Influences of Copolymerization Conditions on the Structure and Properties of Isotactic Polypropylene/Ethylene– Propylene Random Copolymer *In Situ* Blends

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ABSTRACT: A spherical TiCl₄/MgCl₂-based catalyst was used in the synthesis of in situ isotactic polypropylene/ethylene-propylene random copolymer blends by propylene bulk polymerization and subsequent gas-phase copolymerization of ethylene with propylene. Different copolymerization conditions, such as the reaction time, monomer pressure, and composition, were investigated, and their influences on the structure and properties of the products were studied. Raising the monomer pressure was the most effective way of speeding up the copolymerization, but it caused more increases in the random copolymer than the block copolymer fractions. Increasing the ethylene content of the monomer feed also resulted in higher reaction rates and copolymer contents, but the ethylene contents of both the random and block copolymer fractions were also raised. In situ blends that contain more than 50 wt % copolymer were prepared. The mechanical properties of the blends, including the impact strength and flexural modulus, were regulated in a rather broad range with changes in the copolymerization conditions. The properties were highly dependent on the amount, distribution, and chain structure of the copolymer fractions. The impact strength was influenced by both the random copolymer and block copolymer portions in a complicated way, whereas the flexural modulus was mainly determined by the amount of random copolymer. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 445-453, 2002; DOI 10.1002/app.10415

Key words: isotactic polypropylene/ethylene-propylene random copolymer *in situ* blends; polymerization conditions; structure; properties

INTRODUCTION

Blends or alloys of isotactic polypropylene (iPP) with ethylene-propylene random copolymer (EPR) are called *toughened polypropylene* (PP) or *high-impact PP* and are widely applied as high-

performance structural materials with a suitable balance between toughness and rigidity. In comparison with iPP/EPR blends formed by mechanical blending, blends prepared by *in situ* or inreactor blending techniques have been proven to be superior in both mechanical properties and production costs.¹⁻⁴ A typical *in situ* blend is prepared by the sequential homopolymerization of propylene in one reactor, followed by ethylene/ propylene copolymerization in a second reactor. In particular, Montell Company¹ developed an in-reactor blending technique named Catalloy

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that uses a spherical, superactive $TiCl_4/MgCl_2$ based catalyst to prepare multiphase, multipolymer PP alloys spherical in shape. The use of a spherical catalyst allows a wider range of rubber contents in the alloy and better control over the phase structure to be achieved. The resultant spherical resin can be directly processed; this eliminates the need for pelleting. This technique is considered the main advance since the in-reactor PP blend was first developed in the 1960s.

The structure and properties of iPP/EPR blends, made either by mechanical blending or by multistage polymerization, have been extensively studied.³⁻¹⁰ It has been reported that the composition of the blend and the chain structure of the copolymer portion strongly influence the mechanical properties of the material. The effects of structural features, such as the ethylene content and molecular weight distribution of the EPR portion, on the properties of an iPP/EPR mechanical blend were studied by D'Orazio et al.⁸ The relationships between the amount and structure of the rubber phase and the ductility of iPP/EPR blends have been reported.¹⁰ In our previous work,¹¹ we found that there were synergistic effects between the random copolymer portion and block copolymer portion of an in situ iPP/EPR blend that played an important role in enhancing the impact strength of the blend at low temperatures. However, there are very few reports in the literature concerning the influences of polymerization conditions on the structure and properties of in situ iPP/EPR blends. Kawai and Hamielec¹² studied the effects of polymerization conditions on the particle size distribution of in situ iPP/EPR blends and the distribution of rubber phases in the polymer particles.

In a multistage process for synthesizing *in situ* iPP/EPR blends, a direct way to regulate the amount and chain structure of the copolymer portions is to change the conditions of the copolymerization stage. Other ways of regulating the structure and properties of the blend include changing the stereoregularity, molecular weight distribution, and morphology of the iPP matrix phase formed in the first stage;² changing the designs of the reactor and the polymerization process; and adding poisons of the active sites to control their space distribution in the catalyst particles.¹² There is no doubt that the conditions of gas-phase copolymerization are the most important variables and can directly influence the reaction rate and copolymer composition.

In this study, a spherical, high-yield $TiCl_4/MgCl_2$ -based catalyst was used in the synthesis of *in situ* iPP/EPR blends by a two-stage polymerization process. Different conditions in the gasphase copolymerization stage, such as the reaction time, monomer pressure, and monomer composition, were investigated, and their influences on the structure and properties of the *in situ* blends are reported.

EXPERIMENTAL

Polymerization

A high-yield, spherical $TiCl_4/MgCl_2 \cdot ID$ (where ID is an internal donor) catalyst (DQ-1, donated by Beijing Research Institute of Chemical Industry, Beijing, China) was used in the polymerization reactions, with $Al(C_2H_5)_3$ -Ph₂Si(OCH₃)₂ as a cocatalyst. The polymer was synthesized in a twostage reaction process, in which the first stage was propylene homopolymerization in liquid propylene at 70°C in an autoclave and the second stage was successive gas-phase ethylene-propylene copolymerization in a stirred-bed reactor. In the first stage, spherical iPP granules 0.5–3 mm in diameter were produced, and residual propylene in the particles was completely removed before the granules were transferred to the second reactor. In the copolymerization stage, an ethylene-propylene mixture of constant composition was continuously supplied to the gas-phase reactor at a constant pressure. The copolymerization rate was determined by measurement of the flow rate of monomer gas at a constant pressure. In this work, the pressure of the monomer feed gas was regulated in the range of 0.2–0.6 MPa, and the composition of the monomer feed was changed in the range of 20-60 mol % ethylene. The final product after two stages of reaction was still free-flowing, spherical granules. This means that most of the copolymer was formed inside the granules.

Fractionation of the Blend

A modified Kumagawa extractor was used for temperature-gradient extraction fractionation (TGEF) of the polymer.¹³ *n*-Octane was used as the solvent for successive extraction of the sample at different controlled temperatures, from room temperature to around 120°C. Six fractions were collected by the extraction of 3-g samples at 20, 70, 90, 102, 110, and greater than 110° C. Purified fractions were obtained after the concentration of the extract solutions, precipitation of the polymer, and washing and drying of the fractions *in vacuo*.

Extraction by boiling *n*-heptane was adopted for measuring in a rapid way the amount of EPR and block copolymers containing relatively short segments in the blend. About 5 g of a blend sample was extracted in a Kumagawa extractor by the boiling of *n*-heptane for 12 h. The dissolved polymer was precipitated by ethanol and dried *in vacuo*. The weight percentage of the soluble part was used as a measure of the random copolymer content in the blend.

Measurement of the Ethylene Contents

Fourier transform infrared (FTIR) spectra of the blend sample and the fractions were recorded on a Nicolet (Madison, WI) 5DX FTIR spectrometer. A thin film of the sample was prepared through hot pressing. An empirical equation was used for the estimation of the ethylene content based on the infrared spectrum:

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

where C_2 is the molar percentage of ethylene in the polymer. The equation was calibrated by ethylene content data measured by ¹³C-NMR.

Measurement of the Mechanical and Physical Properties

The notched Izod impact strength of the polymer sample was measured on a Ceast (Turin, Italy) impact strength tester according to ASTM Standard D 256. The flexural modulus, flexural strength, tensile strength, tensile modulus, and elongation at break were measured according to ASTM Standard D 790 and ASTM Standard D 638-76 on a Shimadzu AG-500A electronic tester. The sample plates were heat-molded into sheets, which were than cut into pieces, put into a 150 mm \times 150 mm \times 4 mm mold, and pressed under 25 MPa at 180°C for 5 min. The sample was than cooled to room temperature in the mold. Sample strips for the tests were cut from the plate according to the ASTM standard.

The melt flow indices of the blend samples were measured in a melt flow index tester.



Figure 1 Rate profile of copolymerization at 50° C and 0.5 MPa of monomer pressure. Ethylene/propylene (mol/mol) = 1/1.

RESULTS AND DISCUSSION

Influences of the Copolymerization Conditions on the Blend Compositions

In the first stage of polymerization, the bulk polymerization of propylene was conducted in an autoclave at 70°C. Spherical iPP particles 0.5–3.0 mm in diameter were produced. More than 70 wt % of the polymer particles fell within a diameter range of 1.4–2.5 mm. The catalyst efficiency of the polymerization was about 1.7×10^5 g of PP/g of Ti \cdot h. The iPP particles had a porosity of about 15–20%, as measured by volumetric testing. The ethylene–propylene copolymer produced in the gas-phase copolymerization stage mainly existed in tiny holes inside the iPP particles, so the final product still had a spherical shape.

The kinetics of the copolymerization were determined by monitoring of the flow rate of the monomer entering 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. The change in the EPR and ethylene contents with the copolymerization time (Fig. 2) also indicated rapid rate decay. Such rate decay seems not to have resulted from the activity decay of active centers, as the catalyst should have reached its stationary stage after about 2 h of homopolymerization. Therefore, it is more likely that the rate decay was caused by diffusion limitation in the polymer particles. As the copolymerization proceeded, the small holes in the iPP 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 diffu-



Figure 2 Change in the blend composition with the copolymerization time. Temperature = 60° C; monomer pressure = 0.5 MPa; ethylene/propylene (mol/mol) = 1/1.

sion-controlled kinetics of the copolymerization.¹⁴ If there were diffusion limitation in the gas-phase reaction, it influenced the relations between the reaction conditions and the copolymerization behaviors.

Figure 3 shows the effects of the copolymerization temperature on the content of EPR (represented by the weight percentage of the boiling *n*-heptane-soluble part) in the blend. Changing the temperature from 40 to 70°C exerted only a limited influence on the EPR content. Because the copolymer yield was roughly proportional to the EPR content (see Table I), it may be said that changing the temperature had a small effect on the polymerization rate. This may be evidence for the diffusion limitation phenomenon because the diffusion coefficients of the monomers in the particles, which were correlated to the physical properties of the polymer particle and the monomers, were little affected by temperature. Because of the small difference in activity between catalyst batches used in different experiment sets, the EPR content shown in Figure 2 was higher than the corresponding value in Figure 3 under the same conditions. The tendencies shown in Figure 2 and Figure 3 imply that there are limits in regulating the copolymer content with changes in the reaction time or temperature.

As shown in Figure 4, raising the monomer pressure had a much stronger effect on the copolymerization rate. The ethylene content increased almost linearly with increasing monomer pressure. Therefore, changing the monomer pressure, namely, the monomer concentration, may be the most effective way of controlling the copolymer content in the blend. In our experiments, the amount of EPR was easily adjusted within a range of 0-50 wt %.

However, changing the ethylene/propylene ratio in the monomer mixture also strongly affected the copolymerization rate (Fig. 5). As the amount of ethylene in the monomer feed increased, the EPR content in the product increased, and the ethylene content was enhanced even more. This phenomenon can be explained by the much higher polymerization activity of ethylene than of propylene in such Ti-based catalyst systems. It could be expected that the ethylene content of the copolymer in the blend would be raised as the ethylene content in the monomer increased.

Influences of the Copolymerization Conditions on the Polymer Structural Distribution

In a previous study,¹¹ we found that the iPP/EPR blend is composed of three parts: iPP homopolymer formed in the bulk polymerization stage, EPR, and ethylene–propylene block copolymers with polyethylene (PE) and PP segments of different lengths. Similar structural distributions have also been found in other *in situ* iPP/EPR blends.^{3,7} It has also been discovered that the block copolymer fractions play an important role in improving the mechanical properties of the blend, especially the impact strength. Therefore, controlling the structural distribution is an effective way of fine tuning the properties of the final product.

To study the structural distribution of the blend samples, we fractionated each sample into



Figure 3 Effect of the copolymerization temperature on the composition of *in situ* blends. Monomer pressure = 0.5 MPa; ethylene/propylene (mol/mol) = 1/1; time = 2 h.

	Monor	mer Pressure	(MPa) ^b	Ethylene Amount in Monomer (mol %) ^c		
Polymerization Conditions ^a	0.2	0.4	0.6	20	40	60
EPR content (wt $\%$) ^d	16.3	25.2	46.6	9.8	19.1	26.7
C_2 in EPR (mol %) ^e	43.3	45.5	36.3	32.3	39.9	54.6
Block copolymer content (wt %) ^f	18.0	13.0	28.2	17.7	15.1	14.0
C_2 in block copolymer (mol %) ^g	35.9	47.6	18.9	16.0	40.0	76.0
iPP content (wt %) ^h	65.7	61.8	25.2	72.6	65.9	59.4
Weight ratio of EPR/iPP (g/g)	0.25	0.41	1.85	0.14	0.29	0.45
Weight ratio of block						
copolymer/iPP (g/g)	0.27	0.21	1.12	0.24	0.23	0.24
Weight ratio of EPR/block						
copolymer (g/g)	0.91	1.94	1.65	0.55	1.26	1.91
Weight of C_2 from EPR ⁱ	0.055	0.090	0.128	0.024	0.059	0.119
Weight of $\overline{C_2}$ from the block						
copolymer ^j	0.049	0.049	0.038	0.020	0.046	0.095
C_2 from EPR/ C_2 from block						
copolymer ^k	1.12	1.84	3.37	1.20	1.28	1.25

Table I Influence of Reaction Conditions on the Structural Distribution of the In Situ Blends

^a Conditions of gas-phase copolymerization of ethylene with propylene: temperature = 60° C; time = 2 h.

^b Ethylene content in the feed monomer mixture = 50 mol %.

^c Pressure of the monomer gas = 0.5 MPa.

^d Weight percentage of ethylene–propylene random copolymer (the fraction extracted at 20°C) in the final product.

^e Ethylene content in the 20°C fraction measured by FTIR.

^fWeight percentage of block copolymer (defined as the fractions extracted at 75, 90, and 102°C) in the final product.

^g Average ethylene content in the 75, 90, and 102°C fractions measured by FTIR.

^h Weight percentage of propylene homopolymer (defined as the fractions extracted at 110 and >110°C) in the final product.

ⁱ Weight of ethylene that existed in the random copolymer fraction per gram of blend.

^j Weight of ethylene that existed in the block copolymer fractions per gram of blend.

^k Ratio of ethylene from the EPR fraction to that from the block copolymer fraction.

six fractions by TGEF. The fraction distributions of the samples prepared at different monomer pressures are shown in Figure 6. As proved in the previous work,¹¹ the fraction extracted at room temperature (20°C) was random copolymer (EPR), and the fractions extracted at 50-100 °C were composed of ethylene-propylene block copolymers with PE and PP segments of different lengths. The amount of random copolymer evidently increased when the monomer pressure



Figure 4 Effect of the monomer pressure on the composition of *in situ* blends. Temperature = 60° C; ethyl-ene/propylene (mol/mol) = 1/1; time = 2 h.



Figure 5 Effect of the ethylene content in the monomer feed on the composition of *in situ* blends. Monomer pressure = 0.5 MPa; temperature = 60° C; time = 2 h.



Figure 6 Fraction distributions of blends prepared under different monomer pressures. The polymerization conditions are given in Table I.

rose, but the amount of block copolymers, which existed in the 70-102°C fractions, was little influenced by monomer pressure. To understand this phenomenon, we should consider the block copolymer formed at the very beginning of the copolymerization. At the beginning of the copolymerization, many of the active centers still have chemically bonded iPP propagation chains that are formed in the propylene homopolymerization stage. When these active centers meet the ethylene/propylene mixture in the gas-phase reactor, copolymerization will continue on these living PP chains, forming block copolymers with long iPP segments. After a chain-transfer reaction, such block copolymer chains will leave the active centers, and the later formed chains will be mainly random copolymer chains. This fact implies that the amount of block copolymer formed at the switching point from the bulk polymerization to the gas-phase reaction should only depend on the number of active centers, and the copolymerization conditions should not influence it much.



Figure 7 Ethylene weights in the fractions of blend samples prepared under different monomer pressures.



Figure 8 Fraction distributions of blends prepared with different monomer compositions. The polymerization conditions are given in Table I.

Therefore, raising the monomer pressure will relatively favor the formation of random copolymer. This trend becomes more evident if we look at Figure 7, which shows the weight distribution of ethylene among the fractions. The weight of ethylene existing in the 102°C fraction, which was composed of block copolymer with relatively long PE and PP segments,¹¹ was almost unchanged when the monomer pressure increased from 0.2 to 0.6 MPa.

However, changing the ethylene content in the monomer feed exerted a strong influence on both the random copolymer and block copolymer fractions. As shown in Figures 8 and 9, the weight of EPR (i.e., the weight of the 20°C fraction) increased when ethylene content in the monomer feed increased from 20 to 60 mol %; meanwhile, the ethylene weight in the fraction increased even more. The ethylene weight in the other copolymer fractions also greatly increased with the addition of more ethylene in the feed. This means that



Figure 9 Ethylene weights in the fractions of blend samples prepared with different monomer compositions.

Copolymerization Conditions ^a	Monomer Pressure (MPa) ^b				Ethylene Content in Feed (mol %)^c				
	0.2	0.4	0.5	0.6	20	30	40	50	60
EPR content (wt %)	25.2	29.1	42.0	51.2	17.8	19.9	23.2	30.0	34.2
Ethylene content (wt %) ^d	16.2	20.0	23.1	25.6	6.6	8.6	13.4	18.3	26.4
Notched Izod impact strength (J/m)									
23°C	653	NB	NB	NB	425	427	559	606	NB
$-30^{\circ}\mathrm{C}$	347	436	496	510	60	82	171	450	680
Flexural modulus (MPa)	757	688	450	329	964	758	800	732	608
Flexural strength (MPa)	18.3	14.6	11.3	8.5	22.5	20.6	15.6	19.3	14.9
Tensile strength (MPa)	n.d.	n.d.	n.d.	n.d.	25.8	17.9	20.3	18.8	15.9
Tensile modulus (MPa)	n.d.	n.d.	n.d.	n.d.	670	669	598	582	514
Elongation at break (%)	n.d.	n.d.	n.d.	n.d.	247	375	447	470	500
Melt Index (g/10 min)	1.65	1.18	n.d.	0.87	1.54	1.38	1.27	n.d.	0.56

 Table II
 Influence of Copolymerization Conditions on the Mechanical and Physical Properties of the In Situ Blends

NB = not broken; n.d. = not determined.

^a Conditions of gas-phase copolymerization of ethylene with propylene: temperature = 60° C; time = 2 h.

^b Ethylene content in the feed monomer mixture = 50 mol %.

^c Pressure of the monomer gas = 0.5 MPa.

^d Ethylene content of the *in situ* blend (mol %).

regulating the ethylene content of the monomer feed was an effective way of changing the ethylene amount in all the copolymer fractions. However, as shown in Figure 8, the weight ratio of the block copolymer (fractions extracted at $70-102^{\circ}$ C) to EPR was lowered with the ethylene content of the monomer feed being raised.

In Table I, the changes in the polymer structural distribution with the copolymerization conditions are summarized. Raising the monomer pressure caused sensible increases in both the EPR and block copolymer fractions, with the EPR fraction having increased more. As a result, the weight ratio of the block copolymer to the random copolymer decreased. Raising the ethylene content of the feed showed similar effects, but the ratio of ethylene from EPR to that from the block copolymer was almost unchanged. In all cases, the ethylene content of the EPR fraction could only be regulated in a narrow range (ca. 30-55 mol %), but the ethylene content of the block copolymer fractions changed in a broad range. Higher monomer pressure tended to produce block copolymers with low ethylene contents. In contrast, raising the ethylene content of the monomer feed was an effective way of increasing the ethylene content of the block copolymer portion.

Mechanical and Physical Properties of the In Situ Blends

Some important mechanical properties such as the impact strength, flexural modulus, tensile strength, and ductility of the in situ blend samples were measured, and the results are summarized in Table II. The impact strength of the blend was greatly improved by the introduction of more ethylene into the material because of either increasing monomer pressure or increasing ethylene in the feed. It seems that the ethylene content was the most important parameter that determined the impact strength. At ethylene contents of 15 wt % and higher, both the room-temperature and low-temperature impact strength became very high (>200 J/m). As a reference, the impact strength of iPP at room temperature is only about 24 J/m, and it is even lower at -30°C. iPP/EPR blends prepared by mechanical blending also showed much lower impact strengths than the *in* situ blends containing similar amounts of ethylene.⁸ Therefore, in situ blending based on a spherical Ziegler–Natta catalyst is a very effective way of improving the impact properties of iPP.

In Table II, we can also find that there is a limit in improving the impact strength by simply introducing more EPR into the blend. The sample prepared at 0.6 MPa and 50% ethylene in the feed (sample A) contained more EPR than the sample

Sample	Reaction Time (min)	EPR Content (wt %)	Ethylene Content (mol %)	Notched Izod Impact Strength (J/m)	Flexural Strength (MPa)	Flexural Modulus (MPa)
EP1 EP2 EP05	10 30 120	$7.1 \\ 11.6 \\ 42.0$	4.6 8.7 23.1	86.3 302.5 $\rm NB^{b}$	33.4 25.8 11.3	$1674 \\ 1371 \\ 450$

Table III Influence of Copolymerization Time on the Mechanical Properties of the Blends^a

^a Copolymerization conditions: temperature = 60° C; monomer pressure = 0.5 MPa; ethylene content in the monomer feed = 50 mol %.

 $^{\rm b}$ NB = not broken. The notched Izod impact strength of this sample measured at -30° C was 495 J/m.

prepared at 0.5 MPa and 60% ethylene in the feed (sample B; 51 vs 34 wt %), but the former showed lower impact strength than the latter. By examining the data in Table I, we find that the former sample contained much less ethylene in the block copolymer fractions than the latter. This means that the block copolymer fractions also play an important role in improving the impact strength. In a previous work, we reported that there was a synergistic effect between the EPR fraction and the block copolymer fractions in relation to the impact properties. The coexistence of both portions in a suitable ratio is the key to high impact strength both at room temperature and at low temperature.

However, the flexural modulus and flexural strength of the blend were strongly affected by the content of EPR. This is easy to understand because EPR is a kind of elastomeric material with very low strength and modulus. Therefore, simply increasing the EPR portion is an effective way of lowering the flexural modulus, as the aforementioned sample A showed much lower flexural modulus than sample B, although both had similar ethylene contents (25.6 vs. 26.4%). In this way, *in situ* blends may be made that can be applied in cases for which both high toughness and high flexibility are required.

As shown in Table II, the tensile strength and tensile modulus also decreased with the increasing EPR content of the blend, and the ductility was improved when the blend became softer and more flexible.

The polymer structure can also be regulated in a broad range with changes in the copolymerization time, and so can the mechanical properties. As shown in Table III, when the EPR content was lowered to about 10% by shortening of the reaction time, the impact strength of the blend was still quite high; meanwhile, the flexural modulus was only slightly lowered (the flexural modulus of iPP is ca. 1600 MPa). Combining the results in Table II and Table III, we conclude that the mechanical properties of the *in situ* blends can be regulated in a rather broad range simply by changes in the copolymerization conditions. A series of different blends or alloys may be prepared in such a process, ranging from very tough and rigid plastics to soft and flexible materials. Their applications may include car bumpers in the automotive industry, flexible packaging, consumer products, industry products, and textiles.

The melt flow index of the *in situ* blends also depended on the copolymerization conditions. As shown in Table II, the melt index of the blend decreased as the ethylene content of the blend increased. This was likely caused by the molecular weights of the copolymers (both random and blocky) being higher than that of iPP. By examining the data in Table I, we find that the amount of ethylene in the block copolymer fractions is more closely related to the melt index, and the amount of EPR seems to be less important. A possible explanation is that the active centers producing block copolymers have very low chaintransfer constants, so the block copolymer chains are much longer than the random copolymer and iPP chains.

CONCLUSIONS

The conditions of gas-phase ethyene-propylene copolymerization strongly influence the composition and structural distribution of *in situ* iPP/EPR blends based on a spherical, high-yield Ziegler-Natta catalyst. Raising the monomer pressure is the most effective way of speeding up the copolymerization, but it will cause a greater increase in the random copolymer fraction than in the block copolymer fractions. Increasing the ethylene content of the monomer feed also results in higher reaction rates and copolymer contents, but the ethylene content of both the random copolymer and the block copolymer fractions will also be raised. Under some conditions, *in situ* blends that have more than 50 wt % copolymer fractions were prepared. The mechanical properties of the blends, including the impact strength and flexural modulus, can be regulated in a rather broad range with changes in the copolymerization conditions. These properties are highly dependent on the amount, distribution, and chain structure of the copolymer fractions. The impact strength is affected by both the random copolymer and block copolymer portions in a complicated way, whereas the flexural modulus is mainly determined by the amount of random copolymer.

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