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The Isomerization Polymerization of 2-Butene*[1]

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The crystalline polymer has been obtained by polymerizing 2-butene using a Ziegler-type catalyst containing titanium trichloride. 2-Butene was transformed into an equilibrium mixture of 1-butene and *cis*- and *trans*-2-butene by the catalytic action of titanium trichloride. When alkylaluminum was present in the system, isotactic poly-1-butene was obtained. These results can be explained by the concept of isomerization polymerization.

Generally internal olefines like 2-butene do not polymerize to high-molecular-weight crystalline polymers with Ziegler-type catalysts.(1) Recently, Friedlander(2) reported that a solid polymer can be obtained from 2-butene using a Ziegler-type catalyst. However, the structure of the polymer was not been characterized in detail. According to the patent literature,(3) a solid crystalline polymer can be obtained from 2-butene using a catalyst consisting of titanium trichloride, sodium hydride, and aluminum chloride. The structure of this polymer is claimed to be poly-1-butene.

In the present study, the interaction between butene monomers and the titanium trichloride-alkylaluminum catalyst and the reaction processes have been investigated.

During the preparation of our manuscript, Symcox(4) reported the preparation of isotactic poly-1-butene from 2-butene using a Ziegler-type catalyst. More recently, Shimizu *et al.*(5) obtained the same results as those described in this work.

Experimental

Ligroin (bp 95—105°C) and *n*-heptane were used as solvents. They were dried with calcium hydride, distilled and stored over sodium wire under nitrogen. Commercially-available *cis*- and *trans*-2-butene of Phillips Petroleum Co. were used. Gas chromatographic analysis indicated the absence of 1-butene. Titanium trichloride (AA) was supplied by Stauffer Chemical Co. Organoaluminum compounds purchased from Texas Alkyls, Inc., were used without further purification. *Cis*- and *trans*-2-butene were purified by passing the monomers consecutively through a series of columns filled with potassium hydroxide pellets, calcium chloride, activated alumina, and triethylaluminum in liquid paraffin, they were then condensed in a measuring vessel kept in dry ice - acetone bath. Polymerizations were carried out in 200 m*l* pressure-proved glass vessels equipped with a magnetic stirrer. Isomerizations were carried out by continuously rotating reactors (100 m*l* stainless steel vessels with a released valve) in a thermostat. Each 25 m*l* portion of the three *n*-butene isomers was added to *n*-heptane containing titanium trichloride or triethylaluminum. Gas samples for analysis were extracted intermittently from the gas phase of the reaction systems with a syringe and analyzed by gas chromatography using a benzyl ether column 2 m long.

Results

Titanium Trichloride-Alkylaluminum Catalyst System. The reactions were carried out with various catalysts consisting of titanium trichloride and one of the organoaluminum compounds. The polymers obtained have high molecular weights ([η] measured in tetralin at 135°C, 0.5—0.8) and melt at 100—105°C. The infrared spectrum of the polymer obtained from *cis*-2-butene with a titanium trichloride - triethylaluminum catalyst is shown in Fig. 1 in comparison with that of poly-1-butene.

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*[1] Presented at the 13th Annual Meeting of Polymer Science of Japan (June 6, 1964), Preprint, p. 21.

1) G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvasori and A. Zambelli, *J. Am. Chem. Soc.*, **83**, 3344 (1961).

2) H. Z. Friedlander, *Chem. Eng. News*, Feb. 10, 1964, p. 42.

3) Sun Oil Co., U. S. Pat. 2956989 (1960).

4) R. O. Symcox, *Polymer Letters*, **2**, 947 (1964).

5) A. Shimizu, T, Otsu and M. Imoto, *ibid.*, **3**, 449 (1965).

TABLE 1. POLYMERIZATION OF *cis*-2-BUTENE BY TITANIUM TRICHLORIDE-ALKYLALUMINUM CATALYSTS
(Conditions: ligroin 75 m*l*, *cis*-2-butene (condensed at −70°C) 25 m*l*, 50°C, 4 hr)

No.	$TiCl_3$ mmol	Alkylaluminum mmol		Product mg	Residual gas composition (mol%)				
					C_2[a]	C_4[b]	1-Butene	*trans*-2-Butene	*cis*-2-Butene
1	4.38	$AlEt_3$	7.34	387[c]	7.38	—	0.84	12.24	78.8
2	3.97	$AlEt_2Cl$	7.3	9.5	21.4	—	0.6	—	76.4
3	4.03	$AlEtCl_2$	7.37	2	1.98	—	0.16	0.41	97.5
4	4	$Al(i\text{-}Bu)_3$	7.1	1046.5	—	1.5	1.86	25.17	71.5
5	4.13	$Al(Hex)_3$	8	887[d]	—	—	0.14	23.15	75.2

a) Ethane or ethylene from ethylaluminum compounds.
b) Isobutane or isobutene from $Al(i\text{-}Bu)_3$.
c) $[\eta]^{135°C}_{\mathrm{Tetralin}}$ 0.519. d) $[\eta]^{135°C}_{\mathrm{Tetralin}}$ 0.577.

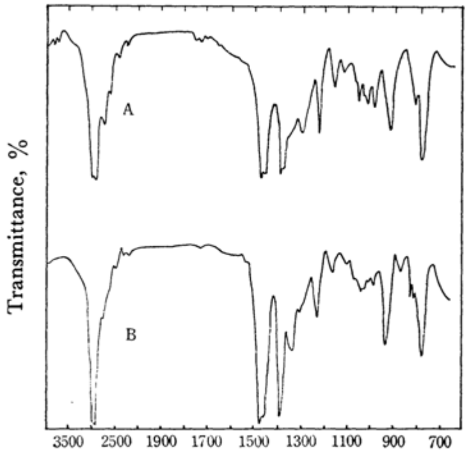

Fig. 1. Infrared spectra of polymers obtained (A) from 1-butene and (B) from 2-butene.

At the end of the polymerization the residual gases were analyzed by gas chromatography. The results are shown in Table 1. 1-Butene was detected in all residual gases. It was found that triisobutylaluminum was the most active cocatalyst in the polymerization.

Isomerizations of *n*-Butene Isomers. Isomerizations of *n*-butene isomers were studied at 50°C and 100°C in the presence of titanium trichloride. At 50°C the rate of isomerization was slow, but at 100°C the isomerization in which 2-butene converts to 1-butene was observed at a measurable rate. After the desired reaction times, the gases in the gaseous phase were analyzed; the results are shown in Fig. 2. In the gas chromatographs a few peaks besides those of the three *n*-butene isomers were observed. They were probably saturated C_4 hydrocarbons, but their identifications and occurrences were not investigated.

The catalytic activity of triethylaluminum for the isomerization was studied at 50°C. After four hours, only about 7.6% of C_2 hydrocarbons (ethane or ethylene) which derived from triethylaluminum was found; besides the starting isomer, no C_4 hydrocarbon has been detected. Since the alkyl group seems to be displaced significantly at the higher temperatures, the isomerization at 100°C was not investigated.

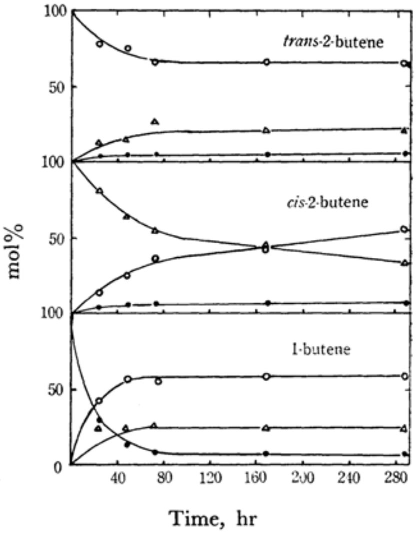

Fig. 2. Composition of three *n*-butene isomers of gaseous phase in the isomerization by $TiCl_3$ at 100°C (mol%).
(●) 1-butene, (△) *cis*-2-butene, (○) *trans*-2-butene

The Isomerization Polymerization of 2-Butene. The effect of the reaction temperature on the polymerization of 2-butene was studied with the catalyst titanium trichloride - triisobutylaluminum. The relationship between the polymer yield and the temperature is shown in Fig. 3. The apparent activation energy of the isomerization of 2-butene is about 2.7 kcal/mol in the 30—80°C range. The compositions of residual gases after the reactions are shown as a function of the

Table 2. Effect of catalyst concentration at constant Al/Ti molar ratio

(Conditions: *n*-heptane 75 m*l*, *cis*-2-butene (condensed at −70°C) 25 m*l*, Al/Ti molar ratio 1.83, 50°C, 4 hr)

No.	$TiCl_3$ mmol	Al(*i*-Bu)$_3$ mmol	Product mg	Residual gas composition (mol%)				*trans*/*cis* ratio
				C_4[a)]	1-Butene	*trans*-2-Butene	*cis*-2-Butene	
6	1.4	2.88	105.7	2.3	1.47	7.34	88.9	0.083
7	2.26	4.17	140.7	3	2.21	11.82	82.97	0.142
8	4	7.1	1046.5	1.5	1.86	25.17	71.46	0.352
9	8.34	15.23	1712.8	4.4	3.56	42.68	48.98	0.872

a) Isobutane or isobutene from Al(*i*-Bu)$_3$.

Table 3. Effect of Al/Ti molar ratio at a constant total catalyst concentration

(Conditions: *n*-heptane 75 m*l*, *cis*-2-butene (condensed at −70°C) 25 m*l*, $TiCl_3$-Al(*i*-Bu)$_3$, 80°C, 4 hr)

No.	Al/Ti molar ratio	Amount of total catalyst mmol	Product mg	Residual gas composition (mol%)			
				C_4[a)]	1-Butene	*trans*-2-Butene	*cis*-2-Butene
10	1.85	11.24	236	5.02	5.97	52.01	37.00
11	0.556	11.3	168.8	3.14	2.12	14.62	80.05
12	0.205	11.3	7.75	2.5	3.87	15.72	77.91

a) Isobutane or isobutene from Al(*i*-Bu)$_3$.

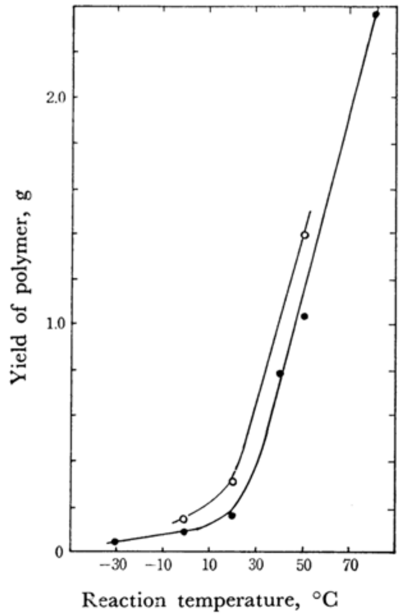

Fig. 3. Effect of reaction temperature, starting material: (●) *cis*-2-butene, (○) *trans*-2-butene. Conditions: *n*-heptane 75 m*l*, $TiCl_3$ 4 mmol, $(i\text{-}C_4H_9)_3Al$ 7.3 mmol, 2-butene (condensed at −70°C) 25 m*l*, 4 hr.

temperature in Fig. 4. It was found that the higher temperature was advantageous for the isomerization. The effects of the catalyst concentration on the reactions at a constant Al/Ti molar ratio are shown in Table 2. The yields of polymers increase with the catalyst concentration.

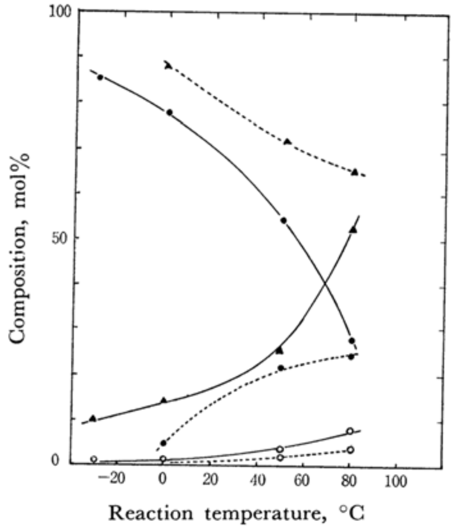

Fig. 4. Composition of residual gas in gaseous phase at various reaction temperatures (mol%), starting material: (—) *cis*-2-butene, (···) *trans*-2-butene, (○) 1-butene, (●) *cis*-2-butene, (▲) *trans*-2-butene.

It was found by the results shown in Table 3 that, as the Al/Ti molar ratios increase, both the polymer yield and the 1-butene content in the residual gases increase.

Discussion

2-Butene was polymerized to a crystalline polymer in the presence of a Ziegler-type catalyst containing titanium trichloride. The polymer obtained is essentially isotactic poly-1-butene. However, the details of the structure of the polymers are somewhat different from those of poly-1-butene. The infrared spectrum shown in Fig. 1B has some absorptions, *e. g.*, 1350, 1080, and 880 cm^{-1}, which were not detected in the spectrum of poly-1-butene shown in Fig. 1A. It is considered that the polymers formed from 2-butene contain a small amount of a comonomer which could possibly be 2-butene and ethylene (when triethylaluminum was used as a cocatalyst). It is apparent from Fig. 2 that titanium trichloride is active in isomerizing *n*-butene to an equilibrium mixture of three *n*-butene isomers. Apparently, only double-bond rearrangements occur and no skeletal rearrangements take place, because isobutene has not been detected in the residual gases. Alkylaluminum alone dose not catalyze the isomerization of 2-butene under the present experimental conditions.⁶⁾

The reaction mechanism probably involves, under the influence of titanium trichloride, the isomerization of 2-butene to 1-butene, which then is immediately polymerized in the presence of the alkylaluminum co-catalyst. Consequently, 1-butene was removed from the equilibrium and more 2-butene could be isomerized. The fact that the residual gases in all experiments contained 1-butene suggested a two-step mechanism, *i. e.*, the isomerization of 2-butene to an equilibrium mixture consisting of *cis*- and *trans*-2-butene and 1-butene and the polymerization of 1-butene. The catalyst system, $TiCl_3$-AlR_3, was apparently bifunctional.

The rate of isomerization and the yield of poly-1-butene increase with the reaction temperature. The effect of the size of the alkyl group of alkylaluminum on the reaction was in agreement with the findings obtained by Medalia⁷⁾ in the polymerization of 1-butene, triisobutylaluminum being the most effective co-catalyst.

It has been established that high temperatures, high catalyst concentrations, and high Al/Ti molar ratios are preferable in the preparation of isotactic poly-1-butene from 2-butene.

The authors wish to express their thanks to Toyo Rayon Co. for permission to publish this work.

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6) H. Zeiss, Ed., "Organometallic Chemistry," Reinhold Publ., New York (1960), p. 217.

7) A. I. Medalia, A. Orzechowski, J. A. Trinchera and J. P. Morley, *J. Polymer Sci.*, **41**, 241 (1959).