Influence of Copolymerization Conditions on the Structure and Properties of Polyethylene/Polypropylene/Poly(ethylene-*co*-propylene) In-Reactor Alloys Synthesized in Gas-Phase with Spherical Ziegler-Natta Catalyst

Zhiqiang Fan, Jian Deng, Yan-Mei Zuo, Zhi-Sheng Fu

Department of Polymer Science and Engineering, The Institute of Polymer Science, Zhejiang University, Hangzhou 310027, People's Republic of China

ABSTRACT: A spherical $TiCl_4/MgCl_2$-based catalyst was used in the synthesis of polyethylene/polypropylene/poly (ethylene-*co*-propylene) in-reactor alloys by sequential homopolymerization of ethylene, homopolymerization of propylene, and copolymerization of ethylene and propylene in gas-phase. Different conditions in the third stage, such as the pressure of ethylene–propylene mixture and the feed ratio of ethylene, were investigated, and their influences on the compositions, structural distribution and properties of the in-reactor alloys were studied. Increasing the feed ratio of ethylene is favorable for forming random ethylene–propylene copolymer and segmented ethylene–propylene copolymer, however, slightly influences the formation of ethylene-*b*-propylene block copolymer and homopolyethylene. Raising the pressure of ethylene–propylene mixture results in the increment of segmented ethylene–propylene copolymer, ethylene-*b*-propylene block copolymer, and PE fractions, but exerts a slight influence on both the random copolymer and PP fractions. The impact strength of PE/PP/EPR in-reactor alloys can be markedly improved by increasing the feed ratio of ethylene in the ethylene–propylene mixture or increasing the pressure of ethylene–propylene mixture. However, the flexural modulus decreases as the feed ratio of ethylene in the ethylene–propylene mixture or the pressure of ethylene–propylene mixture increases. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2481–2487, 2006

Key words: copolymerization; polyolefins; structure; mechanical properties; alloys

INTRODUCTION

Modification of polypropylene (PP) aiming at the improvement of impact strength is a topic of great significance in science and industry.[1–6] Among the ways to toughen PP, in-reactor blending of PP with other polyolefin (e.g., ethylene–propylene random copolymer) by sequential multistage polymerization has been proved superior both in respect of polymer properties and production cost.[7–11] Recently, the synthesis and chain-structure of polyethylene/polypropylene (PE/PP) in-reactor alloy using a super active spherical Ziegler-Natta catalyst have been reported.[12] It was found that the PE/PP in-reactor alloys show much improved impact strength while the flexural modulus was only slightly lowered as compared to PP homo-polymer. Such good balance between toughness and rigidity is very important for applications as high performance structural materials. However, the impact strength of the PE/PP two-component in-reactor alloy is still not high enough for the applications that require high toughness. Introducing certain amount of ethylene–propylene random copolymer (EPR) in the PE/PP alloy may further improve the toughness of the materials. However, preparation of polyethylene/polypropylene/poly (ethylene-*co*-propylene) (PE/PP/EPR) in-reactor alloy using spherical Ziegler-Natta catalyst has not been reported in literatures.

The structure of alloy influences the alloy's mechanical properties strongly. But the composition and chain structure of the alloy is controlled by the polymerization conditions. In a multistage process for synthesizing in-reactor PE/PP/EPR alloys, a direct way to regulate the amount and chain structure of the rubber phase is to change the conditions of copolymerization of ethylene and propylene.

In this study, a spherical, high-yield $TiCl_4/MgCl_2$-based catalyst was used in synthesis of in-reactor PE/PP/EPR alloys by a three-stage gas phase polymerization process. Different conditions in the ethyl-

TABLE I
Size Distribution of PE/PP Alloys Prepared at Different Pressure (wt %)

Sample	Pressure (MPa)	$\overline{D}$(wt %)	≥2 mm	2–1.45 mm	45–1 mm	1–0.45 mm	≤0.45 mm
PEP60	0.6	93.37	2.57	38.15	28.58	26.60	4.09

The first stage: Al/Ti = 60, Al/Si = 25; ethylene pressure = 0.6 MPa; reaction temperature = 60°C; polymerization time = 60 min. The second stage: propylene pressure = 0.8 MPa; polymerization time = 120 min.

ene–propylene copolymerization stage, such as the pressure of ethylene–propylene mixture and the feed ratio of ethylene in ethylene–propylene mixture, were investigated, and their influences on the structure and composition of the in-reactor alloys are reported.

EXPERIMENTAL

Polymerization

Prepolymerized catalyst was made by homo-polymerization of propylene in a well-stirred glass bottle containing 40 mL petroleum ether (bp: 60–90°C) at 50°C and normal pressure for 30 min. A high-yield, spherical $TiCl_4$/$MgCl_2$·ID (ID: internal donor) catalyst (DQ00-189, kindly donated by the Beijing Research Institute of Chemical Industry) was used in the polymerization, with $Al(C_2H_5)_3$-$Ph_2Si(OCH_3)_2$ as a cocatalyst.

In the first stage, polyethylene was prepared after prepolymerized catalyst being transferred to a 0.5-L jacketed Büchiglasuster reactor with a helical stirrer. The reaction rate is calculated from the feed rate required to keep the pressure constant and measured by a mass flow controller. A special helical stirrer has been used to enforce good mixing inside the reactor. Moreover, 50 mL petroleum ether (bp: 60–90°C) has been used for every experiment to prevent prepolymerized catalyst particles from sticking to each other and to the reactor wall. We still call the polymerization as gas-phase processing, because the amount of solvent added was so small that after 20-min polymerization it was absorbed thoroughly by the polymer produced in the reactor. Then most part of the reaction was carried out in gas-phase. In this stage, spherical PE granules with

the diameter of 0.45–2 mm were produced and residual ethylene in the particles was completely removed before the addition of propylene. In the second stage, propylene at constant pressure of 0.7 MPa was continuously supplied to the gas-phase reactor and polymerized for 2 h. In the copolymerization stage, the residual propylene in the particles was completely removed, and then an ethylene–propylene mixture of constant composition was continuously supplied to the autoclave at a constant pressure and copolymerized for 1 h. The copolymerization rate was determined by measurement of the flow rate of monomer gas at a constant pressure. In this work, the pressure of ethylene feed gas was regulate in the range of 0.3–0.7 MPa, and the composition of the monomer feed was changed in the range of 20–50 mol % ethylene. The final product after three stages of reaction was still free-flowing, spherical granules. This means that most of the copolymer was formed inside the granules.

Fraction of the alloy

A modified Kumagawa extractor was used to carry out a temperature-gradient extraction fractionation of the polymer.[13] n-Octane was used as solvent to successively extract the sample at different controlled temperatures (room temperature, 90, 110, and 120°C). Five fractions were collected by extracting 2 g of every sample at 25, 90, 110, 120, and >120°C, and they were named fraction A, fraction B, fraction C, fraction D, and fraction E, respectively. Purified fractions were obtained after concentrating the extract solutions, precipitating the polymer, washing, and drying the fractions in vacuum.

TABLE II
Size Distribution of Different PE/PP/ERP Alloys Prepared at Different Pressure of Ethylene–Propylene Mixture

Sample	Pressure (MPa)	$\overline{D}$	≥2 mm	2–1.45 mm	1.45–1 mm	1–0.45 mm	≤0.45 mm
020129	0.7	88.27	4.95	16.84	26.76	44.66	6.78
020119	0.6	88.48	3.12	26.30	26.34	35.85	8.40
020121	0.5	88.66	0.38	10.34	26.92	51.40	10.96
020131	0.4	85.35	0.30	9.35	16.50	59.49	14.35

The first stage: Al/Ti = 60, Al/Si = 25; ethylene pressure = 0.6 MPa; reaction temperature = 60°C; polymerization time = 60 min. The second stage: propylene pressure = 0.8 MPa; polymerization time = 120 min. The third stage: ethylene:propylene = 1:1; polymerization time = 60 min.

TABLE III
Size Distribution of Different PE/PP/ERP Alloys Prepared at Different
Feed Ratio of Ethylene

Sample	mol %	$\overline{D}$	≥2 mm	2–1.45 mm	1.45–1 mm	1–0.45 mm	≤0.45 mm
020125	20	87.12	0.58	10.09	19.23	57.80	12.30
020126	30	85.33	0.89	14.22	23.20	47.91	13.78
020128	40	89.27	2.63	16.45	25.80	47.02	8.10
020129	50	88.27	4.95	16.84	26.76	44.66	6.78

The first stage: Al/Ti = 60, Al/Si = 25; ethylene pressure = 0.6 MPa; reaction temperature = 60°C; polymerization time = 60 min. The second stage: propylene pressure = 0.8 MPa; polymerization time = 120 min. The third stage: pressure of ethylene–propylene mixture = 0.7 MPa; polymerization time = 60 min.

As proved in our previous work,[14] the fraction extracted at room temperature (20°C) is random co-polymer (EPR), the fraction extracted at 90°C is segmented ethylene–propylene copolymer, the fraction extracted at 110°C mainly contains PE, the fraction extracted at 120°C is ethylene-b-propylene copolymer, and the fraction insoluble at 120°C is mainly PP.

Measurement of the particle porosity

The measurement of the particle porosity was carried out in a density bottle whose weight was W_0. The volume of the density bottle (V) was calibrated by n-butanol. The density bottle was filled with polymer particle weighted W_1, and then filled with n-butanol. After that, the density bottle was put into a thermostatic bath for 4 h, then dried and weighted (W_t). The following equation was used to calculate the bulk density of polymer particles (ρ_b):

$$V = \frac{W_{polymer}}{\rho_b} + \frac{W_t - W_1}{\rho_{n\text{-butanol}}}$$

where $W_{polymer}$ refers to the weight of polymer particles, $\rho_{n\text{-butanol}}$ refers to the density of n-butanol.

The apparent density of polymer particles ρ_{abb} can be measured by substituting mercury for n-butanol. The porosity of polymer particles (P) can be calculated by the equation below:

$$P = 1 - \frac{\rho_{app}}{\rho_b}$$

Measurement of the ethylene content

Fourier transform infrared (FTIR) spectra of the alloy samples and the fractions were recorded on a Bruker Vector 22 FTIR spectrometer. A thin film of the samples was prepared through hot pressing. An empirical equation was used for the estimation of the ethylene content based on the infrared spectrum[9]:

$$\ln A_{1150}/A_{720} = 2.98 - 0.060 \times C_2$$

(C_2—mol % of ethylene in the polymer).

The equation was calibrated by ethylene content data measured by ^{13}C-NMR.

^{13}C-NMR spectra of the fractions were measured on a Bruker AMX400 NMR spectrometer at 100 MHz. o-Dichlorobenzene-d4 was used as a solvent to prepare the polymer solution of 20 wt %. The spectra were recorded at 120°C, with hexamethyldisiloxane as internal reference. Broadband decoupling and a pulse delay of 5 s were employed. Typically 3000 transients were collected.

Measurement of the mechanical and physical properties

Notched Izod impact strength of the alloy samples was measured on a Ceast impact strength tester, according to ASTMD 256. The flexural modulus and flexural strength were measured following ASTMD 709 on a REGER-2000 electronic tester. The sample strips were prepared by injection molding using a mini-injector.

The intrinsic viscosity of polymer fractions was measured using an Ubbelohde viscometer at 135°C with decahydronaphthalene as solvent.

RESULTS AND DISCUSSION

Influences of the copolymerization conditions on the alloy compositions

After two stages of polymerization (ethylene homo-polymerization and propylene homopolymerization), spherical PE/PP in-reactor alloy particles were produced. About 90 wt % of PE/PP particles fell within a diameter range of 0.45–2.0 mm. The PE/PP particles had a porosity of about 50 vol %, as measured

TABLE IV
Porosity of PE/PP/EPR Alloys Prepared Under
Different Conditions

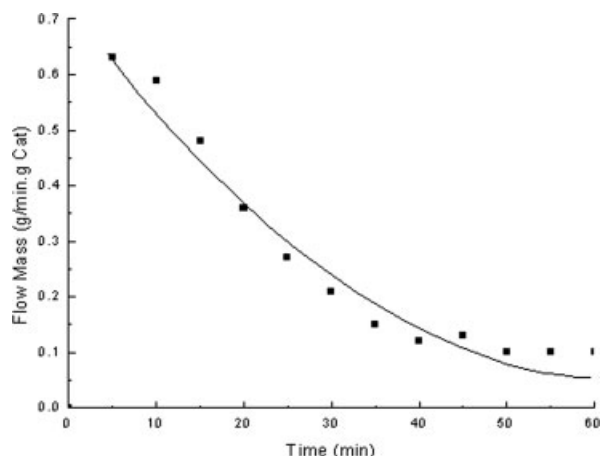| Conditions	Monomer pressure (MPa)			Feed ratio of ethylene (mol %)		
	0.7	0.6	0.4	50	40	20
Porosity (%)	23.1	23.1	32.0	32.0	24.5	23.1

Figure 1 Rate profile of copolymerization at 60°C and 0.7 MPa of monomer pressure. Ethylene/propylene (mol/mol) = 1.

by volumetric testing. That is very suitable for farther blending with other polymers and modifying by polar monomers, which makes it possible for fabricating more and more new materials. The catalyst efficiency of the whole polymerization (three stages) was about $1.13–1.49 \times 10^5$ g polymer/g Ti·h. We measured the size distribution of PE/PP and PE/PP/EPR alloys by sieving particles. Tables I–III show the size distribution of PE/PP alloy, PE/PP/EPR alloy (prepared at different pressure of ethylene–propylene mixture), and PE/PP/EPR alloy (prepared at different feed ratio of ethylene in ethylene-propylene mixture), respectively, where $\overline{D}$ presents weight percent of particles with diameter in the range of 0.45–2.0 mm. Table IV shows the porosity of PE/PP/EPR alloys prepared under different conditions. As shown in Tables I–III, the value of $\overline{D}$ of PE/PP/EPR alloy is slightly smaller than that of PE/PP alloy. And the content of powder (granule diameter ≤0.45 mm) in the PE/PP/EPR alloy is more than that in PE/PP alloy. It is probably due to the longer time (120 min) of agitation of the stirrer. Table IV shows that the porosity of PE/PP/EPR alloy is much lower than that of PE/PP alloy. Hence, we can conclude that the ethylene–propylene copolymer produced in the copolymerization stage mainly existed in tiny holes inside the PE/PP particles, so the final product still had a spherical shape.

The kinetics of the copolymerization was determined by monitoring the flow rate of the monomer fed into the reactor. A typical rate profile of the copolymerization is shown in Figure 1. There was a rapid decay of the polymerization rate during the reaction. It seems that such rate decay is not the result of the activity decay of active centers, as the catalyst should have reached its stationary stage after about 2 h of propylene homopolymerization. Therefore, it is more likely that the rate decay was caused by diffusion limitation in the polymer par-

ticles. As the copolymerization proceeded, the tiny holes in the PE/PP particles were gradually filled with the copolymer, and the monomers had to diffuse through the solid polymer layer before reaching the active sites. This possibly resulted in diffusion-controlled kinetics of the polymerization.[15] If there was diffusion limitation in the reaction, it influenced the relations between the reaction conditions and the copolymerization behaviors.

Figure 2 shows the effects of the monomer pressure in the copolymerization stage on the content of EPR (represented by the weight percentage of the *n*-octane-soluble part at 25°C) and ethylene in the alloys. Changing the monomer pressure from 0.3 to 0.7 MPa exerted only a limited influence on the EPR content and ethylene content. The ethylene content raised from 51.8 to 57.6 wt % as the monomer pressure rose from 0.3 to 0.7 MPa. On the other hand, the EPR content of different alloys prepared at different monomer pressure is quite similar to each other. In our experiments, the amount of EPR was just in the narrow range of 5.67–7.02 wt %. Therefore, changing the monomer pressure, namely, the monomer concentration is not an effective way of controlling the copolymer content in the alloy. It may be said that changing the monomer pressure had hardly effect on the alloy's composition.

However, changing the feed ratio of ethylene–propylene mixture had a much stronger effect on the copolymerization rate (as shown in Fig. 3). The ethylene content of different alloys prepared at different feed ratio increases almost linearly with the increase of feed ratio of ethylene. However, there is a maximum of EPR content in the profile when the feed ratio of ethylene is 40 mol %, which may result from three competitive reactions during the ethylene–propylene copolymerization process: copolymerization of ethylene and propylene, homopolymerization of ethylene, and homopolymerization of propylene. At low
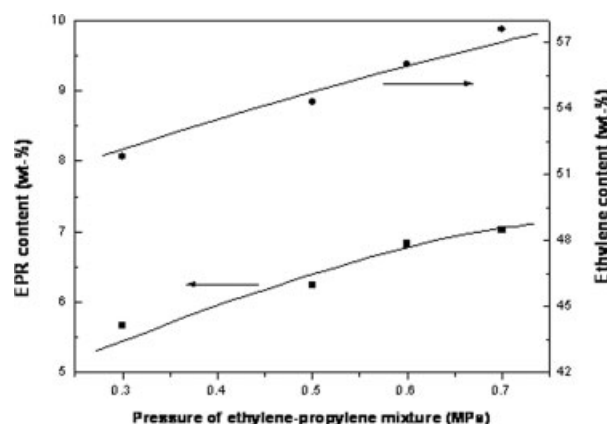

Figure 2 Effect of the monomer pressure on the composition of in-reactor alloys: temperature = 60°C, time = 1 h; propylene/ethylene (mol/mol) = 1.
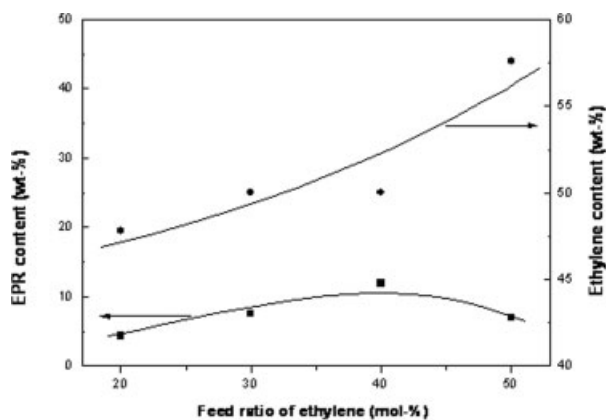
Figure 3 Effect of the feed ratio of ethylene in ethylene–propylene mixture on the composition of in-reactor alloys: reaction temperature = 60°C; monomer pressure = 0.7 MPa; time = 1 h.

levels of ethylene feed ratio (≤ 40 mol %), the copolymerization of ethylene and propylene is the main reaction, and more ethylene leads to higher content of ethylene–propylene random copolymer and segmented ethylene-propylene copolymer, as is represented by EPR and Fraction B, respectively, and listed in Table V. But at high levels of ethylene feed ratio, homopolymerization of ethylene becomes the dominant reaction, because the polymerization activity of ethylene is much higher than that of propylene in such Ti-based catalyst systems. Therefore, the content of polyethylene in the PE/PP/EPR alloy with 50 mol % ethylene in the ethylene–propylene mixture is the highest. But the content of ethylene–propylene random copolymer and polypropylene is relatively lower, as is represented by EPR and Fraction E and listed in Table V. From the results above, it can be concluded that changing the feed ratio of ethylene–propylene mixture is the most effective way of controlling the copolymer content in the alloy.

Influences of the copolymerization conditions on the alloy structural distribution

We found[9] that the segmented ethylene–propylene copolymer portion alone is able to increase the impact strength at room temperature greatly, while the low temperature impact strength can be markedly enhanced only when random copolymer coexists with the segmented copolymer. The synergistic effect between random copolymer and segmented copolymer is a key factor for high impact strength at low temperature. Thus, controlling the structural distribution is an effective way of fine-tuning the properties of final product. To study the structural distribution of the alloy samples, we separated each sample into five fractions by TGEF. The fraction distributions of samples prepared at different feed ratio of ethylene in ethylene–propylene mixture are shown in Figure 4. The amount of EPR (Fraction As) and segmented ethylene–propylene copolymer (Fraction Bs) increased evidently when the feed ratio of ethylene increased. However, the amount of ethylene-*b*-propylene block copolymer (Fraction Ds) decreased slightly and the amount of PP (Fraction Es) decreased evidently. To understand this phenomenon, we should consider that in the third stage (copolymerization of ethylene and propylene) there are homopolyethylene, homopolypropylene, and poly(ethylene-*co*-propylene) formed in the same time. As the amount of ethylene in the ethylene–propylene mixture increases, the concentration of propylene decreases which leads to form less homopolypropylene but more homopolyethylene (as shown in Fig. 4). Increasing the feed ratio of ethylene in the ethylene–propylene mixture is favorable for forming random ethylene–propylene copolymer and segmented ethylene–propylene copolymer, however, has slight influence on the formation of ethylene-*b*-propylene block copolymer. Especially, increment of the amount of ethylene in the mixture restricts the formation of homopolymer.

TABLE V
Influence of Polymerization Conditions on the Mechanical and Physical Properties of the In-Reactor Alloys

Polymerization conditions	Feed ratio of ethylene (mol %)[a]			Pressure of ethylene–Propylene mixture (MPa)[b]		
	30	20	0.7	0.6	0.4	
Ethylene content (wt %)	57.6	57.5	47.8	57.6	50.6	51.8
EPR content (wt %)	7.0	7.6	4.4	7.0	6.8	5.7
Fraction B content (wt %)	14.3	14.2	12.1	14.3	9.8	4.9
Fraction C content (wt %)	24.8	17.2	15.4	24.8	26.5	33.4
Fraction D content (wt %)	47.7	50.8	51.5	47.7	46.1	44.7
Fraction E content (wt %)	6.2	10.3	16.7	6.2	10.8	11.3
Impact strength kJ/m^2	Not broken	112.5	80.4	Not broken	160.3	111.3
Flexual module (MPa)	1113.9	2519.2	2218.5	1113.9	2235.8	2503.2
[η] (1/g mL)	930	910	1180	930	990	1220

[a] The polymerization conditions are given in Table III.
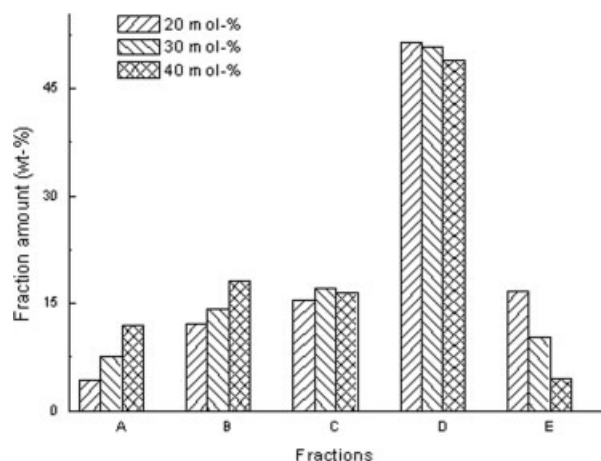[b] The polymerization conditions are given in Table II.

Figure 4 Fraction distributions of alloys prepared at different feed ratio of ethylene in ethylene–propylene mixture. The polymerization conditions are given in Table II.

As shown in Figure 5, the content of random copolymer (Fraction As), segmented copolymer (Fraction Bs) and ethylene-*b*-propylene block copolymer (Fraction Ds) increased as the pressure of ethylene–propylene mixture changed from 0.4 to 0.7 MPa, but the content of both PE (Fraction Cs) and PP (Fraction Es) decreased comparatively. To understand this phenomenon, we should consider the influence of monomer concentration on polymerization rate. As we all know the copolymerization rate of ethylene and propylene (R_{EP}), the homopolymerization rate of ethylene (R_E) and the homopolymerization rate of propylene (R_P) can be, respectively, represented as follows:

$$R_{EP} = k_{EP}[M_E][M_P]$$
$$R_E = k_E[M_E]$$
$$R_P = k_P[M_P]$$

where k_{EP}, k_E, and k_P represents the reaction rate constant of ethylene–propylene copolymerization, ethylene homopolymerization, and propylene homopolymerization, respectively; $[M_E]$, $[M_P]$ represents ethylene monomer concentration and propylene monomer concentration respectively. Increase in the pressure of ethylene–propylene mixture results in increment of ethylene monomer concentration and propylene monomer concentration. As the expressions above show, the increment of R_{EP} is much higher than that of R_E and R_P with the increment of $[M_E]$ and $[M_P]$. Therefore, increasing the pressure of ethylene–propylene mixture leads to more ethylene–propylene copolymer but less homopolyethylene and homopolypropylene in the PE/PP/EPR in-reactor alloys.

Mechanical and physical properties of the in-reactor alloys

Some important mechanical properties such as the impact strength and flexural modulus were measured, and the results are summarized in Table V. The impact strength of PE/PP/EPR in-reactor is more than 80.4 kJ/m^2. As a reference,[16] the impact strength of PE/PP in-reactor alloy at room temperature is about 67.3 kJ/m^2. Therefore, the three-stage process used to prepare PE/PP/EPR in-reactor alloys is a more effective way of improving the impact properties of iPP than the two-stage process used to prepare PE/PP in-reactor alloys.

It seems that the impact strength and the flexural modulus of PE/PP/EPR in-reactor alloys are influenced not only by the amount of random copolymer and segmented copolymer but also by the amount of PP. In Table V, we can find that as the amount of random copolymer and segmented copolymer increases, the impact strength of PE/PP/EPR in-reactor alloys increases and the flexural modulus decreases. Although the content of random copolymer and segmented copolymer is similar in the two PE/PP/EPR in-reactor alloys prepared at different feed ratio of ethylene, 50 and 30 mol %, there is difference between their impact strength and flexural modulus. This may be due to the different content of PP. This means that the amount of random and segmented copolymer fraction is not the only factor in improving the impact strength. The coexistence of random ethylene–propylene copolymer, segmented ethylene–propylene copolymer, and homopolypropylene in a suitable ratio is the key to both high impact strength and high flexural modulus.

The intrinsic viscosity of the in reactor alloys also depend on the polymerization conditions. As shown in Table V, the intrinsic viscosity of the alloys decreases
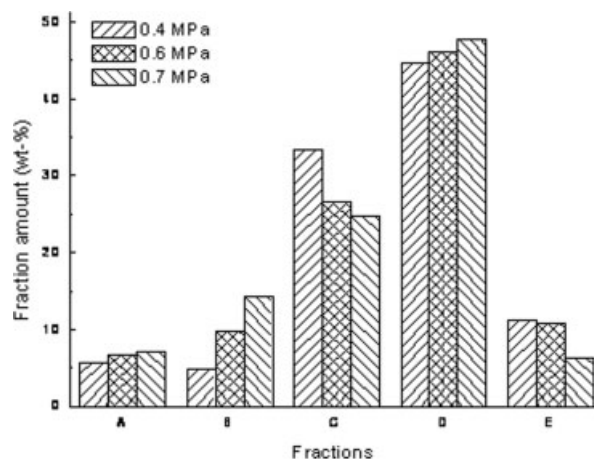

Figure 5 Fraction distributions of alloys prepared at different pressure of ethylene-propylene mixture. The polymerization conditions are given in Table II.

as the content of random ethylene–propylene copolymer and segmented ethylene–propylene copolymer increases. This was likely caused by the low molecular weights of the copolymers (both random and segmented copolymer).

CONCLUSIONS

The conditions of gas-phase ethylene–propylene copolymerization can regulate the ethylene content of PE/PP/EPR in-reactor alloys in a narrow range but strongly influence the structural distribution of PE/PP/EPR in-reactor alloys based on a spherical, high-yield Ziegle-Natta catalyst. Increasing the feed ratio of ethylene in the ethylene–propylene mixture is favorable for forming random ethylene–propylene copolymer and segmented ethylene–propylene copolymer, but shows slight influence on the formation of ethylene-*b*-propylene block copolymer and homopolyethylene. Raising the pressure of ethylene–propylene mixture results in the increment of segmented ethylene–propylene copolymer, ethylene-*b*-propylene block copolymer and PE fractions, but exerts slight influence on both the random copolymer and PP fractions. The mechanical properties of the alloys, including the impact strength and flexural modulus, can be regulated in a broad range with changes in the copolymerization conditions. The impact strength of PE/PP/EPR in-reactor alloys can be markedly improved by increasing the feed ratio of ethylene in the ethylene–propylene mixture or increasing the pressure of ethylene–propylene mixture. However, the flexural modulus decreases as the feed ratio of ethylene in the ethylene–propylene mixture or the pressure of ethylene–propylene mixture increases.

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