Monomer-Isomerization Polymerization. XIV. Monomer-Isomerization Polymerization of 4-Methyl-2-pentene with Ziegler-Natta Catalyst

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4-Methyl-2-pentene (4M2P) was found to polymerize in the presence of $TiCl_3$–$Al(C_2H_5)_3$ catalyst, and to yield a high molecular weight isotactic homopolymer of 4-methyl-1-pentene (4M1P). From the fact that the isomerizations from 4M2P to its positional isomers were also observed, it was concluded that this polymerization was induced by a monomer-isomerization polymerization mechanism, *i.e.* 4M2P isomerized first to 4M1P, which then homopolymerized. The rates of both polymerization and isomerization were affected by the Al/Ti molar ratio of catalyst system, and by the addition of transition metal compounds such as nickel acetylacetonate [$Ni(acac)_2$]. It was concluded that the maximum rates were observed at Al/Ti =3 and Ni/Ti=0.2 in molar ratio.

It has been well known that internal olefins do not polymerize to give high polymers in the presence of any catalysts, including Ziegler-Natta catalyst. Several years ago, however, it was found that some linear internal olefins such as 2-butene, 2-pentene, and 2-hexene polymerize with $TiCl_3$–$Al(C_2H_5)_3$ (Al/Ti≥2) catalysts to give high molecular weight polymers, if allowed to react for a long time at 80 °C.[1–5]

Interestingly, the polymers thus obtained were confirmed to be homopolymers consisting of the corresponding 1-olefin units. In accordance with the observation that the isomerization from the starting 2-olefin to the 1-olefin occurs simultaneously during reaction, it was concluded that these 2-olefins isomerize first to the corresponding 1-olefins, which then homopolymerize. Since this kind of polymerization gives a new route for polymer synthesis, we have proposed that this polymerization proceeds *via* a monomer-isomerization polymerization mechanism.

These monomer-isomerization polymerizations have also been extended to the other higher internal olefins, such as 2-heptene, 3-heptene, and 2-octene.[6] In general, the monomer-isomerization polymerization involves two independent reaction steps: isomerization to the most polymerizable 1-olefin and polymerization of this 1-olefin. Accordingly, the total rate of polymerization is determined by both the rate of isomerization to 1-olefin and its concentration in an equilibrium olefin mixture. Since such a concentration in linear internal olefins is generally higher than that in branched ones, it is usually expected that the former olefins are more favorable to the monomer-isomerization polymerization than are the latter olefins.

However, it was found recently that some branched internal olefins, 4M2P, underwent monomer-isomerization polymerization in the presence of $TiCl_3$–$Al(C_2H_5)_3$ catalyst to give the homopolymer of 4M2P. The present paper describes the results of these monomer-isomerization polymerizations of 4M2P.

Experimental

Materials. 4M2P and 4M1P were purified through a fractional distillation of commercial grade samples. Purities of both monomers determined by gas chromatography were above 99.9%; here the *cis* and *trans* isomers could not be separated.

Triethylaluminum (Ethyl Corp.), titanium trichloride (Stauffer Chem.), and transition metal chelates of acetylacetonate (acac) such as $Ni(acac)_2$ and $Co(acac)_2$ (Dotite reagent) were used without further purification. Solvents were purified by ordinary methods.

Polymerization Procedure. Most polymerizations were carried out in a sealed glass tube with shaking in a thermostat for a given time. The charging of the required reagents into the tube and its sealing under vacuum were performed by methods described in the previous paper.[3] After polymerization the tube was opened and the unreacted olefin monomer was recovered by distillation in order to analyze the isomer distribution by means of gas chromatography, in which a bis(2-methoxyethyl) adipate column was used at 17 °C. The residue of the tube was 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. In these polymerizations, the polymer yield was dependent on the conditions of catalyst preparation, and seemed to contain ±2% error.

Characterization of the Polymers. The structure of the resulting polymers was checked by infrared spectroscopy of their thin films. The isotacticity of the polymers was determined by the weight of the hot *n*-hexane–insoluble polymer.[7] The intrinsic viscosity ($[\eta]$) was determined from a viscosity measurement of the dilute decaline solution at 130 °C with an Ubbelohde viscometer. The number-average molecular weight ($\bar{M}_n$) was calculated from the following equation:[7]

$$[\eta] = 1.95\times 10^{-4}\bar{M}_n^{0.75}$$

Results and Discussion

Polymerization and Isomerization of 4M2P with $TiCl_3$–$Al(C_2H_5)_3$ Catalyst. The results of polymerization and isomerization of 4M2P with $TiCl_3$–$Al(C_2H_5)_3$ catalyst in *p*-xylene or *n*-heptane are summarized in Table 1. As can be seen from this table, the yields of polymers in both solvents increase as a function of polymerization time, and those in *n*-heptane are somewhat higher than in *p*-xylene. Upon comparing these results with those of 4M1P under similar conditions, as shown in Table 2, the polymerization of 4M2P was found to proceed with a much slower rate.

Figure 1 shows the infrared spectra of the polymers obtained from 4M2P and 4M1P with the $TiCl_3$–$Al(C_2H_5)_3$ catalyst. From this figure, the infrared spectra of both polymers are quite identical. It is clear therefore that the polymers obtained from 4M2P and 4M1P

Table 1. Monomer-isomerization polymerization of 4-methyl-2-pentene with $TiCl_3$–$Al(C_2H_5)_3$ catalyst at 80 °C[a)]

Solvent	Time (hr)	Yield (%)	Composition of methylpentenes recovered after polymerization, %[b)]				
			2MP	4MIP	4M2P	2M2P	2M1P
p-Xylene	5	3.6	0.2	0.3	98.8	0.7	0.0
p-Xylene	10	5.4	0.2	0.2	98.5	1.1	0.0
p-Xylene	20	7.6	0.7	0.6	96.5	2.2	0.0
p-Xylene	45	11.8	1.2	0.5	95.1	3.2	0.0
p-Xylene	60	16.7	0.5	0.4	94.1	5.0	trace
n-Heptane	5	5.2	1.5	0.5	93.1	4.6	0.3
n-Heptane	10	10.6	1.8	0.5	88.7	8.3	0.7
n-Heptane	20	15.9	2.5	0.4	84.5	11.5	1.1
n-Heptane	45	16.5	2.3	0.5	83.5	13.1	0.6
n-Heptane	60	20.4	0.6	0.6	91.2	6.8	0.6
				0.5[c)]	3.7[c)]	82.6[c)]	13.2[c)]

a) Polymerization conditions: $[TiCl_3]=117$ mmol/l, $[4M2P]=2.7$ mol/l, Al/Ti=3.0 in molar ratio. b) Determined by gas chromatography of the unreacted monomer mixture recovered after polymerization. c) Equilibrated concentrations calculated from free energies of formation of the isomer.

Table 2. Polymerization of 4-methyl-1-pentene with $TiCl_3$–$Al(C_2H_5)_3$ catalyst in *p*-xylene[a)]

Al/Ti molar ratio	Time (hr)	Temp. (°C)	Polymer Yield (%)
0.5	0.07	80	100
1.0	0.07	80	100
2.0	0.07	80	100
3.0	1.00	30	94.8

a) Polymerization conditions: $[TiCl_3]=117$ mmol/l, $[4M1P]=3.0$ mol/l.

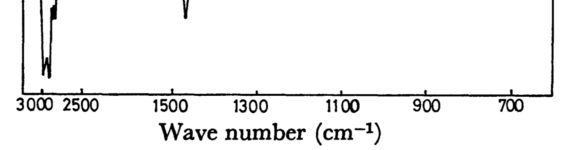


Fig. 1. Infrared spectra of polymers with $TiCl_3$–$Al(C_2H_5)_3$ catalyst (1) obtained from 4M1P, (2) obtained from 4M2P (film).

consist of the same recurring unit, 4M1P. Like the polymers obtained from 4M1P with Ziegler-Natta catalyst, the polymers from 4M2P are observed to contain isotactic polymers which have molecular weights of 4—11.5×10^4 (Table 3), and melt at 213 °C.

Table 3. Some properties of the polymers obtained from 4M2P with $TiCl_3$–$Al(C_2H_5)_3$ catalyst in *p*-xylene at 80 °C for 60 hr[a)]

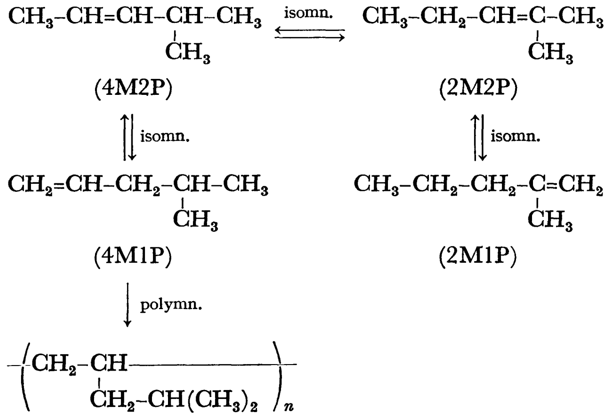
Al/Ti molar ratio	Ni/Ti molar ratio	Yield (%)	Solvent extraction		$[\eta]$ (dl/g)	$\bar{M}_n$ ($\times 10^{-4}$)
			n-hexane soluble (%)	*n*-hexane insoluble (%)		
2.0	0.15	35.6	73.5	26.5	1.21	11.45
2.0	0.20	35.9	56.8	43.2	—	—
2.0	0.0	24.4	61.7[b)]	38.3	—	—
3.0	0.0	27.5	56.9[b)]	43.1	0.68	3.89

a) Polymerization conditions: $[TiCl_3]=117$ mmol/l, $[4M2P]=2.7$ mol/l. b) $[4M2P]=3.0$ mol/l.

As is also shown in Table 1, the isomerizations of 4M2P to its positional isomers are observed to proceed with a time in proportion to the polymer yield. In *n*-heptane, 2-methyl-1-pentene (2M1P) isomer was found during polymerization of 4M2P, but only a trace of this isomer was observed in *p*-xylene. Contrary to the results of the polymerization of 2-butene to poly-1-butene, the observed isomer distributions are seen to approach with a very slow rate to those in an equilibrium olefin mixture. However, it is obvious from Table 1 that the rate of isomerization to 4M1P, which is the most polymerizable isomer, is much greater than that to 2-methyl-2-pentene (2M2P), which is the most stable isomer.

Accordingly these results strongly indicate that 4M2P undergoes monomer-isomerization polymerization to give high molecular weight isotactic poly (4M1P), *i.e.* 4M2P isomerizes to 4M1P prior to polymerization and then this olefin homopolymerizes. In this case, it is interesting that 4M2P and 2M2P serve only as a diluent, and the high molecular weight homopolymer of 4M1P is obtained, although the observed concentration of 4M1P isomerized from 4M2P is as low as 0.5%. This result can be expected from the fact that the isomerization to 4M1P is sufficiently fast to replenish the consumed 4M1P.

The monomer-isomerization polymerization of 4M2P is expressed by the following reaction scheme:



More recently it has been found that both 2M2P and 2M1P also undergo the monomer-isomerization polymerization with a very slow rate to give poly (4M1P).

Table 4. Effect of Al/Ti molar ratio on monomer-isomerization polymerization of 4-methyl-2-pentene with $TiCl_3$–Al $(C_2H_5)_3$ catalyst in *p*-xylene at 80 °C for 60 hr[a]

Al/Ti molar ratio	Yield (%)	Composition of methylpentenes recovered after polymerization, %[b]				
		2MP	4M1P	4M2P	2M2P	2M1P
0.25	0.0	1.1	0.1	98.1	0.7	0.0
0.5	trace	trace	trace	99.9	trace	0.0
1.0	10.6	0.2	0.2	92.3	7.0	0.3
2.0	24.4	0.8	0.4	91.3	7.0	0.5
3.0	27.5	0.4	0.1	84.8	14.1	0.6
3.5	33.1	0.5	0.2	87.7	11.4	0.2
4.0	17.6	1.2	0.8	89.7	8.0	0.3
5.0	10.2	2.5	2.1	86.0	9.0	0.4

a) $[TiCl_3]=117$ mmol/l, $[4M2P]=3.0$ mol/l. b) Determinaed by gas chromatography.

Table 5. Effect of isomerization catalyst (MeX) on the monomer-isomerization polymerization of 4-methyl-2-pentene with $TiCl_3$–Al $(C_2H_5)_3$ catalyst at 80 °C in *p*-xylene; Al/Ti=3.0 in molar ratio

MeX	$TiCl_3$ (mmol/l)	Monomer (mol/l)	Me/Ti molar ratio	Time (hr)	Yield (%)
None	70	4.0	0	96.5	11.0
$Ni(acac)_2$	70	4.0	0.5	96.5	6.4
$Co(acac)_2$	70	4.0	0.5	96.5	4.0
$Mn(acac)_2$	70	4.0	0.5	96.5	trace
None	105	3.0	0	100.0	24.6
$Ni(acac)_2$	105	3.0	0.5	100.0	14.4
$Fe(acac)_3$	105	3.0	0.5	100.0	5.9
$Co(acac)_3$	105	3.0	0.5	100.0	trace

Effect of Al/Ti Molar Ratios on Monomer-Isomerization Polymerization of 4M2P. In the monomer-isomerization polymerization of 2-butene with $TiCl_3$–$Al(C_2H_5)_3$ catalyst, it was found that the rate of polymerization was affected by the Al/Ti molar ratios used. A similar result was also reported in the polymerization of 4M1P with $TiCl_3$–$Al(C_2H_5)_3$ catalyst in which the rate went through a maximum at the Al/Ti molar ratio of 3.0.[8]

To check this point, the effects of Al/Ti molar ratio on the monomer-isomerization polymerization of 4M2P were investigated. The results are shown in Table 4, from which it is found that the maximum rates of both polymerization and isomerization are observed at a molar ratio Al/Ti of about 3.0—3.5. This finding is in agreement with that observed in the polymerization of 4M1P.[8]

From Table 4, at the Al/Ti molar ratio lower than 1.0, neither polymerization nor isomerization occured. The polymers obtained at the Al/Ti molar ratios higher than 1.0 were found to consist of poly (4M1P).

Effect of Metal Acetylacetonates $[Me(acac)_x]$ on Monomer-Isomerization Polymerization of 4M2P. Since, in monomer-isomerization polymerization of 2-olefin, the isomerization to 1-olefin must occur before its polymerization,[4] the addition of isomerization catalyst is expected to accelerate this polymerizarion. As is shown in Table 5, however, the polymerizations of 4M2P slowed down in the presence of $Me(acac)_x$ in which the Me/Ti molar ratio was kept constant at 0.5. This observation is different from the observed accelerating effect on the monomer-isomerization polymerization of 2-butene.[4]

Table 6. Effect of $Ni(acac)_2$ on the monomer-isomerization polymerization of 4-methyl-2-penetene with $TiCl_3$–$Al(C_2H_5)_3$–$Ni(acac)_2$ catalyst at 80 °C in *p*-xylene for 60 hr[a]

Ni/Ti molar ratio	Yield (%)	Composition of methylpentenes recovered after polymerization, %[b]				
		2MP	4M1P	4M2P	2M2P	2M1P
0	18.5	0.9	0.5	92.0	6.3	0.3
0.06	20.9	1.9	1.2	89.3	7.0	0.6
0.15	35.6	1.4	0.8	68.2	26.8	2.8
0.20	35.9	—	—	—	—	—
0.30	18.6	1.3	2.3	70.9	22.3	3.2
0.40	3.5	0.7	4.5	78.6	13.9	2.3
0.50	1.0	0.5	2.8	75.0	16.7	5.0
Ni/Al=1/8	0.0	0.2	4.7	85.0	7.9	2.2

a) Polymerization conditions: $[TiCl_3]=117$ mmol/l, $[4M2P]=2.7$ mol/l, Al/Ti=2.0 in molar ratio. b) Determied by gas chromatography. c) In the absence of $TiCl_3$.

To test further the effect of $Me(acac)_2$, the polymerization and isomerization of 4M2P with $TiCl_3$–$Al(C_2H_5)_3$ (Al/Ti=2) catalyst in the presence of various Ni/Ti molar ratios of $Ni(acac)_2$ were investigated. The results are shown in Table 6. It is found that the rates of both polymerization and isomerization are dependent on the Ni/Ti molar ratio added, and their maximum rates are observed at an Ni/Ti molar ratio of about 0.15—0.2.

This observation seems to originate from the fact that $Ni(acac)_2$ behaves as both activator and deactivator of active sites for polymerization of 4M1P and isomerization from 4M2P to 4M1P, because $TiCl_3$ and $Ni(acac)_2$ react competitively with $Al(C_2H_5)_3$ in the catalyst system. Accordingly, it is found that at the molar ratio Ni/Ti of 0.5, the active sites for polymerization are destoroyed.

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