Compositional Differences of Propylene–Ethylene Block Copolymers Manufactured by Degradation and Hydrogenation Techniques

Chuanzhi Zhang,[1] Fusheng Yu,[1,2] Li-Qun Wang,[1] Kehua Tu[1]

[1]*Institute of Polymer Science, Zhejiang University, Hangzhou, 310027, China*
[2]*Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, China*

Received 23 June 2005; accepted 15 November 2005
DOI 10.1002/app.23841
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The purpose of the present work is to investigate the compositional difference of polypropylene–polyethylene block copolymers (PP-*b*-PE) manufactured industrially by the process of degradation and hydrogenation, respectively. Each of the PP-*b*-PE copolymers was fractionated into three fractions with heptane and chloroform. The compositions of the three fractions were characterized by ^{13}C nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, as well as differential scanning calorimetry (DSC) and thermal fractionation. The results showed that the Chloroform-soluble fraction was amorphous ethylene-propylene rubber, and the content of the rubber in PP-*b*-PE manufactured by hydrogenation was less than that by degradation. The degree of crystallinity of the chloroform-insoluble fraction of the PP-*b*-PE manufactured by hydrogenation is higher than that of by degradation. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3301–3306, 2006

Key words: polypropylene–copolymers; degradation and hydrogenation; compositional characterization

INTRODUCTION

Polypropylene (PP) is a kind of polymer material with very poor impact property at low temperature. It is now well known that the improvement of the toughness of PP can be fulfilled in a two-step copolymerization technique, where propylene is polymerized first and then it is copolymerized with ethylene *in situ* to form polypropylene–polyethylene block copolymer.[1–3] Industrially, hydrogenation and degradation processes are the two widely adopted methods in producing the toughened PP product. Although large amounts of the product have been successfully used in commerce, little information concerning their compositional difference has been published. Accordingly, relatively comprehensive characteristic data are presented in this paper to get a perspective on the difference in molecular structures of the two originated products, and which will benefit the end-use of this commercially important product.

Chain structures of the propylene–ethylene block copolymers from diverse origins have been studied by several authors.[4–9] An abundance of information about the molecular structure of the propylene–ethylene block copolymers was revealed by using temperature rising elution fractionation (TREF) method in combination with Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy.[7–10] However, it is recognized that TREF separation becomes less effective when the crystallinity of polymers is decreased. Recently, a clean and clear-cut thermal fractionation technique has been successfully used to investigate the microstructures of ethylene copolymers[10,11] and their blends.[12–14]

The present study focuses on the compositional differences of the two commercial block PP samples manufactured respectively, by hydrogenation and degradation techniques. The samples were fractionated into three fractions by heptane and chloroform. The compositional differences of the fractions were characterized in detail by ^{13}C NMR, FTIR, and differential scanning calorimetry (DSC). The chloroform-insoluble fraction was studied by the technique of thermal fractionation.

EXPERIMENTAL

Materials

Two commercial block PP samples manufactured by hydrogenation (A) and degradation (B), respectively, were employed in this work. Each sample was first fractionated with heptane into two fractions, which are assigned as HS for heptane-soluble part and HI for the insoluble part. The heptane-soluble fraction was

Correspondence to: L. Q. Wang (lqwang@zju.edu.cn).

© 2006 Wiley Periodicals, Inc.

TABLE I
The Content of the Heptane and Chloroform Extract Fractionations of the IPP Copolymers

IPP copolymer	HI- (wt %)	CS- (wt %)	CI- (wt %)
A (Hyd)	79.02	7.66	12.28
B (Deg)	82.28	10.05	6.37

Total recovery: 96–99%.

then fractionated into two parts with chloroform and assigned as CS for chloroform-soluble fraction and CI for the insoluble fraction.

Fractionation of the block PP copolymers

About 2.5 g of the block PP sample stabilized with the antioxidant was dissolved in 250 mL of xylene at 403 K. The solution was cooled to room temperature and precipitated into methanol. After being filtrated, the residual solvent was removed at 313–323 K. The precipitate was then extracted by boiling heptane for 8 h. Both soluble (HS) and insoluble (HI) parts were dried at 313–323 K. The heptane-soluble fraction was further separated with chloroform at room temperature. A typical process is that about 40 mL chloroform was poured into the beaker containing HS fraction. After being stirred vigorously for 4 h, the precipitate (CI) was separated from the solution (CS). The precipitate was then mixed with another 40 mL fresh chloroform, stirred, and filtrated. The procedure was repeated till the CS and CI fractions were completely separated. The fractions were then dried in vacuum at 303 K. The contents of the fractionations are summarized in Table I.

Measurements

Fourier transform infrared (FTIR) spectra were obtained with Bio-Rad FTS-135 spectrometer with a resolution of 4 cm^{-1} and 64 scanning times. All of the samples were measured at room temperature, except that the chloroform-insoluble fractions were measured at elevated temperature especially. The temperature ranged from 293 to 423 K.

^{13}C NMR spectra were measured on a 400 MHz Bruker AV 400 spectrometer at 403 K. The pulse angle was 90°, and the pulse repetition time was 6 s. Deuterated *o*-dichlorobenzene was used as a solvent and hexamethyl-siloxane as the internal reference (20.3 downfield from the resonance of tetra-methyl-silane). The ^{13}C NMR results calculated following Cheng[15] and Sun's methods[6] are compiled in Table II.

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin–Elmer Pyris 1 instrument. The specimens were weighted in about 10 mg. The temperature reading and calorific measurement were calibrated by using standard indium. The scanning temperature ranged from 198 to 453 K for CS fraction and from 323 to 453 K for the other fractions with a scanning rate of 283 K/min. All the specimens were first heated to 453 K at a rate of 283 K/min and were held at this temperature for 5 min, then quenched to the lower temperature limit to eliminate the previous thermal history. For the thermal fractionation, all the specimens were first melted at 453 K for 5 min and then cooled to 298 K at a rate of 293 K/min. After this, the specimens were reheated at the same rate to 403 K, held for 5 min and then cooled to 298 K at a rate of 293 K/min. The specimens were then heated at the rate of 293 K/min to 398 K for 5 min and then cooled to 298 K at a rate of 293 K/min. The process was repeated at every 278 K lower in the upper limited temperature than that in the previous procedure until 333 K was reached.

RESULTS AND DISCUSSION

Heptane-insoluble fractions of the two originated PP block copolymers

Each of the two originated PP samples was first fractionated into two parts by boiling heptane. The hep-

TABLE II
Sequences Distribution of the Fractions

Fractions sequences	HI-		CS-		CI-	
	A	B	A	B	A	B
P	0.959	0.969	0.572	0.646	0.712	0.605
E	0.041	0.031	0.428	0.354	0.288	0.395
PP	0.953	0.964	0.336	0.427	0.617	0.454
EP	0.013	0.011	0.473	0.452	0.189	0.302
EE	0.034	0.025	0.190	0.124	0.186	0.243
PPP	0.945	0.959	0.223	0.300	0.680	0.573
PPE	0.01	0.008	0.250	0.262	0.032	0.032
EPE	0.005	0.002	0.099	0.084	0	0
EEE	0.030	0.022	0.071	0.044	0.105	0.133
EEP	0.006	0.006	0.231	0.172	0.130	0.216
PEP	0.004	0.003	0.121	0.139	0.030	0.043

tane-soluble fraction was further fractionated into another two parts, and the results will be discussed in the following section. The concentrations of comonomer, dyad, and triad of heptane-insoluble fraction are listed in Table II. It can be seen that [P] is 0.959, which is apparently higher than [E] that is 0.041, suggesting that the heptane-insoluble fraction is mainly PP. The data also demonstrate clearly that heptane-insoluble fractions from the two originations contain almost only propylene structure. No significant difference can be found in the compositional structure of HI-A and HI-B, though the weight percentage of extract of HI-B is a little more than that of HI-A.

Chloroform-soluble fractions of the two originated PP block copolymers

Since the heptane-insoluble fraction contains mainly PP, the PP–PE copolymers are accordingly contained in the heptane-soluble fraction. The heptane-soluble fraction was further fractionated with chloroform into two fractions, which are assigned as CS for chloroform-soluble part and CI for chloroform-insoluble part. Chloroform is used to separate PP-PE rubber phase from PP–PE block copolymers based on the assumption that chloroform is a good solvent for PP–PE rubber. The content of the chloroform-extracted fractions is summarized in Table I. A distinct difference between the extracted weight percentages of CS fractions from the two originated block PP samples can be found. The chloroform-soluble extract (CS-B) from the sample by degradation technique is 10.05 wt%, which is much higher than that of CS-A (6.37 wt%) from the sample by hydrogenation technique.

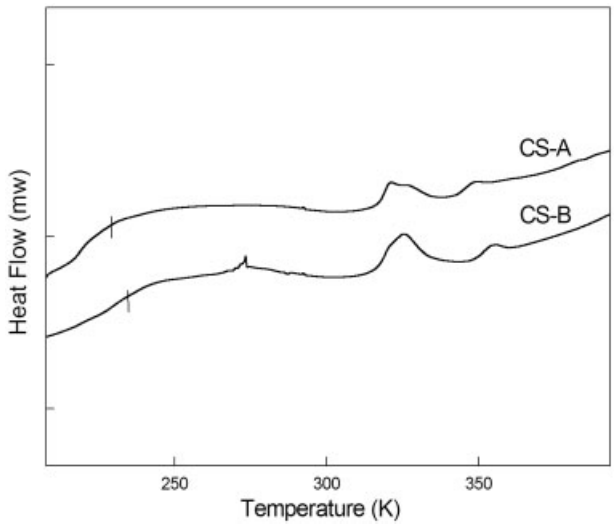

Figure 1 DSC curves of the chloroform-soluble fraction with the first scanning. (The lines in figure are the about location of $T_{g.}$)

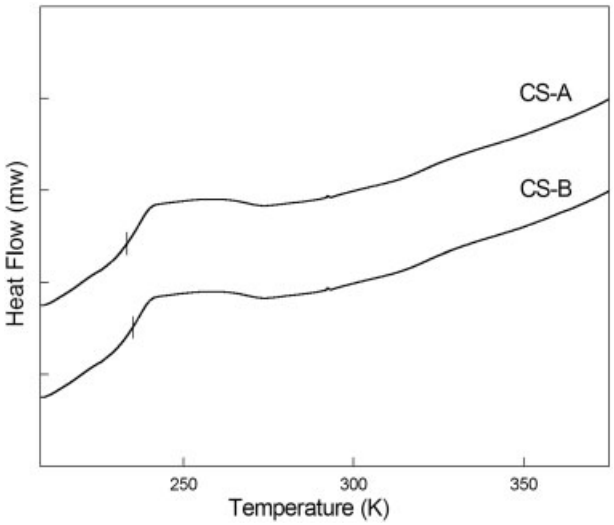

Figure 2 DSC curves of the chloroform-soluble fraction with the second scanning. (The lines in figure are the about location of $T_{g.}$)

The concentrations of comonomer, dyad, and triad of the CS fractions of the two originated samples were characterized by ^{13}C NMR. The result listed in Table II demonstrates that [EP] are 0.473 for CS-A and 0.452 for CS-B. The values are quite the same. In contrast, [EEE] are 0.071 and 0.044 for CS-A and CS-B, respectively, which demonstrates that the CS fractions for both of the originated samples are mainly in the nature of EP rubber. No significant difference is exhibited in the molecular structure of the CS fractions for the two originated block PPs.

DSC experiments were carried out for both of the CS samples. Two glass transitions at about 233 K are exhibited in the DSC curves of the two CS fractions (Figs. 1 and 2). According to the authors,[16–19] it should be the glass transition temperature of EP rubber. Although weak melting peaks were shown in both of the CS samples at the first scan, they vanish in the second scanning, indicating that the CS fraction is mainly in the nature of EP rubber with very defective crystallizability.

FTIR spectra of the CS fractions of the two originated PPs were measured and shown in Figure 3. It is known that the bands at 720 and 729 cm^{-1} are the characteristics of ethylene structure corresponding to different lengths of the ethylene sequence. Specific absorption bands related to the critical length of at least 5 PP units are observed at 975 cm^{-1}, 11–12 PP units at 998 cm^{-1} and 13–15 PP units at 841 cm^{-1}.[20]

The contents of ethylene in the fractions can be estimated by an empirical equation based on the FTIR spectra:

$$\text{The content of ethylene} = \frac{A_{720}}{A_{720} + A_{973} + A_{998} + A_{841}}$$

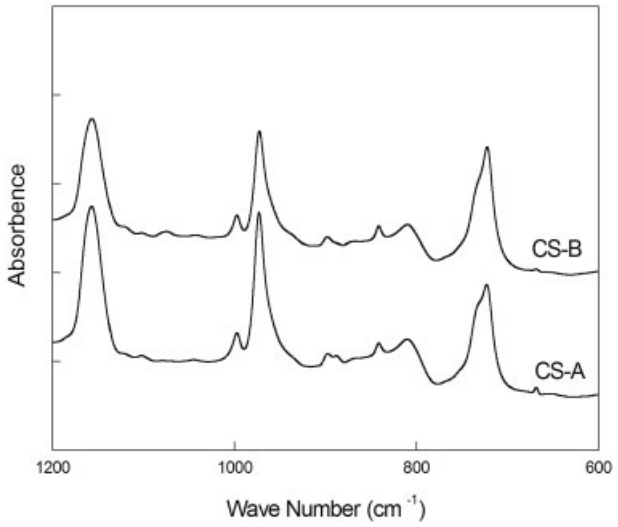

Figure 3 FTIR spectra of the fractions of CS.

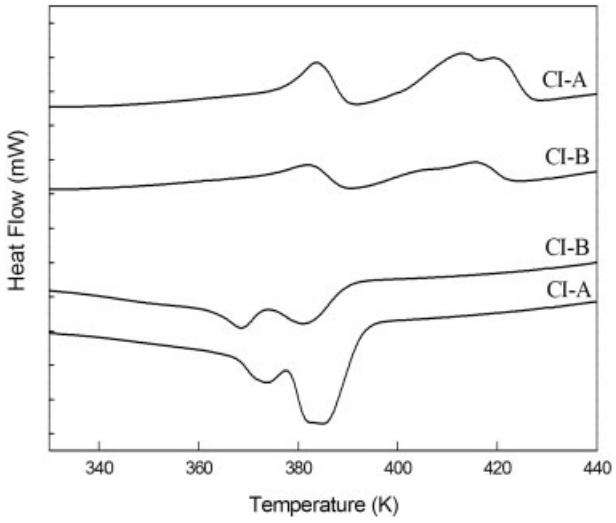

Figure 4 The heat melting curves and the cooling crystal curves of the chloroform-insoluble fraction.

where A_{720}, A_{841}, A_{973}, and A_{998} are the absorbance at 720, 841, 973, and 998 cm^{-1}, respectively.

It was proposed that the absorption at 998 cm^{-1} is originated from the methyl rocking mode in isotactic PP and 972 cm^{-1} from the amorphous PP.[16] Accordingly, the degree of crystallinity of PP can be calculated on FTIR spectrum by A_{998}/A_{973}. The data are summarized in Table III. The band at 998 cm^{-1} corresponding to the fraction CS is very weak, implying the low crystallinity of PP. Therefore, fraction CS is mainly amorphous rubber.

Chloroform-insoluble fractions of the two originated samples

Since chloroform is a good solvent for the statistical EP rubber, it is believed that the CI fraction should be in block nature. The NMR data listed in Table II show that the concentration of the triad [PEP] and [EPE] of the CI fractions of the two block PP samples are remarkably lower than that of the CS fractions, indicating that the CI fraction is indeed mainly PP–PE block copolymer. It is also found that the contents of EP are 0.189 for CI-A and 0.302 for CI-B, revealing that EP joints appear more frequently in the chain of the sample by degradation technique. In addition, PPP in CI-A is 0.680, which is much higher than that in CI-B where the value is 0.233. Therefore, it is believed that the hydrogenation method would result in longer PP chains, when compared with the degradation technique. It is supposed that the long PP chains are degraded into short ones in the presence of peroxid in the degradation process.

TABLE III
The Content of Ethylene and Crystallinity Calculated on FTIR Spectra

	CS-A	CS-B	CI-A	CI-B
Content of ethylene (mol %)	59.53	51.15	51.28	66.80
Crystallinity of propylene (mol %)	7.85	7.35	70.78	55.56

It is seen in Figure 4 that two peaks exhibit in both the heating and cooling curves of the two CI fractions, which should correspond respectively, to the molecular motion of PE segment at the lower position and PP segment at the higher site. To get a perspective of the relationship between the difference of the molecular structure and the thermal properties of the samples, the method of thermal fractionation was employed.

Thermal fractionation is a temperature-dependent segregation process based on recrystallization and reorganization of ethylene and propylene sequences from the melt. It is similar to temperature rising elution fractionation (TREF), but the segregation mode is different. In the stepwise annealing process, the segments of a copolymer, having been first melted, are allowed to recrystallize at a series of controlled temperatures. In a typical thermal fractionation thermogram, the number of peaks in the melting curves correspond to the number of controlled crystallization steps.[21] Each endotherm represents a population of crystals with almost the same thermodynamic stability and the melting temperature.[22] It is generally recognized that the difference among the endotherm is mainly caused by the distribution of crystal size and lamellar thickness.

The melting curves obtained after thermal fractionation for two CI fractions are shown in Figure 5. All curves show a large peak preceded by a series of small lower temperature peaks in the range of 333 to 393 K. The right-hand large peak (T_m = 413 K) refers to PP

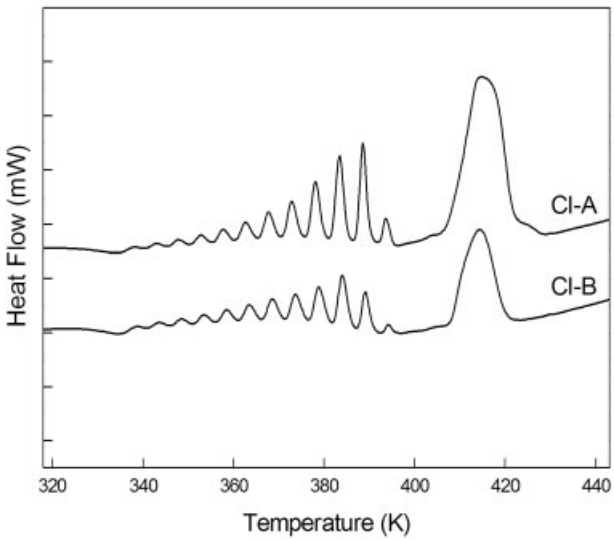

Figure 5 The melting curves obtained after fractionation of chloroform-insoluble.

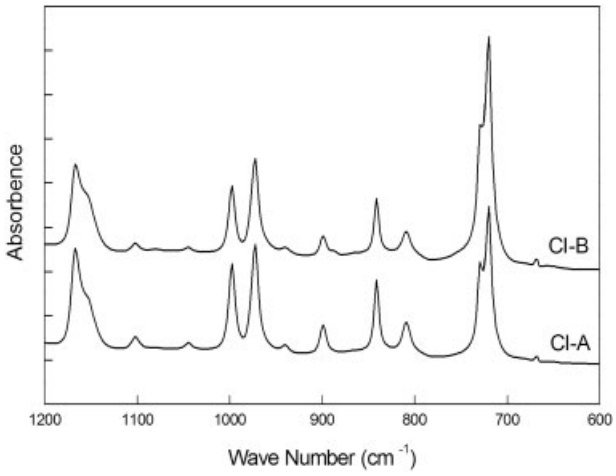

Figure 6 FTIR spectra of the fractions of CI.

with a minor amount of ethylene monomer and a series of lower temperature peaks refer to PE with a minor amount of propylene monomer. The long E sequences of these blocks increase with increasing fraction temperature. The multiple broad peaks of the melting endotherm curves demonstrate that the comonomer distribution is heterogeneous.

It is seen in Table IV and Figure 5 that the content of various sequences of the crystallized PE of CI-A is lower than that of CI-B, and the PP content of CI-A (71.44%) is higher than that of CI-B (59.13%). The order is consistent with the results of ^{13}C NMR and FTIR.

The FTIR spectra of Figure 6 for CI fractions show that the peaks at 720 and 729 cm^{-1} become evident and sharp, suggesting the existence of the long ethylene structure and the crystalline PE. The DSC and the thermal fractionation measurements also show apparently the crystallization of PP and PE segments. Therefore, CI fractions are mainly the ethylene and propylene block copolymer.

Table III lists the content and the crystallinity of PP of the CS fractions. It is seen that the content of ethylene in CS-B is 51.15%, which is lower than that in CS-A, where the value is 59.53%. Accordingly, the content of ethylene in CI-B is higher than that in CI-B (66.8% for CI-B and 51.28% for CI-A, respectively). The data suggest that the crystal of PP in CI-A is much perfect than that in CI-B.

The FTIR spectra of the CI fractions were also recorded at different temperature (Figs. 7a and 7b). The results demonstrate that the crystalline peaks at 729, 841, and 998 cm^{-1} vanished gradually with the elevation of temperature, indicating the existence of the crystals with different sizes and the lamellas with various thicknesses in the polymer.

TABLE IV
Melting Enthalpy and Content of Each Endotherm of Two CI Fractions after Stepwise Isothermal Crystallization

		Melting enthalpy (J/g)		Contents (%)	
Peak	T_m (K)	CI-A	CI-B	CI-A	CI-B
1	338	0.159	0.193	0.34	0.83
2	343	0.175	0.196	0.37	0.84
3	348	0.257	0.261	0.55	1.12
4	353	0.369	0.384	0.79	1.64
5	358	0.529	0.528	1.13	2.26
6	363	0.765	0.689	1.63	2.96
7	368	1.147	0.919	2.44	3.94
8	373	1.610	1.347	3.43	4.86
9	378	2.452	1.564	5.22	6.71
10	383	3.487	2.121	7.42	9.09
11	388	3.548	1.362	7.55	5.84
12	393	0.833	0.219	1.77	0.94
13	413	31.645	13.756	67.36	58.97

CONCLUSIONS

It was shown that the propylene–ethylene block copolymers manufactured by degradation and hydrogenation techniques in the industry are in fact the blend of polypropylene homopolymer with negligible ethylene homopolymer, the great mass of PP (crystalline) with a minor amount of ethylene, various sequence length of crystalline PE with a minor amount of propylene, and amorphous ethylene–propylene rubber.

The results also show that in the propylene–ethylene block copolymer manufactured by hydrogenation, the content of ethylene–propylene rubber, which is CS, and the content of various sequence of crystalline PE, which is CI, are lower than that by degradation.

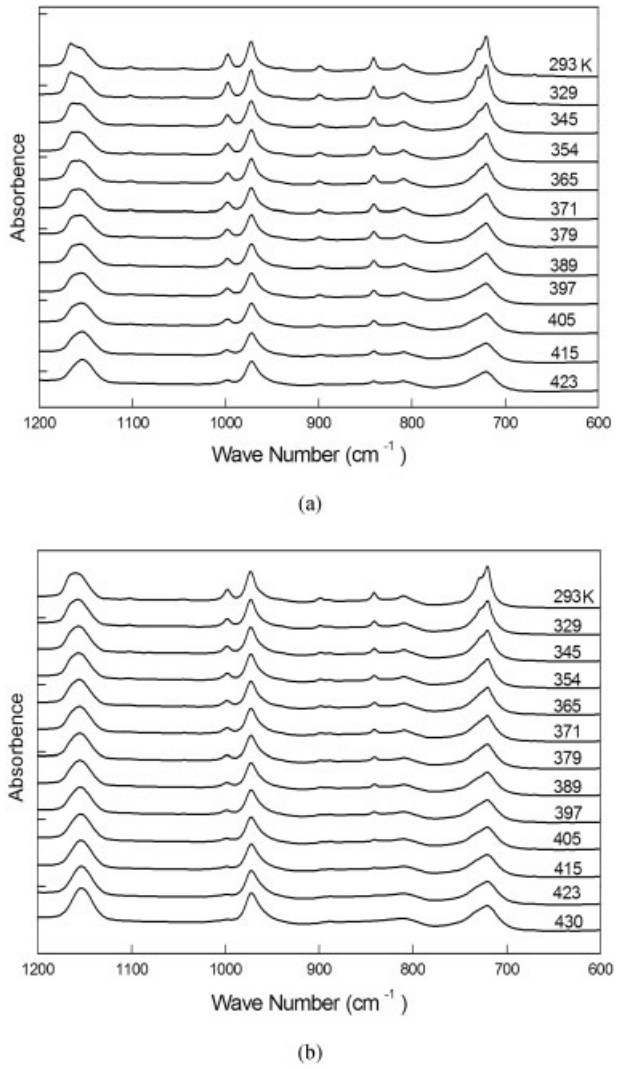

Figure 7 FTIR spectra of chloroform-insoluble fractions at various temperatures (a) CI-A; (b) CI-B.

The crystallinity of PP of CI fraction from the sample manufactured by hydrogenation is higher than that by degradation.

DSC thermal fractionation shows an effective method for elucidating the components of unidentified blends, especially when it is used in combination with other analytical techniques, such as IR and NMR spectroscopies.

References

1. Fernando, P. L.; Williams, J. G. Polym Eng Sci 1981, 21, 1003.
2. Bramuzzo, M. Polym Eng Sci 1989, 29, 1077.
3. Ma, D. Z.; Li, X. Q.; Luo, X. L. Chin J Polym Sci 1994, 12, 164.
4. Cheng, H. N.; Lee, G. H. Macromolecules 1987, 20, 436.
5. Hayashi, T.; Lnoue, Y.; Chûjô, R. Polymer 1988, 29, 1848.
6. Sun, Z.; Yu, F.; Qi, Y. Polymer 1991, 32, 1059.
7. Cai, H. J.; Luo, X. L.; Ma, D. Z. J Appl Polym Sci 1999, 71, 93.
8. Feng, Y.; Hay, J. N. Polymer 1998, 39, 6723.
9. Mirabella, F. M., Jr. Polymer 1993, 34, 1729.
10. Shanks, R. A.; Amarasinghe, G. J Therm Anal Calorimetry 2000, 59, 471.
11. Cser, F.; Hopewell, J. L.; Shanks, R. A. J Therm Anal 1998, 54, 707.
12. Shanks, R. A.; Amarasinghe, G. Polymer 2000, 41, 4579.
13. Drummond, K. M.; Hopewell, J. L.; Shanks, R. A. J Appl Polym Sci 2000, 78, 1009.
14. Keating, M.; Lee, I. H.; Wong, C. S. Thermochim Acta 1996, 284, 47.
15. Cheng, N. H. Macromolecules 1984, 17, 1950.
16. Wang, L. X.; Huang, B. J Polym Sci Part B: Polym Phys 1990, 28, 937.
17. Paukkeri, R.; Lehtinen, A. Polymer 1994, 35, 1673.
18. Maurer, J. J. Rubber Chem Technol 1965, 38, 979.
19. Ronarc'h, D.; Audren, P.; Moura, J. L. J Appl Phys 1985, 58, 466.
20. Monasse, B.; Haudin, J. M. Polypropylene: Structure, Blends and Composites. In: Karger-Kocsis, J., Ed.; Chapman and Hall: London, 1995; p 20.
21. Chen, F.; Shanks, R. A.; Amarasinghe, G. Polymer 2001, 42, 4579.
22. Starck, P.; Rajanen, K.; Löfgren, B. Thermochim Acta 2003, 395, 169.