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COPOLYMERIZATION OF ETHYLENE WITH α -OLEFINS AT HIGH TEMPERATURE AND CHARACTERIZATION OF COPOLYMERS

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Key Words: Copolymerization; Ethylene; α -Olefin; High temperature; Comonomer composition distribution; Temperature rising elution fractionation

ABSTRACT

Ethylene copolymerizations were performed with butene-1,4-methylpentene-1 (4MP1), hexene-1, and octene-1 at a high temperature. Comonomer incorporation is markedly poor for 4MP1, but there are negligible differences among the other comonomers. The densities of copolymers having the same comonomer mole content increase with a decrease of molecular weight of the comonomers, whereas the melt temperature of the copolymers decrease except for 4MP1 which has the highest melt temperatures. From an analysis of the copolymers by TREF combined with GPC and ^{13}C -NMR, it is assumed that the copolymers from heavier comonomers comprise heptane-soluble amorphous copolymers and ethylene-rich semicrystalline ones which lead to lower densities and higher melt temperatures, respectively. Therefore, it can be said that heavier comonomers (4MP1 in particular) tend to be incorporated more heterogeneously, resulting in a wider distribution of comonomer composition.

INTRODUCTION

Studies of the copolymerization of ethylene with α -olefins have been intensively performed using various types of Ziegler–Natta catalysts. In recent years, copolymers called LLDPEs (linear low density polyethylenes) have grown in importance in the polyolefin market because of their good mechanical and optical properties together with their inexpensive material and production costs.

Such polymerization processes as gas phase, slurry, solution, high pressure, etc. have been employed for the industrial production of LLDPEs. Solution polymerization is usually carried out at a temperature higher than 140°C whereas the other polymerization temperatures are usually below 100°C.

A solution polymerization system is homogeneous under high temperature conditions [1, 2]. This homogeneity makes the diffusion control of monomers to an active site on a catalyst less influential with an increase in the volume of polymers, as well as a difference in the diffusion rates of the monomers [3]. At higher temperatures the reactivity of a comonomer increases and a larger amount of comonomer is incorporated into the copolymer [4, 5], resulting in smaller values of reactivity ratio products, $r(\text{ethylene}) \times r(\text{comonomer})$. Kashiwa reported [1] that copolymerization at 170°C consumes a comonomer in a higher amount in the following order: propylene > butene-1 > 4-methylpentene-1(4MP-1). On the other hand, Luft reported [4] that with a high temperature and a high pressure of ethylene, a heavier comonomer with butene-1, hexene-1, octene-1, and decene-1 is more abundantly incorporated.

It is generally known that Ziegler–Natta-type supported catalysts have multi-active sites. If polymerization is performed at a high temperature, only thermally stable active sites will remain, resulting in a more homogeneous catalyst. Hence, it is expected that copolymers obtained at a high temperature will have more homogeneous comonomer compositions. Despite our expectation, there is a report [6] that at the same values of copolymer density, a larger molecular weight comonomer was found to give a more heterogeneous comonomer composition according to analysis using a differential scanning calorimeter (DSC) and a method of temperature rising elution fractionation (TREF).

Until now, there have been very few studies of high temperature homo and copolymerizations of ethylene with α -olefins using Ziegler–Natta catalysts [1–9]. In particular, no detailed reports of the fundamental structural and property differences of copolymers from various α -olefins exist. The present paper describes the detailed analytical results of copolymers obtained at 130°C with a Ziegler–Natta catalyst. It also includes a discussion of the physical properties of the copolymers.

EXPERIMENTAL

Copolymerizations were carried out in an autoclave equipped with an electric furnace. The following chemicals were introduced. Heptane as a medium, a comonomer, diethylaluminumchloride as a cocatalyst, hydrogen and ethylene (5 kg/cm²) saturated in heptane, and finally, at 130°C, an ampule containing a magnesium-chloride-supported titanium catalyst (prepared by reacting titanium tetrachloride with a support, and obtained by a method described elsewhere [10]) was broken.

The comonomer contents of the copolymers were obtained by $^1\text{H-NMR}$ on a JEOL-FX200 FT-NMR instrument by determining the peak intensity ratios of methyl, methylene, and methine protons. $^{13}\text{C-NMR}$ analysis on a JEOL-GSX400 FT-NMR instrument was also carried out at 120°C to obtain the comonomer contents and triad comonomer sequences under the following conditions: 20,000 Hz frequency, $9.5\ \mu\text{s}$ pulse width, 20,000 scans using C_6D_6 and *o*-dichlorobenzene with tetramethylsilane as an internal standard.

Densities were determined according to a method of JIS K6760 using films of 0.3 mm thickness. Melt temperatures of the copolymers were determined as an endothermic peak of differential scanning calorimetry (DSC) with a MAC SCIENCE DSC-3100 under the following conditions: first, preheat a sample at $10^\circ\text{C}/\text{min}$ to 160°C , hold for 10 minutes, cool by $5^\circ\text{C}/\text{min}$ to 30°C , again heat at $10^\circ\text{C}/\text{min}$ to 160°C to measure the endothermic peaks. The preheated samples were also used for observation with an Hitachi H-7000 transmission electron microscope (TEM).

In order to determine the molecular weights (MW) and the molecular weight distributions (M_w/M_n) of the copolymers, and the comonomer composition distribution temperature rising elution fractionation (TREF) combined with gel permeation chromatography (GPC) was performed on a MITSUBISHI PETROCHEMICAL CFC (T-150-A) with a data processing system [11]. Fractions at 28 elution temperatures (0, 10, 20, 30, 40, 45, 49, 52, 55, 58, 61, 64, 67, 70, 73, 76, 79, 82, 85, 88, 91, 94, 97, 100, 102, 105, 120, and 135°C) were directly sent to GPC with Shodex AT-80M/S as a column using *o*-dichlorobenzene.

RESULTS AND DISCUSSION

Table 1 shows the copolymerization conditions, yields, and properties of copolymers produced: comonomer content in mole and weight percents, molecular weight (MW), molecular weight distribution (M_w/M_n), density, and melt temperature (T_m). A total of 20 copolymers having five different density levels (0.93, 0.92, 0.90, 0.89, and 0.88) were obtained from four different comonomers: butene-1(B-1), 4-methylpentene-1(4MP-1), hexene-1(H-1), and octene-1(O-1).

The densities of the copolymers were controlled by varying the comonomer concentration supplied for copolymerizations. All copolymerizations were carried out up to conversions of ethylene and comonomers of around 30 to 40% and several percent, respectively. Therefore, the ethylene/comonomer ratio changed in the course of each copolymerization. Nevertheless, we think that the copolymer properties of the four different comonomers can be profitably compared. The ratios of ethylene/comonomer decreased in nearly the same degree regardless of the comonomer as the copolymerizations proceeded. Furthermore, the molecular weights of all the copolymers were controlled to a level of 120,000 with a deviation of 30% by adjusting the amount of hydrogen fed. Thus, differences in copolymer properties can be discussed without considering the effect of polymer molecular weight.

Figure 1 shows plots of supplied comonomer concentration vs incorporated comonomer content in a mole percent. 4-MP-1 is less abundantly incorporated into copolymers compared to the other three comonomers. The reactivities among the three comonomers appear to be nearly equivalent. It is generally understood that

TABLE 1. Copolymerizations of Ethylene with Various α -Olefins

| Sample | Polymerization conditions | | | | Copolymer properties | | | | | | |
|--------|---------------------------|-----|------------------------|----------|----------------------|-----------|----------------------------|-------------------|------|----------------------|-------|
| | Comonomer in feed | | Ethylene conversion, % | Yield, g | MW $\times 10^{-5}$ | M_w/M_n | Density, g/cm ³ | Comonomer content | | Melt temperature, °C | |
| | Comonomer mol% | wt% | | | | | | mol% | wt% | | |
| 1 | Butene-1 | 26 | 41 | 41 | 10.1 | 1.1 | 3.27 | 0.9334 | 0.91 | 1.80 | 124.4 |
| 2 | 4-MP-1 | 37 | 64 | 32 | 7.9 | 1.3 | 4.06 | 0.9327 | 1.17 | 3.43 | 128.0 |
| 3 | Hexene-1 | 15 | 34 | 39 | 8.4 | 1.1 | 3.68 | 0.9364 | 0.52 | 1.54 | 127.9 |
| 4 | Octene-1 | 15 | 41 | 36 | 8.8 | 1.0 | 3.48 | 0.9360 | 0.54 | 2.31 | 128.5 |
| 5 | Butene-1 | 48 | 65 | 40 | 10.1 | 0.94 | 4.09 | 0.9200 | 2.48 | 4.84 | 121.6 |
| 6 | 4-MP-1 | 56 | 79 | 31 | 7.9 | 1.1 | 4.53 | 0.9213 | 2.19 | 6.30 | 127.6 |
| 7 | Hexene-1 | 41 | 68 | 44 | 11.1 | 0.81 | 3.82 | 0.9232 | 1.56 | 4.59 | 124.9 |
| 8 | Octene-1 | 41 | 74 | 36 | 9.5 | 1.0 | 3.97 | 0.9212 | 2.17 | 8.15 | 125.6 |
| 9 | Butene-1 | 68 | 81 | 44 | 11.8 | 1.2 | 4.36 | 0.9051 | 6.09 | 11.5 | 121.4 |
| 10 | 4-MP-1 | 69 | 87 | 40 | 11.3 | 1.2 | 5.33 | 0.9050 | 5.04 | 13.7 | 127.0 |
| 11 | Hexene-1 | 61 | 83 | 36 | 9.9 | 1.2 | 4.48 | 0.9031 | 5.05 | 13.8 | 125.2 |
| 12 | Octene-1 | 62 | 84 | 40 | 11.5 | 1.2 | 4.52 | 0.9060 | 4.51 | 15.9 | 126.1 |
| 13 | Butene-1 | 75 | 86 | 30 | 8.1 | 1.1 | 4.27 | 0.8993 | 5.99 | 11.3 | 119.9 |
| 14 | 4-MP-1 | 77 | 91 | 35 | 10.1 | 1.4 | 5.97 | 0.8964 | 5.87 | 15.8 | 127.0 |
| 15 | Hexene-1 | 69 | 87 | 32 | 9.3 | 1.1 | 4.55 | 0.8971 | 6.35 | 16.9 | 124.6 |
| 16 | Octene-1 | 62 | 87 | 40 | 11.6 | 1.3 | 5.08 | 0.8987 | 4.75 | 16.1 | 126.0 |
| 17 | Butene-1 | 79 | 88 | 35 | 10.0 | 0.98 | 3.90 | 0.8882 | 8.79 | 16.2 | 120.6 |
| 18 | 4-MP-1 | 80 | 92 | 38 | 11.2 | 1.4 | 5.26 | 0.8903 | 7.68 | 20.0 | 127.3 |
| 19 | Hexene-1 | 75 | 90 | 33 | 10.2 | 1.5 | 5.40 | 0.8848 | 9.18 | 23.3 | 124.9 |
| 20 | Octene-1 | 69 | 90 | 41 | 12.9 | 1.4 | 5.38 | 0.8882 | 7.09 | 23.4 | 126.1 |

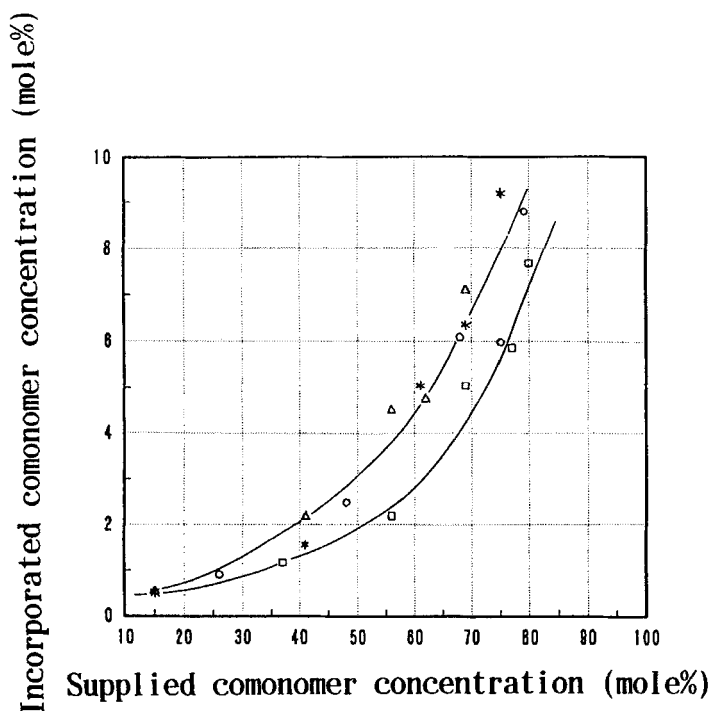


FIG. 1. Supplied comonomer concentration vs incorporated comonomer concentration: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

the reactivity of α -olefin is influenced by its molecular weight and bulkiness, and this may be why 4-MP-1 is the least reactive.

The present result indicating that both O-1 and H-1 have the same high reactivity as butene-1 is very interesting. Luft et al. [4] reported that the reactivities of α -olefins at high temperature is in the following order: O-1 > H-1 > B-1. In high temperature copolymerization using heptane as the medium, copolymers may dissolve, depending upon the copolymer properties. As will be shown in Fig. 3, a comonomer having a larger molecular weight gives a lower density and amorphous copolymer which is certainly more soluble in the medium. Hence, diffusion of the comonomer to a catalyst active site is fast; consequently, heavier comonomers are fairly well incorporated in spite of their poor reactivities.

Figure 2 shows the dependence of the T_m of copolymers on comonomer content. A T_m which corresponds to a DSC endothermic peak in the highest temperature region is said to consist of those of an ethylene homopolymer, if present, and copolymers having smaller amounts of a comonomer. Also, it is known that the higher a T_m is, the thicker the lamellas of a crystalline copolymer are. Photographs 1 to 4 and Table 2 indicate the dependence of T_m on lamella thickness for copolymers having the same density levels. In particular, a copolymer from 4-MP-1 exhibits a high T_m and thick lamellas.

A T_m decreases with an increase of comonomer content because side chains ascribed to comonomers interfere with the growth of lamellas and hence they remain

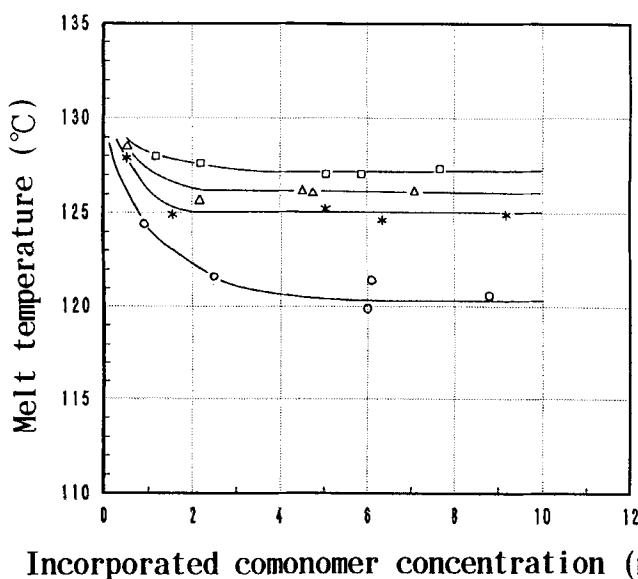
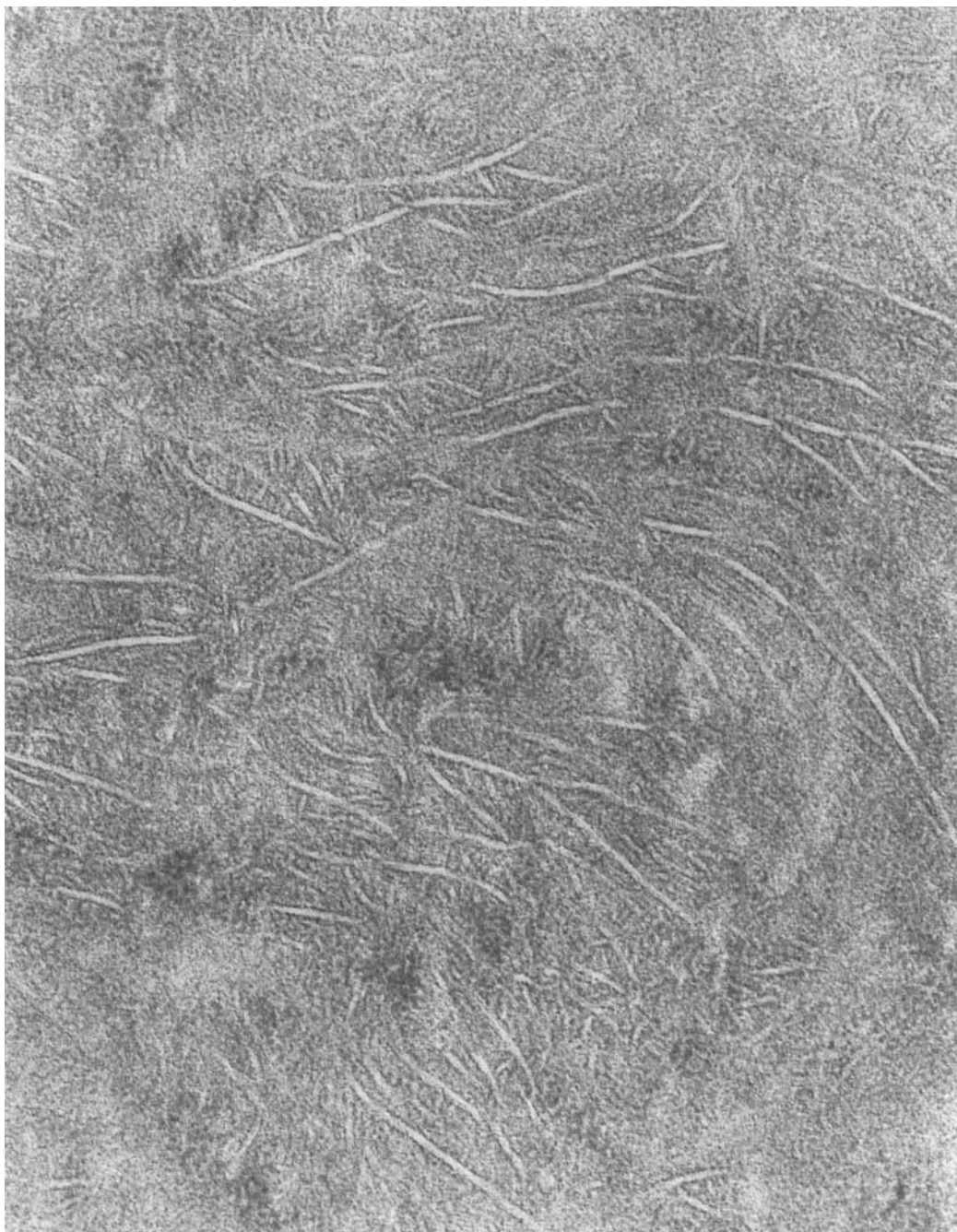


FIG. 2. Dependence of melt temperature on comonomer content: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

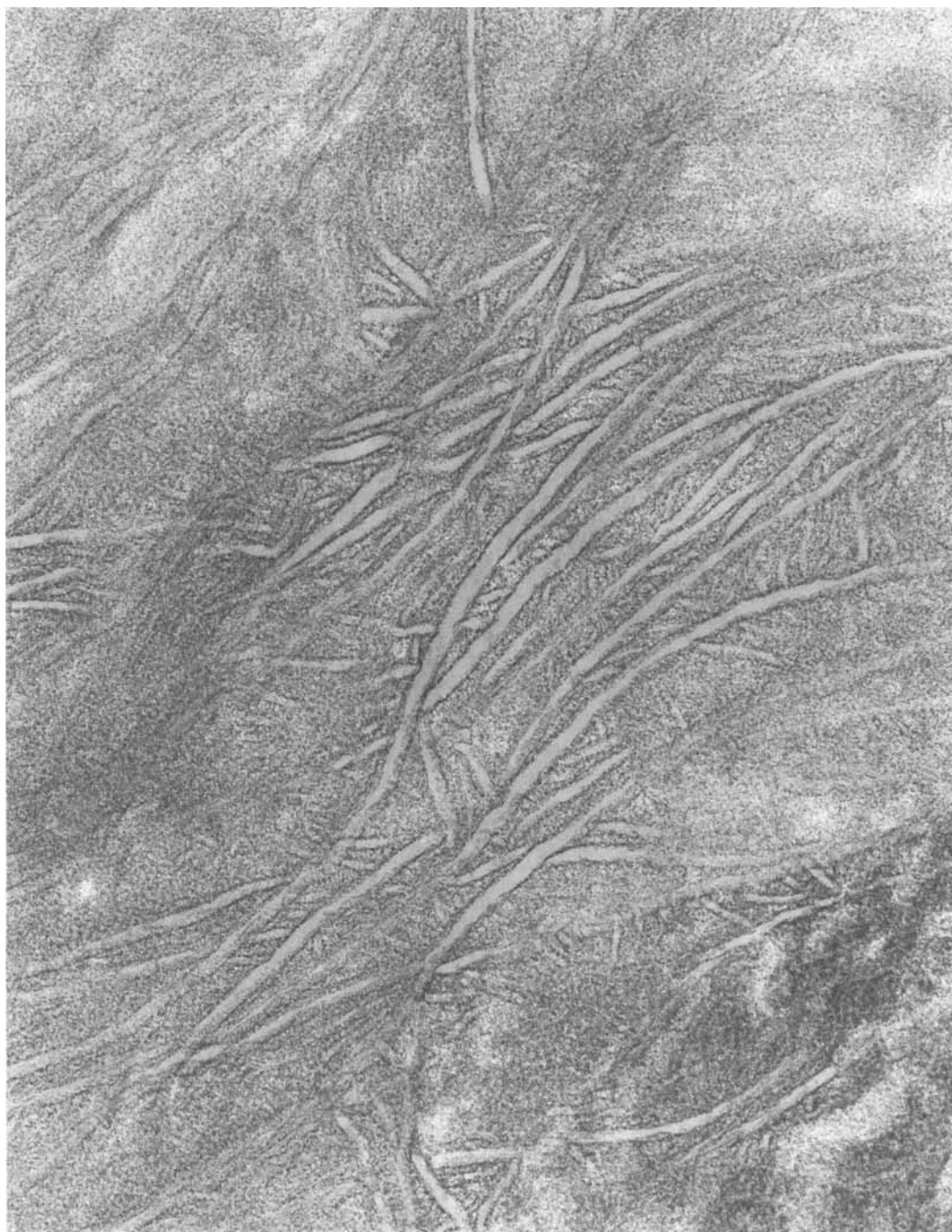
thin. Hosoda investigated the effect of side chains on the formation of lamellas [13, 14]. From the relationships between T_m and comonomer content for copolymers having a molecular weight of about 100,000 according to temperature rising elution fractionation, and further identification by ^{13}C -NMR of organic compounds obtained by selectively etching the amorphous part of lamellas with fuming nitric acid, he concluded that the side chains from comonomers are eliminated from lamellas in the following order: isobutyl, dodecyl to hexyl > butyl > ethyl > methyl.

Our present results (Fig. 2) definitely contradict Hosoda's results. That is, the larger or bulkier the side chains for comonomers, the higher the T_m 's in the same degree of comonomer incorporation in mole percent. From these findings it can be said that the comonomer content determined by ^1H -NMR for each sample is average and does not directly reflect those of crystalline copolymers. In high temperature copolymerization in our present study, copolymers obtained from ethylene copolymerization have broad distributions of comonomer composition. Actually, this heterogeneity is quite common for LLDPEs from a slurry or a gas-phase polymerization since the catalysts used are heterogeneous.

In the present case, the heterogeneity of comonomer composition differs among the comonomers. The differences are simply assumed by the molecular weight distributions (M_w/M_n) shown in Table 1. The M_w/M_n values are likely larger in the following order: 4-MP-1 > O-1, H-1 > B-1. Moreover, Fig. 2 shows that the melt temperatures are independent of the incorporation of comonomer at contents of more than 4 mol%, indicating the limitation of comonomer incorporation in ethylene-rich copolymers. Comonomer incorporation generally depends upon comonomer concentration in the feed for any active site. Therefore, the independence of the melt temperature may be assigned to greater comonomer incorporation



Photograph 1 (Sample No. 9) 0.1 μ —



Photograph 2 (Sample No. 10)



Photograph 3 (Sample No. 11)



Photograph 4 (Sample No. 12)

TABLE 2. Lamella Thickness

| Sample | Comonomer | Maximum lamella thickness, Å | Melt temperature, °C |
|--------|-----------|------------------------------|----------------------|
| 9 | Butene-1 | 111 | 119.9 |
| 10 | 4-MP-1 | 183 | 127.0 |
| 11 | Hexene-1 | 167 | 124.6 |
| 12 | Octene-1 | 144 | 126.0 |

into comonomer-rich amorphous copolymers at higher comonomer concentrations. Comonomer composition distribution will be discussed in detail later in this paper.

Figures 3 and 4 show the dependence of density on comonomer content in mole and weight percents, respectively. When a comonomer is incorporated into a polymer, the lamella becomes thinner as the volume of the amorphous part increases, and the specific volume as a reciprocal of the density value increases. Ross [12] reported that a specific volume (V) is expressed by two equations:

$$V \propto N \times MW^{0.5}$$

where N is the number of side chains and MW is the molecular weight of the side chains, provided that N is relatively small and the density is 0.92 or more.

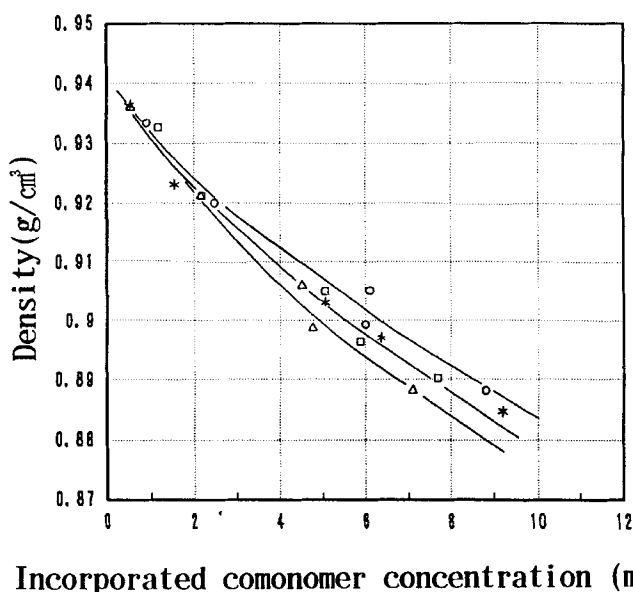


FIG. 3. Dependence of density on comonomer mole content: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

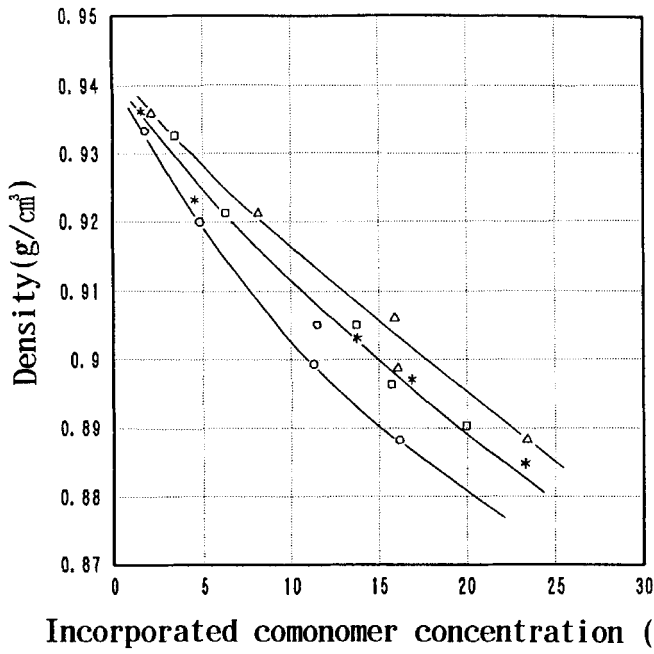


FIG. 4. Dependence of density on comonomer weight content: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

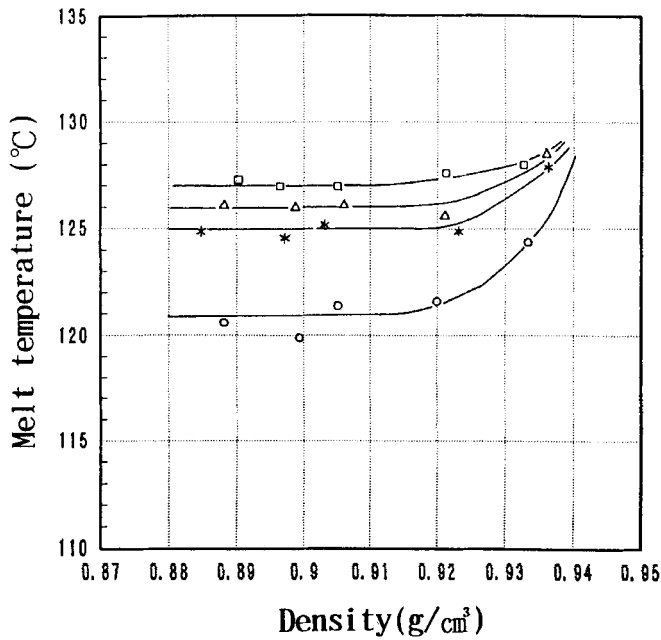


FIG. 5. Density vs melt temperature: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

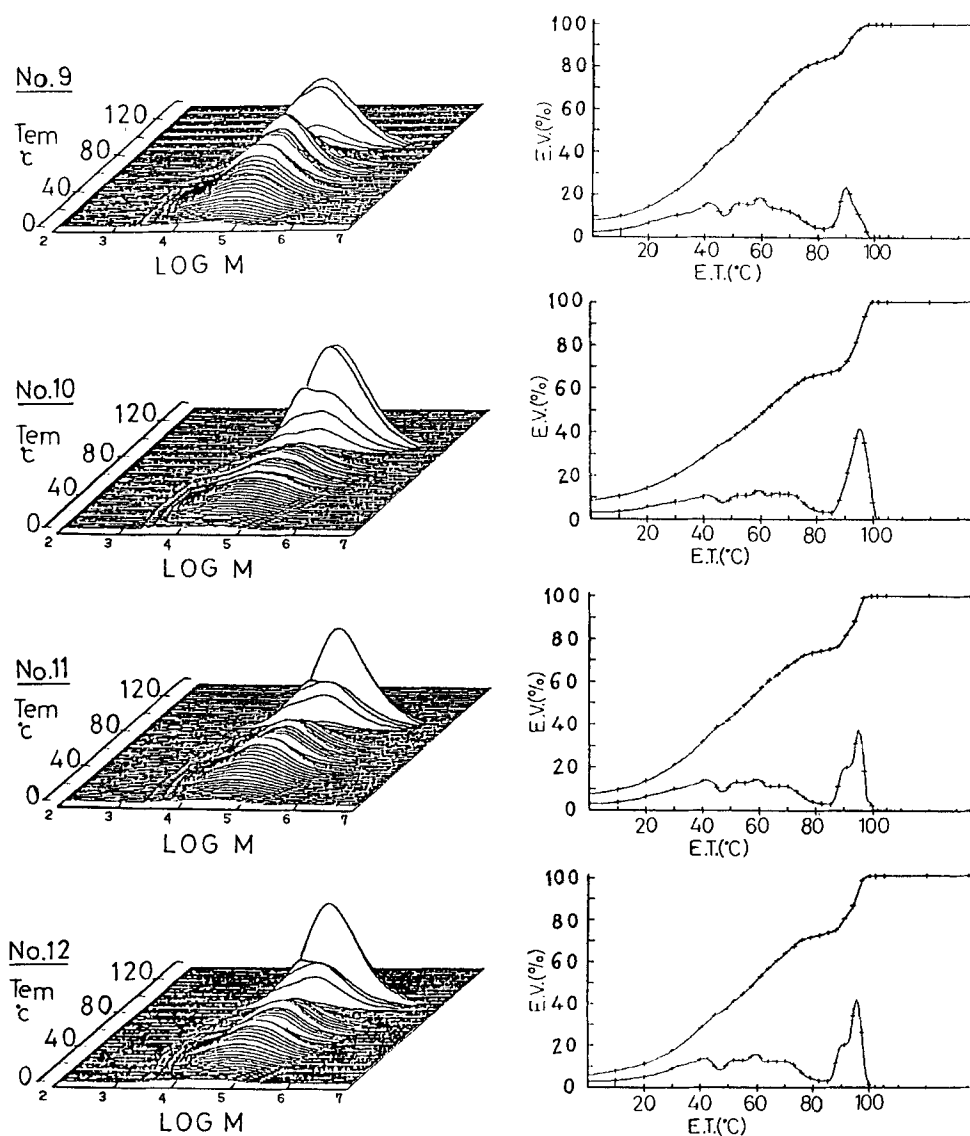


FIG. 6. TREF/GPC data of copolymers having similar densities: Sample No. 9, butene-1; No. 10, 4-methylpentene-1; No. 11, hexene-1; No. 12, octene-1.

$$V \propto N$$

when N is larger.

The present results indicate that the specific volume depends on both the molecular weight of the side chains (Fig. 3) and the number of side chains (Fig. 4), in a wide range of densities from 0.88 to 0.93. A difference between H-1 and 4-MP-1 was not observed.

TABLE 3. TREF Data of Various Copolymers

| Sample | Comonomer | Density, g/cm ³ | ET50, °C | EV0, % | EVH, % | ETX, °C | σ |
|--------|-----------|-------------------------------|-------------|-----------|-----------|------------|----------|
| 1 | Butene-1 | 0.9334 | 87 | 0 | — | 84.5 | 8.42 |
| 2 | 4-MP-1 | 0.9327 | 93 | 0 | — | 86.8 | 11.3 |
| 3 | Hexene-1 | 0.9363 | 93 | 0 | — | 89.9 | 6.73 |
| 4 | Octene-1 | 0.9360 | 93 | 0 | — | 89.7 | 7.23 |
| 5 | Butene-1 | 0.9200 | 73 | 0.67 | 22.2 | 70.2 | 16.9 |
| 6 | 4-MP-1 | 0.9213 | 79 | 0.78 | 41.6 | 75.5 | 20.3 |
| 7 | Hexene-1 | 0.9232 | 75 | 0.58 | 32.9 | 73.0 | 19.0 |
| 8 | Octene-1 | 0.9212 | 75 | 0.50 | 34.8 | 73.5 | 19.0 |
| 9 | Butene-1 | 0.9051 | 54 | 7.03 | 16.5 | 54.9 | 25.1 |
| 10 | 4-MP-1 | 0.9050 | 64 | 7.62 | 33.0 | 65.4 | 28.6 |
| 11 | Hexene-1 | 0.9031 | 58 | 6.50 | 25.2 | 59.6 | 27.9 |
| 12 | Octene-1 | 0.9060 | 60 | 4.92 | 27.5 | 62.0 | 27.5 |
| 13 | Butene-1 | 0.8993 | 46 | 9.17 | 11.8 | 49.7 | 25.0 |
| 14 | 4-MP-1 | 0.8964 | 56 | 15.4 | 28.8 | 62.5 | 30.6 |
| 15 | Hexene-1 | 0.8971 | 48 | 12.1 | 20.0 | 55.2 | 29.1 |
| 16 | Octene-1 | 0.8987 | 52 | 10.6 | 23.4 | 57.8 | 29.1 |
| 17 | Butene-1 | 0.8882 | 32 | 24.0 | 8.15 | 43.0 | 25.7 |
| 18 | 4-MP-1 | 0.8903 | 62 | — | 32.8 | 60.2 | 31.8 |
| 19 | Hexene-1 | 0.8848 | 34 | 27.2 | 18.5 | 52.1 | 31.3 |
| 20 | Octene-1 | 0.8882 | 40 | 21.1 | 20.7 | 54.7 | 30.7 |

Figure 5 is plots of density vs T_m . As seen in Figs. 3 and 4, the differences in the relationships between density and comonomer content among the copolymers are not remarkable. The differences among the copolymers, however, are apparent in Fig. 5 as observed in Fig. 2 with respect to T_m .

In order to determine more details of the distributions of comonomer composition and to compare them among different comonomers, analyses for copolymers were performed by temperature rising elution fractionation (TREF) combined with gel permeation chromatography (GPC). The TREF technique has recently been widely used for the characterization of ethylene copolymers. Many explanations have been proposed for comonomer composition and the behavior of crystallinity and melt temperature from TREF data [15–18]. However, TREF analysis of ethylene copolymers obtained by high temperature polymerization is seldom reported.

The right column of Fig. 6 shows plots of the elution temperature vs both the differential and integration elution fraction volumes for copolymer samples 9 to 12. The left column of Fig. 6 shows three-dimensional views of TREF–GPC for the same series of samples.

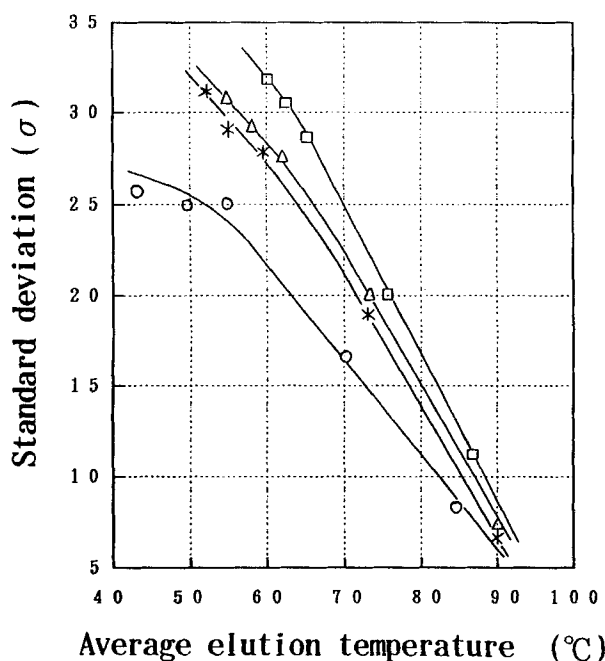


FIG. 7. Relationship between average elution temperature and standard deviation: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

Each copolymer has very similar densities, but the results for sample 9, where a comonomer is B-1, are clearly different from those of the others. In the case of B-1, the elution temperature of the fractionation peak in the highest temperature region is lower and the elution fraction volume is also smaller. Also, the distribution of elution volumes over a fractionated temperature range is more moderate. On the contrary, for the other comonomers, the elution peak temperature in the highest temperature region is invariably 95°C and the elution volumes are comparatively large. Even a careful study of the figures does not reveal discernible differences among the three comonomers.

Table 3 summarizes the TREF data for all copolymers with respect to ET50 (a temperature at an integrated elution volume of 50%), EV0 (an elution volume percent at less than 0°C), EVH (an elution volume percent corresponding to the highest temperature peak area), and ETX [an average elution temperature expressed by $\Sigma(T \times V)/\Sigma V$, where T is each elution temperature and V is each elution volume]. σ is the standard deviation.

Regardless of the comonomers, the values of ET50 become lower with a lower density, the values of EV0 increase markedly, and those of EVH decrease as the densities decrease, indicating that the solubility of the copolymers largely depends on the content of the comonomer rather than on the molecular weights of the copolymers. Larger increases in the values of EV0 correspond well with larger decreases in those of EVH for B-1, whereas for the other three comonomers (in

TABLE 4. ^{13}C -NMR Data of Various Copolymers

| Sample | Comonomer | Content, mol% | $\frac{[\text{ECC}] + [\text{CCC}]}{[\text{C}]}$, % | $r_1 r_2$ |
|--------|-----------|------------------|---|-------------|
| 1 | Butene-1 | 1.6 | 2.5 | 0.79 |
| 2 | 4-MP-1 | 1.5 | 4.0 | 1.41 |
| 3 | Hexene-1 | 1.1 | <u>12.7</u> | <u>6.42</u> |
| 4 | Octene-1 | 0.97 | <u>12.9</u> | <u>7.72</u> |
| 5 | Butene-1 | 3.9 | 4.8 | 0.60 |
| 6 | 4-MP-1 | 3.2 | 8.5 | 1.40 |
| 7 | Hexene-1 | 3.3 | 8.0 | 1.24 |
| 8 | Octene-1 | 3.2 | 6.4 | 1.01 |
| 9 | Butene-1 | 8.4 | 12.8 | 0.76 |
| 10 | 4-MP-1 | 6.3 | 15.9 | 1.38 |
| 11 | Hexene-1 | 6.9 | 12.9 | 0.96 |
| 12 | Octene-1 | 5.9 | 10.8 | 0.93 |
| 13 | Butene-1 | 9.2 | 13.8 | 0.75 |
| 14 | 4-MP-1 | 7.7 | 19.1 | 1.38 |
| 15 | Hexene-1 | 8.5 | 15.4 | 0.93 |
| 16 | Octene-1 | 7.1 | 13.3 | 0.97 |
| 17 | Butene-1 | 12.6 | 18.2 | 0.71 |
| 18 | 4-MP-1 | 9.4 | 22.6 | 1.36 |
| 19 | Hexene-1 | 11.0 | 19.6 | 0.92 |
| 20 | Octene-1 | 9.3 | 15.2 | 0.83 |

particular, for 4-MP-1), moderate decreases in EVH are not compensated for by larger increases in EV0. This indicates that 4-MP-1 is poorly incorporated in copolymers having a high ethylene content. In other words, the copolymer composition distribution is much wider, forming amorphous copolymers of high comonomer content as well as crystalline copolymers of very low comonomer content.

Figure 7 is plots of ETX vs σ . A smaller σ means that the variation of elution volumes above and below ETX is larger; accordingly, the copolymer composition distribution is narrower. As shown in Fig. 7, the homogeneity of comonomer incorporation is in the following order: B-1 \gg H-1 $>$ O-1 $>$ 4-MP-1.

^{13}C -NMR analysis was carried out for the copolymers to determine the comonomer sequence distribution and monomer reactivity ratio [19]. Table 4 lists the comonomer contents from ^{13}C -NMR, the triad sequence distributions (where E and C are an ethylene unit and a comonomer unit, respectively, and [C] is the comonomer content), and reactivity ratio products ($r_1 r_2$). The relationships between the former two factors are shown in Fig. 8. The data of H-1 and O-1 at their lowest contents (underlined in Table 4) are excluded from Fig. 8 because the NMR peak

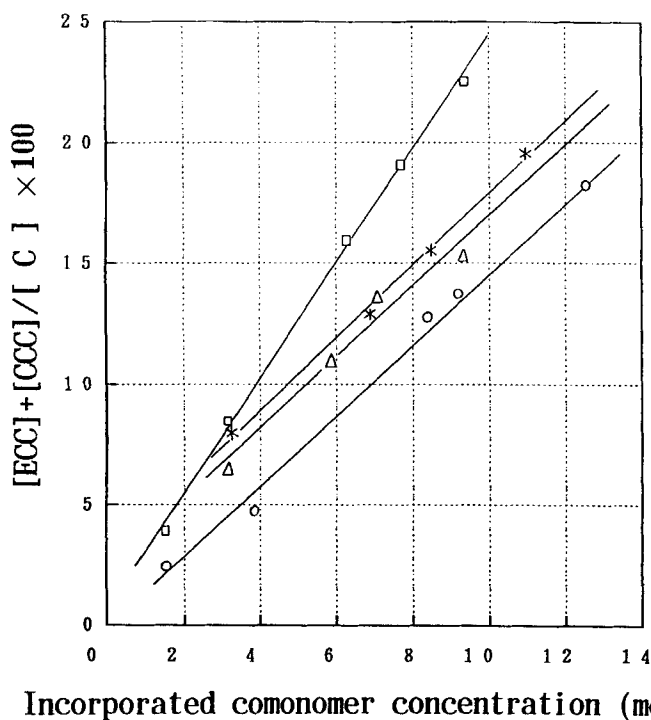


FIG. 8. Comonomer sequence distribution vs comonomer mole content: (○) butene-1, (□) 4-methylpentene-1, (*) hexene-1, (△) octene-1.

intensities are too weak to measure with accuracy and these values deviate remarkably from linear relationships. This figure shows that heavier olefins are incorporated more heterogeneously; this is more apparent at higher 4-MP-1 contents.

As described before, Ziegler-Natta-type solid catalysts generally have various active sites which produce copolymers having different comonomer compositions. Even in the present study of high temperature copolymerization, a remarkable heterogeneity of comonomer composition and differences in composition among the various comonomers were observed. The copolymers obtained comprise semicrystalline copolymers having higher ethylene contents and amorphous copolymers having higher comonomer contents. The former copolymers are likely insoluble in heptane as a polymerization medium, and the latter copolymers are much more soluble. It seems that each comonomer has a different diffusion rate as well as polymerization reactivity. The diffusion rate (DL) of a comonomer into a semicrystalline copolymer is lower than that (DH) into an amorphous copolymer, and it is known that DH/DL is higher for a heavier comonomer [20, 21]. In consideration of the present results, it can be said that 4-MP-1 has the largest DH/DL value compared to the other olefins. This may be a plausible explanation for the wider comonomer composition distribution of a heavier comonomer, in particular, 4-MP-1.

It would be reasonable to say that the kind of solvent used in polymerization has a large influence on the distribution of comonomer composition. In solution copolymerization where an appropriate medium is employed to dissolve even semi-crystalline copolymers, the copolymers produced should be more homogeneous. On the other hand, gas-phase copolymerization is likely to give rather heterogeneous copolymers.

CONCLUSION

Copolymerizations of ethylene with B-1, 4-MP-1, H-1, and O-1 were carried out at 130°C using a magnesium-chloride-supported titanium catalyst. 4-MP-1 showed the least reactivity whereas the other comonomers had the same reactivity. Investigations of density, melt temperature, molecular weight, ¹H-NMR, ¹³C-NMR, and TREF-GPC for the copolymers indicate that heavier comonomers give more heterogeneous copolymers. 4-MP-1 yields the most heterogeneous ones.

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