more or less visible for the CPPB sample. Similarly to the spectra of fraction A, the band at 720 cm^{-1} of CPPJ's fraction B is weaker; that is, the content of long ethylene sequence of CPPJ's fraction B is lower than that of CPPB fraction B. Polypropylene crystal-

line bands of fraction B are much weaker than those of ICPP; thus, we can deduce that fraction B is ethylene–propylene segmented copolymer with a short ethylene and propylene block.

3. The spectra of both fraction Cs show that not only PP segments but also polyethylene segments can crystallize. The PP crystalline bands of fraction C are weaker than those of ICPP. The doublet at 720 and 730 cm^{-1} becomes evident and sharp for CPPB's fraction C. That doublet of CPPJ's fraction C is much weaker than that of CPPB's fraction C, but it is stronger than that of ICPP. The differential scanning calorimetry (DSC) measurements also prove the obvious crystallization of PP and PE segments in fractions (seen in the next work). These mean that fraction C is EP block copolymers.

4. The spectra of both fraction Ds show that PP segments strongly crystallize. Their PP crystalline bands are similar to those of ICPP. The bands at 720 and 730 cm^{-1} are very weak, almost invisible. That means that ethylene content and the content of long ethylene segment are so low in fraction D that ethylene segments cannot crystallize.

The ^{13}C-NMR spectra of the first 3 fractions of CPPJ and CPPB are shown in Figures 4–6. The calculated results according to the work of Carman and Wilkes are compiled in Table V.

The chain structure characteristics of the fractions of CPPJ and CPPB are as follows.

1. In fraction A, B, and C of ICPP, the ethylene content of the CPPJ sample is lower than that of the CPPB sample.
   The ethylene content of original CPPJ sample is a little higher than that of CPPB. It can be concluded that the ethylene content of CPPJ's fraction D should be a little higher than that of CPPB's fraction D.

2. For the fraction A of 2 ICPPs, both propylene and ethylene sequence distributions in all triads are relatively homogeneous. This confirms that fraction A is EP rubber.

3. For the 2 fraction Cs, both propylene and ethylene sequence distributions in all triads are evidently heterogeneous, particularly for CPPB's fraction C. The content of

Table V   The Content of the Propylene, Ethylene Monomer, and Triad Sequence Distributions

ICPP	Fraction A		Fraction B		Fraction C	
	CPPB	CPPJ	CPPB	CPPJ	CPPB	CPPJ
P	0.547	0.635	0.658	0.694	0.545	0.831
E	0.453	0.365	0.342	0.306	0.455	0.169
PPP	0.176	0.300	0.470	0.482	0.527	0.716
PPE	0.203	0.208	0.125	0.154	0.018	0.094
EPE	0.167	0.127	0.063	0.058	0	0.025
PEE	0.195	0.122	0.090	0.111	0.030	0.018
PEP	0.081	0.142	0.033	0.073	0	0.011
EEE	0.177	0.101	0.220	0.123	0.425	0.140

PPP and the content of EEE are much higher than other triads. The results convincingly prove the essence of the EP block copolymer for the 2 fraction Cs.

The chain structure characteristic of fraction B is between that of fraction A and fraction C. Thus, we are sure that fraction B is a segmented copolymer.

It is very interesting that both propylene sequence distribution and ethylene sequence distribution change gradually from fraction A to fraction B and fraction C for these ICPPs. The change of propylene sequence distribution and ethylene sequence distribution among fractions exhibits some continuity. This is an important characteristic of the *in-situ* polymerization method for ICPP. Propylene sequence distribution and ethylene sequence distribution change more continuously among fractions of CPPJ than among fractions of CPPB.

In order to understand the chain structure of *in-situ* prepared ICPP more clearly, the following calculation is suggested.

For each long propylene sequence $[\text{---}(P)_m\text{---}$, $m \geq 3]$, there are 2 PPE triads, so the average length of long propylene sequence should be equal to $L_p = 2(\text{PPP})/(\text{PPE}) + 2$. The same way, the length of long ethylene sequence $[\text{---}(E)_m\text{---}$, $m \geq 3]$ should be equal to $L_E = 2(\text{EEE})/(\text{EEP}) + 2$. The results of these calculations are shown in Table VI.

The average length of long propylene sequence and that of long ethylene sequence increase gradually from fraction A to fraction C for both CPPJ and CPPB. The change of average length of long propylene sequence and that of long ethylene sequence also exhibit some continuity among fractions of CPPJ and CPPB, and the continuity of CPPJ sample is comparatively strong.

CONCLUSIONS

Impact copolymer polypropylene comprises multiple fractions that are different in composition and chain sequence structure, that is, EP rubber, EP segmented copolymer, EP block copolymer, and PP. Between different fractions, the composition and sequence structure change gradually, and we call that the continuity in the change of composition and chain sequence structure. Polydispersity and continuity are 2 aspects of the characteristics of the ICPP's chain structure.

Table VI   The Average Length of Ethylene and Propylene Segment (Containing at Least 3 Monomers)

ICPP	Original Sample		Component A		Component B		Component C	
	L_E	L_P	L_E	L_P	L_E	L_P	L_E	L_P
CPPB	4.5	19.5	3.8	3.7	6.9	9.5	30.6	60.6
CPPJ	3.8	13.3	3.7	4.9	4.2	8.3	17.4	17.2

The suggested method of separating *in-situ,* prepared ICPP into fractions is convenient and effective for the investigation of chain structure of impact copolymer PP.

Analyzing the chain structure of the fractions allows us to understand the chain structure of *in-situ,* prepared ICPP much more clearly and deeply than directly analyzing the chain structure of the ICPP as a whole.

The results obtained by the method mentioned in this work will make the understanding of aggregate structure of *in-situ,* prepared ICPPs clearer and more precise as well. That will be studied further in our next work.

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