

Polymerization of Butadiene in Toluene with Nickel (II) Stearate-Diethyl Aluminum Chloride Catalyst. I. Catalytic Behaviors

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Synopsis

The polymerization of butadiene with nickel (II) stearate- Et_2AlCl catalyst has been studied in a batch reactor. The rate of polymerization is first order with respect to monomer and increases with the addition of water. In this system, no appreciable termination reaction has been found and the chain transfer to monomer dictates the molecular weight distribution of the polymer products. Molecular weight increases with conversion and water content. The cis-1,4 content was found to be a function of the extent of polymerization.

INTRODUCTION

In polymerization, the Ziegler-Natta catalyst has been known for its capability of producing highly stereoregulated polymers. Depending on the proper choice of transition metal and organometallic compound, a polymer of a specific microstructure can be obtained. For example, in the polymerization of butadiene a combination of titanium tetraiodide and triisobutyl aluminum will produce a polymer having a nearly pure cis-1,4 structure, whereas a high trans-1,4 structure prevails when iodide is replaced with chloride.^{1,2} For the cobalt acetyl acetonate system, changing from AlR_2Cl to AlR_3 will result in a change of a 97% cis-1,4 to a mainly 1,2 structure.

The choice of transition-metal compound also has a significant effect on the molecular weight of the polymer. Unlike the cobalt- or titanium-based catalyst, the nickel compound normally gives polybutadiene of low molecular weight.³ The practical interest in low-molecular-weight polybutadiene is in the coating industry.

There are many nickel-based catalysts known to be effective for the polymerization of butadiene. Two are notably successful in commercial applications: one developed by the Bridgestone Tire Co. using a ternary system $\text{Ni}(\text{naphth})_2-(\text{C}_2\text{H}_5)_3\text{Al}-\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ to produce polybutadiene of 97% cis content,⁴ and the other developed by the Chemische Werke Hüls with $\text{Ni}(\text{acac})_2-(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$ to produce liquid polybutadiene having a cis-1,4 content of 70–80%.⁵ However, little information has been published on the general behavior of the nickel-based catalysts and the kinetics of the polymerization reactions.

In this work, a systematic investigation of the butadiene polymerization in toluene initiated by nickel (II) stearate-diethyl aluminum chloride was carried out in a bench-scale batch reactor. Polymerization rates were measured against

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time. The effects of aluminum compound and the addition order of the catalyst components and monomer were studied first to determine the most favorable polymerization conditions, followed by a study of the effects of catalyst composition on conversion, molecular weight, and microstructure. Further work was also done as to the influence of temperature and additives on the polymerization.

In the second part of this publication, a kinetic model is proposed in order to study quantitatively the conversion data and to try to explain some experimental observations concerning the changes of microstructure and molecular weight during the course of polymerization.

EXPERIMENTAL

Materials

Toluene used as solvent was ACS certified analytical reagent grade obtained from Fischer Scientific Co. To remove moisture, the toluene was refluxed with sodium metal under nitrogen atmosphere for at least one day. The dryness of the toluene was tested by adding to it a few drops of benzophenone. The toluene, if dry, would turn into a dark blue color as a result of the formation of metal ketyls.⁶ The toluene was then distilled from the dark blue ketyl solution under nitrogen and collected in a dry flask just before an experimental run.

Butadiene-1,3 of rubber grade with 99 mol % purity containing 0.02 wt % *t*-butyl catechol as an inhibitor was obtained from Phillips Petroleum Co. It was dried by passing through a column containing a mixture of phosphorus pentoxide and drierite.

Diethyl aluminum chloride (DEAC), obtained from Ethyl Corp., was specified to contain 22.0 wt % aluminum and 28.8 wt % chloride, and was used without further purification.

Nickel (II) stearate with 99% purity was obtained from Pfaltz and Bauer, Inc. and dried over phosphorous pentoxide for a period of several days.

Experiments were all run under nitrogen atmosphere. The moisture in the N₂ gas was removed by passing it through a column filled with P₂O₅ and drierite. The overall moisture content in the system was estimated to be about 5 ppm.

Equipment

The reactor system consisted of the reactor itself, a temperature control unit, and the apparatus for preparing monomer and catalyst solutions. The reactor had a capacity of about 1 liter and was made of borosilicate glass with an aluminum cover. All connections, for feed and sampling devices, the cooling coil, the nitrogen or vacuum line, the manometer lead for pressure measurement, and the thermistor probe for temperature measurement and control, were made through the cover. The mixing was accomplished by a magnetic stirrer which had the advantage of not using lubricant oil, thereby reducing the possibility of contamination.

The reaction temperature was controlled at the desired levels to within $\pm 0.5^\circ\text{C}$ by a YSI model 71A temperature controller in connection with a constant temperature bath which provided cooling water of a controlled temperature. The

best result was obtained by adjusting the proper setting of the temperature of the cooling water and regulating the rate of the cooling water by a bypassing valve.

The apparatuses used in preparing the catalyst and monomer solutions were simple graduated flasks. Preparation was always done in a controlled atmosphere box under nitrogen and then transferred to the reactor.

Polymerization Procedure

The reactor and other glasswares were cleaned and dried in a vacuum oven overnight at 150°C. They were assembled while still hot. After cooling, the whole system was purged with dry nitrogen several times. The temperature controller was turned on at the same time. At the beginning of the polymerization, the bypassing valve for the cooling water was wide open and was gradually closed down as the polymerization proceeded.

A desired amount of nickel (II) stearate was mixed with a predetermined quantity of toluene in a measuring flask. DEAC was prepared in a similar fashion except that it was measured by volume using a syringe. The monomer solution was prepared by first adding a known quantity of dry toluene to the condensing flask, which was at the dry-ice methanol temperature, and then allowing the butadiene to be distilled over slowly from the butadiene cylinder. The amount of butadiene transferred was measured by the difference in volume. Before entering the condensing flask butadiene vapor was passed through a drying tube filled with drierite and P_2O_5 .

Nickel compound was always added first to the reactor, followed by either DEAC or monomer according to the order of addition.

Water was added in the form of water-saturated toluene and was added before the butadiene and DEAC solutions were introduced.

During the polymerization, the pressure was always kept slightly positive (~1 kPa) with nitrogen.

The monomer conversion was followed by sampling the reaction mixture at convenient time intervals. The methanol was added to the sample as a stopper for the polymerization. A small amount of phenyl-2-naphthylamine was also added as antioxidant. The unreacted monomer, solvent, and methanol were removed by evaporation. The final drying was done in a vacuum oven at 40°C. The percent conversion of butadiene was calculated by taking the difference between the weight of aliquot withdrawn and the weight of dry polymer after the correction for the weight of the catalyst residues remaining in the polymer.

Molecular Weight Measurement

Spectra-Physics SP8000 liquid chromatograph with Waters μ -Styragel columns was used for the determination of the molecular weights of the polymer products.

The gel permeation chromatograph (GPC) was operated at 25°C using toluene as a solvent. The flow rate was maintained at 1 ml/min, and the sample concentration was kept at about 0.1%. The sample loop had a capacity of 0.5 ml.

The calibration of GPC was done according to the universal calibration

method,⁷ using standard polystyrene samples obtained from Waters and five broadly distributed polybutadiene standard samples from Phillips Petroleum Co.

The instrumental spreading of each sample was not corrected for this study. The detailed procedures for GPC calibration were given by Hsu et al.²

Microstructure

The microstructure of polybutadiene was determined using a Beckman AccuLab 6 IR spectroscope. The method follows the procedures described by Silas.⁸ Polybutadiene was dissolved in carbon disulfide with a concentration of about 2.0%. The potassium bromide cell with 0.5 mm path length was used, along with a reference cell of adjustable path length. It was found in this study and also by Potapov⁹ that satisfactory results could be obtained using the adsorption bands of 10.3, 11.0, and 13.5 μm without taking the area bound by the two wavelengths between 12.0 and 16.0 μm , as described by Silas.

With this modulation of the Silas method, IR was calibrated against five standard samples (supplied by Phillips Petroleum Co.) of known compositions of microstructure. The maximum deviation of the calculated percentage of microstructure was found to be $\pm 2.0\%$.

RESULTS AND DISCUSSION

The reactivities of the catalysts in combining nickel (II) stearate with different organoaluminum compounds were first examined. It was found that the halogen-free compounds of triethyl and triisobutyl aluminum do not initiate the butadiene polymerization, a result very similar to the organoaluminum-nickel (II) acetylacetonate system.⁵ It appears that the reactivity of the catalyst depends on the formation of a halogen-bridged complex, as suggested by Pennington and Howell.¹⁰ A similar result was also obtained by Kormer et al.,¹¹ who found that no polybutadiene was obtained using $(\text{C}_4\text{H}_7\text{NiOCOC}_{17}\text{H}_{33})_2$ alone, but butadiene was readily polymerized in the presence of TiCl_4 . $(\text{C}_4\text{H}_7\text{NiOCOC}_{17}\text{H}_{33})_2$ can be considered as π -allyl nickel complex similar to the nickel (II) stearate.

On the other hand, a combination of nickel (II) stearate with diethyl aluminum chloride will initiate the polymerization of butadiene to a high degree of conversion.

It is well known that for such a system the order of addition of the catalysts and the monomer could have a profound effect on polymerization. In this work the nickel was always added first in the form of suspension in toluene, followed by either monomer or DEAC solution. In method A butadiene was added before the addition of DEAC. The order is reversed in method B.

The physical appearance of the reaction mixture is different for the two addition methods. In method A, the light green color of partially soluble nickel catalyst remained after the addition of butadiene. The color of the mixture turned orange as soon as DEAC was added. As the polymerization proceeded the solid suspension gradually disappeared and the color of the mixture turned darker. Some temperature fluctuations were observed at the instant of DEAC addition. This probably was due to the rapid formation of complexes.

In method B, the light green color of nickel (II) stearate changed to dark brown as soon as DEAC was added. A sudden increase in temperature was also observed. When stirring was stopped, the insoluble solids settled quickly at the bottom. The suspended solids remained undissolved over the entire period of the polymerization reaction.

Addition method B was further complicated by the effect of catalyst aging. Figure 1 shows the conversion-time curves for different aging times. It is quite evident that the rate of polymerization at a given reaction time decreases with increasing aging time. However, no further deterioration of catalytic reactivity was observed beyond 30 min of aging time.

In the study of complex formation from nickel (II) carboxylate and alkyl aluminum chloride, Pennington et al.¹⁰ found that the complex in benzene is slowly reduced to metallic nickel in the absence of monomer, following a first-order reaction with a rate constant of $4 \times 10^{-6} \text{ sec}^{-1}$, which amounts to a half-life of about 44 hr. Thus, the aging effect observed here cannot be attributed to the reduction reaction. In 1959, Orzechowski¹² investigated the effect of aging on the activity of the TiCl_4 -(*i*-Bu)₃Al system in ethylene polymerization, and found that the activity of catalyst prepared at 50°C at an Al/Ti ratio of 2.8 dropped to half its initial value after aging for a few minutes. On the other hand, Simon and Ghymes¹³ found that the aging effect may also depend upon the nature of the aluminum compound. For triethyl aluminum, aging time does not exert any appreciable effect on polymerization of ethylene in the presence of TiCl_4 . However, a marked effect was observed with catalyst prepared with Et_2AlCl or EtAlCl_2 . They concluded that the aging effect became more pronounced as the chlorine content of aluminum compound increased.

The nature of aging observed in this investigation is obviously different from that reported by either Orzechowski or Simon and Ghymes. In the latter case, the activity of the catalyst with no aging remains high, whereas in this work the activity of the catalyst, for aging time less than 30 min, decreases slowly with time

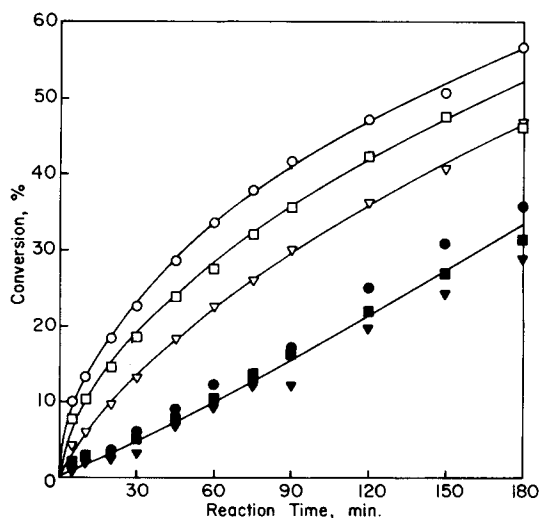


Fig. 1. Time-conversion curve for different aging time (20°C). $[\text{Ni}(\text{stearate})_2] = 4.81 \times 10^{-3}$ mole/liter, $[\text{Et}_2\text{AlCl}] = 3.03 \times 10^{-2}$ mole/liter, $[\text{M}]_0 = 1.43$ mole/liter, $[\text{Al}]/[\text{Ni}] = 6.30$. Aging time (min): (○) 2.0; (□) 5.0; (▽) 15.0; (●) 30.0; (■) 60.0; (▼) 125.0.

and then approaches a constant level. For a long aging time, the initial deactivation was not observed and the polymerization rate remained fairly constant from the onset of polymerization.

In comparing the polymerization data between two addition methods, the percentage conversions were plotted against reaction time in Figure 2, while other conditions were kept constant. Obviously, the slope of the conversion-time curve decreases faster in method A than in method B though the general behavior of the two curves is very much the same. This, together with the color differences in the reaction mixture, led us to believe that depending on whether the monomer is present or not, the reaction between two catalyst components will yield different active species for polymerization. In the polymerization of propylene using $\text{TiCl}_4\text{-Et}_3\text{Al}$ as a catalyst, Korotkov¹⁴ observed that the polymerization was less stereospecific when the two catalysts were mixed in the presence of the monomer. Further evidence showing such an effect was given by Inoue and co-workers,¹⁵ who used the same catalyst as Korotkov did in the study of styrene polymerization. They attributed the rapid production of amorphous polystyrene, when TiCl_4 and Et_3Al were mixed in the presence of monomer, to a radical type of polymerization. For the system in Ni (II) stearate-DEAC different addition orders yield no appreciable difference in the nature of polymerization; the only difference was in the reactivity of the catalyst.

For both addition methods, the formation of active complexes can be considered instantaneous, because no induction period has been observed in all experiments except in one case where the catalyst was aged for 2 hr. The induction period shown in this particular experiment is apparently caused by other unknown reasons.

To avoid the effect of aging on polymerization, method A was adopted for further study of the catalyst behavior. A summary of the experimental results was presented in Table I. The conversion was reported at the end of 2 hr of polymerization time. The molecular weight of polybutadiene normally varies

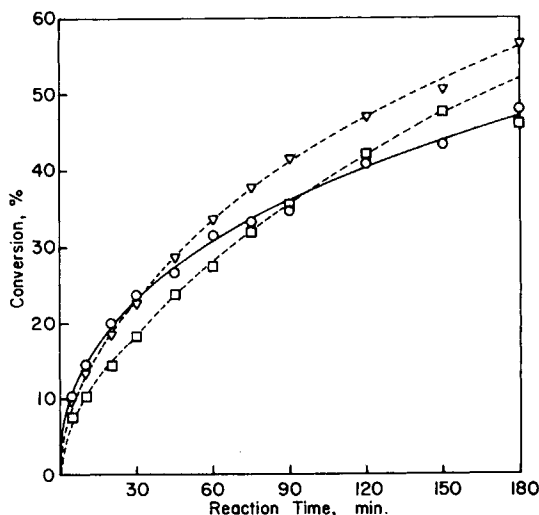


Fig. 2. Time-conversion curve for different addition methods (20°C). $[\text{Ni}(\text{stearate})_2] = 4.81 \times 10^{-3}$ mole/liter, $[\text{Et}_2\text{AlCl}] = 3.03 \times 10^{-2}$ mole/liter, $[\text{M}]_0 = 1.43$ mole/liter, $[\text{Al}]/[\text{Ni}] = 6.30$. (○) Addition method A; (▽) addition method B (aging 2 min); (□) addition method B (aging 5 min).

TABLE I
 Results of Polymerization under Different Reaction Conditions

Experiment No.	[Ni] × 10 ³ (mole/liter)	[A] × 10 ² (mole/liter)	[M] ₀ (mole/liter)	[H ₂ O] × 10 ³ (mole/liter)	Temperature (°C)	Conversion ^a (%)	\bar{M}_n ^a	cis-1,4 ^a (%)
A 52	4.81	3.03	0.57	0.5	20	41.2	1806	
53			1.00			41.8	2130	
27			1.43			40.9	2482	77.7
33			1.43			38.3	1985	
54			1.86			36.1	2964	
55			2.29			37.8	3299	
B 36	1.60	1.01	1.43	0.5	20	16.3	2083	84.9
58	2.41	1.52				22.4		
57	5.62	3.54				41.0		
35	9.63	6.07				62.0	1774	76.8
59	12.84	8.09				77.6	1957	
C 41	4.81	1.01	1.43	0.5	20	6.5	2583	95.6
60		1.52				11.4		
44		5.06				49.3		
61		8.09				64.5	2537	76.7
56		12.14				63.1	2292	74.5
D 49	1.60	3.03	1.43	0.5	20	30.8	2181	84.9
50	8.02					34.4		
51	9.63					25.0	1786	74.5
E 72	4.81	3.03	1.43	2.0	20	62.5	2129	84.2
73				4.0		64.3		
74				7.7		77.2		
80				15.0		95.1	2073	85.5
F 64	4.81	3.03	1.43	0.5	10	42.4	1759	
65					25	38.0		
63					30	43.2		
62					40	45.3		

^a Data are based on 2 hr polymerization time.

with the conversion, but has a number average in the order of 2000. Polymerization follows a first-order reaction with monomer as is usually the case for Ziegler-Natta systems.¹⁶ Initial monomer concentration has little effect on conversion but its increase results in higher molecular weight. On the other hand, relative amounts of the two catalysts have a decisive effect on conversion, but are rather insensitive to molecular weight. Water content greatly influences conversion and generally favors the cis-1,4 polymerization. Temperature, in general, plays a minor role in the polymerization. A detailed discussion of those factors will be given in the following sections.

Living Polymer

A typical first-order plot, viz., $\ln(M_0/M)$ vs. time t is given in Figure 3, where M is the monomer concentration at time t and the subscript zero indicates the initial concentration. It was found in all experiments that the slope or the rate of polymerization decreases in the early stage of polymerization but remains constant after about 30 min. In other words, a constant polymerization rate was reached after a period of catalytical deactivation. Further evidence showed that the system can be considered to contain living polymers. In fact, a complete conversion can be achieved without forming an appreciable amount of gel for an estimated reaction time of 6–8 hr.

The existence of living polymers can further be demonstrated by Figure 4. In the plot it shows that the conversion reaches ~86% after 300 min. The lower curve is the result of adding monomer solution after the reaction mixture was left overnight (~19 hr). After 19 hr, the conversion was complete. The addition of fresh monomer restarted the polymerization. It is interesting to see that the curve remains linear for a period of 4 hr. The slope is only slightly less than that

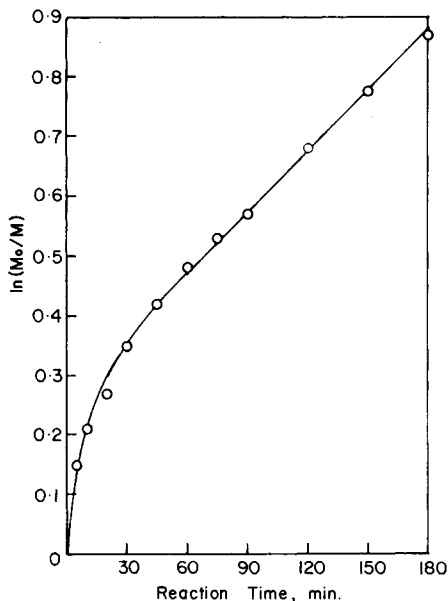


Fig. 3. $\ln(M_0/M)$ as a function of polymerization time (20°C). $[\text{Ni}(\text{stearate})_2] = 4.81 \times 10^{-3}$ mole/liter, $[\text{Et}_2\text{AlCl}] = 3.3 \times 10^{-2}$ mole/liter, $[M]_0 = 1.43$ mole/liter.

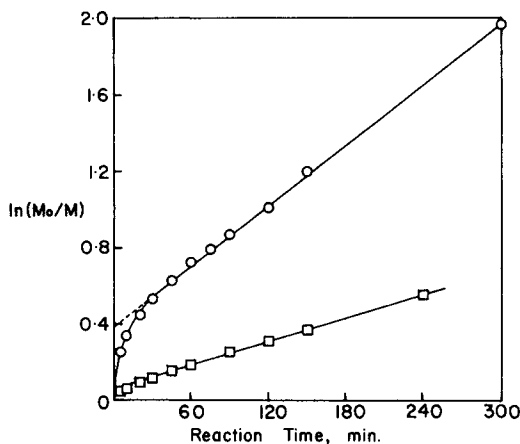


Fig. 4. $\ln(M_0/M)$ as a function of time at 20°C. The lower curve (\square) represents $\ln(M_0/M)$ vs. t after the second addition of monomer solution, 19 hr after the first (\circ) addition of monomer.

of the upper curve. The decline in the polymerization, however, is not necessarily due to the decrease in reactivity; it is more likely due to the dilution effect by introducing additional solvent.

The molecular weight plot of the two-stage polymerization is given in Figure 5 and it shows a gradual increase in molecular weight with no discontinuity at the addition of additional monomer. It should be noted that the measured molecular weight is cumulative. Thus, from these experimental results it can be unequivocally concluded that the active species remain active with no termination reaction. Similar findings were obtained by Yoshimoto and co-workers⁴ for nickel (II) naphthenate- $\text{BF}_3\text{-Et}_2\text{O-Et}_3\text{Al}$ system. For the $\text{V}(\text{acac})_3\text{-Et}_2\text{AlCl}$ system Doi et al.¹⁷ were able to obtain a living polymer system producing polymers of low polydispersity, 1.19 ± 0.05 , without any detectable chain transfer or termination reaction. The polydispersity of the polymer ob-

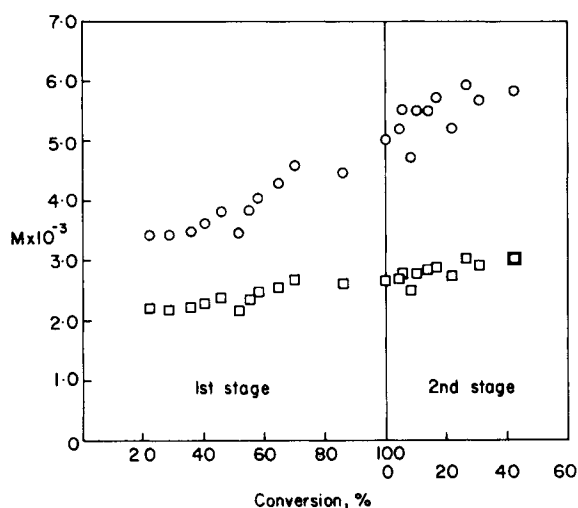


Fig. 5. Variation of average molecular weights with conversion for a two-stage polymerization. (\circ) \bar{M}_w ; (\square) \bar{M}_n .

tained in this work is in the range 1.5–2.0, indicating a possible chain transfer reaction.

Effects of Ni and Al Concentrations on Polymerization

As the data show in Table I, for those experiments (experimental set B) where the Al/Ni ratio was kept at 6.30, the nickel concentration has no effect on the molecular weight, but the conversion over a period of 2 hr increases from 16.3 to 77.6% as the Ni concentration increases from 1.6 to 12.84 mmole/liter. This expected increase is of course due to the direct increase in the concentration of the active complexes because of increasing availability of nickel compound. If the polymerization rate of the constant rate region is plotted against Ni concentration in a log–log plot (Fig. 6), a linear relation is obtained. However, the deviation from the linearity becomes obvious at both ends of the scale, particularly toward the lower limit of nickel concentration. Thus, the number of active complexes is directly proportional to the initial nickel added only in a certain range of Ni concentration.

From the molecular weight data, it is easy to see that DEAC does not influence the molecular weight, thus clearly indicating that DEAC is not a chain termination agent as many Ziegler catalysts have shown.^{1,2}

Effects of DEAC

In Table I, the experimental set C shows the effect of DEAC concentration on polymerization. Conversion increases with increasing DEAC concentration, but the molecular weight remains unaffected. The conversion reaches to a maximum when Al/Ni increases to about 17. This increase in polymerization is not a result of higher reactivity, but rather a result of forming more active complexes at a higher concentration of DEAC. This can be shown by the following experiment.

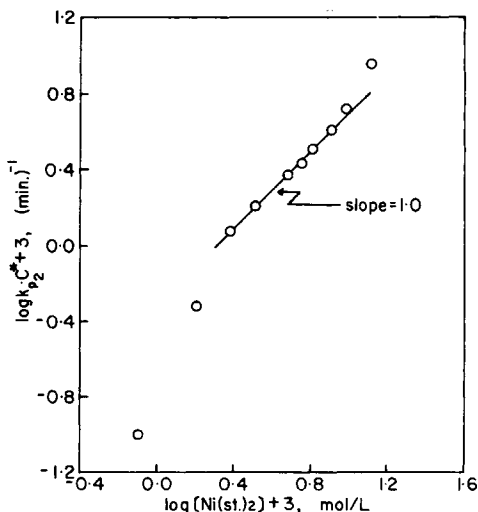


Fig. 6. Constant polymerization rate as a function of nickel concentration at 20°C. [Al]/[Ni] = 6.30.

Figure 7 shows an example of such an experiment where additional DEAC was added after 63 min of reaction time with an amount of equal to that initially added. Initially, the Al/Ni ratio was 6.3. It can be seen that the additional DEAC has little effect on conversion compared to the case when no additional DEAC was added. Figure 7 also includes the results from the experiment in which the amount of DEAC added initially equals the total amount of DEAC added in two stages. The conversion in the former case is much higher than the latter. To explain this, we view the reactions between nickel and aluminum compounds to be irreversible. The amount of nickel converted to the active species is determined by the amount of DEAC initially present and further addition of DEAC has no impact on the nickel that has already converted to the compound inactive to the initiation of polymerization.

Role of Water in Polymerization

It is well known that water plays an important role in many of the Ziegler-Natta polymerizations.^{1,18-20} Figure 8 depicts how the water affects the reactivity of the catalyst studied in this work. At water concentration below 12 mmole/liter, the effect on the polymerization rate is nearly linear. Beyond that, there is a sharp upturn of the rate until the concentration reaches 20 mmole/liter. However, it is difficult to tell whether the rate reaches its true maximum. In this region, the increasing sensitivity of water toward the polymerization rate and also the inherent difficulties in controlling the exact water concentration make a precise relationship between the rate and the water concentration impossible to obtain.

It is almost impossible to remove the water completely from the system. Thus, no direct proof can be shown that water is necessary to activate the catalyst. However, from the extrapolation to zero water content from Figure 8, it seems that the catalyst is capable of initiating polymerization in the absence of water. It can then be concluded that water will enhance the polymerization, but is not a necessary ingredient.

Many previous investigators have attempted to explain the role water plays in that kind of polymerization. Gippin¹⁹ believed that in the presence of water, aluminum alkyl is hydrolyzed to form AlCl_3 or $\text{EtAl}(\text{OH})\text{Cl}$ depending on the

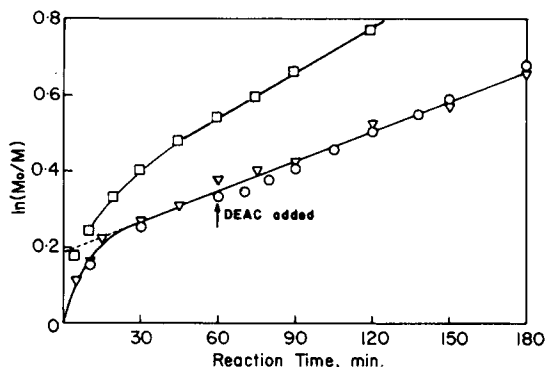


Fig. 7. Effect of second addition of DEAC on polymerization. DEAC, 1.5 ml, dissolved in 20 ml toluene was added after 63 min of polymerization. (○) Addition of Et_2AlCl after 63 min; (▽) no addition; (□) $[\text{Al}] = 0.06$ mole/liter.

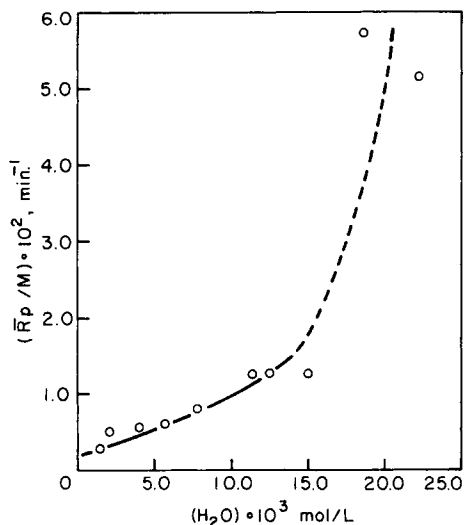


Fig. 8. Effects of water on catalyst reactivity at 20°C. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$, $[\text{M}]_0 = 1.43$ mole/liter.

ratio of $[\text{Al}]/[\text{H}_2\text{O}]$, and the formation of $\text{EtAl}(\text{OH})\text{Cl}$ increases the Lewis acidity. On the other hand, Rancanelli and Porri²¹ proposed that one of the functions of water is to form aloxane *in situ* from the results that the slow hydrolysis of aluminum alkyl can produce aloxane.²² Medvedev¹⁸ stated that no bonding of water into any stable compounds occurs as a result of interaction of water with R_2AlCl , however, a few unstable active compounds of enhanced ability of accepting electron may be formed. The explanation by Gippin is probably more appropriate for the catalyst we studied.

Even in the presence of water, it seems that no appreciable amount of gel is formed for this system, in contrast with cobalt-based systems^{23,24} and the $\text{Ni}(\text{acac})_2\text{-Et}_3\text{Al}_2\text{Cl}_3$ system.⁵

Molecular Weight and Polydispersity

The molecular weights of polybutadiene obtained under different reaction conditions as given in Table I are generally low, and the polydispersity (\bar{M}_w/\bar{M}_n) is usually in the range 1.5–2.0. As shown in Figure 9, the molecular weight of the product increases slightly with conversion. If we plot $(M_0 - M)/\bar{M}_n$ versus percentage conversion (Fig. 10), where $(M_0 - M)/\bar{M}_n$ can be considered to be a quantity corresponding to the number of polymer molecules in the system, the population of polymer molecules increases by a factor of 5 over a conversion range of 10–80%. It is then evident that the low molecular weight of the products can be attributed to the significant chain termination or transfer reaction. As previously pointed out, the molecular weight is independent of DEAC concentration; the transfer reaction to DEAC is negligible. Thus, in the absence of a termination reaction, the transfer to monomer is likely the only chain-terminating reaction.

With the transfer to monomer as the only chain-terminating reaction for a living polymer system, the degree of polymerization can be written as

$$\frac{1}{P_n} = \frac{k_{fm}}{k_p} + \frac{C^*}{[\text{M}]_0 x} \quad (1)$$

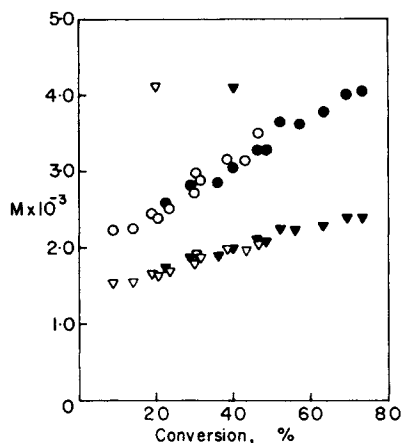


Fig. 9. Average molecular weight as a function of conversion at 20°C. For experiment Nos. 33 [(○) \bar{M}_w ; (▽) \bar{M}_n] and 56 [(●) \bar{M}_w ; (▼) \bar{M}_n], respectively, [Ni], mmole/liter: 4.81 and 4.81; [Al]/[Ni]: 6.3 and 25.8; $[M]_0$, mole/liter: 1.43 and 1.43.

where x is the fractional conversion, $[M]_0$ is the initial monomer concentration, C^* is the concentration of active species, and k_{fm} and k_p are the rate constants for transfer to monomer and propagation, respectively.

According to eq. (1) the number-average molecular weight should increase with conversion as well as initial monomer concentration, which in fact is the case shown in Figures 11 and 12. Similar results have been obtained for the system of nickel (II) naphthenate–boron trifluoride etherate–triethyl aluminum catalyst.⁴

The effects of water content on molecular weight are shown in Figure 13. The increase in molecular weight with the amount of water can be explained with

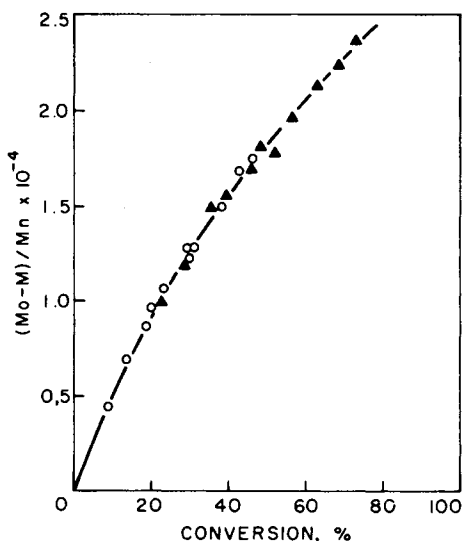


Fig. 10. Plot of the population of polymer chains against conversion at 20°C and $[M]_0 = 1.43$ mole/liter. [(○) Experiment No. 33: Ni, 4.81 mmole/liter; Al, 30.3 mmole/liter; (▲) experiment No. 56: Ni, 4.81 mmole/liter; Al, 121.4 mmole/liter.

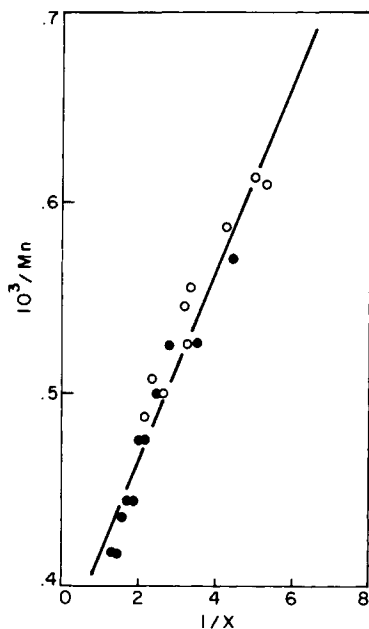


Fig. 11. Plot of $1/\bar{M}_n$ vs. $1/x$ for experiment Nos. 33 and 56 for the polymerization conditions given in Fig. 9.

increased activity of catalyst by enhanced electron-acceptor ability. For the $(i\text{-Bu})_2\text{AlCl}-\text{CoCl}_2\cdot\text{EtOH}$ complex system, molecular weight was found to be directly proportional to water concentration.²³ Figure 13 also shows a moderate increase in polydispersity with water. This increase is understandable because water to some degree also acts as a transfer agent.¹

The effect of temperature on molecular weight is shown in Figure 14. It is interesting to see that the molecular weight of polybutadiene increases with increasing reaction temperature, which is contrary to those observed in the free radical polymerization for the case where the chain transfer to monomer dominates the chain termination reaction. Obviously then, of the systems of interest, the activation energy of the propagation reaction is greater than that of the chain transfer reaction.

Microstructure of Polybutadiene

The microstructure of the polymer products is generally determined not only by the transition metal itself but also by the nature of the active species as a whole, which in turn is influenced by the nucleophilic or electrophilic additives and by the ligands bound to the metal atoms, such as the monomer, counterion, and solvent.

For polybutadiene, there are three possible structures; *cis*-1,4, *trans*-1,4, and vinyl-1,2. In this investigation, the composition was determined using IR, and it was found that the vinyl-1,2 structure in the polymer is usually no more than 3%, but the relative composition of *cis* and *trans* varies with reaction time as shown in Figure 15. The polymer formed at the onset of polymerization is almost exclusively in *cis* structure. *Cis* content progressively decreases with time. The

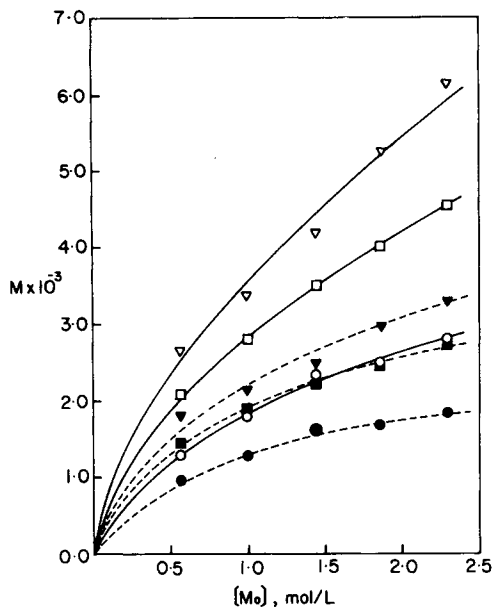


Fig. 12. Effect of initial monomer on molecular weight at 20°C. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$. Conversion (%): 10 ± 2 (○) \bar{M}_w , (●) \bar{M}_n ; 20 ± 2 (□) \bar{M}_w , (■) \bar{M}_n ; 40 ± 3 (▽) \bar{M}_w , (▼) \bar{M}_n .

change of composition during the course of polymerization was also noted by other investigators. In the study of nickel (II) octanoate- $\text{Et}_3\text{Al}-\text{BF}_3-\text{OEt}_2$ system, Saltman and Kuzma²⁴ found that the cis content increases while the trans and vinyl contents decrease as the number-average molecular weight increases. On the other hand, Dolgoplosk and his co-workers²⁵ reported that, for some nickel- and titanium-based catalysts, lowering the initial monomer concentration resulted in lowering cis-1,4 polymerization. Dawans and Teyssie²⁶ attempted

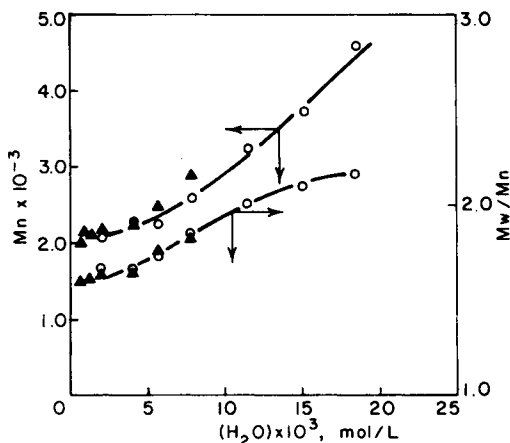


Fig. 13. Effect of water on number average molecular weight and polydispersity at 20°C. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$. Conversion (%): (○) 60 ± 3 ; (▲) 40 ± 2 .

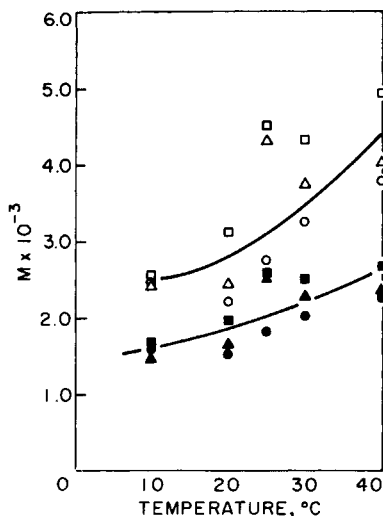


Fig. 14. Effect of temperature on average molecular weight. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$. Conversion (%): 10 ± 2 (O) M_w , (●) M_n ; 20 ± 2 (Δ) M_w , (\blacktriangle) M_n ; 30 ± 2 (\square) M_w , (\blacksquare) M_n .

to explain this phenomenon based on the characteristics of butadiene coordination on transition metal. Dolgoplosk et al.,²⁷ on the other hand, assumed that trans units in the polymer chain were determined by the ratio of the propagation rate to the anti-syn isomerization rate. In his assumption, the initial monomer insertion into the active species is always in anti configuration leading to a cis polymerization. However, if the transformation from anti to syn configuration occurs before the next insertion of monomer, then the trans configuration will result. Accordingly, as the conversion increases or the monomer concentration diminishes, the rate of polymerization also decreases as compared to the isomerization rate, which in turn reduces the cis content. This explains the general results obtained in this work. However, it is difficult to explain some other works where cis content increases with conversion. Furthermore, we should expect that the initial cis content of the polymers obtained under the conditions that give a higher initial polymerization rate will be higher as compared to lower initial rate. It was, in fact, not found to be the case here.

As mentioned previously, the reaction between nickel and aluminum compounds forms two or more active species, and their activities and stereospecificity are not expected to be the same. One of the species may in fact have limited

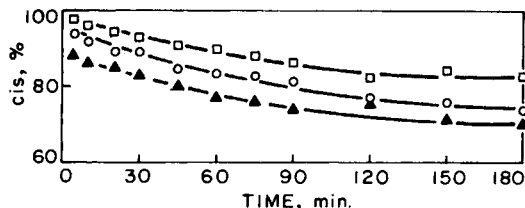
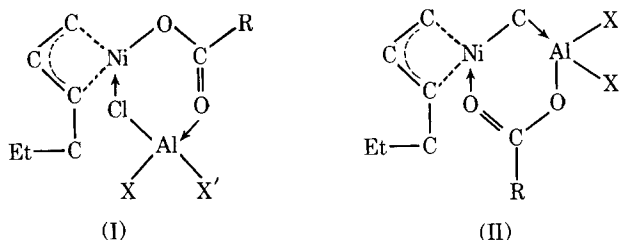


Fig. 15. Percentage cis content as a function of polymerization time at 20°C . $[\text{Al}]/[\text{Ni}] = 6.3$. (Ni), mmole/liter: (\blacktriangle) 1.60; (O) 4.81; (\square) 9.63.

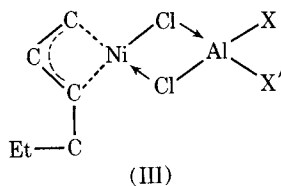
solubility, as we have observed from the appearance of the reaction mixture at the first 15 min of polymerization. Normally the alkylation reaction of the transition metal in the presence of organometallic produces metallic compounds of difference valance states.²⁸ The organo-aluminum compounds in this case fulfill two functions²⁹: the alkylation of transition metal will ensure the formation of π -allyl complexes; and the charge-transferred complex (or anion) formation takes place on participation of alkylaluminum halides and the efficiency of the latter increases in sequence of $R_2AlCl > RAlCl_2 > AlCl_3$. The π -allyl transition metal complex is a reactive intermediate for the polymerization of butadiene,^{26,30,31} and its mononuclear complex formed from the interaction with monomer is usually the active species for the polymerization of butadiene.^{32,33}

Thus, it seems possible that the following π -allyl nickel complexes are formed in the system studied here:



where R is $C_{17}H_{35}$ of the stearate group and X = Et, Cl, stearate group, etc. A very similar complex structure has been proposed by Throckmorton and Farson³⁴ for the nickel (II) octanoate- Et_3Al -HF system.

Type (III) complex as shown below can also be formed:



In a study of the $NiCl_2$ - Et_2AlCl catalyst, the type (III) complex produces 90% *cis*-polybutadiene.³⁵ The formation of (III) from Ni (II) stearate is very slow and its concentration can be neglected in the initial stage of polymerization but gradually builds up. This was seen from the increasing *cis* content for the polymer formed after 20 hr.³⁵

From the polymerization rate data and the microstructure of the polymers, we can then assume that, when the catalyst components are mixed, complex (I) is first formed with high reactivity. Type (I) complexes are gradually transformed into type (II), a relatively stable complex, but less reactive. The active species (I) has limited solubility while type (II) remains soluble in the reaction medium. Another example for which the solubility is changed with its structure has been found in the case of a π -allylic complex of iron.³⁶ π - $C_4H_{13}Fe(CO)_3ClO_4$, which has a strong electron attracting group, is an ionic compound insoluble in hydrocarbon, while π - $C_4H_{13}Fe(CO)_3Cl$, having a covalent structure, is soluble in hydrocarbon.

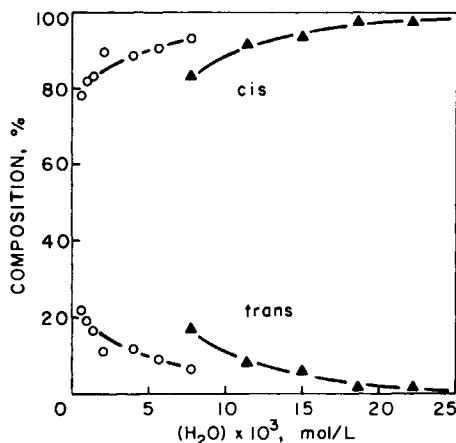


Fig. 16. Effect of water on microstructure at 20°C. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$. Conversion (%): (○) 40 ± 2 ; (▲) 80 ± 3 .

Based on the proposed structure, it can be considered that the electron density of the nickel atom in species (I) is smaller than that in species (II) because of the electron-attractive carboxylic group. Thus, reactive species (I) is more active and may act mainly as a cis regulating center, while species (II) tends to be less stereospecific and less active. This explains the decrease in cis content as the extent of polymerization increases.

In the presence of added water, the cis content of polybutadiene at a given conversion was plotted in Figure 16 against the concentration of water added. It was found that the cis content was increased with water content. Water is normally considered an electron acceptor. According to Matsumoto and Furukawa,³⁷ the electron acceptor causes the increase of activity as well as the stereoregulating ability.

The temperature effect on microstructure at constant conversion was also examined as shown in Figure 17. The cis content decreases with increasing reaction temperature as a result of shifting the type (I) species to type (II).

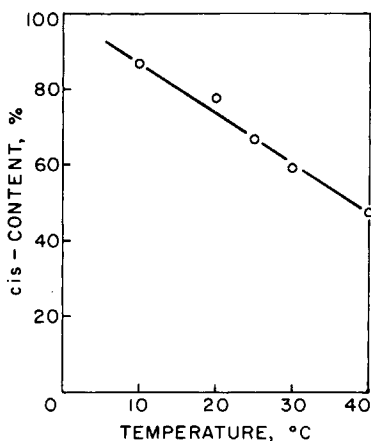


Fig. 17. Temperature effect on microstructure. $[\text{Ni}] = 4.81$ mmole/liter, $[\text{Al}]/[\text{Ni}] = 6.3$.

CONCLUSION

Nickel (II) stearate and diethyl aluminum chloride form two or more active species. The addition of water will enhance the reactivity. The type I complex, which acts mainly as a cis regulating center, is highly active. The reactivity decreases as type I is gradually shifted to type II and reaches a constant polymerization rate. Because the type II species is less stereospecific, the cis content decreases as the extent of polymerization increases.

Initiation reaction can be considered instantaneous and the propagation reaction is first order with respect to the monomer. The polymerization belongs to a living polymer system with no termination. The molecular weight is regulated by the chain transfer to monomer.

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