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Monomer-Isomerization Polymerization. 32. The Role of Nickel Compounds (NiX_2) in Monomer-Isomerization Polymerization of 2-Butene with $TiCl_3$–NiX_2–$(C_2H_5)_3Al$ Catalyst

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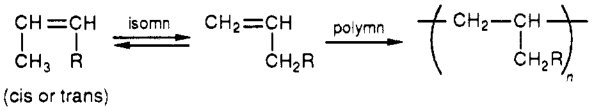
ABSTRACT: The effects of nickel(2+) compounds, NiX_2 (X = chloride, acetylacetonate, and dimethyl glyoximate) on monomer-isomerization polymerization of *cis*-2-butene with $TiCl_3$–$(C_2H_5)_3Al$ catalyst were studied. NiX_2 affected both isomerization and polymerization processes. Thus, addition of $NiCl_2$ increased the yields of polymer, poly(1-butene), and a maximum yield (72.3% for 24 h) was obtained at Ni/Ti and Al/Ti molar ratios of 1 and 3, respectively ([Ti] = 50 mmol/L). These polymers have high molecular weights [(40–85) × 10^4] and contain a significant isotactic fraction. Analysis of the composition of unpolymerized butene isomers in the reaction mixture indicates that their equilibrium concentrations determine the rate of reactions. The $NiCl_2$–$(C_2H_5)_3Al$ catalyst induced the isomerization of *cis*-2-butene at a rate comparable to the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst but did not produce a polymer.

Introduction

We have reported[1-10] that a number of 2-olefins undergo monomer-isomerization polymerizations with Ziegler–Natta catalysts to give polymers of the corresponding 1-olefin units (eq 1), where R is an alkyl group.



$$\underset{\text{(cis or trans)}}{\underset{CH_3\quad R}{CH{=}CH}} \xrightleftharpoons{\text{isomn}} \underset{CH_2R}{CH_2{=}CH} \xrightarrow{\text{polymn}} \left(CH_2-\underset{CH_2R}{CH} \right)_n \qquad (1)$$

The monomer-isomerization polymerizations are composed of two distinct reactions, isomerization and polymerization, which occur at different active sites. 1-Olefins consumed by the polymerization are replenished by the isomerization of 2-olefins.[3] The advantage of this procedure is a "one-pot" polymer synthesis of the 1-olefin polymers using the 2-olefins.

For monomer-isomerization polymerization of *cis*-2-butene (c2B), $TiCl_3$–R_3Al (R = C_2H_5 and *i*-C_4H_9) showed a high catalytic activity among Ziegler–Natta catalysts examined.[9] Polymer yields are also accelerated by the addition of transition-metal compounds of group VIII[5,6,9,10] which catalyze the isomerization. Among them, some nickel compounds (NiX_2) are known to be excellent isomerization catalysts.[11-14]

Since the monomer-isomerization polymerization consists of two sequence reactions, it is important to elucidate (1) the determining step and (2) the effect of NiX_2. We report here on the monomer-isomerization polymerization of c2B with the $TiCl_3$–NiX_2–$(C_2H_5)_3Al$ catalyst.

Experimental Section

Materials. 1-Butene (1B), c2B, and *trans*-2-butene (t2B) were purified by a distillation over CaH_2 before use. Alkylaluminums (Ethyl Co.) and hydrogen-activated titanium trichloride (Stauffer Chem. Co.) were used without further purification. Nickel chloride (Tokyo Kasei Co.) was dried before use at 150 °C for 3 h under a high vacuum. Other transition-metal salts (Tokyo Kasei Co.) were used without further purification. Solvents were purified by washing with sulfuric acid and aqueous sodium hydroxide and distilling over CaH_2 and were stored on a sodium wire.

Polymerization Procedures. The polymerizations were carried out in a sealed glass tube. Charging of required amounts of reagents into the tube and isolation of the resulting polymers were performed by the methods described in a previous paper.[2] The composition of unpolymerized butenes recovered after reactions was determined by GC method using a stainless column (i.d. ϕ 5 × 2 m) packed with VZ-7 60/80 mesh purchased from Gasukuro Kogyo Co. at 0 °C. The polymer yields were determined by gravimetric methods and are based on the amount of c2B charged.

Characterization of Polymer. The intrinsic viscosity of the polymers was determined by viscosity measurement in a dilute heptane solution at 60 °C with an Ubbelohde viscometer. The molecular weights of polymers were calculated from the following equation:[15]

$$[\eta] = (1.50 \times 10^{-4})\bar{M}_n^{\,0.69} \qquad (2)$$

The structure of the resulting polymers was checked by IR and ^{13}C NMR spectra.

Results and Discussion

Effect of Nickel Compounds. Table I shows the results of the addition effects of NiX_2 to $TiCl_3$–$(C_2H_5)_3Al$ on monomer isomerization and polymerization of c2B. The effects of NiX_2 on both reactions were observed, and the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst showed an accelerating effect on polymer yields as compared with yields from reactions in the absence of $NiCl_2$.

The structure of polymers obtained from c2B were confirmed to consist of 1B units from their IR and ^{13}C NMR spectra.[9] Namely, monomer-isomerization polymerization of c2B occurred according to eq 1. From extraction with diethyl ether, the resulting polymers contained considerable amounts of the insoluble fraction. Namely, isotactic poly(1B) was produced through the monomer-isomerization polymerization of c2B, which was confirmed by their ^{13}C NMR spectra. From the viscosity measurement, the molecular weights of the polymers obtained with the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst are higher than those obtained in the absence of $NiCl_2$.

On the other hand, nickel dimethyl glyoximate [Ni(DMG)$_2$] and nickel acetylacetonate [Ni(acac)$_2$] containing catalysts did not showed an accelerating effect on the polymer yields. Since the isomerization has proceeded with a comparable rate to reactions in the absence of the nickel compounds, excess addition of these compounds are considered to destroy polymerization sites.

Ethylene can be dimerized by some NiX_2 in combination with alkylaluminums to give 1B due to a preference for

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Table I
Effect of NiX_2 on Monomer-Isomerization Polymerization of c2B with the $TiCl_3$–NiX_2–$(C_2H_5)_3Al$ Catalyst in Heptane at 80 °C for 24 h[a]

NiX_2	Ni/Ti molar ratio	polymer yield (%)	Et_2O insoluble		composition of unpolymerized butenes (%)		
			wt %	MW × 10^{-4}	1B	t2B	c2B
–	–	34.4	46.8	35.0	3.2	60.0	36.8
$NiCl_2$	0.5	47.7	64.3	44.3	4.5	62.0	33.5
$NiCl_2$	1.0	72.3	71.3	71.9	5.4	71.2	23.4
$Ni(DMG)_2$	0.5	3.4	–	–	11.9	43.7	44.4
$Ni(DMG)_2$	1.0	0.0	–	–	3.4	55.2	41.4
$Ni(acac)_2$	0.5	0.8	–	–	5.4	73.4	21.2
					(5.1	72.4	22.5)[b]

[a] Conditions: [c2B] = 4.0 mol·L^{-1}, [$TiCl_3$] = 50 mmol·L^{-1}, Al/Ti = 3.0 in molar ratio. Initial c2B contains 2.7% t2B. [b] Equilibrium concentration calculated from free energies of the formation at 80 °C.[2]

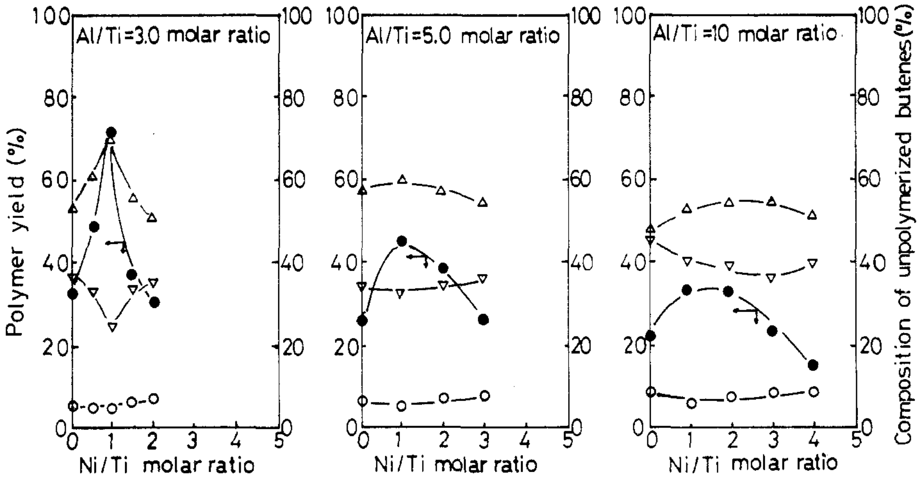

Figure 1. Effect of Ni/Ti molar ratio on monomer-isomerization polymerization of c2B with the $TiCl_3$–$(C_2H_5)_3Al$ catalyst in heptane at 80 °C for 24 h: (△) t2B, (▽) c2B, (○) 1B. Conditions: [c2B] = 4.0 mol·L^{-1}, [$TiCl_3$] = 50 mmol·L^{-1}, Al/Ti = 3.0 in molar ratio.

β-hydrogen elimination.[11,16,17] Some bis(ylid)nickel compounds can cause oligomerization of ethylene.[18] However, in the monomer-isomerization polymerization of c2B, such transfer reactions were not observed. The addition of $NiCl_2$ to the $TiCl_3$–$(C_2H_5)_3Al$ catalyst enhanced both the molecular weights of the resulting polymers and the polymer yields, suggesting that $NiCl_2$ does not interfere the polymerization process.

Effects of Ni/Ti Molar Ratios. Since alkylaluminums react with $TiCl_3$ to create polymerization sites and with $NiCl_2$ to create isomerization sites, the effect of Ni/Ti molar ratio is considered to influence the catalytic activity on monomer-isomerization polymerization. So the effects of the Ni/Ti molar ratios were examined with the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst by varying the Al/Ti molar ratios from 1 to 10, and the results are shown in Figure 1. Both isomerization and polymerization were affected by the Ni/Ti molar ratios. At the Ni/Ti and the Al/Ti molar ratios of 1 and 3, respectively, the highest catalytic activity was observed, i.e., the polymer yield reached 72.3% for 24 h.

When the polymerizations of c2B were carried out with the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst (Al/Ti > 3.0), optimum Ni/Ti molar ratios for the polymer yield were not changed significantly, but the maxima yields decreased with an increase of the Al/Ti molar ratios as indicated in Figure 1.

Such phenomenon may be explained by an increase of Ti^{2+} complexes produced by the reduction with $(C_2H_5)_3Al$, since it was proven that Ti^{3+} complexes are active for polymerization of 1-olefins but not for Ti^{2+} complexes.[19-21]

Although evidence for the maxima in the polymer-yield curves for all $(C_2H_5)_3Al$-containing catalysts was not found, some sort of Ni–Ti bimetallic complex is considered to be produced, which is similar to the reaction of nickel carbonyl with $TiCl_4$ to form a bimetallic coordination catalyst.[22,23]

Figure 2 shows the relations between the molecular weight of polymers after extraction with diethyl ether and Ni/Ti molar ratios. All polymers obtained have considerable amounts of isotactic fraction and high molecular weights. The change of insoluble fraction and the molecular weights is consistent with that of the polymer yields.

The effect of Ni/Ti molar ratios on the polymerization of c2B was also examined with the $TiCl_3$–$(i\text{-}C_4H_9)_3Al$ catalyst, and the results are shown in Figure 3. In contrast to the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst, the $TiCl_3$–$NiCl_2$–$(i\text{-}C_4H_9)_3Al$ catalyst showed different polymerization behavior. The isomerization was accelerated by the addition of $NiCl_2$, but the polymer yields decreased with an increase of Ni/Ti molar ratios.

To clarify this point, the polymerizations of 1B and c2B with the $TiCl_3$–$(C_2H_5)_3Al$ and the $TiCl_3$–$(i\text{-}C_4H_9)_3Al$ catalysts were performed in the absence of $NiCl_2$, and the results are listed in Table II. In the polymerizations of both olefins, the catalytic activity of the $TiCl_3$–$(i\text{-}C_4H_9)_3Al$ catalyst is higher than that of the $TiCl_3$–$(C_2H_5)_3Al$ catalyst.

On the other hand, with the $TiCl_3$–$NiCl_2$–$(i\text{-}C_4H_9)_3Al$ catalyst (Ni/Ti > 1.0), the composition of unpolymerized butenes recovered after the reactions gave the equilibrium mixtures, but with the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst, the composition did not give the equilibrium mixtures (see Figures 1 and 3).

We supposed from these findings that more $(i\text{-}C_4H_9)_3Al$ was consumed to create an isomerization site as compared with $(C_2H_5)_3Al$, and this reduced the amount of polymerization sites. Although this is considered to cause such

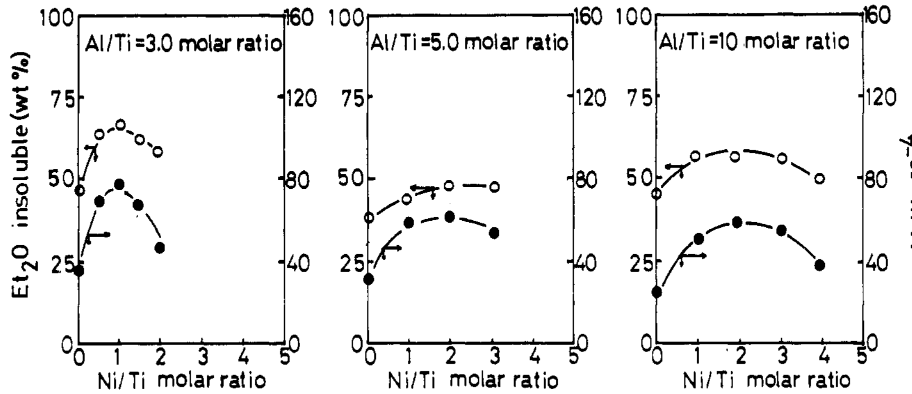

Figure 2. Effect of Ni/Ti molar ratio on the properties of the resulting polymers.

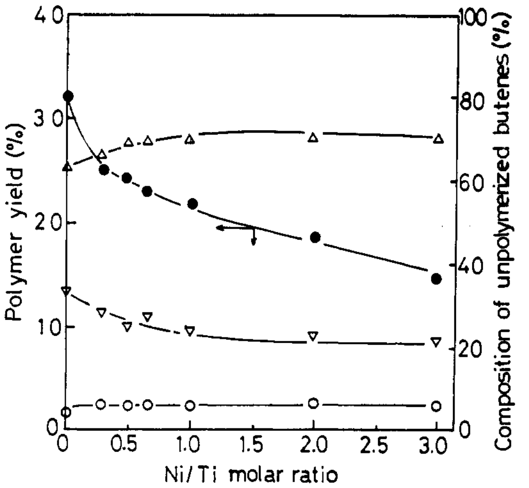

Figure 3. Effect of Ni/Ti molar ratio on monomer-isomerization polymerization of c2B with the $TiCl_3$–$NiCl_2$–$(i\text{-}C_4H_9)_3Al$ (Al/Ti = 3.0 in molar ratio) catalyst in heptane at 80 °C for 24 h: (△) t2B, (▽) c2B, (○) 1B. Conditions: [c2B] = 4.0 mol·L^{-1}, [$TiCl_3$] = 50 mmol·L^{1}, Al/Ti = 3.0 in molar ratio.

Table II
Polymerizations of Butenes with the $TiCl_3$–$(C_2H_5)_3Al$ Catalyst and the $TiCl_3$–$(i\text{-}C_4H_9)_3Al$ Catalyst in Heptane at 80 °C[a]

			polymer yield (%)	
butene	[$TiCl_3$] (mmol·L^{-1})	time (h)	$TiCl_3$–$(C_2H_5)_3Al$	$TiCl_3$–$(i\text{-}C_4H_9)_3Al$
1B	20	0.17	65.0	98.3
c2B	50	8.0	19.8	27.9

[a] [Butene] = 4.0 mol·L^{-1}, Al/Ti = 3.0 in molar ratio.

differences in catalytic activity, further study will be need to confirm this point.

Polymerization and Isomerization with $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$. Figure 4 shows the results for the monomer-isomerization polymerization of c2B with $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ and $TiCl_3$–$(C_2H_5)_3Al$ catalysts. With both catalysts, the polymer yields increased as a function of reaction time, but the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst gave higher polymer yields than the $TiCl_3$–$(C_2H_5)_3Al$ catalyst. This seems to be due to the acceleration effect of isomerization by the addition of $NiCl_2$. To clarify this point, the isomerization was traced by GC.

With the $TiCl_3$–$(C_2H_5)_3Al$ catalyst, the isomerization proceeded with the time, but the composition of unpolymerized butenes recovered after the reactions slowly approached the equilibrium values. On the other hand, with the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst, the isomerization proceeded rapidly, and after 2.0 h the composition gave the equilibrium mixture.[2]

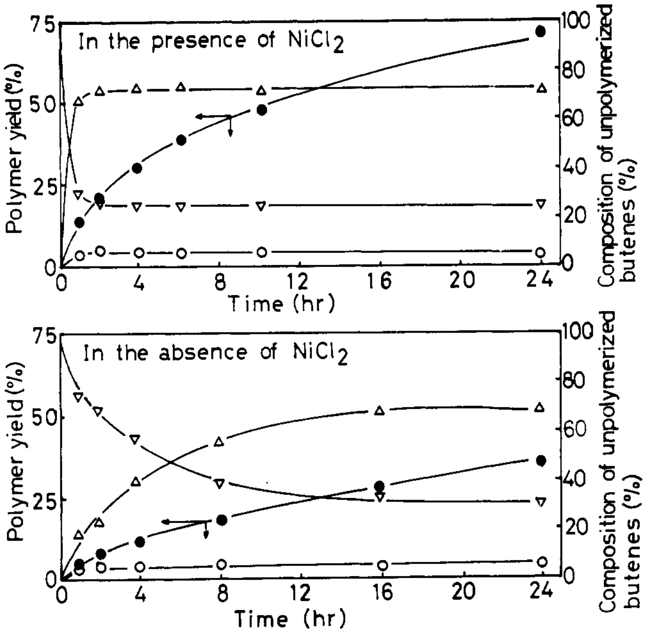

Figure 4. Polymerization and isomerization of c2B with the $TiCl_3$–$(C_2H_5)_3Al$ catalyst in heptane at 80 °C: (△) t2B, (▽) c2B, (○) 1B. Conditions: [c2B] = 4.0 mol·L^{-1}, [$TiCl_3$] = 50 mmol·L^{-1}, Al/Ti = 3.0 in molar ratio, Ni/Ti = 1.0 in molar ratio.

After that the equilibrated concentration remained constant throughout the reactions, but the polymer yields increased with reaction time. These findings indicate that 1B consumed by the polymerization is constantly and rapidly replenish by the isomerization to keep the equilibrium concentration, so that the monomer-isomerization polymerization proceeds continuously to give poly(1B) in high yields. Under these conditions, it is considered that the polymerization is a rate-determining step for this reaction.

Estimation of $NiCl_2$ as Isomerization Catalyst. To elucidate the role of $NiCl_2$ in the monomer-isomerization polymerization of c2B, the reactions were carried out with various catalysts. The results are summarized in Table III. A single-component catalyst, $(C_2H_5)_3Al$ and $NiCl_2$, was not effective for the isomerization. When the $NiCl_2$–$(C_2H_5)_3Al$ catalyst was used, geometric and positional isomerizations took place, but neither skeletal isomerization to isobutene nor polymerization of 1B was observed.

The isomerization was also observed with the $NiCl_2$–$TiCl_3$ catalyst in low activity. Since each compound alone did not catalyze isomerization, this suggests that a certain bimetallic compound of Ni and Ti may be produced.

Since the $NiCl_2$–$(C_2H_5)_3Al$ catalyst showed a high catalytic activity for isomerization, the isomerizations were

Table III
Isomerization of c2B with Various Catalysts in Heptane at 80 °C[a]

catalyst	time (h)	composition of butenes after polymerization (%)			polymer yield (%)
		1B	t2B	c2B	
$NiCl_2$–$(C_2H_5)_3Al$	1.0	6.1	55.1	38.8	0.0
$NiCl_2$	24.0	0.0	3.0	97.0	0.0
$(C_2H_5)_3Al$	24.0	0.0	2.7	97.3	0.0
$NiCl_2$–$TiCl_2$	24.0	2.8	12.3	84.9	0.0
$TiCl_3$	24.0	0.5	5.9	93.6	0.0
$TiCl_3$–$(C_2H_5)_3Al$	1.0	2.6	20.0	77.4	2.4
$TiCl_3$–$(C_2H_5)_3Al$–$NiCl_2$	1.0	3.2	62.8	34.0	17.8

[a] Conditions: [c2B] = 4.0 mol·L^{-1}, [$TiCl_3$] = 50 mmol·L^{-1}, [$(C_2H_5)_3Al$] = 150 mmol·L^{-1}, [$NiCl_2$] = 50 mmol·L^{-1}.

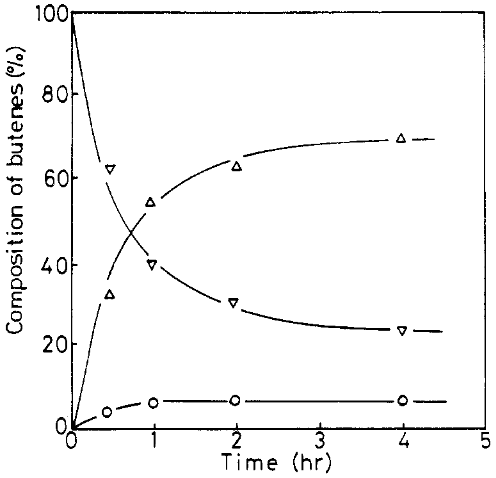

Figure 5. Isomerization of c2B with the $NiCl_2$–$(C_2H_5)_3Al$ catalyst in heptane at 80 °C: (△) t2B, (▽) c2B, (○) 1B. Conditions: [c2B] = 4.0 mol·L^{-1}, [$NiCl_2$] = 50 mmol·L^{-1}, Al/Ni = 3.0 in molar ratio.

examined in detail. The results are shown in Figure 5, from which geometric and positional isomerizations took place concurrently, and the amount of 1B was always lower than that of t2B during the reaction. Moreover, a small amount of butane was observed in the reaction products.

For the isomerization of olefins, two mechanisms have been postulated: one is σ-alkylmetal complexes[16,24,25] and the other is π-allylmetal complexes.[16,26,27] The results obtained with the $NiCl_2$–$(C_2H_5)_3Al$ catalyst indicate that the isomerization proceeded through σ-alkylmetal complexes, which required Ni–H bonds as active sites for the isomerization. The formation of the Ni–H bond as an active site was reported in the isomerization of olefins with NiX_2 and alkylaluminums.[12,13] This bond may be formed as a result of β-hydrogen elimination from alkylnickel complexes produced by the reaction of $NiCl_2$ and alkylaluminums.

The secondary insertion of 1-olefins into the Ni–H bond was reported to occur easily due to the high d population of nickel compounds.[16] This insertion mode is necessary for the isomerization of olefins. Thus, with Ni-based catalysts the isomerization takes place readily as compared with Ti-based catalysts.

The catalytic activity for the isomerization of the $NiCl_2$–$(C_2H_5)_3Al$ catalyst was similar to that of the $TiCl_3$–$NiCl_2$–$(C_2H_5)_3Al$ catalyst (see Figures 4 and 5), but the binary catalyst did not induce the polymerization of 1B. Moreover, only when the catalyst which contains both $TiCl_3$ and $(C_2H_5)_3Al$ was used was monomer-isomerization polymerization of c2B induced to give poly(1B). On the basis of these results, it is clear that the complexes of $NiCl_2$ and alkylaluminums participate in the isomerization but not in the polymerization.

Conclusion

$NiCl_2$ itself did not catalyze isomerization of butenes. When it was combined with alkylaluminums, active sites for isomerizations were produced, but they do not interfere with the polymerization of 1B. The addition of $NiCl_2$ to $TiCl_3$–$(C_2H_5)_3Al$ is considered to form some bimetallic compounds of Ni + Ti, and the rate-determing step changed from isomerization to polymerization by acceleration of isomerization.

References and Notes

(1) Shimizu, A.; Otsu, T.; Imoto, M. *J. Polym. Sci., Part B* **1965**, *3*, 449.
(2) Otsu, T.; Shimizu, A.; Imoto, M. *J. Polym. Sci., Part A-1* **1966**, *4*, 1579.
(3) Kennedy, J. P.; Otsu, T. *Adv. Polym. Sci.* **1970**, *7*, 369.
(4) Otsu, T.; Nagahama, H.; Endo, K. *J. Polym. Sci., Part B* **1972**, *10*, 601.
(5) Otsu, T.; Endo, K.; Nagahama, H.; Shimizu, A. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2470.
(6) Endo, K.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2083.
(7) Endo, K.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1615.
(8) Endo, K.; Tsujikawa, H.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1633.
(9) Endo, K.; Otsu, T. *J. Polym. Sci., Part A, Polym. Chem.* **1991**, *29*, 847.
(10) Otsu, T.; Shimizu, A.; Imoto, M. *J. Polym. Sci., Part A-1* **1969**, *7*, 3111.
(11) Jolly, P. W.; Wilke, G. In *The Organic Chemistry of Nickel, Vol II*; Academic Press: New York, 1975; Chapter 1.
(12) Takegami, Y.; Suzuki, T.; Shirai, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1478.
(13) Suzuki, T.; Takegami, Y. *Kogyo Kagaku Zasshi* **1971**, *74*, 1371.
(14) Kanai, H.; Choe, B.; Klabunde, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 2019.
(15) Stivala, S.; Valles, R.; Levi, D. *J. Appl. Polym. Sci.* **1963**, *7*, 97.
(16) Henrici-Olive, G.; Olive, S. In *Coordination and Catalysis*; Verlag Chemie: Weinheim, 1977; pp 126 and 158.
(17) Fischer, K.; Jonas, K.; Misbach, P.; Stabba, R.; Wile, G. *Angew. Chem.* **1973**, *85*, 1002.
(18) Starzewski, K. A. O.; Witle, J.; Reichert, K. H.; Vasilion, G. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 349.
(19) Soga, K.; Sano, T.; Ohnishi, R. *Polym. Bull.* **1981**, *4*, 157.
(20) Kashiwa, N.; Yoshitake, J. *Makromol. Chem.* **1984**, *185*, 1133.
(21) Weber, S.; Chien, J. C. W. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 45.
(22) Greco, A.; Perego, G.; Cesari, M.; Cesca, S. *J. Appl. Polym. Sci.* **1979**, *23*, 1319.
(23) Greco, A.; Bertolini, G.; Bruzzone, M.; Cesca, S. *J. Appl. Polym. Sci.* **1979**, *23*, 1333.
(24) Manuel, T. A. *J. Org. Chem.* **1962**, *27*, 3941.
(25) Cramer, R.; Lindsey, R. V. *J. Am. Chem. Soc.* **1966**, *88*, 3534.
(26) Bonnemann, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 736.
(27) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 2248.

Registry No. c2B, 590-18-1; c2B (homopolymer), 25989-99-5; 1B (homopolymer), 9003-28-5; t2B, 624-64-6; 1B, 106-98-9; $TiCl_3$, 7705-07-9; $(C_2H_5)_3Al$, 97-93-8; $(i\text{-}C_4H_9)_3Al$, 100-99-2; $NiCl_2$, 7718-54-9; Ni(acac)$_2$, 3264-82-2; Ni(DMG)$_2$, 13478-93-8.