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Monomer-Isomerization Polymerization of Some Branched Internal Olefins with a Ziegler-Natta Catalyst

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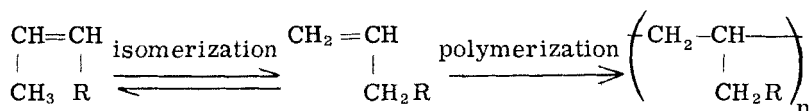
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ABSTRACT

New examples for the monomer-isomerization polymerizations of some branched internal olefins, 4-methyl-2-pentene and 4-phenyl-2-butene, are presented. When these olefins are polymerized with $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ ($[\text{TiCl}_3] = 120$ mmole/liter, $\text{Al/Ti} = 3.0$) catalyst at 80°C , considerable amounts of high polymers [27.5%/60 hr ($[\eta] = 0.68$ dl/g) and 35.6%/100 hr, respectively] were obtained. From the additional fact that the isomerization from these 2-olefins to the mixture of their positional isomers including 1-olefins was observed during the polymerization, it is assumed that the polymerizations from these 2-olefins are performed with the 1-olefins which isomerized from the starting 2-olefins.

INTRODUCTION

In previous papers [1-4] it has been reported that internal olefins such as 2-butene, 2-pentene, 2-hexene, 2-heptene, 3-heptene, and 2-octene can homopolymerize in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ ($\text{Al/Ti} = 2$ to 3) catalyst to give high polymers consisting of the corresponding 1-olefin units:



where $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{and } \text{C}_5\text{H}_{11}$.

In these monomer-isomerization polymerizations, two independent steps on the two independent catalyst sites are involved. In the first step the internal olefin is isomerized to an equilibrium mixture of various olefins, including 1-olefin; in the second step, this 1-olefin is polymerized. Accordingly, the total rate of polymerization of the internal olefin is determined by its isomerization rate, its concentration in an equilibrium mixture, and the polymerizability of the 1-olefin formed by isomerization. Since the concentration of 1-olefin in an equilibrium mixture isomerized from linear 2-olefin is generally higher than that from branched 2-olefins, it is expected that the former olefins are more favorable to monomer-isomerization polymerization than the latter olefins [2, 5, 6].

We have recently found that some branched internal olefins such as 4-methyl-2-pentene and 4-phenyl-2-butene undergo monomer-isomerization polymerization in the presence of a Ziegler-Natta catalyst. The present paper deals with the results of monomer-isomerization polymerizations of these branched internal olefins.

EXPERIMENTAL

Material

4-Methyl-1-pentene, 4-methyl-2-pentene, 4-phenyl-1-butene, and 4-phenyl-2-butene were used after fractional distillation over calcium hydride of the respective commercial reagents. Purities determined by gas chromatography were 99.9, 99.9, 96.0, and 99.9%, respectively; 4-phenyl-2-butene consisted of 97.3% cis and 2.7% trans isomers.

Triethylaluminum, ethylaluminum dichloride (Ethyl Corp.), diethylaluminum chloride (Texas Alkyls), titanium trichloride (Stauffer Chem. Co.), and transition metal compounds (commercial pure grade reagents) were used without further purification. Solvents and precipitants were used after purification by the conventional method.

Polymerization Procedure

Titanium trichloride in a sealed small ampule, and if necessary a transition metal compound, was placed in a glass tube provided with a rubber stopper and with a connection to the vacuum system. The required amount of solvent was added through a syringe after degassing, and the required amount of alkylaluminum solution was charged through a syringe in a dry nitrogen atmosphere. The TiCl_3 ampule was destroyed, and the mixture was aged for an hour at room temperature. After aging, olefin monomer was charged through a syringe. The system was then sealed under vacuum.

Polymerizations were carried out by shaking in a thermostat maintained at a constant temperature for a given time. The tube was opened after polymerization, and the unreacted olefin was recovered by distillation and its isomer distribution was analyzed by gas chromatography by using a bis(2-methoxyethyl)-adipate column at 17°C for methylpentenes and Bentone 34 and tricresylphosphate columns at 110°C for phenylbutenes. The residues of the tube were then poured into a large amount of methanol containing hydrochloric acid in order 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 checked by the IR spectra of their films. The isotacticity of the resulting polymer was determined from the weight of hot n-hexane-insoluble polymer [7]. The intrinsic viscosity of the polymer was determined by viscosity measurement of dilute Decalin solution at 130°C with an Ubbelohde viscometer.

RESULTS AND DISCUSSION

Monomer-Isomerization Polymerization of 4-Methyl-2-pentenePolymerization and Isomerization

The results of polymerization of 4-methyl-2-pentene by $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ catalyst in n-heptane are shown in Table 1, in which the results of isomerization are also indicated.

From Table 1 it is observed that this olefin easily polymerizes and the yield increases with an increase of the reaction time. For comparison, the corresponding 1-olefin, 4-methyl-1-pentene, was polymerized at a very fast rate (95.8%/1 hr at 30°C) without isomerization under similar conditions. The polymer obtained from this 2-olefin shows the same IR spectrum as the polymer obtained from 4-methyl-1-pentene, as is seen from Fig. 1. The polymers are also found to contain the hexane-insoluble fractions (43.1%) which consist of a high molecular weight isotactic structure ($[\eta] = 0.68$ dl/g).

TABLE 1. Results of Polymerization and Isomerization of 4-Methyl-2-pentene by $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ Catalyst^a

Time (hr)	Yield (%)	Composition of methylpentenes recovered after polymerization (%) ^b				
		4M1P	4M2P	2M2P	2M1P	2MP
5	5.2	0.5	93.1	4.6	0.3	1.5
10	10.6	0.5	88.7	8.3	0.7	1.8
20	15.9	0.4	84.5	11.5	1.1	2.5
40	16.5	0.5	83.5	13.1	0.6	2.3
60	20.4	0.8	91.2	6.8	0.6	0.6
		0.5 ^c	3.7 ^c	82.6 ^c	13.2 ^c	

^aPolymerization conditions: $[\text{TiCl}_3] = 117$ mmole/liter, $\text{Al/Ti} = 3.0$, $[\text{4M2P}] = 2.7$ mole/liter at 80°C.

^bAbbreviations are as follows: 4M1P, 4-methyl-1-pentene; 4M2P, 4-methyl-2-pentene; 2M2P, 2-methyl-2-pentene; 2M1P, 2-methyl-1-pentene; 2MP, 2-methylpentane.

^cCalculated from the thermodynamic stabilities of the isomers.

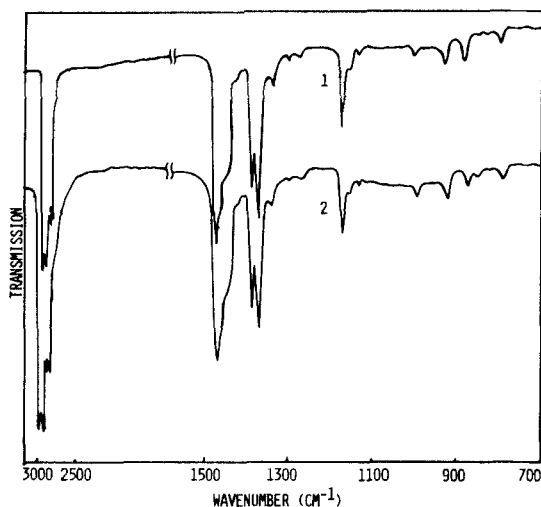
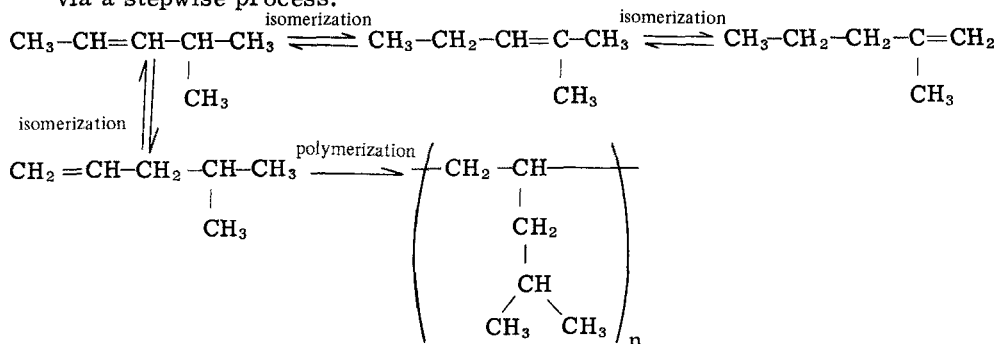


FIG. 1. IR spectra of polymers: (1) obtained from 4-methyl-1-pentene with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst; (2) obtained from 4-methyl-2-pentene with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst.

It is also found from Table 1 that the isomerization of the starting olefin to the corresponding positional isomers and the formation of a saturated alkane, 2-methylpentane, are observed during the polymerization, and that the concentration of 4-methyl-1-pentene isomer is in good agreement with that (0.5%) calculated from the thermodynamic stabilities of these isomers. From these results it is clear that this polymerization is an example of the monomer-isomerization polymerization, similar to those of linear internal olefins such as 2-butene [2].

From the change in isomer distribution of this 2-olefin with polymerization time (Table 1), the isomerization seems to proceed via a stepwise process:



It is also interesting that the rate of isomerization from 4-methyl-2-pentene to 4-methyl-1-pentene is faster than that to 2-methyl-2-pentene, which is the most stable of these isomers. In connection with this result, it was found that 2-methyl-2-pentene and 2-methyl-1-pentene can undergo monomer-isomerization polymerization at a very slow rate [8].

Effect of Al/Ti Molar Ratio and Transition Metal Compounds

The effect of the Al/Ti molar ratio in the catalyst system on the polymerization and the isomerization of 4-methyl-2-pentene is shown in Table 2.

From this table it is seen that the maximum rates of both polymerization and isomerization are observed at a molar ratio of Al/Ti of about 3.0 to 3.5. The result regarding the polymerization rate is in good agreement with that reported for the polymerization of 4-methyl-1-pentene by $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ catalyst [9].

TABLE 2. Effects of Al/Ti Molar Ratio on the Monomer-Isomerization Polymerization of 4-Methyl-2-pentene^a

Al/Ti molar ratio	Yield (%)	Composition of methylpentenes recovered after polymerization (%) ^b				
		4M1P	4M2P	2M2P	2M1P	2MP
0.5	0	0	99.8	0	0	0
1.0	10.6	0.2	92.3	7.0	0.3	0.2
2.0	22.4	0.4	91.3	7.0	0.5	0.3
3.0	27.5	0.1	84.8	14.1	0.6	0.4
3.5	33.1	0.2	87.7	11.4	0.2	0.5
4.0	17.6	0.8	89.7	8.0	0.3	1.2

^aPolymerization conditions: $[\text{TiCl}_3] = 117$ mmole/liter, $[4\text{M}2\text{P}] = 2.7$ mole/liter, in p-xylene at 80°C for 60 hr.

^bAbbreviations as in Table 1.

TABLE 3. Effects of Transition Metal Compounds^a

Me(acac) _x	Yield (%)
None	24.6
Ni(acac) ₂	14.4
Fe(acac) ₃	5.9

^aPolymerization conditions: Al(C₂H₅)₃-TiCl₃ catalyst, [TiCl₃] = 105 mmole/liter, [4M2P] = 3.0 mole/liter, Al/Ti = 3.0, Me/Ti = 0.5, in p-xylene at 80°C for 100 hr.

As shown in Table 3, transition metal compounds such as metal acetylacetonates [Me(acac)_x] are found to exhibit a retarding effect on the rate of this polymerization (Me/Ti = 0.5), contrary to the marked accelerating effect they showed on the monomer-isomerization polymerizations of 2-butene and 2-pentene [3]. To check this point further, the effect of the Ni/Ti molar ratio of the catalyst system [Al(C₂H₅)₃-TiCl₃-Ni(acac)₂, Al/Ti = 3.0] on the rate of polymerization and isomerization of 4-methyl-2-pentene was investigated. The results are shown in Fig. 2.

From Fig. 2 it is seen that both polymerization and isomerization are affected by the concentration of Ni(acac)₂, and their maximum rate is also found to appear at a molar ratio Ni/Ti of ~0.2. Accordingly, it seems that Ni(acac)₂ behaves as both activator and deactivator in the formation of the active sites as a function of its concentration, and when the concentration of Ni(acac)₂ increases to more than a molar ratio Ni/Ti of 0.5, the active sites for isomerization and polymerization are completely destroyed.

Monomer-Isomerization Polymerization of 4-Phenyl-2-butene

Polymerization with Various Catalyst System

The results of the polymerization of 4-phenyl-2-butene with various Ziegler-Natta-type catalysts are shown in Table 4, as are the results for 4-phenyl-1-butene.

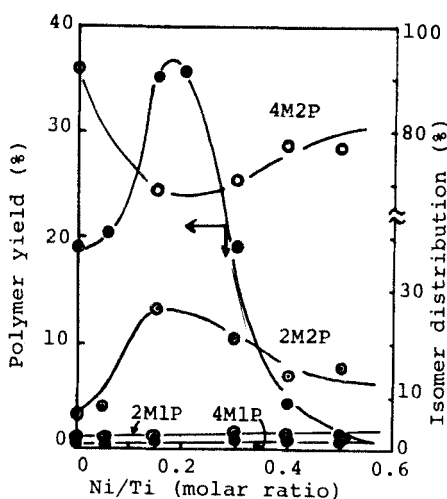


FIG. 2. Effects of Ni/Ti molar ratio on the polymerization and the isomer distribution when 4-methyl-2-pentene is reacted with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 - $\text{Ni}(\text{acac})_2$ as the catalyst: $[\text{TiCl}_3] = 117$ mmole/liter $\text{Al}/\text{Ti} = 2.0$, $[\text{4M2P}] = 2.7$ mole/liter at 80°C for 60 hr.

TABLE 4. Polymerization of Phenylbutenes^a

Monomer ^b	Catalyst system	Time (hr)	Yield (%)
4Ph1B	$(\text{C}_2\text{H}_5)_3\text{Al}-\text{TiCl}_3$	0.25	100
4Ph2B	$(\text{C}_2\text{H}_5)_3\text{Al}-\text{TiCl}_3$	100	35.6
4Ph2B	$(\text{C}_2\text{H}_5)_2\text{AlCl}-\text{TiCl}_3$	100	Trace
4Ph2B	$\text{C}_2\text{H}_5\text{AlCl}_2-\text{TiCl}_3$	100	0.5

^aPolymerization condition: $[\text{TiCl}_3] = 120$ mmole/liter, $\text{Al}/\text{Ti} = 3.0$, $[\text{Monomer}] = 3.0$ mole/liter, in heptane at 80°C .

^bAbbreviations are as follows: 4Ph1B, 4-phenyl-1-butene; 4Ph2B, 4-phenyl-2-butene.

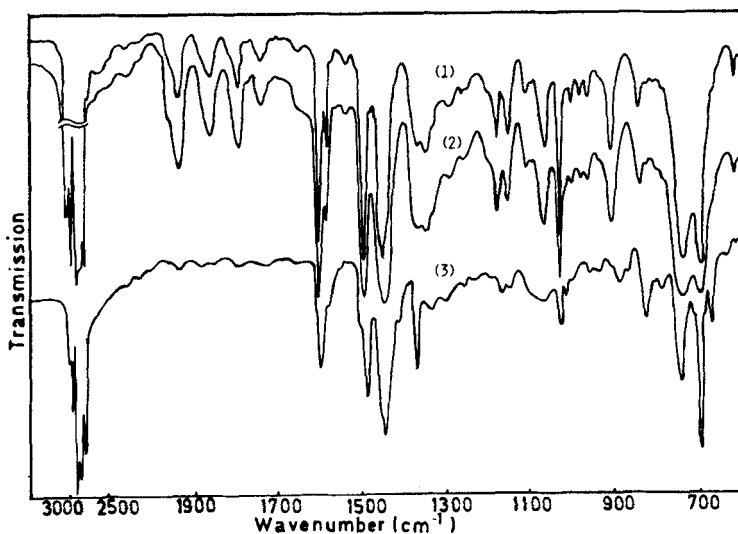


FIG. 3. IR spectra of polymers: (1) obtained from 4-phenyl-1-butene with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst; (2) obtained from 4-phenyl-2-butene with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst; (3) obtained from 4-phenyl-2-butene with $\text{C}_2\text{H}_5\text{AlCl}_2$ - TiCl_3 catalyst.

As can be seen from Table 4, 4-phenyl-1-butene quite readily polymerizes with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst, but 4-phenyl-2-butene gives polymer at a slower rate under similar conditions. The catalyst systems consisting of $(\text{C}_2\text{H}_5)_2\text{AlCl}$ and $\text{C}_2\text{H}_5\text{AlCl}_2$ instead of $\text{Al}(\text{C}_2\text{H}_5)_3$ show very weak activity for the polymerization of 4-phenyl-2-butene, and the polymer obtained by the latter system was a viscous brownish material which was confirmed from IR spectrum (Fig. 3) to be an oligo(4-phenyl-2-butene).

However, the polymers obtained from both phenylbutenes with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst show an identical IR spectrum (Fig. 3), indicating that 4-phenyl-2-butene underwent monomer-isomerization polymerization with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst. This conclusion was also supported by the fact that the rate of polymerization corresponded to that of isomerization (see Table 5):

TABLE 5. Results of Polymerization and Isomerization of 4-Phenyl-2-butene with $\text{Al}(\text{C}_2\text{H}_5)_3$ - TiCl_3 catalyst^a

Al/Ti molar ratio	Time (hr)	Yield (%)	Composition of phenylbutenes recovered after polymerization (%) ^b					
			4Ph1B	cis- 4Ph2B	trans- 4Ph2B	cis- 1Ph1B	trans- 1Ph1B	BuBz
2.0	60	17.5	1.1	61.2	26.7	0.3	10.5	0.2
3.0	100	35.6	2.2	50.3	15.4	0.3	31.7	0.1
4.0	60	14.4	2.5	51.2	15.5	1.5	24.7	2.6
5.0	60	14.9	1.0	65.7	19.8	0.4	12.8	1.0

^aPolymerization conditions: $[\text{TiCl}_3] = 120$ mmole/liter, $[4\text{Ph2B}] = 3.0$ mole/liter, in p-xylene at 80°C .

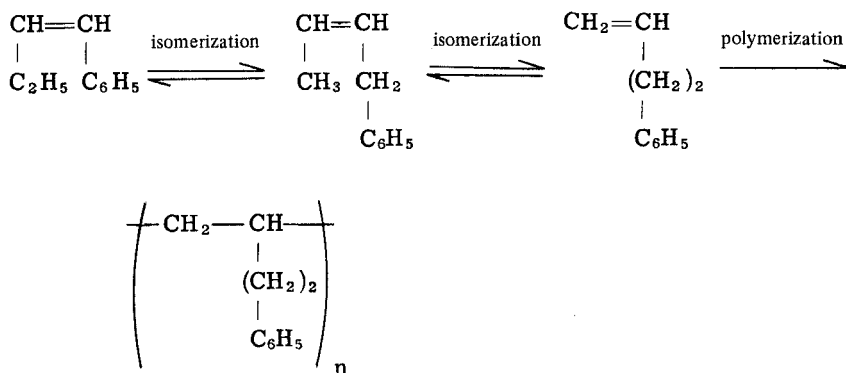
^bAbbreviations are as follows: 1Ph1B, 1-phenyl-1-butene; BuBz, n-butylbenzene; 4Ph1B and 4Ph2B, see Table 4.

TABLE 6. Effects of Transition Metal Compounds (MeX) on the Monomer-Isomerization Polymerization of 4-Phenyl-2-butene^a

MeX	Yield (%)	Composition of phenylbutenes recovered after polymerization (%) ^b					
		4Ph1B	cis- 4Ph2B	trans- 4Ph2B	cis- 1Ph1B	trans- 1Ph1B	BuBz
None	12.5	1.9	52.7	15.8	0.4	25.3	3.5
Ni(acac) ₂	12.7	1.9	36.3	10.4	0.7	47.5	3.2
Ni(DMG) ₂	15.9	1.0	17.9	4.0	1.9	69.9	5.3
Co(acac) ₃	20.6	1.9	52.1	15.6	0.4	27.6	2.4
Fe(acac) ₃	13.5	2.3	49.2	15.5	0.4	27.2	5.5

^aPolymerization conditions: $[\text{TiCl}_3] = 120$ mmole/liter, Al/Ti = 3.0, $[4\text{Ph2B}] = 3.0$ mole/liter, MeX/Ti = 0.1, in n-heptane at 80°C for 60 hr.

^bAbbreviations as in Tables 4 and 5.



Effects of Al/Ti Molar Ratio and Transition Metal Compounds

The effects of the Al/Ti molar ratio in the $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_3$ catalyst on the polymerization and the isomerization of 4-phenyl-2-butene are shown in Table 5.

From Table 5 it is also observed that the rate of polymerization goes through a maximum at a molar ratio of Al/Ti of 2 to 3.

The effect of transition metal compounds on this monomer-isomerization polymerization is shown in Table 6. It is found that $\text{Ni}(\text{DMG})_2$ and $\text{Co}(\text{acac})_3$ serve as accelerators for this polymerization when the Me/Ti molar ratio is 0.1, but the other compounds are not effective. However, the effect of the concentration of these metal compounds on polymerization is uncertain.

CONCLUSION

Although from a consideration of the thermodynamic stabilities of isomers in 4-methyl- and 4-phenyl-branched 2-olefins the isomerization of the 2-olefin to the most unstable but polymerizable 1-olefin seemed to occur very slightly as compared with that to the most stable 3-olefin, 4-methyl-2-pentene and 4-phenyl-2-butene were found to undergo monomer-isomerization polymerization easily to give high molecular weight homopolymers of 4-methyl-1-pentene and 4-phenyl-1-butene, respectively. From gas chromatographic analysis of olefin isomers in the reaction mixture during the polymerization, it was confirmed that the rate of isomerization from 2-olefin to 1-olefin was larger than that to 3-olefin, and hence the concentration of the 1-olefin necessary to homopolymerize was always supplied through the fast isomerization. The mechanism of isomerization and polymerization in these monomer-isomerization polymerizations seemed to be similar to that reported for 2-butene.

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