A study of the structure and crystallinity of 4-methyl-1-pentene copolymers with 1,5-hexadiene by ^{13}C nuclear magnetic resonance and X-ray diffraction methods

Akira Mizuno*†, Jun-ichi Yoshitake‡, Takeshi Muranaka†, Hiroaki Kitani‡ and Norio Kashiwa‡
† Materials Science and Analysis Laboratories, and ‡ Iwakuni Polymer Research Laboratories, Mitsui Petrochemical Industries Ltd, Waki-cho, Kuga-gun, Yamaguchi-ken 740, Japan
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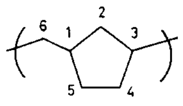
The structures of two 4-methyl-1-pentene copolymers with 1,5-hexadiene prepared with a Ziegler catalyst system have been studied by ^{13}C nuclear magnetic resonance spectroscopy. The copolymers have been found to have two repeat units, i.e. 4-methyl-1-pentene (A) and 1-methylene-3-cyclopentyl (B) units. The introduction of the rigid cyclic unit into the 4-methyl-1-pentene sequences brings about significant changes in the structure and properties. The resulting two copolymers, which are composed of A and B units in the ratios 83/17 and 57/43, form ordered molecular aggregates in the amorphous states as confirmed by X-ray diffraction patterns. This result is in contrast to the well known fact that 4-methyl-1-pentene copolymer with 20 mol% of 1-hexene has a crystallinity of about 50%.

(Keywords: ^{13}C nuclear magnetic resonance; X-ray diffraction; copolymer; 4-methyl-1-pentene; 1,5-hexadiene; structure; amorphous state)

INTRODUCTION

Poly(4-methyl-1-pentene) prepared with a Ziegler catalyst system has a predominantly isotactic structure, which forms a 7_2 helix conformation in the crystal structure[1,2], and shows a high heat resistance. On the other hand, the polymerization of 1,5-hexadiene catalysed by a Ziegler system produces a polymer composed of 1-methylene-3-cyclopentyl units with both *cis* and *trans* placements present in the ratio of 54/46[3]:



1-methylene-3-cyclopentyl unit

Therefore, the copolymerization of 4-methyl-1-pentene with a small amount of 1,5-hexadiene may produce an amorphous or less crystalline polymer because the formation of a 7_2 helix conformation consisting of 4-methyl-1-pentene repeat units is expected to be effectively interrupted by the rigid 1-methylene-3-cyclopentyl units derived from 1,5-hexadiene. This copolymerization technique may open a new route for controlling the crystallinity of poly(4-methyl-1-pentene).

From this expectation, we have prepared copolymers of 4-methyl-1-pentene with 1,5-hexadiene in the present study, and investigated their structure and crystallinity with the aid of high-field ^{13}C n.m.r. and X-ray diffraction methods.

EXPERIMENTAL

Polymerization

Into a 500 ml autoclave were added 240 ml (run no. 1) or 220 ml (run no. 2) of 4-methyl-1-pentene, 10 ml (run no. 1) or 30 ml (run no. 2) of 1,5-hexadiene, 0.5 mmol of triethylaluminium, 0.5 mmol of trimethylmethoxysilane, 0.005 mmol of titanium catalyst component in terms of titanium atom and 500 ml of H_2, and then the polymerization was carried out at 50°C for 30 min. The amount of monomer in the feed was kept at more than 20 times as much as that of consumption by polymerization to hold the monomer composition constant throughout a run. The polymerization was then terminated by addition of methanol, and the whole amount of polymer was precipitated in a large amount of methanol and separated by filtration, followed by drying.

Poly(1,5-hexadiene) and poly(4-methyl-1-pentene), which were used as standard polymers for the n.m.r. structural analysis of the copolymers, were also prepared with the same catalyst system.

N.m.r. analysis

The ^{13}C n.m.r. sample was prepared by dissolving ~50 mg of the polymer at 120°C in ~0.5 ml of hexachlorobutadiene, including ~0.05 ml of deuteriobenzene, which was used for field stabilization, in a 5 mm o.d. glass tube. The ^{13}C (^{1}H) n.m.r. spectra were recorded on a JEOL GX-500 spectrometer operating at 125.8 MHz in Fourier-transform mode. Instrumental

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* To whom correspondence should be addressed

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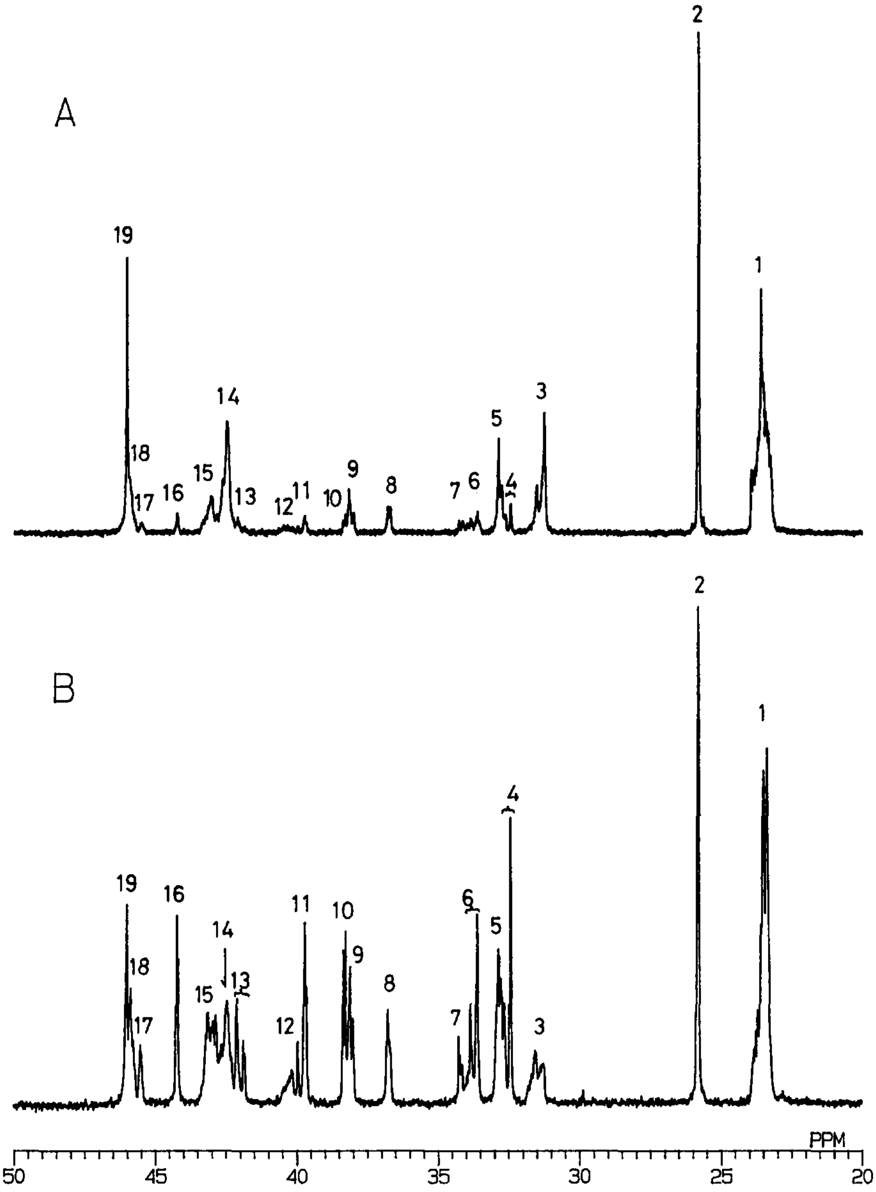


Figure 1 ^{13}C n.m.r. spectra of 4-methyl-1-pentene copolymers with 1,5-hexadiene: (A) run no. 1; (B) run no. 2

conditions were as follows: pulse angle, 45°; pulse repetition time, 5.0 s; spectral width, 18000 Hz; number of scans, 10000; data points, 64000. The ^{1}H decoupled d.e.p.t. (distortionless enhancement by polarization transfer) ^{13}C n.m.r. method was also used for the sample of run no. 2 to discriminate the types of carbon species.

The ^{1}H n.m.r. spectrum of the sample of run no. 2 was also measured in order to observe alkene proton resonances, because the corresponding alkene carbon resonances may be hidden under the solvent resonances of hexachlorobutadiene in the ^{13}C n.m.r. spectrum.

X-ray diffraction analysis

The 0.1 mm sheets of copolymer samples for X-ray diffraction measurements were made between heated plates in a moulding press at about 200°C. The X-ray pattern was measured by a Rigaku RU-300 X-ray diffractometer. Instrumental conditions were as follows: Cu target/point focus, 50 kV and 300 mA; divergence slit, 0.5°; receiving slit, 0.15 mm; scatter slit, 0.5°; goniometer speed, 2° min^{-1}; measurement angle, 5–35°.

RESULTS AND DISCUSSION

N.m.r. analysis of copolymers

The ^{13}C n.m.r. spectra of two copolymer samples are shown in *Figure 1*. Carbon species of each peak were determined by d.e.p.t. measurement. The alkene carbon resonances were found to be unnecessary to take into account because no alkene proton resonances with notable intensity were observed in the proton n.m.r. spectrum (not shown).

The ^{13}C n.m.r. spectra of the copolymers were analysed on the assumption that each copolymer is composed of two repeat units, i.e. 4-methyl-1-pentene (A) and 1-methylene-3-cyclopentyl (B) units. In the analysis of the n.m.r. spectrum, in the first place, attention was focused on the peaks resonating in the range between 31 and 34.5 ppm. Since the peaks resonating at 31.2–31.9 ppm, 32.7–33.2 ppm and 34.1–34.4 ppm are assigned to methine peaks by d.e.p.t. measurement, these peaks are attributed to the methine groups belonging to the main chain of 4-methyl-1-pentene unit with reference

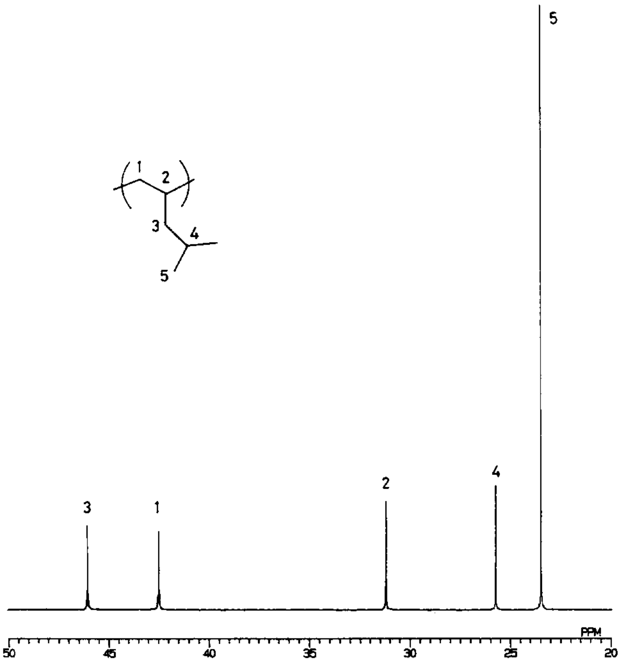
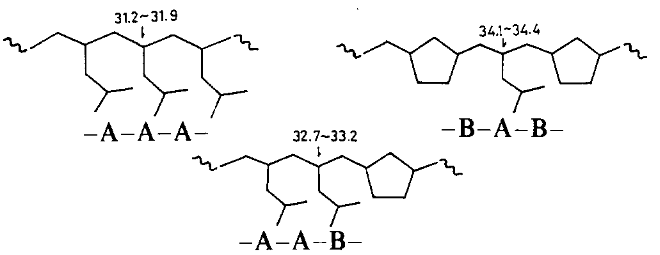


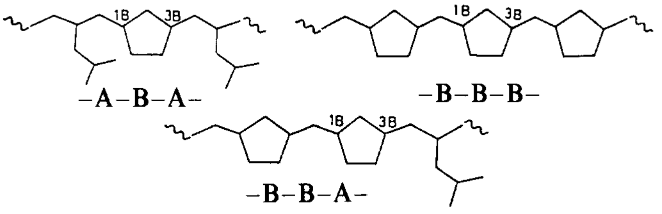
Figure 2 ^{13}C n.m.r. spectrum of poly(4-methyl-1-pentene). The peak assignments were cited from ref. 8

to the spectral data of poly(4-methyl-1-pentene) in *Figure 2*. The appearance of peaks in the three regions in the spectrum might reflect the difference in the sequential distributions shown below:



From the ^{13}C chemical shifts of methine peaks, it is estimated that the substitution of 4-methyl-1-pentene unit to 1-methylene-3-cyclopentyl unit induces a chemical shift change (about 1.5 ppm) on the main-chain methine peak of the neighbouring 4-methyl-1-pentene unit.

Similarly, the peaks observed in the range of 36.5–39.9 ppm were assigned to 1B and 3B carbon resonances of 1-methylene-3-cyclopentyl unit as follows, on the basis of the results of spectral analysis of poly(1,5-hexadiene)^3 in *Figure 3* and the substitution effect as mentioned above:



	Chemical shift
1B,3B(-A-B-A-), 3B(-B-B-A-) = 1B(-A-B-B-)	36.6–37.0 ppm (*trans*) 37.9–38.2 ppm (*cis*)
1B(-B-B-A-) = 3B(-A-B-B-), 1B,3B(-B-B-B-)	38.2–38.5 ppm (*trans*) 39.6–39.9 ppm (*cis*)

Here, the chemical shift change induced by the substitution is also estimated to be about 1.5 ppm. The other peaks are likewise assigned with the aid of d.e.p.t. data and the peak intensity changes accompanied by the comonomer contents shown in *Figure 1*. The results of all the peak assignments are summarized in *Table 1*.

From the peak assignments shown in *Table 1*, the content of 4-methyl-1-pentene unit (A) of each copolymer is determined by:

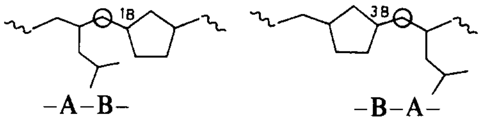
$$[A] = \frac{I_{17}+I_{18}+I_{19}}{(I_8+I_9+I_{10}+I_{11})2+I_{17}+I_{18}+I_{19}} = (I_{17}+I_{18}+I_{19})/S \qquad (1)$$

where I_{17} is, for instance, the area of peak 17 in *Figure 1* and S represents $(I_8+I_9+I_{10}+I_{11})/2+I_{17}+I_{18}+I_{19}$.

Next, the contents of the dyad comonomer sequences such as AA, AB and BB are estimated in the following way. The content [AA] of AA sequence is simply given by:

$$[AA] = [AAA] + [AAB]/2 = (I_3 + I_5/2)/S \qquad (2)$$

The dyad sequence of AB is expressed by the circled carbon atom in the structures below:



As each circled carbon atom is bonded with either a 1B or 3B carbon atom of the five-membered ring, regardless of *cis* or *trans* placement, the content [AB] is given by*:

$$[AB] = (I_8 + I_9)/S \qquad (3)$$

Similarly, the dyad sequence of BB is represented by the bridge carbons between the five-membered rings. However, in this case, the bridge carbon is bonded with

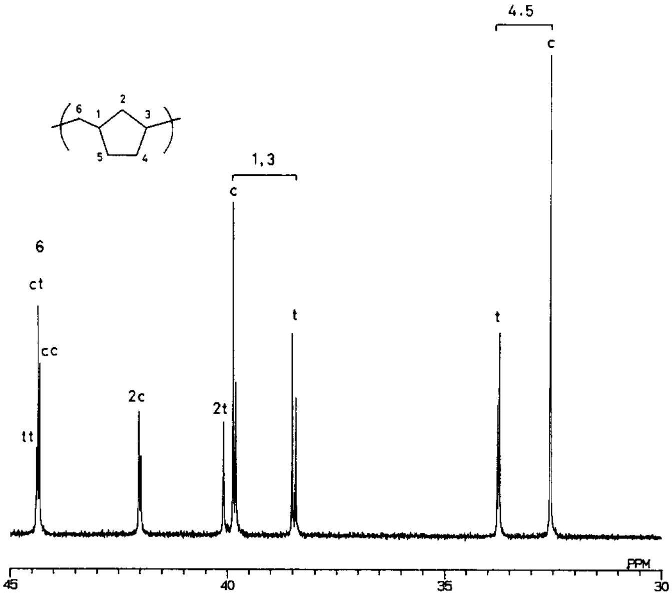


Figure 3 ^{13}C n.m.r. spectrum of poly(1,5-hexadiene). The peak assignments were cited from ref. 3

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* The peak areas of I_9 and I_{10} were separated in this work by a vertical line drawn from the valley between peaks 9 and 10 to the baseline

both 1B and 3B irrespective of *cis* or *trans* placement. Therefore, the content [BB] is expressed by*:

$$[\mathrm{BB}] = (I_{10} + I_{11})/2S \qquad (4)$$

From the dyad distribution determined, the monomer reactivity ratio product is calculated by the following equation:

$$r_1 \times r_2 = [\mathrm{AA}]\{[\mathrm{BB}]/([\mathrm{AB}]/2)^2\} \qquad (5)$$

on the assumption that the statistical stationary condition is satisfied and the copolymerization reaction proceeds according to first-order Markovian statistics. Moreover, r_1 and r_2 are given by the following equations[4,5] as a function of the monomer feed composition X and the probability parameters P_{12} and P_{21}:

$$r_1 = (1 - P_{12})/P_{12}X \qquad (6)$$

$$r_2 = (1 - P_{21})X/P_{21} \qquad (7)$$

where subscripts 1 and 2 designate 4-methyl-1-pentene and 1,5-hexadiene, respectively, X = (feed 4-methyl-1-pentene)/(feed 1,5-hexadiene) and P_{mn} is the probability that a chain ending in m will add n-monomer. The probability parameters are estimated from the monomer and dyad compositions in the polymer as shown in the equations below:

$$P_{11} = [\mathrm{AA}]/[\mathrm{A}] = 1 - P_{12} \qquad (8)$$

$$P_{22} = [\mathrm{BB}]/[\mathrm{B}] = 1 - P_{21} \qquad (9)$$

In *Table 2* are summarized the monomer compositions, dyad distributions, monomer reactivity ratios r_1 and r_2 and their products for two copolymers of 4-methyl-1-pentene and 1,5-hexadiene. The products of r_1 and r_2 of copolymers of runs no. 1 and no. 2 are calculated to be 1.9 and 1.7, respectively, indicating that the 1-methylene-3-cyclopentyl unit is somewhat randomly distributed through the whole polymer chains. The contents [AAA], [AAB] and [BAB] of triad sequences, which are estimated from the areas of peaks 3, 5 and 7, are compared with the calculated values based on first-order Markovian and Bernoullian statistics in *Table 3*. The first-order Markovian statistics reproduces the observed values relatively well, compared with Bernoullian statistics. The small discrepancies between the observed values and the calculated ones by the first-order Markovian scheme, which are found especially in run no. 2, may reflect the presence of complex multiple active sites in the catalyst. Since 1,5-hexadiene is more reactive than 4-methyl-1-pentene from the viewpoint of monomer reactivity ratio, the formation of a long 4-methyl-1-pentene sequence is less probable in the polymerization, and the intervention of the rigid cyclic unit in the

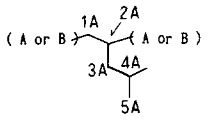
Table 1 ^{13}C chemical shifts of 4-methyl-1-pentene copolymer with 1,5-hexadiene

Peak no.[a]	Chemical shift (ppm)	Assignment[b,c] (triad sequence[b])
1	23.0–24.0	5A (AAA, AAB, BAB)
2	25.8	4A (AAA, AAB, BAB)
3	31.2–32.9	2A (AAA)
4	32.3–32.7	$4B_c$, $5B_c$ (ABA, ABB, BBB)
5	32.7–33.2	2A (AAB)
6	33.7–34.1	$4B_t$, $5B_t$ (ABA, ABB, BBB)
7	34.1–34.4	2A (BAB)
8	36.6–37.0	$1B_t$, $3B_t$ (ABA) $1B_t$ (ABB) = $3B_t$ (BBA)
9	37.9–38.2	$1B_c$, $3B_c$ (ABA) $1B_c$ (ABB) = $3B_c$ (BBA)
10	38.2–38.5	$1B_t$, $3B_t$ (BBB) $1B_t$ (BBA) = $3B_t$ (ABB)
11	39.6–39.9	$1B_c$, $3B_c$ (BBB) $1B_c$ (BBA) = $3B_c$ (ABB)
12	39.9–40.6	$2B_t$ (ABA, ABB, BBB)
13	41.7–42.2	$2B_c$ (ABA, ABB, BBB)
14	42.2–42.8	1A (AAA, AAB)
15	42.8–43.5	1A (BAA, BAB) = $6B_c$, $6B_t$ (ABA, ABB)
16	44.2	$6B_c$, $6B_t$ (BBB, BBA)
17	45.5	3A (BAB)
18	45.9	3A (AAB)
19	46.1	3A (AAA)

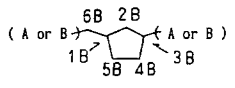
[a] The peak number is shown in *Figure 1*

[b] Numbering of carbon atoms is as follows:

4-methyl-1-pentene unit (A)



1-methylene-3-cyclopentyl unit (B)



[c] Subscripts *c* and *t* mean *cis* and *trans* placements of B unit, respectively

Table 2 Monomer composition, dyad distribution and r_1 and r_2 values for two 4-methyl-1-pentene copolymers with 1,5-hexadiene

Sample	[A]	[B]	[AA]	[AB]	[BB]	r_1	r_2	$r_1 \times r_2$
Run no. 1	0.83	0.17	0.71	0.25	0.04	0.25	7.4	1.9
Run no. 2	0.57	0.43	0.35	0.43	0.22	0.22	7.7	1.7

A: 4-methyl-1-pentene unit
B: 1-methylene-3-cyclopentyl unit

Table 3 Observed and calculated triad distributions

	[AAA]			[AAB]			[BAB]		
Sample	Obs.	Calc. 1	Calc. 2	Obs.	Calc. 1	Calc. 2	Obs	Calc. 1	Calc. 2
Run no. 1	0.61	0.60	0.58	0.19	0.21	0.23	0.03	0.02	0.02
Run no. 2	0.24	0.22	0.18	0.24	0.27	0.28	0.09	0.08	0.11

A: 4-methyl-1-pentene unit
B: 1-methylene-3-cyclopentyl unit
Calc. 1: first-order Markovian statistics
Calc. 2: Bernoullian statistics

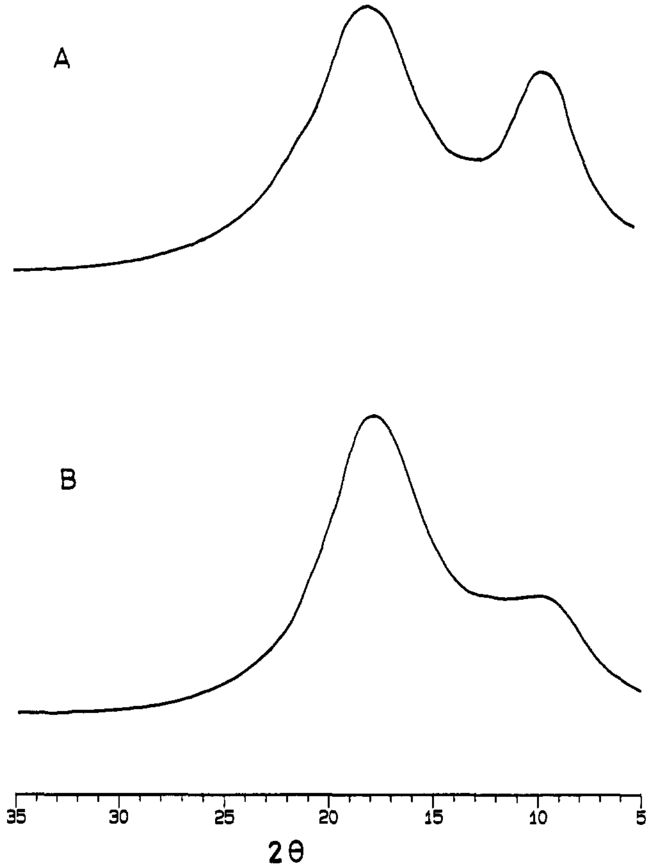


Figure 4 X-ray diffraction patterns of 4-methyl-1-pentene copolymers with 1,5-hexadiene: (A) run no. 1; (B) run no. 2

4-methyl-1-pentene sequences may effectively hinder the formation of a 7_2 helix conformation leading to the crystal. In order to check this idea, the crystallinity of two copolymers was measured by X-ray diffractometry as described in the following section.

X-ray diffraction analysis of copolymers

The X-ray diffraction patterns of both copolymers of runs no. 1 and no. 2 are shown in *Figure 4*. Both patterns exhibit two broad diffraction peaks at 2θ of 5–13° and 13–27°. By reference to the X-ray diffraction study on the structure of amorphous and molten states of poly(4-methyl-1-pentene) by Wilkes and Lehr[6], the 4-methyl-1-pentene sequences in the present copolymers are interpreted as forming ordered molecular aggregates in the non-crystalline states with looser packing than in the crystal phase in poly(4-methyl-1-pentene). On the other hand, a 4-methyl-1-pentene copolymer containing, for example, 20 mol% of 1-hexene unit shows a crystallinity of about 50% (ref. 7). From this comparison, it is clear that the rigid cyclic structure derived from 1,5-hexadiene effectively hinders the formation of the crystal structure consisting of the 4-methyl-1-pentene sequences.

The difference in the patterns of the two copolymers in *Figure 4* reflects the comonomer compositions, because the broad diffraction patterns[6] of 4-methyl-1-pentene unit appear at 5–13° and 13–27° while the pattern of 1-methylene-3-cyclopentyl unit only appears at 13–27°.

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