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Synthesis and characterization of ethylene–propylene random copolymers with isotactic propylene sequence

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Abstract

Novel ethylene–propylene random copolymers with isotactic sequence of propylene were synthesized with a $MgCl_2$-supported $Cr(acac)_3$ catalyst. The propylene content was controlled by the monomer concentration. The crystallinity of these copolymers showed a minimum around 50 mol% content of propylene or ethylene. According to differential scanning calorimetry and wide-angle X-ray diffraction, crystals of polyethylene (PE) and polypropylene (PP) do not coexist, and ethylene-rich copolymers exhibit the orthorhombic form of PE and propylene-rich copolymers exhibit the monoclinic form of PP. It was found that the mechanical properties of these changed drastically between 70 and 53 mol% of propylene content. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chromium catalyst; Copolymerisation; Ethylene propylene random copolymer

1. Introduction

Polypropylene (PP) and polyethylene (PE) multiphase polymer systems have been widely investigated with growing use of these polyolefins. In particular, much attention has been paid to random copolymers of PP and PE for improving the performance of existing polyolefin-based materials [1–7]. In general, stereoregularity of the PP sequence in typical ethylene–propylene random copolymers is much lower and typical ethylene/propylene random copolymers show considerably low crystallizability.

Recent development of catalysts for PP/PE copolymerization enabled us to control the content and stereoregularity of the PP sequence in ethylene–propylene copolymers. According to Soga et al. [8–10], $Cr(acac)_3$ supported on $MgCl_2$ activated by diethylaluminium chloride (DEAC) promoted not only ethylene and propylene polymerization but also ethylene–propylene copolymerization. In particular, the addition of external donor such as ethylbenzoate (EB) makes it possible to convert non-stereospecific into highly isospecific sites being accompanied by a considerable increase in the activity. Moreover, the addition of EB did not affect the activity and the molecular weight in the ethylene polymerization. As a result, the $Cr(acac)_3$ catalyst was found to produce ethylene–propylene copolymers having a narrow molecular weight distribution and a high stereospecificity in propylene sequence

In this work, ethylene–propylene random copolymers with a wide composition range were synthesized with the catalyst system consisting of $Cr(acac)_3/MgCl_2$–DEAC–EB. The influence of propylene content (P-content) on the mechanical properties as well as morphology of these ethylene–propylene copolymers were studied by dynamic mechanical analysis, tensile behavior, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and other techniques.

2. Experimental section

2.1. Materials

$MgCl_2$ (surface area measured by Brunauer–Emmett–Teller (BET) method = 80 m^2/g) and $Cr(acac)_3$ were donated from Toho Titanium Co. and Kanto Chemicals, respectively. Diethylaluminium chloride (DEAC) donated by Tosho Akzo Co. was used without further purification. Ethylbenzoate (EB) and *n*-heptane commercially obtained from Kanto Chemical Co. Ltd. were purified by refluxing CaH_2 over 24 h followed by distillation, and stored over molecular sieves under nitrogen. Propylene and ethylene of commercial grade (Takachiho Chem. Co.) were further purified through columns of NaOH and P_2O_5.

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Table 1
Results of ethylene/propylene copolymerization with Cr(acac)$_3$/MgCl$_2$–DEAC–EB catalyst system (Conditions: Cr(acac)$_3$ = 0.02 mmol, [Al]/[Cr] = 400, [EB]/[Cr] = 200, polymn. time = 18 h, polymn. temp. = 40°C, *n*-heptane = 30 cm^3, in 100 cm^3 stainless autoclave)

Run No	Monomer(l)		T_m[b] (K)	T_γ[c] (K)	T_β[c] (K)	M_w (10^4)	M_w/M_n	P. Cont. (mol%)	$r_P r_E$
	E[a]	P[a]							
PP	0	10.0	439.3		275.0	18.0	2.6	100	
P92	0.5	9.5	392.8		261.6	20.0	2.9	92.2	7.16[d]
P89	0.7	9.3	378.9		258.9	18.7	2.7	89.3	1.14
P77	1.0	9.0	329.5	135.1	238.8	25.8	1.9	76.5	1.11
P70	2.0	8.0	–	128.3	220.7	41.1	2.7	70.0	1.06
P53	3.0	7.0	–	135.8	209.9	40.8	2.3	52.5	1.09
P42	5.0	5.0	–	136.6	212.7	43.4	2.9	42.4	1.08
P31	5.0	2.5	383.1	134.7	215.8	19.9	3.0	30.9	1.12
P23	5.0	1.5	386.8	139.0	217.1	23.2	3.1	22.6	1.13
P11	5.0	0.5	392.5	138.6	220.7	24.5	2.9	11.1	8.46[e]
PE	10.0	0	408.8	148.7	254.2	25.8	2.8	0	

[b] Determined by DSC.
[c] Determined by DMA.
[a] L(STP).
[d] r_P.
[e] r_E.

2.2. Polymerization and sample characterization

Ethylene–propylene random copolymers with a wide composition range were synthesized with a catalyst system consisting Cr(acac)$_3$/MgCl$_2$–DEAC–EB according to the literature [8–10]. Homopolymerization and copolymerization were conducted in a 100 cm^3 stainless steel autoclave equipped with a magnetic stirrer. After the reactor was filled with nitrogen, an appropriate amount of EB (4 mmol), DEAC (8 mmol of Al), heptane (30 ml), and the supported Cr catalyst was added to the reactor in this order. The reactor was then evacuated at liquid nitrogen temperature, and propylene and ethylene were introduced into the reactor. Polymerization was carried out at 40°C for 1 h. Depending on the pressure and ratio of two monomers, copolymers varying the P-content from 11.1 to 92.2 mol% were successfully synthesized. The polymers were quenched by adding the dilute solution of hydrochloric acid in methanol. The polymers thus prepared were repeatedly washed with methanol and dried under vacuum at 60°C for 8 h.

The resulting polymers were extracted with boiling *o*-dichlorobenzene solution and the purified homopolymers and copolymers were dried under vacuum at 60°C for 6 h.

The content of propylene and the reactivity ratios ($r_P r_E$) in the copolymers were estimated by ^{13}C-NMR analysis according to the literature [11]. The ^{13}C-NMR spectra of the samples were recorded at 140°C using a Varian Gemini 300 spectrometer operating at 75 MHz. The polymers were dissolved in 1,2,4-trichlorobenzene/benzene-d_6(vol. ratio = 9/1) up to 10 wt%.

The average of molecular weight M_w and M_w/M_n of the polymer were determined from GPC (Senshu Kagaku, SSC-7100) measurements at 418 K using *o*-dichlorobenzene as solvent. The calibration curve of the copolymers was made with standard polystyrene samples. The molecular characteristics of these polymers are summarized in Table 1.

2.3. Measurements

The samples were melt-pressed in a laboratory hot press at 463 K and at 12 MPa. The film sheets with the thickness of about 300 μm were prepared by quenching from the melt-pressed samples into an ice-water bath.

DSC measurements were carried out using a Mettler DSC 820 to examine the melting behavior. The samples of 10 mg sealed in aluminium pans, which were cut from the sheets, were heated from room temperature to 473 K at a scanning rate of 10 K/min under nitrogen atmosphere.

Densities of the sheets were determined by a floatation method. The binary medium prepared from various ratios of distilled water and ethyl alcohol was used. The crystallinity of these copolymer films can be determined using their density data:

$$\chi_v = \frac{\rho - \rho_a}{\rho - \rho_c} \tag{1}$$

where χ_v is the degree of crystallinity in volume fraction, and ρ is the density of the sample, ρ_a is the density of amorphous region and ρ_c is the density of crystal [12,13]. Since PE and PP crystals do not coexist in copolymers according to WAXD profiles, the density of monoclinic unit cell, 936 kg/m^3, were used as ρ_c for P-rich copolymers and that of the orthorhombic unit cell, 1000 kg/m^3, were used for E-rich copolymers. The value of ρ_a was taken to be 854 kg/m^3, which is the density of an amorphous ethylene–propylene random copolymer [14].

WAXD measurements were performed at room temperature using a Mac Science MXP18 X-ray diffractmeter. The

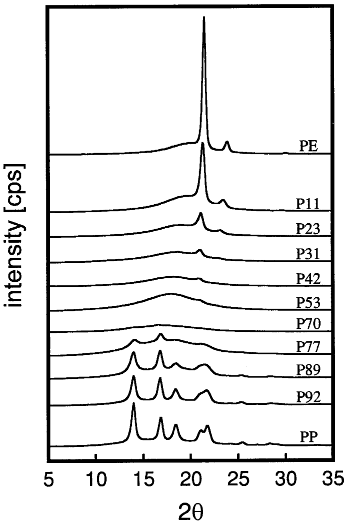

Fig. 1. X-ray diffraction patterns of PP, PE and their random copolymers.

experiments were carried out using CuKα radiation operating at 40 kV and 150 mV at a scanning rate 2°/min over 2θ range from 5 to 35°.

Dynamic mechanical properties were investigated using a dynamic mechanical analyzer (Rheology Co., Ltd. DVEV-4) on sample specimens of the following dimensions: the length of 20 mm, the width of 3 mm and the thickness of about 300 μm. The temperature dependencies of the storage modulus E' and loss modulus E'' were measured between 208 and 448 K at a constant frequency of 10 Hz and heating rate of 2 K/min. The activation energies (ΔH) were calculated from the frequency dependence of the E'' peak in the temperature range from 203 to 303 K.

The uniaxial tensile behavior was investigated using a Shimadzu AGS-5 kN. The sample specimens were cut with a dumbbell shape in which the gauge length is 10 mm. The tensile strain was calculated from the ratio of the increment of the length between clamps to the initial gauge length. The tensile stress was determined by dividing the tensile load by the initial cross section. The strain–stress curves at 298 K were measured at a constant cross-head speed of 20 mm/min. The tensile strain was calculated from the ratio of the length between clamps to the initial gauge length.

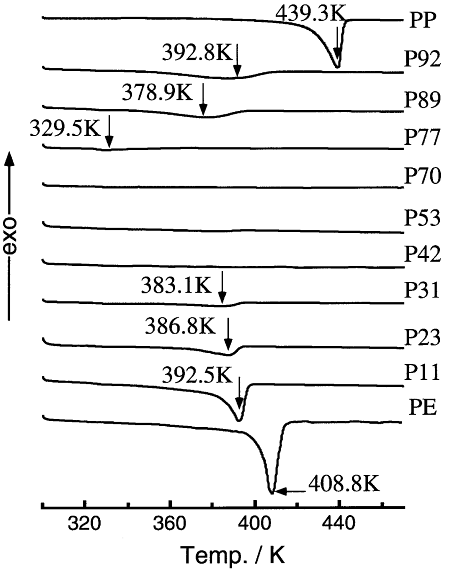

Fig. 2. DSC curves of PP, PE and their random copolymers.

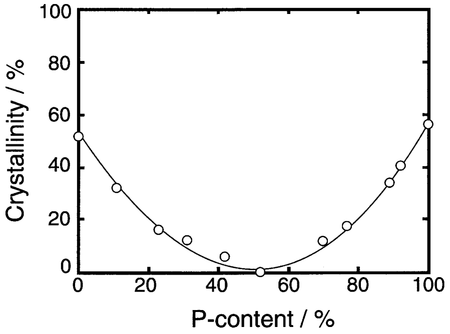

Fig. 3. The propylene content dependence of the degree of crystallinity in volume fraction.

3. Results and discussion

The molecular weight distribution of copolymers and homopolymers produced with the present catalyst system was quite narrower than that of typical polyolefins produced by heterogeneous Ziegler–Natta catalysts. It should be noted here that reactivity ratios of these copolymers except for P92 and P11 were around unity as seen in Table 1, indicating that these copolymers are completely random copolymers. Since P92 and P11 copolymers have no ethylene and propylene sequences, respectively, according to ^{13}C-NMR spectra, the values of r_P and r_E are listed for P92 and P11, respectively, in Table 1.

As shown in Fig. 1, WAXD patterns on these random copolymers demonstrated that ethylene-rich (E-rich) copolymers show the orthorhombic form of PE whilst propylene-rich (P-rich) copolymers show the monoclinic form of PP. It was found that both the crystals do not coexist but the peak intensities decrease with increasing P-content in E-rich copolymers and with increasing E-content in P-rich copolymers.

The DSC curves of these samples are presented in Fig. 2. These copolymers have one endothermic melting peak, attributable to the melting of PP crystal in the P-rich copolymers and that of PE crystal in the E-rich copolymers according to WAXD profile. The increase of ethylene-content (E-content) in P-rich copolymers weakened the melting peak of PP and markedly shifted to lower temperatures, indicating drastically thinning of PP crystal lamellae. In the middle component of PP and PE polymers, the melting peak disappeared, suggesting that the middle component

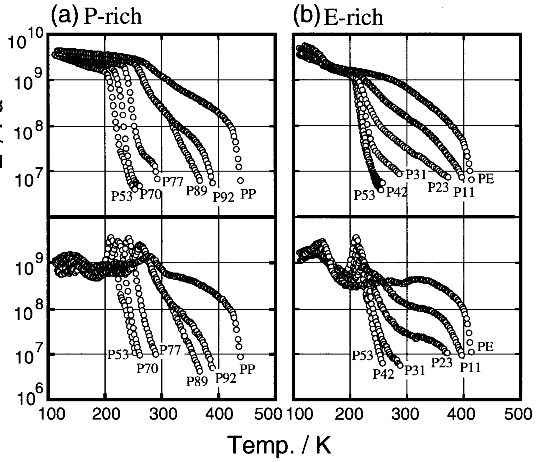

Fig. 4. Dynamic mechanical properties for (a) P-rich copolymers and PP and (b) E-rich copolymers and PE.

copolymers are amorphous as is also indicated from the WAXD data. This is due to the fact that the sequence of PP or PE is impeded by numerous propylene–ethylene connections. Furthermore, as the E-content increases, the melting peak corresponding to PE developed and shifted toward to the melting temperature of pure PE.

As shown in Fig. 3, the χ_v versus P-content curve was symmetric and showed a minimum at around 50 mol% of P-content. This behavior is in conformity with the presence of PP or PE crystallites on WAXD diffraction spectra and melting points on DSC curves.

Fig. 4 shows the overall dynamic mechanical behaviors of these copolymers. In these mechanical spectra, there are three relaxation processes assigned as α, β, and γ in the order of decreasing temperature. The α-process, which is ascribed to the relaxation process of crystals, reduces with increasing E-content in P-rich copolymers and with increasing P-content in E-rich copolymers. The α-process depends strongly on the crystallizability. The variations of loss modulus E'' at the β and γ relaxation processes with composition of the copolymers are shown in Figs. 5 and 6. In the P-rich copolymers, as the E-content increases, the temperature of the β-process shifted from the glass transition (T_g) of PP to the T_g of a completely amorphous PE with many short chain branches [14,15]. The P-rich copolymers form PP crystals so that the polymer chains in the amorphous phase may be E-rich chains. This means that the amorphous chains are considered as linear low-density PE (LLDPE) chains so that the P-rich copolymer is essentially different from semicrystalline PP materials. These data suggest a potential application of the copolymers as a high-impact type of PP materials. On the other hands, in the E-rich copolymers the β-process shifted from T_g of amorphous PE to the β-relaxation temperature of typical LLDPE with increasing E-content. Finally, the β-process disappeared in the pure PE with no P-content, which is the consistence with typical mechanical spectra of high-density PE (HDPE) materials. The γ-process developed with increasing E-content, demonstrating that the γ-process is attributed to the segmental motion of ethylene sequence. It should be noted here that homo-PP has no γ peak and HDPE has no β peak.

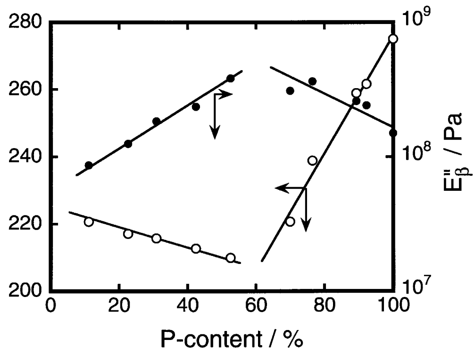

Fig. 5. The composition dependence of E'' and temperature at the β relaxation process.

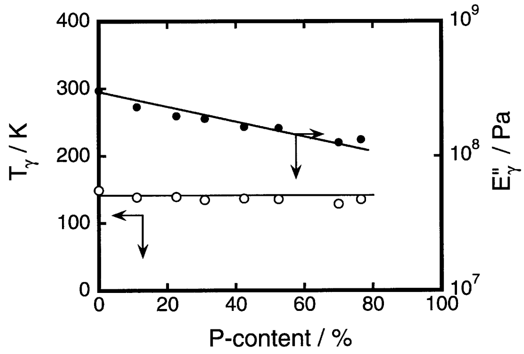

Fig. 6. The composition dependence of E'' and temperature at the γ relaxation process.

In Fig. 7, the composition dependence of the activation energy for the β-process was shown. It is very interesting to note that the value of ΔH_β is drastically changed at around 50% of P-content, suggesting that the molecular mobility in the amorphous region of E-rich copolymers is much greater than that of P-rich copolymers. Considering that the chains in the amorphous phase of P-rich copolymers become E-rich chains, the crystallizability of E-sequence in the amorphous chains may lead to the reduction of molecular motion. When

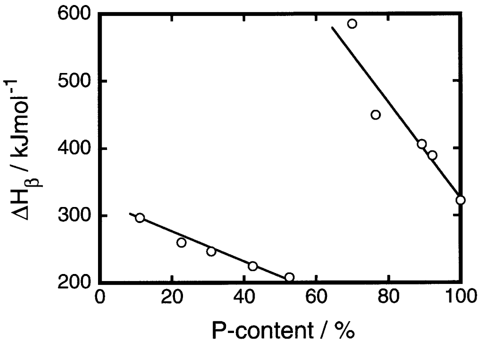

Fig. 7. The composition dependence of the activation energy of β-process.

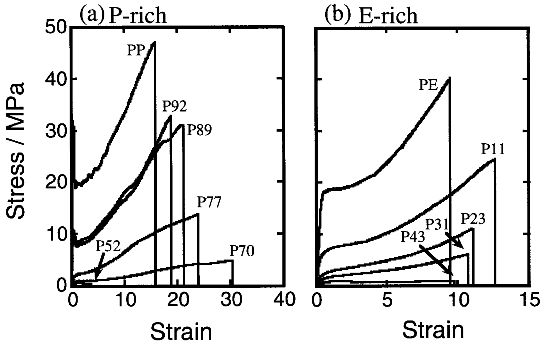

Fig. 8. Stress–strain curves for (a) P-rich copolymers and PP and (b) E-rich copolymers and PE.

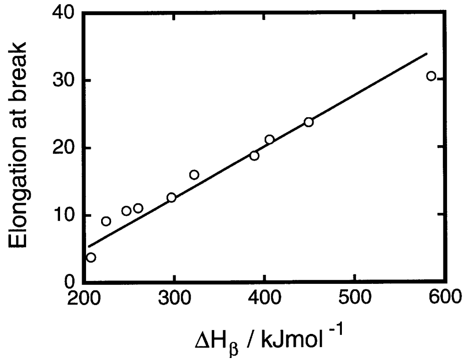

Fig. 9. Plot of the elongation at break versus the activation energy of β-process.

P-rich copolymers change into E-rich copolymers, the polymers in amorphous phases are transformed from LLDPE with many methyl branches to random block PP with many ethylene mers. As a result, the transformation is possibly responsible for the drastic changes in ΔH_β at around 50 mol%.

The shape of the stress–strain curve of PP is much different from that of PE, in such a way that PP shows a single yield peak while PE shows a broad yielding peak as shown in Fig. 8. The shapes of the yield peak of P-rich copolymers and of E-rich copolymers are similar to those of homopolymers of PP and PE, respectively. This is likely because the yield process is accompanied by the fragmentation of crystalline lamellae, which are composed of PP crystal for P-rich copolymers and of PE crystal for E-rich ones. In addition, the overall stress or the yield stress increased with increasing P-content in P-rich copolymers and with decreasing P-content in E-rich copolymers. The ultimate strength of these materials showed a minimum at around 50 mol% of P (or E) content. These results indicate that the crystallizability governs the mechanical strength and stress. Fig. 9 shows the plot of the elongation at break versus activation energy ΔH_β. All the data falls on the straight line, suggesting that the mobility in amorphous chains plays a central role in drawability.

4. Summary

A series of ethylene–propylene random copolymers with isotactic sequence of PP over the wide range of the composition was synthesized with $Cr(acac)_3/MgCl_2$ catalyst system. DSC and WAXD results demonstrate that the P-rich copolymers form PP crystal and E-rich ones form PE crystal, and there is no coexistence of PP and PE crystals in these copolymers. The crystallizability of these copolymers showed a minimum around 50 mol% content of propylene or ethylene. It was found that the overall stress level and the ultimate strength in the stress–strain behavior were governed by crystallizability while the ultimate elongation was associated with the activation energy of the mechanical relaxation in amorphous phase.

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