

Cocrystallization and Crystalline Transformations in Copolymers of Butene-1 and Olefins

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The crystallization phenomena in olefin copolymers due to isomorphism of monomer units are discussed from the point of chain conformation. Copolymerizations of butene-1 and 4-methyl-1-pentene, 3-methyl-1-butene, styrene and propylene were carried out with stereospecific catalytic system. An interesting feature of the copolymers of butene-1 and 4-methyl-1-pentene or 3-methyl-1-butene is an ability to crystallize in type of the modification II of polybutene-1. It is reasonably assumed that the modification II which is usually less stable than I in butene-1 homopolymer is stabilized owing to incorporation of those comonomer units into the crystal lattice of the modification II. On the contrary, it is observed that styrene or propylene units in a copolymer promote the transformation from the Form II to I. These facts imply that cocrystalline copolymer can not be formed from copolymerization of butene-1 and styrene or propylene. It is likely to account for those facts by viewing the chain conformations in the crystals of each homopolymer.

Crystallizability and variations of lattice parameters in crystal phases are studied in copolymers of butene-1 and 4-methyl-1-pentene. It is found that this system is crystalline over the whole range of monomer composition, and its crystal lattice constant is changed in relation to the composition. The physical properties of those copolymers are discussed, correlating with their cocrystallization behavior.

INTRODUCTION

It is widely known that for mineral mixtures or organic low molecular weight substance mixtures as well *isomorphism* phenomena or solid solution formations occasionally are observed. These are not characteristic only of low molecular weight substance systems but similar phenomena have been recognized also for polymeric systems. It was reported, for example, by G. Natta¹⁾ that some parameters of crystal lattice for copolymers of styrene and ring-substituted styrene copolymerized with stereospecific catalysts, were varied continuously in accord with the comonomer ratio. It indicates that a kind of isomorphism occurred between styrene and ring-substituted styrene units both distributed randomly in a molecular chain of the copolymers. He refers also that such isomorphism phenomena in copolymers will occur in the following cases. The phenomena will take place if copolymerizing monomer units can be replaced each other isomorphously in a unit crystal cell of each homopolymer. In this case the crystal structures of each homopolymer must be analogous each other with almost equivalent fiber periods and only slightly different lattice constants.

As the other type of isomorphism there is sometimes observed an analogous phenomena for a copolymer system, even if homopolymers of each comonomer have different crystal structures. For such systems, the observed crystal structure

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is essentially characteristic of homopolymers of the major component monomer, although the crystal lattice is deformed slightly owing to incorporation of the minor comonomer units. This particular type of isomorphism is called *isodimorphism*. For an example, the crystal structures of homopolymers of styrene and *p*-fluorostyrene are little different each other, the former being in a threefold helical form and the later in a fourfold helical form. However, the copolymer system of these two monomers indicates crystallinity in the whole range of comonomer ratios, of which crystalline structure is essentially intrinsic of the major component. Threefold helical conformation for the copolymer of high styrene content and fourfold helical conformation for that of high *p*-fluorostyrene content are recognized.

This paper is concerned with cocrystallization phenomena as *isomorphism* or *isodimorphism* for butene-1 copolymer systems with 4-methyl-1-pentene, 3-methyl-1-butene, propylene and styrene. All comonomers studied here are olefins to give isotactic polymer respectively by homopolymerization. The chain conformations of molecules in crystalline forms for those homopolymers are more or less different each other, as well known those molecular chains are confined in helical or planar zig-zag form. Therefore, for cocrystallization of a copolymer system of two components the monomer units of the low content must be able to incorporate into the crystal lattice of the major component.

Since we are mainly concerned with the cocrystallization for copolymer systems of high butene-1 content, the crystalline structure of its homopolymer must be first considered. For isotactic polybutene-1 three kinds of crystalline modifications are known; the one is a crystalline structure with 3_1 helix (designated as modification I)²⁾, the second with 11_2 helix (designated as modification II), and the third with unknown conformation (designated as modification III). Mutual transformation of these crystalline modifications can easily be performed each other without much energy change.

The modification II whose crystal is assigned to tetragonal can be obtained by rapid quenching of the polymer melt into dry ice-methanol mixture. This modification is not stable at room temperature and naturally transformed to the modification I of hexagonal form³⁾ on standing for a long period of time or by drawing at room temperature. These facts may indicate that the modification II is stable only in a lower temperature range well below room temperature and the modification I is a stable form in a wide temperature range above the transition temperature from the modification II to I (below room temperature) up to the melting temperature of the modification I. The other type of crystalline form, modification III is obtained by crystallization from the solution⁴⁾, precipitating from the solution or evaporating its solvent by casting. The detailed form of this modification is not known at present but it is tentatively assigned to orthorhombic form. It is reported recently⁵⁾ that the modification III is converted to the other forms by annealing. It is converted to the modification I by slow heating, involving solid-solid transformation, but to the modification II through a melt state by rapid heating, involving a solid-liquid-solid transformation. In Table 1 and 2 the crystallographic parameters of these three modifications of polybutene-1 and other olefin homopolymers are summarized.

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Table 1. Crystallographic parameters of unit cell in the different modifications of polybutene-1.

	Modification I	Modification II	Modification III
Melting point	130-140°C	120-126°C	90-96
Unit cell	Hexagonal	Tetragonal	Orthorhombic
Helix	3 ₁	11 ₃	?
a	17.70 Å	14.98 Å	12.49 Å ?
b	17.70 Å	14.98 Å	8.96 Å ?
c	6.50 Å	20.87 Å	7.6 Å ?
Monomer units per turn	3	3.7	
Length parallel to c per monomer unit	2.17	1.90	
Transverse area per chain	67.36 Å ²	56.10 Å ²	

Table 2. Crystallographic parameters of unit cell in polyolefin crystals

Character	Poly(4-methyl-1-pentene)	Poly(3-methyl-1-butene)	Polypropylene	Polystyrene
Melting point	240 °C	300 °C	168 °C	235 °C
Unit cell	Tetragonal	Monoclinic	Monoclinic	Rhombohedral
a	18.60 Å	19.1 Å	6.65 Å	21.90 Å
b	18.60 Å	17.8 Å	20.96 Å	21.90 Å
c	13.86 Å	6.85 Å	6.50 Å	6.63 Å
	$\gamma=90^\circ$	$\gamma=116^\circ$	$\beta=99^\circ 20'$	$\gamma=120^\circ$
Monomer units per turn	7 ₂ =3.5	*	3 ₁ =3	3 ₁ =3
Length parallel to c per monomer unit	1.98		2.17	2.21
Transverse area per chain	86 Å ²		34.4 Å ²	139 Å ²

* The chain conformation of poly(3-methyl-1-butene) is defined as planer zigzag, according to R.L. Miller and L.E. Nielsen. (*J. Polymer Sci.*, 55, 643 (1961)).

Incorporation of foreign comonomers to the chain sequence of butene-1 by copolymerization must necessarily induce great change in crystallizability in the each crystalline form and in mutual transformations thereof. We have studied the cocrystallizability and the the crystalline structure and the mutual transformation of the the crystalline modifications of butene-1 copolymers with the above described olefins mainly by X-ray techniques. For these copolymer systems of butene-1, some cocrystallization phenomena as an *isodimorphism* have been confirmed. We,

therefore, wish to report the experimental results and discuss the *isodimorphism* phenomena in terms of molecular conformation of each component homopolymer.

EXPERIMENTAL

Copolymerization

The copolymerization was carried out with stereospecific catalytic system of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{TiCl}_3$ ($\approx 2.5/1$ molar ratio) in an autoclave of 500 ml. capacity under nitrogen atmosphere, using *n*-heptane as a diluent. The batch technique was so chosen as to give random copolymer. Butene-1 gas supplied from Showa Denko Co. was purified through molecular-sieves. After a mixture of *n*-heptane and catalysts was brought to a predetermined reaction temperature of 50°C , was added a monomer mixture, then the reaction was continued for 5 hours at the temperature. The reaction was ceased by injection of great amounts of *n*-propyl alcohol. The polymer was precipitated from the reaction mixture with a solution of methanol and hydrochloric acid during a day and the precipitated product was further purified by washing with methanol, and dried. The homopolymers of each comonomer were removed from the crude products by use of difference in solubility of each component for various solvents. The monomer composition ratio was determined by infrared spectra. As an example, in Fig. 1 is shown the curve for a copolymer of butene-1 and 4-methyl-1-pentene.

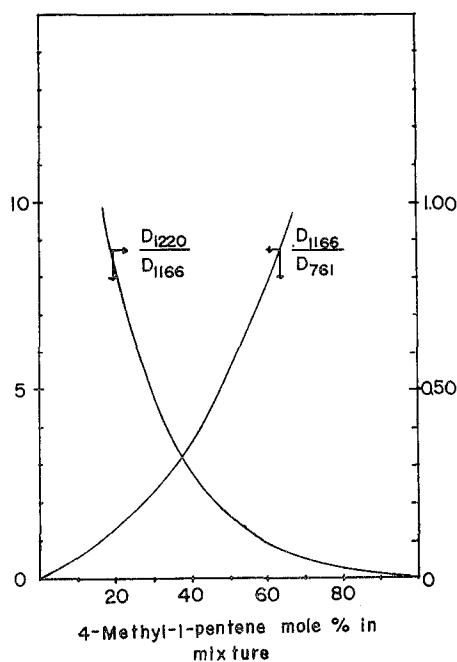


Fig. 1 Relation between 4-methyl-1-pentene content in polybutene-1-poly(4-methyl-1-pentene) mixture and D_{1220}/D_{1166} , D_{1166}/D_{761} in infrared spectra.

The copolymerization of butene-1 and propylene with $\text{Al}(\text{C}_2\text{H}_5)_3/\text{TiCl}_3$ catalytic system was reported by I. Hayashi and K. Ohno⁶⁾. It was confirmed that the both homopolymers of propylene and butene-1 were not contained in the crude products.

The copolymerization of butene-1 and styrene and the isolation of a true copolymer were already reported elsewhere⁷⁾.

The copolymerization of butene-1 and 3-methyl-1-butene and the isolation of a true copolymer were carried out, according to Ketley⁸⁾.

The copolymerization of butene-1 and 4-methyl-1-pentene was achieved by changing feeding monomer mixture ratios. Batch technique for copolymerization was employed in order to give a copolymer in which two monomer units were distributed along the macromolecular chain as randomly as possible. It is, however, considered that the comonomer units may be distributed in block rather than in random in a chain sequence of the copolymer, since it is reasonable to think that polymerization reactivity of butene-1 monomer is larger than that of 4-methyl-1-pentene. It was examined whether each homopolymer of butene-1 and 4-methyl-1-pentene coexisted in the crude products or not from their solubilities in ether and *n*-heptane. After a copolymerized product was extracted by a Soxhlet extractor with ether, the ether-insoluble part was further extracted with *n*-heptane. In Fig. 2 are plotted the soluble weight % against butene-1 content (mole %) in the crude pro-

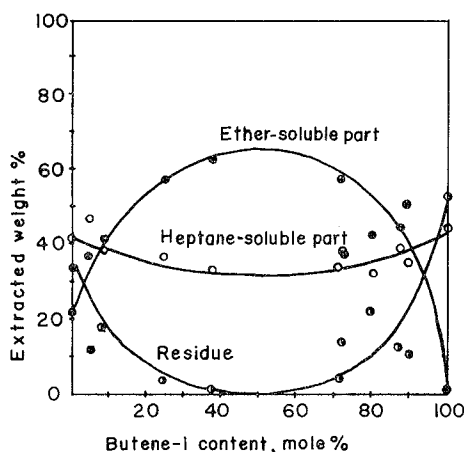


Fig. 2 Extraction of crude products by butene-1 and 4-methyl-1-pentene copolymerization with ether and *n*-heptane. The horizontal line shows butene-1 content in crude product.

ducts. As seen in the figure, in the vicinity of 50 mole percents of butene-1 content, the extracted residue almost diminishes and the ether-extractable part increases. This fact shows that homopolymer of butene-1 and 4-methyl-1-pentene does not exist, but only exists a real copolymer having a chain sequence with poor stereoregularity. Although it is known that the stereoregularities of polybutene-1 and poly(4-methyl-1-pentene) both soluble in *n*-heptane are very poor, they are not completely noncrystalline but slightly crystalline. The fact that the weight percents of *n*-heptane-soluble parts are at an almost equivalent level over the whole composition range may suggest that all the copolymers are more or less crystalline. The copolymerized product of 72.5 mole % butene-1 content was extracted with various solvents, in order of ether, *n*-hexane, cyclohexane and *n*-heptane successively (Table 3). It is recognized that all the fractions contain the both compositions of butene-1 and 4-methyl-1-pentene.

Table 3. Successive extraction of a copolymer of butene-1 and 4-methyl-1-pentene with various solvents at boiling points.*)

Extraction	Extraction temperature °C	Extracted weight %	Butene-1 content in fractions mole %
Ether-soluble	30	40.8	64.3
<i>n</i> -Hexane-soluble	67	27.4	79.8
Cyclohexane-soluble	79	7.2	71.2
<i>n</i> -Heptane-soluble	95	4.1	37.8
Residue	—	20.5	18.1

*) The original sample contains 72.5 mole % butene-1.

X-ray diffraction technique

X-ray diffraction measurements were performed using a ADG-101 type of Toshiba Electronic Company X-ray Diffractometer with nickel-filtered Cu-K α radiation. As specimens for the measurements were used films of about 2 m.m. in thickness and 5 m.m. in width. The scattered radiation was detected with a proportional counter over a range of $2\theta=5\sim 30^\circ$. For scanning angular rate, $1^\circ/\text{min.}$ was used when the crystalline transformation being studied, and $0.25^\circ/\text{min.}$ when the degree of crystallinity and crystal lattice constants being determined.

Density measurement

The density of same samples used for X-ray analysis was measured with a density gradient column of propylene glycol and *n*-propyl alcohol at 30°C.

EXPERIMENTAL RESULTS AND DISCUSSION

The crystalline transformation from the modification II to I in butene-1 copolymers.

By quenching of films of butene-1 homopolymer molded at about 200°C into a dry ice-methanol mixture, formation of the modification II is observed in X-ray diffraction patterns. In the same manner, were prepared quenched films of copolymers of butene-1 with 4-methyl-1-pentene (3.2 mole %), 3-methyl-1-butene (0.5 mole %), propylene (4.0 mole %) and styrene (12.8 mole %). The X-ray diffractions of the films shows characteristic patterns of the modification II of butene-1 homopolymer, although they were somewhat different in position of the peaks in their patterns. As described in the introduction, the modification II of butene-1 homopolymer is transformed to the modification I by annealing at room temperature. Analogous transformation from the modification II to I was observed also for the copolymers studied. These transformations could be estimated quantitatively by calculating of ratios of the areas of the two peaks in $2\theta=11.9^\circ$ characteristic of the modification II, and in $2\theta=10^\circ$ of I in X-ray spectra as a function of annealing time at 30°C. The experimental result is shown in Fig. 3. According to a dilatometric study²⁾, it is reported that dependence of the transformation rate of the modification II to I of polybutene-1 on temperature is maximum in the vicinity of 15°C. The relative transformation from II to I was attained to an equilibrium value of 87.5% by annealing at 30°C for about 80 hours. The crystalline form of

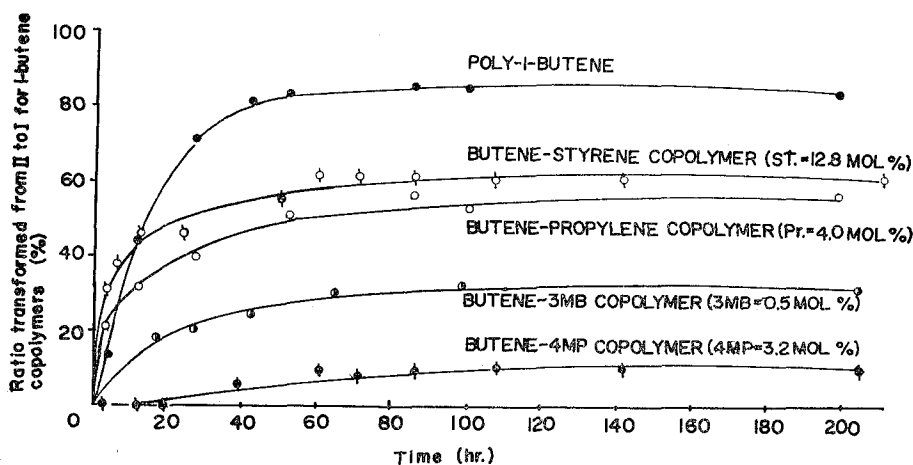


Fig. 3 Rates of conversion from Modification II to Modification I for copolymers of 1-butene with olefins of low content.

the copolymers was transformed to the modification I characteristic of butene-1 homopolymer on standing at 30°C as mentioned above, but the aspects of those transformation differed greatly from that of the homopolymer, depending on the kinds of copolymers. In a copolymer of butene-1 with styrene or propylene, the initial rate of the transformation was greater than that of the homopolymer, and reached an equilibrium value more fast. The slightly lower equilibrium value for the copolymers shown from the figure than that of the homopolymer may indicate that crystallization of the copolymer of butene-1 major composition in the modification I is disturbed, owing to copolymerization. On the contrary, it is recognized that either transformation rate or equilibrium conversion is lower for the copolymer of butene-1 and 4-methyl-1-pentene or 3-methyl-1-butene, despite whose contents are much low. In Fig. 4 is shown the variation of densities of butene-1 homopolymer and its copolymers versus time during annealing at 30°C. The an-

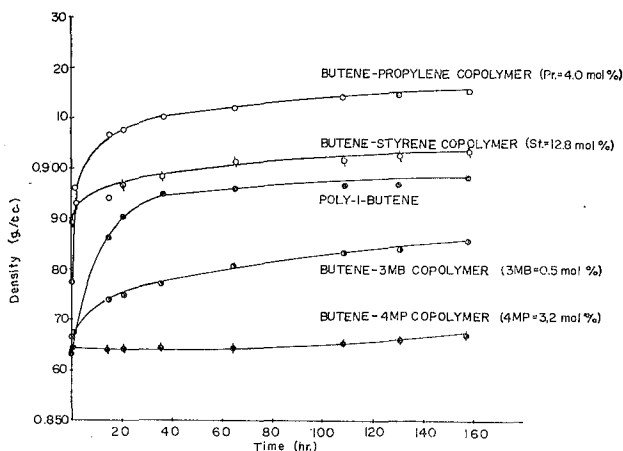


Fig. 4 Variations of density as a function of time on annealing of butene-1 copolymers at 30°C.

nealing and density measurements were carried out conveniently in a density gradient column at 30°C simultaneously. The figure shows the same tendency as in the case of the result of X-ray study. It comes to a conclusion, therefore, that in the copolymers of butene-1 and 4-methyl-1-pentene or 3-methyl-1-butene, the modification II may be formed with easy, but formation of the modification I may be difficult due to incorporation of the comonomer units into the crystal lattice of the modification II of butene-1. This conclusion will be confirmed also by an experimental result, as described later, that a dimension of the crystal lattice varies in accord with the composition ratio. However, it will be obvious from the X-ray spectra that in the butene-1 copolymer with styrene or propylene, the incorporation of the comonomer units may promote transformation from the modification II to I, and may not cause *isomorphism*. On the other hand, in the case of copolymers of butene-1 with 4-methyl-1-pentene or 3-methyl-1-butene, in viewing of chain conformation in each homopolymer, it is considered that the copolymers can cocrystallize in a modification II type of polybutene-1 at high degree of crystallinity.

The crystalline transformation from modification III to II or I of butene-1 copolymers.

The modification III of polybutene-1 is observed in a film casted from the toluene solution. The X-ray diffraction patterns characteristic of the three modifications are designated in the peaks at $2\theta=10.0^\circ$, 17.3° , 20.5° for the modification I, $2\theta=11.0^\circ$, 16.7° , 18.2° for II and $2\theta=12.2^\circ$, 14.3° , 17.2° for III respectively. The X-ray spectra change showing transformation of the modification III to II or I for polybutene-1 by annealing on slow rate heating of 5°C/24 hrs. is depicted in Fig. 5.

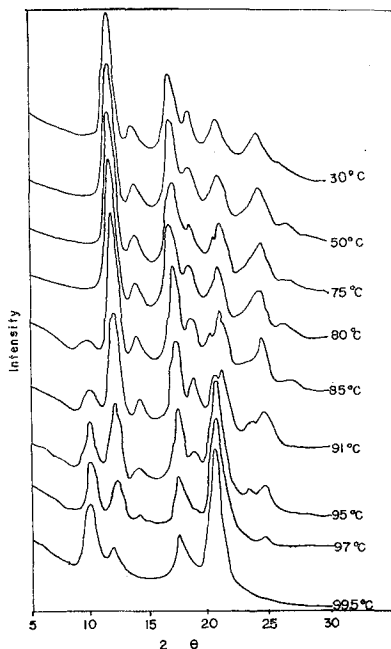


Fig. 5 X-ray scanning curves showing the transformation of modification III to modification I by slow heating of 5°C/24 hrs. for polybutene-1.

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The first appreciable change occurs at about 85°C, where the crystalline form of III is transformed almost into I. It is also confirmed by X-ray spectra that the films of butene-1 copolymers prepared by casting display the same crystalline form as the modification III of the homopolymer. The annealing of these films also was examined in a same manner. The same result as in the case of butene-1 homopolymer was obtained for the copolymer of butene-1 and propylene (Fig. 6). It

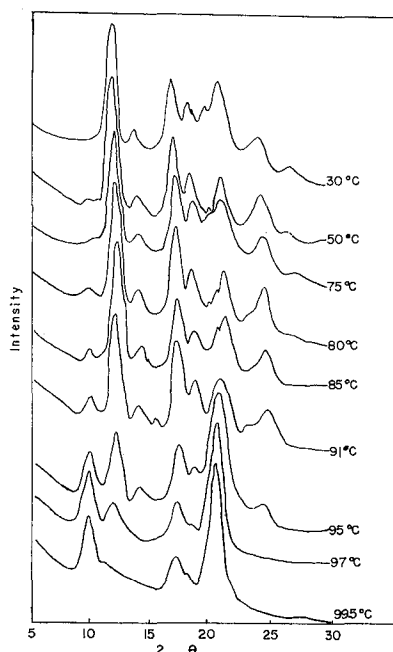


Fig. 6 X-ray scanning curves showing the transformation of modification III to modification I by slow heating of 5°C/24 hrs. for the copolymer of butene-1 with propylene which contains 4.0 mole-% propylene content.

has been manifestly pronounced, by a differential thermal analysis with rapid rate heating of about 1°C/min., that this transformation phenomenon of polybutene-1 involves the transformation: III→melt→II→I⁹⁾. X-ray spectra change for the transformation of the modification III of the butene-1 copolymer with 4-methyl-1-pentene to other modifications as a function of temperature is inserted in Fig. 7, which shows that this copolymer system also involves the same transformation as shown for polybutene-1 or the copolymer of butene-1 and propylene. Since for this copolymer, it has been already confirmed from the result of Fig. 4 not to be transformed from the modification II to I due to the stabilization by cocrystallization of the two monomer units, this transformation may also involve a process, III→melt→II. Either homopolymer or any copolymer of butene-1 studied herein has same tendency of transformation, and the crystal lattice constants are not altered regardless of the kinds of comonomers. These results will suggest that cocrystallization in a type of the modification III can occur. Although the crystalline structure in the modification III of polybutene-1 has not been clear as yet, it is pointed

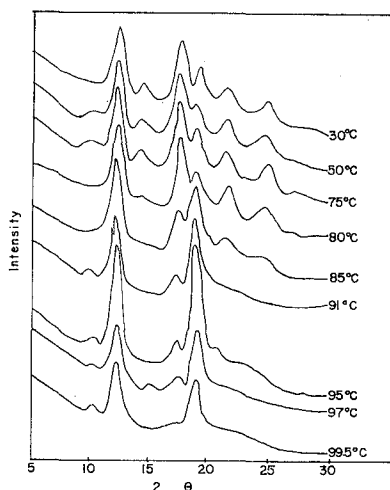


Fig. 7 X-ray scanning curves showing the transformation of modification III to modification I by slow heating of 5°C/24 hrs. for the copolymer of butene-1 with 4-methyl-1-pentene which contains 3.2 mole-% 4-methyl-1-pentene content.

out by R.L. Miller and V.F. Holland¹⁰ that the crystalline form, which belongs to orthorhombic system, has the lattice constants of $a=12.49$ Å and $b=8.96$ Å. If these values are correct, viewing of the crystallographic parameters for poly(4-methyl-1-pentene) and poly(3-methyl-1-butene) in Table 2, it is recognized that these crystallographic parameters are remarkably different from those of the modification III of polybutene-1. Thus, it is plausible to consider that cocrystallizing behavior can not be occurred in the modification III type of polybutene-1.

The crystalline structure of the copolymers of butene-1 and 4-methyl-1-pentene over the whole composition range.

It was cleared from the results in regard to the crystalline transformation of copolymers of butene-1 and 4-methyl-1-pentene that the copolymers in the composition range of high contents of butene-1 could cocrystallized in a crystalline structure of the modification II. In this section, we will further examine the crystalline structure such as the crystallinity and variation of the crystal lattice constants of the copolymers over the whole composition range of the comonomers.

The degree of crystallinity was evaluated from the ratio of areas of X-ray scanning curves for amorphous and crystalline polymers (Fig. 8). Acetone-soluble poly(4-methyl-1-pentene) and atactic polybutene-1 both soluble in ether were used as the amorphous polymers of each homopolymer, respectively (curve d and c in Fig. 8). Curve a in Fig. 8 shows a X-ray scanning curve for crystalline isotactic poly(4-methyl-1-pentene). As shown in Fig. 8-b, a dotted straight line was drawn between $2\theta=5^\circ$ and 30° along the scanning areas as the back ground. And an area surrounded by the straight line scanning curve was divided into amorphous (A) and crystalline (C) areas. The degree of crystallinity was taken simply as $C/(C+A)$ after air scattering correction and without further corrections, where the composite curves of the amorphous state of the copolymers with different compositions were drawn according to the suggestion of the amorphous curves for each homopolymer.

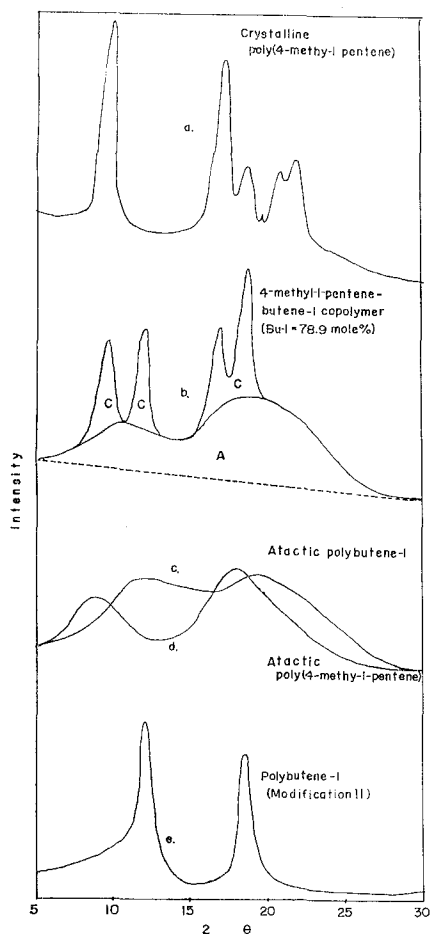


Fig. 8 X-ray scanning curves of homopolymers of butene-1 and 4-methyl-1-pentene and the copolymer.

The degree of crystallinity of butene-1 homopolymer was determined for the crystalline structure of the modification II (curve e in Fig. 8). The samples of poly(4-methyl-1-pentene) and copolymers examined were prepared by annealing of quenched films at 100°C for 3 hours. Crystallinity was observed for the copolymers over the whole composition range (Fig. 9). This series of copolymers are unique in cocrystallizability in contrast to general olefin copolymers such as copolymers of styrene and linear α -olefins which generally do not cocrystallize²⁷.

The identification of each crystal phase was achieved by use of d-spacing from a strong reflection, (200) in X-ray spectra for each homopolymer, characteristic $a=9.2$ Å ($2\theta=9.5^\circ$) for crystalline isotactic poly(4-methyl-1-pentene) and $a=7.5$ Å ($2\theta=11.93^\circ$) for the modification II of polybutene-1 respectively. The reflection (200) is suitable to determine a length of a-axis in unit cell of each homopolymer. In order to examine an expansion or shrinkage of the crystal lattice by copolymerization, variations of length of $a=18.4$ Å for poly(4-methyl-1-pentene) and $a=14.93$ Å for polybutene-1 were measured. In Table 4 are shown the results. It is of particularly interest that the length of a-axis expands for the copolymers

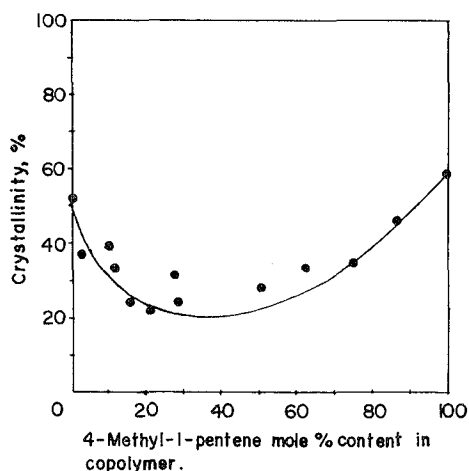


Fig. 9 Degree of crystallization for copolymers of 4-methyl-1-pentene and butene-1.

Table 4. Variations of unit cell dimensions for copolymers of butene-1 and 4-methyl-1-pentene over the whole composition.

Comonomer content, molar ratio	Spacing of a-axis for butene-1 major copolymer.		Spacing of a-axis for 4-MP. major copolymer.	
	2θ	d (Å)	2θ	d (Å)
Bu-1/4MP.				
100/0	11.925	14.752	—	—
96.8/ 3.2	11.800	14.982	—	—
89.5/10.5	11.700	15.109	—	—
87.5/12.5	11.695	15.148	—	—
84.0/16.0	11.525	15.338	—	—
78.9/20.2	11.575	15.274	9.525	18.576
72.5/27.5	11.625	15.206	9.58	18.466
71.2/28.8	11.925	14.752	9.58	18.466
49.6/50.4	11.925	14.752	9.58	18.466
37.8/62.2	—	—	9.58	18.466
24.5/75.5	—	—	9.57	18.468
18.1/81.9	—	—	9.53	18.544
12.9/87.1	—	—	9.51	18.596
8.0/92.0	—	—	9.51	18.596
0/100	—	—	9.500	18.622

of high butene-1 content but, in the contrary, shrinks for the copolymers of high 4-methyl-1-pentene content. Therefore, it must come to a conclusion that the monomer units can be displaced each other isomorphously in a crystal lattice of unit cell of each homopolymer.

CONCLUSION

It would be concluded that copolymers of 4-methyl-1-pentene and butene-1

were manifestly capable of occurrence of isomorphism or cocrystallization. Reviewing of crystallographic study of chain conformations in the crystalline structures of butene-1 and 4-methyl-1-pentene homopolymers, it can be found that the crystalline structure of isotactic poly(4-methyl-1-pentene) is assigned to tetragonal symmetrical form (Table 2), while the crystalline structure of polybutene-1 in a tetragonal system is the modification II (Table 1). The crystalline structures of both polymers have an almost equivalent number of monomer units per a turn of helical chain, $11_2=3.7$ for the modification II of polybutene-1, and $7_2=3.5$ for poly(4-methyl-1-pentene) respectively. If the crystallographic parameters of both homopolymers are compared each other, it would be reasonable to consider that two different kinds of monomer units could be replaced each other in a unit cell without changing of large free energy. It may be a necessary condition for this isomorphism that mutual compatibility of side chains of each monomer is relatively good. It seems important but difficult to know with what degree of mutual replacement two kinds of monomer units are participated in a crystalline structure. It is apparent that if monomer units of the minor content are distributed consecutively or in a blockwise manners in a chain sequence of copolymers, they can not participate in a crystal lattice characteristic of homopolymers of the major component. Therefore, it is useful in studying these phenomena to know whether the comonomers participated in a crystalline structure are distributed in a random manner or in a blockwise manner. Although a polymerization technique was employed so as to produce a random copolymer, the copolymerization could not be considered to have occurred at perfectly random, because it was plausibly presumed that the monomer reactivity of polymerization for butene-1 was higher than that for 4-methyl-1-pentene. Hence, some extensive degree of blockwise displacement is probably present in a chain. It is considered that the crystallinity of copolymers of butene-1 and 4-methyl-1-pentene is much lower than those of each homopolymer. However, crystalline structure was more or less observed for the copolymer of butene-1 and 4-methyl-1-pentene over the whole composition range of each comonomer, hence it was considered that the extent of blockwise copolymerization was not so much high.

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