

# Synthesis and Characterization of Propylene- $\alpha$ -Olefin Random Copolymers with Isotactic Propylene Sequence. II. Propylene–Hexene-1 Random Copolymers

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**ABSTRACT:** A series of novel hexene-1–propylene random copolymers with isotactic sequence of propylene was synthesized with a MgCl<sub>2</sub>-supported Cr(acac)<sub>3</sub> catalyst. The molecular weight distribution of copolymers and homopolymers was considerably narrower than that of typical polyolefins produced by heterogeneous Ziegler–Natta catalysts. The crystallizability of the copolymers having a propylene-unit content of more than 50 mol % drastically decreased with decreasing propylene-unit content, and the copolymers with a propylene content of less than 50 mol %

were completely amorphous. In the present novel type of random copolymers with crystallizable and noncrystallizable units, a single glass transition was observed between pure polypropylene and polyhexene-1, and a major component was found to govern the final morphology and the mechanical characteristics. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2949–2954, 2004

**Key words:** catalysts; block copolymers; poly(propylene) (PP); copolymerization; mechanical properties

## INTRODUCTION

The recent investigation of isotactic polypropylene (iPP)-based materials has concentrated on improving the mechanical properties of existing polymeric materials. A new type of copolymerization with various  $\alpha$ -olefin monomers is desirable for development of soft polyolefin materials. According to Soga et al.,<sup>1,2</sup> Cr(acac)<sub>3</sub> supported on MgCl<sub>2</sub> activated by diethylaluminum chloride (DEAC) promoted not only ethylene and propylene polymerizations but also PP-based copolymerizations, such as ethylene–propylene copolymerization. In particular, the addition of external donors such as ethylbenzoate (EB) made it possible to convert nonstereospecific sites into highly isospecific ones, which are 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. Consequently, the Cr(acac)<sub>3</sub> catalyst was found to produce copolymers having a narrow molecular weight distribution, around unity of monomer reactivity ratios ( $r_1r_2 \approx 1$ ), and a high stereospecificity in propylene sequence.

Previously, we synthesized a new type of ethylene–propylene (EP) random copolymers with iPP sequence

over a wide range of compositions using the Cr(acac)<sub>3</sub> catalyst.<sup>3</sup> The novel EP copolymers were found to have much different properties from those of commercially available EP copolymers because both components of the novel EP copolymer are crystallizable. As a result, the crystallinity of these copolymers showed a minimum around 50 mol % content of propylene or ethylene and the miscibility of iPP and EP copolymers could be modified by the content of the propylene unit.

Continuing this work, a series of novel hexene-1–propylene (HP) random copolymers with iPP sequence thus synthesized by the previous copolymerization techniques are characterized in this article. According to Yamaguchi et al.,<sup>4</sup> the ethylene–hexene-1 random copolymers with a high content of hexene-1 component were miscible with iPP chains in the amorphous region. Therefore, the resulting morphology and bulk properties of HP copolymers are expected to be much different from those of other PP-based copolymers such as ethylene–propylene rubbers.

## EXPERIMENTAL

### Materials

MgCl<sub>2</sub> [surface area measured by Brunauer–Emmett–Teller (BET) method = 80 m<sup>2</sup>/g] and Cr(acac)<sub>3</sub> were donated by Toho Titanium Co. (Japan) and Kanto Chemicals (Japan), respectively. DEAC, donated by

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TABLE I  
Results of Hexene-1/Propylene Copolymerization with Cr(acac)<sub>3</sub>-AlEt<sub>2</sub>Cl-EB Catalyst System<sup>a</sup>

Sample	Monomer (mol)		$T_m^b$ (K)	$T_g^c$ (K)	$T_g^c$ $T_\beta^c$ (K)	$M_w^d$ ( $\times 10^4$ )	$M_w/M_n^d$	P-Cont. <sup>e</sup> (mol %)	$r_P r_H$
	He	P							
iPP	—	0.312	439.3	—	283.1	18.0	2.6	100	—
HP93	0.08	0.223	409.7	—	275.7	22.3	2.5	93.2	—
HP87	0.08	0.134	392.6	—	270.6	23.6	2.5	87.3	—
HP77	0.08	0.076	382.2	118.7	263.6	24.1	2.3	77.2	1.04
HP69	0.08	0.045	374.5	120.5	257.7	24.1	2.6	68.9	1.03
HP53	0.08	0.040	—	120.6	253.9	25.6	2.6	53.4	1.05
HP45	0.08	0.036	—	120.7	248.7	24.7	2.7	44.9	1.09
HP36	0.08	0.029	—	118.4	248.3	24.1	2.5	35.9	1.04
HP21	0.08	0.022	—	120.7	247.7	23.5	2.1	21.0	1.00
HP15	0.08	0.013	—	119.0	245.9	26.4	2.8	14.5	—
PH	0.08	—	—	122.9	236.6	19.6	2.4	0	—

<sup>a</sup> Polymerization conditions: Cr(acac)<sub>3</sub> = 0.02 mmol, [Al]/[Cr] = 400, [EB]/[Cr] = 200, *n*-heptane = 30 cm<sup>3</sup>, in 100-cm<sup>3</sup> stainless autoclave. Ageing at 30 min and washing.

<sup>b</sup> Determined by DSC.

<sup>c</sup> Determined by DMA (100 Hz).

<sup>d</sup> Determined by GPC analysis at 140°C using polystyrene standards and ODCB as the eluant.

<sup>e</sup> Determined by <sup>13</sup>C-NMR.

Tosho Akzo Co. (Japan), was used without further purification. Ethylbenzoate (EB) and *n*-heptane, commercially obtained from Kanto Chemicals, were purified by refluxing CaH<sub>2</sub> over 24 h followed by distillation, and stored over molecular sieves under nitrogen. Propylene (commercial grade; Takachiho Chemical Co., Japan) was further purified through columns of NaOH and P<sub>2</sub>O<sub>5</sub>. Hexene-1 (purchased from Tokyo Chemical Industry, Japan) was refluxed and distilled over CaH<sub>2</sub>.

#### Polymerization and sample characterization

Hexene-1-propylene random copolymers, over a wide range of compositions, were synthesized with a catalyst system consisting of Cr(acac)<sub>3</sub>/MgCl<sub>2</sub>-DEAC-EB according to the literature.<sup>3</sup> Homopolymerization and copolymerization were conducted in a 100-cm<sup>3</sup> stainless-steel autoclave equipped with a magnetic stirrer. After the reactor was filled with nitrogen, appropriate amounts of EB (4 mmol), DEAC (8 mmol of Al), heptane (30 mL), and the supported Cr catalyst were 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 the two monomers, copolymers varying the P-unit content from 14.5 to 93.2 mol % were successfully synthesized. The polymers were quenched by adding a 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*-dichloroben-

zene solution, after which their purified homopolymers and copolymers were dried under vacuum at 60°C for 6 h.

The content of propylene and the reactivity ratios ( $r_P r_H$ ) in the copolymers were estimated by <sup>13</sup>C-NMR analysis according to the literature.<sup>5</sup> <sup>13</sup>C-NMR spectra of the samples were recorded at 140°C using a Varian Gemini 300 spectrometer (Varian Associates, Palo Alto, CA) operating at 75 MHz. The polymers were dissolved in 1,2,4-trichlorobenzene/benzene-*d*<sup>6</sup> (vol. ratio = 9/1) up to 10 wt %. Sample codes for HP copolymers used in this study are as follows: for example, HP53 is hexene-1-propylene copolymer containing 53.4 mol % propylene.

The weight-average molecular weight  $M_w$  and polydispersity  $M_w/M_n$  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 weight distributions of copolymers and homopolymers produced with the present catalyst system were considerably narrower than those of typical polyolefins produced by heterogeneous Ziegler-Natta catalysts. It should be noted here that the reactivity ratios of these copolymers (except for HP93, HP87, and HP15, which had much higher contents of propylene or hexene-1 unit) were around unity, as seen in Table I, indicating that these copolymers were completely random copolymers. Because HP93 and HP87 copolymers have no hexene-1 sequence and HP15 copolymer has no propylene sequence, the values of  $r_P r_H$  for HP93, HP89, and HP15 are not listed in Table I.

## Measurements

Differential scanning calorimetry (DSC) measurements were carried out using a Mettler DSC 820 (Mettler Instruments, Greifensee, Switzerland) to examine the melting behavior. The 10 mg samples, cut from the sheets and sealed in aluminum pans, were heated from room temperature to 473 K at a scanning rate of 20 K/min under nitrogen atmosphere.

Densities of the sheets were determined by a flotation 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:

$$\chi_v = \frac{\rho - \rho_a}{\rho - \rho_c} \quad (1)$$

where  $\chi_v$  is the degree of crystallinity in volume fraction,  $\rho$  is the density of the sample,  $\rho_a$  is the density of the amorphous region, and  $\rho_c$  is the density of the crystal.<sup>6,7</sup> The density of monoclinic unit cell, 936 kg/m<sup>3</sup>, was used as  $\rho_c$  for P-rich copolymers. The value of  $\rho_a$  was taken to be 854 kg/m<sup>3</sup> of polyhexene-1, which coincides with the density of an amorphous PP.

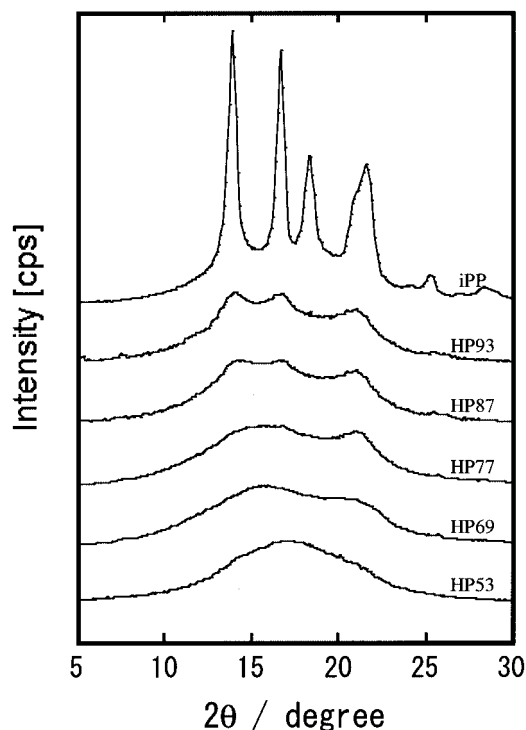
Dynamic mechanical properties were investigated using a dynamic mechanical analyzer DVE-V4 (Rheology Co. Ltd., Kyoto, Japan) on sample specimens of the following dimensions: 20 × 3 × about 300 μm (length × width × thickness). The temperature dependency of the storage modulus  $E'$  and loss modulus  $E''$  were measured between 208 and 448 K at a constant frequency of 10 Hz and heating rate of 2 K/min.

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Mac Science MXP18 X-ray diffractometer. The experiments were carried out using Cu-K $\alpha$  radiation operating at 40 kV and 150 mV at a scanning rate of 2°/min over  $2\theta$  range from 5 to 35°.

The uniaxial tensile behavior was investigated using a Shimadzu AGS-5kN (Shimadzu, Kyoto, Japan). The sample specimens were cut into dumbbell shapes in which the gauge length was 10 mm. The stress-strain curves at 298 K were measured at a constant crosshead speed of 20 mm/min.

## RESULTS AND DISCUSSION

Figure 1 shows the WAXD profiles of iPP and propylene-rich (P-rich) copolymers containing P-unit contents of more than 50 mol %. The iPP homopolymer (homo-PP) displays the well-known monoclinic  $\alpha$ -phase because there are no peaks at  $2\theta = 16.1$  associated with the  $\beta$ -form (hexagonal) and at  $2\theta = 20.1$  associated with the  $\gamma$ -form (triclinic).<sup>8,9</sup> A broadening of the characteristic X-ray peaks with decreasing P-unit content is observed, resulting from a decrease in



**Figure 1** X-ray diffraction patterns of iPP and P-rich random copolymers.

size and perfection of crystalline morphology. The pure polyhexene-1 (PH) and hexene-1-rich (H-rich) copolymers with hexene-1 unit (H-unit) contents of more than 50 mol % have no crystalline peak, suggesting that these samples thus prepared here are amorphous.

Figure 2 shows the DSC curves for the homo-PP and the H-rich copolymers. The copolymers demonstrated that the P-rich copolymers have a single endothermic peak, which can be attributable to the melting of PP crystal according to the WAXD profile. As the P-unit content decreases, the melting temperature and the enthalpy of crystallization decrease to a considerably low value, indicating the severe thinning of PP crystalline lamellae. When the concentration of P-unit content is less than about 50 mol %, no crystallization peaks were detected. Indeed, random introduction of the  $\alpha$ -olefin comonomer into the iPP chain effectively disrupts the crystalline structure of iPP because the uncrystallizable unit will impart defects to the crystallizing chains, creating obstacles for the crystalline organization. This effect becomes more intense with an increase in the H-unit content for these random copolymers.

As shown in Figure 3, the crystallinity  $\chi_v$  of copolymers monotonically decreased with decreasing the P-unit content and became zero at less than around 50 mol % of the P-unit content. This behavior is in conformity with the presence of PP crystals on WAXD

diffraction spectra and the melting point on DSC curves. It is evident that the introduction of the non-crystallizing counts into the crystallizable chain leads to a very rapid and continuing decrease in crystallinity. It is interesting to note that the crystallizability of the copolymers disappears to the extent that the content of the noncrystallizable unit is just greater than that of the crystallizable unit.

The mechanical relaxation spectra at 100 Hz of iPP, PH, and their copolymers are shown in the form of storage modulus and loss modulus in Figure 4. In these dynamic mechanical spectra, there are three relaxation processes, assigned as  $\alpha$ ,  $\beta$ , and  $\gamma$ , in order of decreasing temperature. The  $\alpha$ -process, ascribed to the relaxation of the crystalline phase, decreased with an increase in the H-content in P-rich copolymers, and disappeared in the H-rich copolymers of more than 50 mol % hexane, reflecting the absence of iPP crystals. The  $\beta$ - and  $\gamma$ -relaxations of homo-PP and P-rich copolymers are observed in the temperature range from 250 to 300 K and narrow temperature range from 120 to 150 K, respectively. The  $\beta$ -relaxation is ascribed to the glass-transition temperature ( $T_g$ ) for these PP-based materials. The  $\gamma$ -relaxation is attributed to the localized molecular relaxation such as minute vibration of branch parts and chain segments.

The  $\beta$ -relaxation was observed in all the samples but  $\gamma$ -relaxation was found to be absent only in pure iPP. The dependencies of the P-unit content on the  $\beta$ -

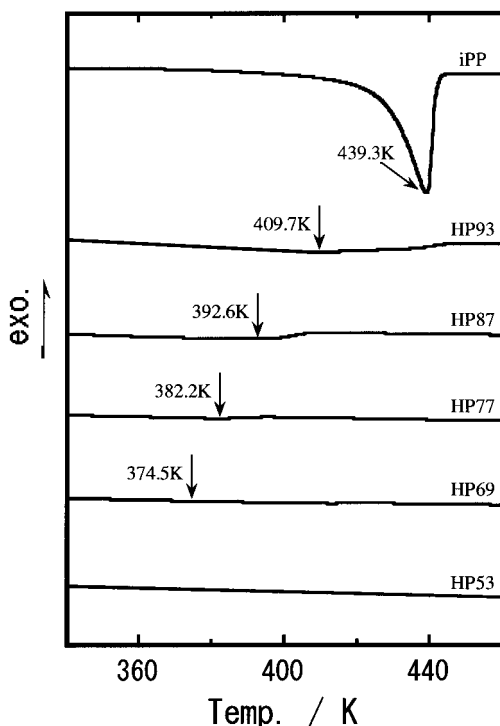


Figure 2 DSC curves of iPP and P-rich random copolymers.

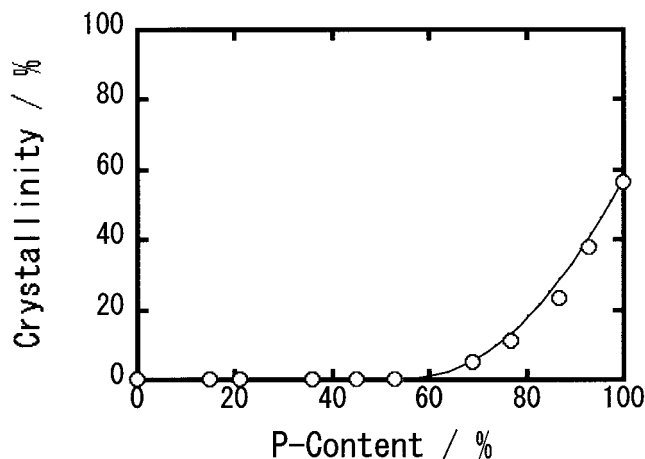


Figure 3 Propylene content dependency of the degree of crystallinity in volume fraction.

and  $\gamma$ -relaxations of the copolymers are plotted in Figures 5 and 6, respectively. As the P-unit content increases, the temperature of the  $\beta$ -relaxation linearly increases for all the copolymers. This result implies that the glass relaxation process of the copolymers occurs cooperatively. The P-unit content dependency of the  $E''$  values of  $\beta$ -relaxation is different between P-rich and H-rich copolymers. The magnitude of  $E''$  increases with decreasing P-unit content for P-rich copolymers, whereas the  $E''$  value of the H-rich copolymers are almost the same as that of homo-PH, being independent of the P-unit content. The increase of the amorphous fraction with a decrease in the P-unit content intensifies the  $\beta$ -relaxation peak and lowers the  $T_{\beta'}$ , reflecting the enhancement of molecular mobility. On the other hand, because the H-rich copolymers are completely amorphous, the intensity of  $E''$  at the temperature location of the  $\beta$ -process ( $T_g$  process) is independent of the P-unit content and remains the same at that of homo-PH.

As seen in Figure 4, the results that the  $\gamma$ -relaxation developed with increasing H-unit content led us to conclude that the  $\gamma$ -process is attributed to the localized molecular motion around the short-chain (butyl) breaches introduced by copolymerized hexene-1 monomer. In addition, considering that homo-PP has no  $\gamma$ -peak and homo-PH has no  $\alpha$ -peak, the H-unit in the P-rich copolymers effectively lowers the crystallizability of copolymers, whereas the P-unit in the H-rich copolymers affects the segmental mobility in the hexane-1 sequence. Thus, as expected, by these dynamic mechanical data, impact properties of iPP potentially can drastically change as a consequence of introducing the hexane-1 unit into the iPP main chain.

The stress-strain curves of iPP and P-rich copolymers at room temperature are shown in Figure 7. It should be noted here that it is impossible to obtain suitable specimens, using homo-PH and H-rich copol-

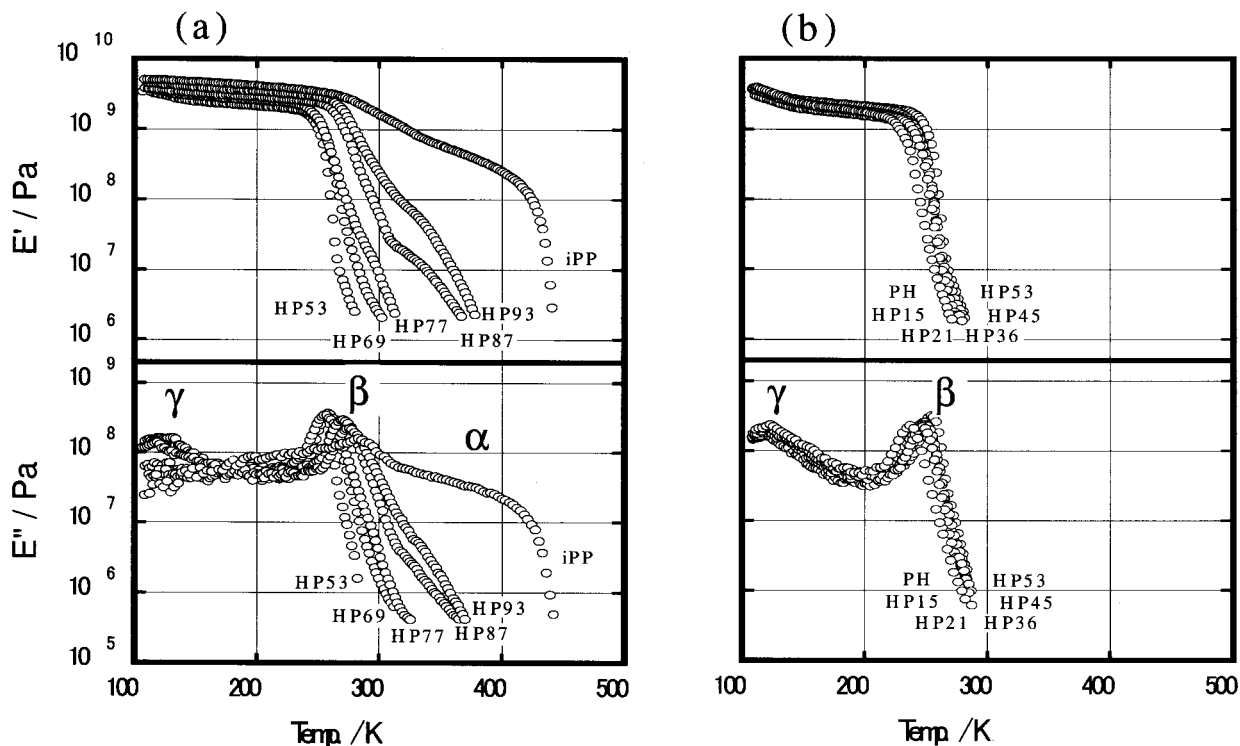


Figure 4 Dynamic mechanical spectra for (a) P-rich copolymers and iPP and (b) H-rich copolymers and PH.

ymers, to suit the intended experiment because of flow at room temperature. It was found that the Young's modulus and the yield stress decrease with decreasing P-unit content. Pure iPP showed a well-defined yield peak, followed by neck formation, and stress-whitening occurred at the strain around 0.3. The magnitude of a load drop at the yield point decreases with increasing the H-unit content and HP69 shows no load drop. The lamellar thinning by the copolymerization with hexane-1 reduces the mechanical energy required for fragmentation of lamellar crystals, leading to lowering and broadening of the yield peak.

CONCLUSIONS

In this work, we synthesized a new type of hexene-1-propylene (HP) random copolymers with isotactic PP sequence over a wide range of compositions using the Cr(acac)<sub>3</sub> catalyst. According to DSC and WAXD measurements, the crystalline thickness and crystallinity of the HP copolymers drastically decreased with increasing content of hexane-1 unit (H-unit) and the crystallizability of the HP copolymers disappeared as much to the extent that the content of noncrystallizable H-unit is just greater than that of crystallizable propylene unit (P-unit). The glass-transition tempera-

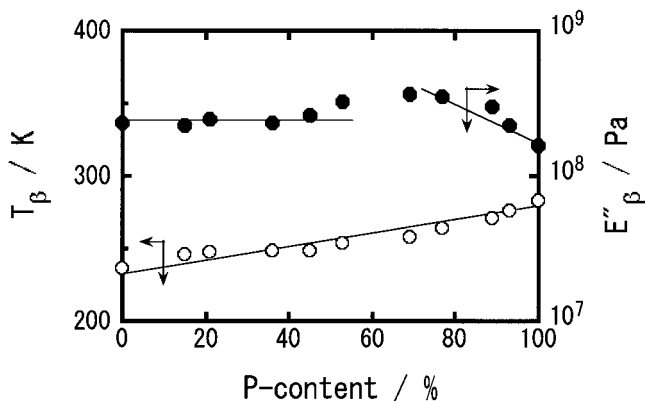


Figure 5 Composition dependency of  $E''$  and temperature at the  $\beta$ -relaxation process.

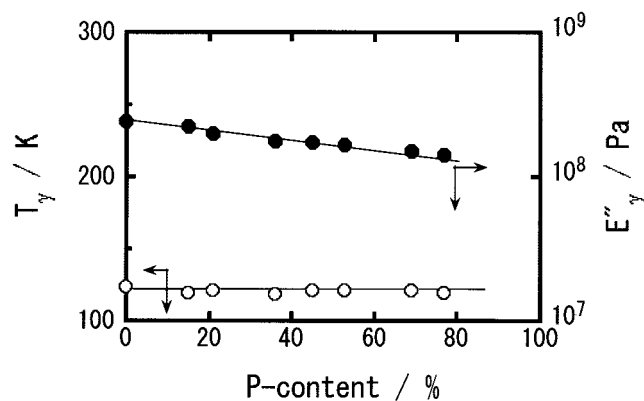


Figure 6 Composition dependency of  $E''$  and temperature at the  $\gamma$ -relaxation process.

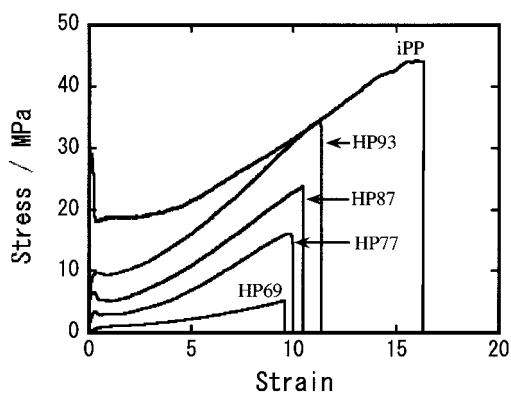


Figure 7 Stress-strain curves of iPP and P-rich copolymers.

ture of these HP copolymers monotonously decreased to  $T_g$  of pure polyhexene-1 by the introduction of the H-unit, indicating that the H-unit and P-unit are cooperatively relaxed in the amorphous region of the HP copolymers. The Young's modulus and the yield stress of these HP copolymers decreased with increasing H-unit content, reflecting their morphological features.

The novel HP copolymers were found to have much different properties from those of commercially available polyolefinic copolymers such as ethylene-propylene rubbers (i.e., EPR and EPDM). This is because

the isotacticity of PP units in the novel copolymers is very high and the hexane-1 copolymer chains exist in the amorphous phase between the PP crystalline lamellae. Thus, the present HP copolymers offer the possibility of constituting a new type of PP-based soft materials; moreover, the addition of HP copolymers to isotactic PP is expected to be a powerful tool for the modification of mechanical properties of isotactic PP and to make it possible to produce a new type of iPP-based thermoplastics, which will be the subject of a future study.

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