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Takayuki Otsu[a]; Hiroharu Nagahama[a]; Kiyoshi Endo[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University Sugimotocho, Osaka, Japan

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Monomer-Isomerization Polymerization. XII. Monomer-Isomerization Polymerizations of 2-Heptene and 3-Heptene with Ziegler-Natta Catalyst

TAKAYUKI OTSU, HIROHARU NAGAHAMA, and KIYOSHI ENDO

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimotocho, Sumiyoshi-ku, Osaka, Japan

ABSTRACT

A study of the monomer-isomerization polymerizations of 2-heptene and 3-heptene has been investigated with $(C_2H_5)_3Al-TiCl_3$ catalyst at 80°C. It was found that 2-heptene and 3-heptene underwent monomer-isomerization polymerization to give a high molecular weight polymer consisting of 1-heptene units. In these polymerizations the isomerization of both olefinic monomers was observed. The addition of the isomerization catalyst nickel acetylacetonate $[Ni(acac)_2]$ accelerated these polymerizations. The rate of polymerization of heptene isomers decreased in the following order; 1-heptene $\gg$ 2-heptene $>$ 3-heptene. The rate of polymerization and the isomer distribution of unreacted olefinic monomer after polymerization occurred via a stepwise double bond migration mechanism. It was also found that the monomer-isomerization copolymerization occurred between trans-2-butene and 2-heptene to give a copolymer cosisting of 1-butene and 1-heptene units. From the results of this copolymerization, the apparent monomer reactivity ratios were obtained as $r_1 = 1.45 \pm 0.05$ and $r_2 = 0.50 \pm 0.10$, where M_1 is trans-2-butene and M_2 is 2-heptene.

INTRODUCTION

In previous papers [1-5] it was shown that linear 2-olefins such as 2-butene, 2-pentene, and 2-hexene first isomerize to the corresponding 1-olefins in the presence of Ziegler-Natta catalyst and then homopolymerize as 1-olefins to give high molecular weight polymers consisting of the recurring unit of the corresponding 1-olefins.

If the 2-olefins are higher than 2-hexene, these monomer-isomerization polymerizations have difficulty in decreasing the concentration of 1-olefin in an equilibrium mixture. To clarify this point, the possibility of monomer-isomerization polymerization of 2-heptene was investigated. It was found that 2-heptene undergoes monomer-isomerization polymerization and copolymerization with 2-butene.

In the monomer-isomerization polymerization of 2-heptene, the isomerization from 2-heptene to 1-heptene and 3-heptene was observed. Therefore, 3-heptene, as a 3-olefin, is also expected to undergo monomer-isomerization polymerization to give poly-1-heptene.

In the light of the above considerations, the present paper deals with the results of monomer-isomerization polymerizations of 2-heptene and 3-heptene with Ziegler-Natta catalyst, and of the monomer-isomerization copolymerization of 2-heptene and 2-butene.

EXPERIMENTAL

Materials

The olefinic monomers were used after fractional distillation of the respective commercial grade samples over calcium hydride. The purities of 1-heptene, 2-heptene, 3-heptene, 1-butene, and trans-2-butene were 96.6, 97.2, (73.3% cis and 23.9% trans isomers), 99.1 (66.8% cis and 32.3% trans isomers), 97.9, and 99.3% respectively. Triethylaluminum (Ethyl Corp.), titanium trichloride (Stauffer Chemical), and transition metal compounds (Dotite reagents) were used without further purification. Solvents and precipitant were used after purification by conventional methods.

Polymerization Procedure

The polymerizations were carried out in a sealed glass tube with shaking for a given time. The charging was performed by methods described in the previous paper [3]. After polymerization, the tube was opened, unreacted olefinic monomers were recovered by distillation, and the isomer distribution was analyzed by gas chromatography by use of bis(2-methoxylethyl)adipate and $AgNO_3$-ethylene glycol columns at 40 and 20°C, respectively.

The contents of tube were then poured into a large amount of methanol containing hydrochloric acid to precipitate the polymer formed. The polymer yield was calculated from the weight of the dry polymer obtained.

Characterization of the Polymers

The structure of the resulting polymers was analyzed by IR and NMR spectroscopy. The intrinsic viscosity of polymer was determined by viscosity measurement of a dilute benzene solution at 30°C with an Ubbelohde viscometer.

The composition of resulting copolymers was analyzed by IR spectra. The ratio in optical density at 724 cm^{-1} (based on the C_5H_{11} group) and 1380 cm^{-1} (based on the CH_3 group) was used as a measure of the 1-butene unit content in the resulting copolymers.

RESULTS AND DISCUSSION

Monomer-Isomerization Polymerizations of 2-Heptene and 3-Heptene

The results of polymerizations of 1-heptene, 2-heptene, and 3-heptene with $(C_2H_5)_3Al-TiCl_3$ catalyst (Al/Ti = 3.0 molar ratio) are shown in Table 1. From this table, 2-heptene was found to polymerize at a slow rate as compared with 1-heptene. It is also

TABLE 1. Polymerizations of Heptene Isomers by $(C_2H_5)_3Al$-$TiCl_3$-Ni(acac)$_2$ Catalyst in p-Xylene[a]

Ni/Ti molar ratio	Temp (°C)	Time (hr)	Yield (%)	[η] (dl/g)	Composition of heptenes after polymerization (%)[b]					
					1H	c-2H	t-2H	c-3H	t-3H	Ha[c]
			1-Heptene		(96.6	0.8	0.9	1.0	0.0	0.9)[d]
0	30	1	35.7	0.51	96.6	0.8	0.9	1.0	0.0	0.9
0	80	0.17	57.5	-	96.6	0.8	0.9	1.0	0.0	0.9
			2-Heptene		(0.3	73.3	23.9	0.2	0.1	0.4)[d]
0	80	20	6.9	-	2.0	21.4	54.9	4.9	14.8	2.0
0	80	36	10.6	-	2.0	22.6	49.2	5.4	19.8	0.5
0.5	80	20	20.7	-	0.6	18.0	46.5	7.3	23.3	2.4
0.5	80	36	25.3	0.72	4.5	17.2	46.8	7.0	22.3	2.4
			3-Heptene		(0.0	0.0	0.0	66.8	32.3	0.9)[d]
0	80	108	Trace	-	-	-	-	-	-	-
0.5	80	103	4.6	-	2.0	15.9	28.5	14.6	38.0	1.2
					2.4[e]	12.2[e]	35.3[e]	10.0[e]	39.1[e]	

[a] $[TiCl_3]$ = 70 mmole/liter, [olefin] = 4.0 mole/liter, Al/Ti = 3.0.

[b] Determined by gas chromatography.

[c] c = cis, t = trans, H = heptene, Ha = heptane.

[d] Indicates the isomer composition of the starting heptenes.

[e] Equilibrated concentrations calculated from thermodynamic stabilities of heptene isomers.

observed that the isomerization from the starting cis- or trans-2-heptene to 1-heptene and cis- or trans-3-heptene occurs during the polymerization of 2-heptene, but in the rapid polymerization of 1-heptene no isomerization is seen. Such a result is similar to that observed for the polymerizations of 1- and 2-butenes [3].

From Table 1, 3-heptene is also found to polymerize with monomer isomerization, even though the polymer yield is quite low. It can be seen that both 2- and 3-heptenes undergo geometric and positional isomerizations during their polymerizations, and the observed isomer distributions of the unreacted heptenes approach those of an equilibrium mixture (see Table 1).

Figure 1 shows the IR spectra of the polymers obtained from 1-, 2-, and 3-heptenes. All IR spectra are completely the same, and the NMR spectra of the polymers obtained from 1- and 2-heptenes are also identical, as is shown in Fig. 2. Accordingly, it is clear that the polymers obtained from 1-, 2-, and 3-heptenes consist of the

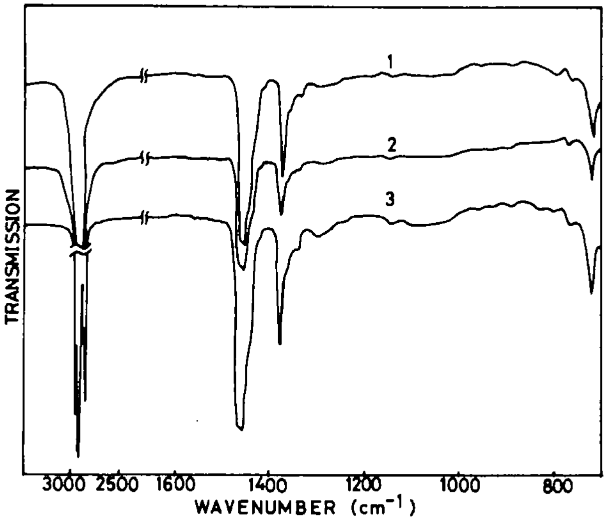
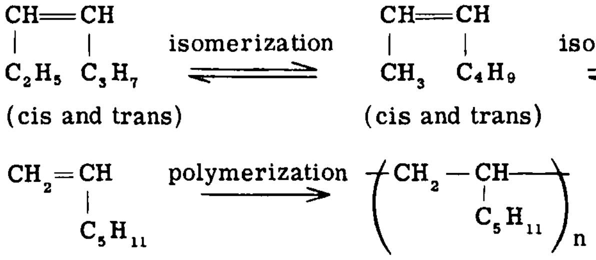


FIG. 1. IR spectra of polymers with $(C_2H_5)_3$-$TiCl_3$ catalyst: (1) obtained from 1-heptene, (2) obtained from 2-heptene, and (3) obtained from 3-heptene (film).

same recurring unit, i.e., 1-heptene, and that both 2- and 3-heptenes can undergo monomer-isomerization polymerization according to



$$\underset{\text{(cis and trans)}}{\underset{C_2H_5\quad C_3H_7}{CH{=}CH}} \xrightleftharpoons{\text{isomerization}} \underset{\text{(cis and trans)}}{\underset{CH_3\quad C_4H_9}{CH{=}CH}} \xrightleftharpoons{\text{isomerization}} \underset{C_5H_{11}}{CH_2{=}CH} \xrightarrow{\text{polymerization}} \left(CH_2-\underset{C_5H_{11}}{CH} \right)_n$$

It is also observed from Table 1 that the rate of monomer-isomerization polymerizations of 2- and 3-heptenes with $(C_2H_5)_3Al$-$TiCl_3$ catalyst is accelerated by the addition of $Ni(acac)_2$ as an isomerization catalyst. A similar result was obtained in the monomer-isomerization polymerization of 2-butene [4]. These observations strongly indicate that there are two independent active sites for isomerization of the 2- and 3-olefin monomers and polymerization of the isomerized 1-olefin.

The observed concentration of the polymerizable 1-heptene in these polymerization mixture is as low as about 0.5 to 4.5% (Table 1) which is in fairly good agreement with that (2.4%) calculated from the thermodynamic stabilities of heptene isomers [6]. The fact that a high molecular weight poly-1-heptene is obtained from 2-heptene under

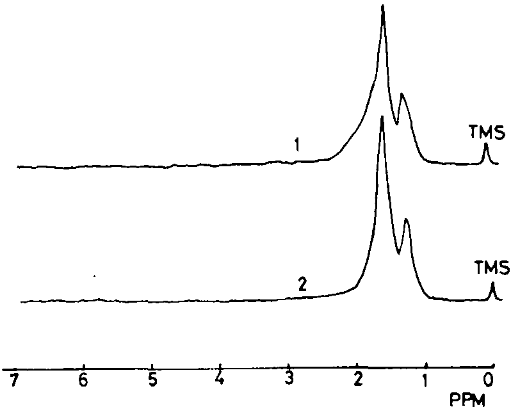


FIG. 2. NMR spectra of polymers with $(C_2H_5)_3$-$TiCl_3$ catalyst: (1) obtained from 1-heptene and (2) obtained from 2-heptene.

such conditions (Table 1) may be explained from the observation that the positional isomerization from 2-heptene to 1-heptene is sufficiently fast compared with that to 3-heptene to replenish the 1-heptene consumed.

Monomer-Isomerization Copolymerization of 2-Heptene with 2-Butene

In the previous paper [3], 2-butene was found to undergo monomer-isomerization polymerization under conditions similar to those used in this study. In order to check whether both 2-olefins can copolymerize with monomer isomerization, the copolymerization of trans-2-butene with 2-heptene was attempted with $(C_2H_5)_3Al-TiCl_3-Ni(acac)_2$ catalyst at 80 °C. As can be seen from Fig. 3, as an example, the IR spectrum of the copolymers obtained from the copolymerization of 2-butene with 2-heptene is found to be quite identical to that of 1-butene with 1-heptene. Accordingly, it is clear that both 2-olefins isomerize to the corresponding 1-olefin monomers preceding

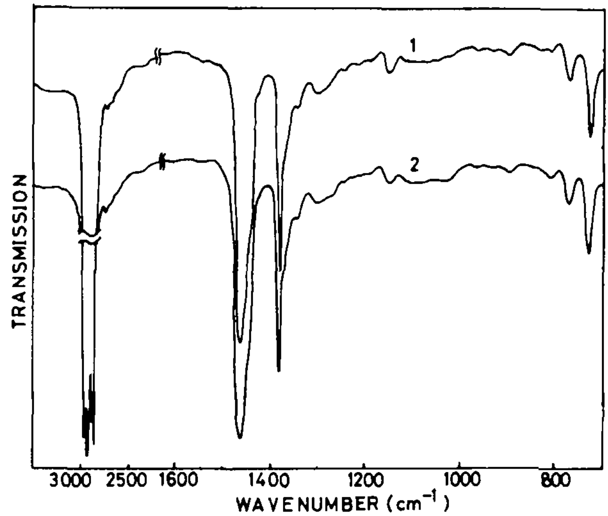
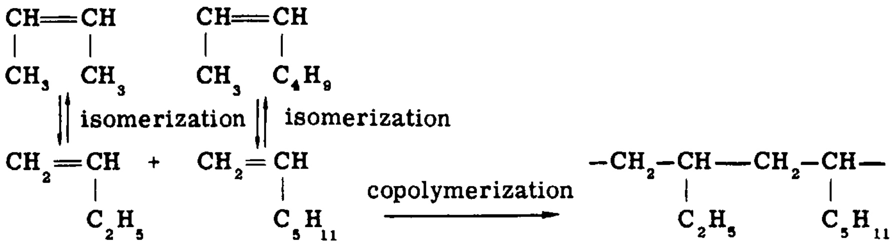


FIG. 3. IR spectra of polymers: (1) obtained from 1-butene and 1-heptene and (2) obtained from trans-2-butene and 2-heptene (film).

polymerization, and then copolymerize between 1-butene and 1-heptene as follows:



The 2-olefins do not participate in this copolymerization, and they act solely as inert diluents, similar to the monomer-isomerization copolymerizations of 2-butene with 2-pentene or 2-hexene [7].

The results of these monomer-isomerization copolymerizations of trans-2-butene (M_1) with 2-heptene (M_2) are shown in Table 2, in which the composition of the resulting copolymers was determined by the optical densities of the absorption bands due to the methyl group (1380 cm^{-1}) and the pentyl group (724 cm^{-1}) in their IR spectra.

Although in Table 3 the results of the copolymerization of 1-butene (M_1) with 1-heptene (M_2) under similar conditions are also shown, the rate of this copolymerization is faster than that of the monomer-isomerization copolymerization of 2-butene with 2-heptene, in which

TABLE 2. Monomer-Isomerization Copolymerization of trans-2-Butene (M_1) with 2-Heptene (M_2) by $(C_2H_5)_3Al$-$TiCl_3$-$Ni(acac)_2$ Catalyst in p-Xylene at 80°C[a]

$[M_1]$ in comonomer (mole %)	Time (min)	Yield (%)	$[M_1]^b$ in copolymer (mole %)
20.2	180	9.5	21.0
38.9	180	15.1	51.0
49.4	180	15.3	60.5
58.6	180	16.7	69.0
79.3	180	22.2	84.0

[a] Polymerization conditions: $[TiCl_3]$ = 70 mmole/liter, [total monomer] = 4.0 mole/liter, Al/Ti = 2.0, Ni/Ti = 0.5 (molar ratio).

[b] Stands for 1-butene unit.

TABLE 3. Copolymerization of 1-Butene (M_1) with 1-Heptene (M_2) by $(C_2H_5)_3Al-TiCl_3$ Catalyst in p-Xylene at 30°C[a]

$[M_1]$ in comonomer (mole %)	Time (min)	Yield (%)	$[M_1]$ in copolymer (mole %)
19.7	10	8.1	14.0
41.0	10	9.7	37.0
50.7	10	9.8	51.0
60.1	10	19.8	62.9
80.7	10	31.2	85.0

[a] Polymerization conditions: $[TiCl_3]$ = 70 mmole/liter, [total monomer] = 4.0 mole/liter, Al/Ti = 2.0 (molar ratio).

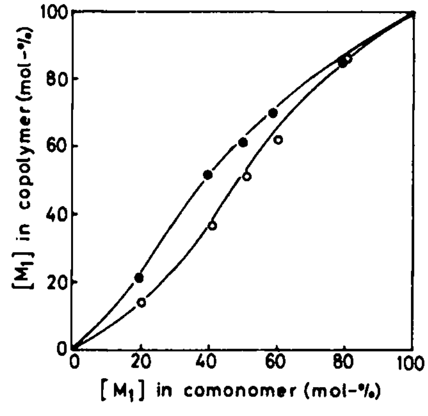


FIG. 4. Copolymer composition curves for the copolymerization of butenes (M_1) and heptenes (M_2): (○) copolymerization of 1-butene and 1-heptene, and (●) copolymerization of trans-2-butene and 2-heptene.

the rate of copolymerization increases with an increase of the 2-butene concentration in the monomer feed. The properties of the resulting copolymers changed from a viscous solid to a crystalline solid with an increase of their 1-butene content.

Figure 4 shows the copolymer composition curves in the

TABLE 4. Monomer Reactivity Ratios for the Copolymerizations of Butenes with Heptenes

M_1	M_2	r_1	r_2
trans-2-Butene	2-Heptene	1.45 ± 0.05	0.50 ± 0.10
1-Butene	1-Heptene	1.90 ± 0.29	2.05 ± 0.30

copolymerization of butenes and heptenes. The observed 1-butene content in the copolymers obtained from monomer-isomerization copolymerization between 2-olefins is somewhat higher than those from ordinary copolymerizations between 1-olefins at the same monomer feed compositions. Such a difference may originate from the isomerization rates of the 2-olefins and also from the concentrations of the corresponding 1-olefins (5.1 and 2.4% for 1-butene and 1-heptene, respectively) in their equilibrium mixtures.

The copolymerization parameters in both copolymerizations are shown in Table 4 in which the monomer reactivity ratios in the monomer-isomerization copolymerization of 2-butene with 2-heptene are apparent values because no corrections were made for the true concentrations of 1-olefins in the neighborhood of the catalyst system. It is interesting, however, that the monomer reactivity ratios of these olefins change depending on whether both 1-olefins or both 2-olefins are used as the feed monomer mixtures.

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