Polymerization of Isoprene in *n*-Heptane with Triethylaluminum–Titanium Tetrachloride Catalyst. I. Effect of Al / Ti Ratio on Stereoregularity, Conversion, Molecular Weight, and Molecular Weight Distribution

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Synopsis

The influence of the Al/Ti ratio of the heterogeneous Ziegler–Natta catalyst system $AlEt_3$–$TiCl_4$ on the isoprene polymerization in *n*-heptane at 30°C in a bench scale reactor was investigated. Each batch run consisted of 50 mL isoprene, 200 mL *n*-heptane with 0.45 and 0.5 g catalyst. Conversion of isoprene and molecular weights of polyisoprene increased with increasing Al/Ti ratio, reaching their maxima values at 1.0 and 1.2, respectively. Conversion and molecular weights decreased remarkably at a higher ratio of Al/Ti. As this ratio decreases from the value of 1.2 to 0.4, the *cis*-1,4 content in polyisoprene decreased from 97 to 25%. When the ratio of Al/Ti increased from 1.2 to 2.2 the *cis*-1,4 structure of polyisoprene decreased from 97 to 85%.

INTRODUCTION

The heterogeneous polymerization of isoprene to a stereoregular polymer of 96% or more *cis*-1,4 structure by Ziegler–Natta coordination complex of triethylaluminum ($AlEt_3$) and titanium tetrachloride ($TiCl_4$) is one of the most important processes for producing isoprene–rubber (IR). The second process is based on the homogeneous polymerization of isoprene to high *cis*-1,4 polyisoprene by alkyllithium catalysts.[1,2]

IR has become an important polymer for the rubber industry due to its increasing use as a substitute to natural rubber (NR) and production growth is likely to exceed the world wide capacity of 1 million tons per annum.[3] To select and develop an industrial process for IR production, it is necessary to investigate on a practical scale the role of different polymerization parameters. Our first concern was the alkyllithium process.[4–7] The main purpose of the present study was to reveal experimentally the role of the Al/Ti ratio of the Ziegler–Natta catalyst system on the course of isoprene polymerization in

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n-heptane at 30°C. These data and the result of alkyllithium processes will be used to develop a mathematical model needed for an effective design and control system for an industrial reactor.

Despite some important published work on diene polymerization by Ziegler–Natta systems,[8–10] the considerable experimental difficulties, and still imperfect knowledge of several parameters during polymerization as well as the relative paucity of literature describing process control and model development,[11,12] it was necessary to provide some new experimental results.

EXPERIMENTAL

The experimental methods employed in the purification of isoprene and *n*-heptane in the present investigation are similar to that used in our earlier work on anionic living polymerization.[4,13,14] Extra care was taken to avoid the presence of water, oxygen, and other impurities which effect polymerization or react with the catalyst system.

A 1-L polymerization glass reactor was cleaned and dried at 120°C before use. Nitrogen of purity more than 99.999 (v/v) was dried through a series of columns of calcium hydride particles, phosphorous pentoxide, and Linde molecular sieves type 5A (Union Carbide), bubbled through living α-methylstyryl sodium tetramer before being introduced to the reactor. Prescribed amounts of $TiCl_4$ and $AlEt_3$, in that order, were charged at 0°C under a dry nitrogen stream. One hour after the reddish-brown coordination complex catalyst was formed, the temperature of the reactor was raised to 30 ± 0.1°C before 200 mL of *n*-heptane and 50 mL of isoprene were syringed into the reactor through a syringe port in that order. The polymerization was timed from the addition of isoprene and terminated after 180 min by introducing methanol to the well-stirred reactor. All polymerizations were conducted at 30 ∓ 0.1°C and 1 atm pressure in a 1-L batch reactor. Polyisoprene was purified after each run several times by dissolution–reprecipitation with the chloroform–methanol system and dried before characterization. Stereoregularity of polyisoprenes obtained in this work was determined carefully from their proton and carbon-13 spectra, which were recorded on 90 MHz NMR spectrometer equipped with Fourier transfer accessory, according to the method described earlier.[4]

The molecular weights and molecular weight distributions were determined on a gel permeation chromatograph Waters Model 150C (Milford, MA) equipped with six ultra-Styragel columns of pore size 100, 500, 10^3, 10^4, 10^5, and 10^6 Å and refractive index detector. Details of measurements are similar to that described recently.[15] Data Module Mz 30 (Waters Assoc.) was used to calculate number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), viscosity average molecular weight ($\overline{M}_v$), *z*-average molecular weight ($\overline{M}_z$), and molecular weight distribution (MWD) expressed as polydispersity (Q). Because polyisoprene standards were not available in this laboratory during GPC measurements, the calibration was made by polystyrene standards obtained from Pressure Chemical with the use of the principle of the Benoit relation and Mark–Houwink constant as described earlier[16] and used recently[17] for polyisoprenes of different stereoregularity.

RESULTS

Our first concern in this study was to provide accurate data on the isoprene polymerization with the commercial catalyst system $AlEt_3$–$TiCl_4$ and to establish that slight change in this complex catalyst could effect some of the most important parameter of commercial polymer product, viz., conversion (yield) as well as the two most important characteristics of the resulting polymer, i.e., stereoregularity and molecular weight. Figure 1 shows the observed change in the monomer percent conversion into polyisoprene with the change in the Al/Ti molar ratio. Conversion increased with increasing Al/Ti ratio up to 1, and then decreased with further increase in this ratio. Increasing the catalyst complex charge from 0.45 to 0.5 g has only a little influence on the percent conversion of isoprene into polyisoprene.

The dependency of the steroregularity of polyisoprene obtained on the Al/Ti ratio of 0.45 and 0.5 g of the complex catalyst are shown in Figures 2 and 3. The highest *cis*-1,4 polyisoprene (97–98%) was obtained at Al/Ti molar ratio of 1.2 for both charges of the catalysts systems. As the ratio of Al/Ti decreases down to the value of 0.4, the content of *cis*-1,4 in the polymer decreases too, reaching values as low as 25–26%. However, when the ratio of Al/Ti increased from 1.2 up to 2.2, only 10% reduction in the *cis*-1,4 content was observed. Results of Tables I and II indicate an outstanding dependency of the molecular weight of polyisoprene obtained from different Al/Ti with only a little influence (again) of the concentration of the catalyst system in the range used in this work. The highest values of $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_v$, and $\overline{M}_z$ were obtained at Al/Ti molar ratio of 1.2. However, only a slight decrease from the highest conversion value of isoprene at Al/Ti ratio was observed. As the Al/Ti ratio increased from 0.4 to 1.2, molecular weights increased too. However, once the ratio of Al/Ti becomes greater than 1.2, a remarkable decrease in all molecular weights started, leading to the eventual formation of liquid polyisoprene. Further, the values of MWD, i.e., $\overline{M}_w/\overline{M}_n$ increased with

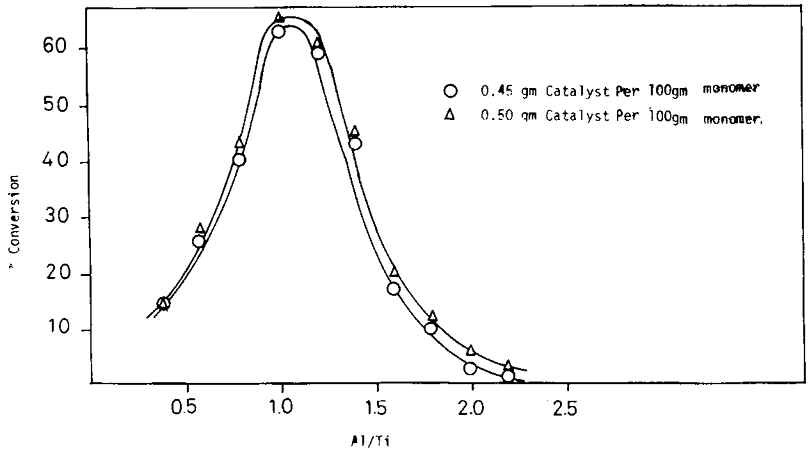

Fig. 1. Effect of the molar ratio Al/Ti on the conversion of isoprene into polyisoprene in a 1-L batch reactor at 30 ± 0.1°C and 1 atm pressure, 180 min reaction time, and 1/4 (v/v) monomer/solvent ratio.

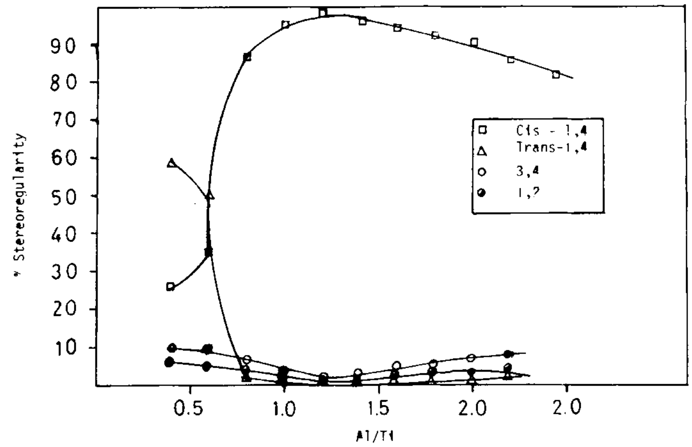

Fig. 2. Effect of the molar ratio Al/Ti of 0.45 g catalyst system on the stereoregularity of polyisoprene in a 1-L batch reactor at 30 ± 0.1°C and 1 atm pressure. 180 min reaction time, and 1/4 (v/v) monomer/solvent ratio.

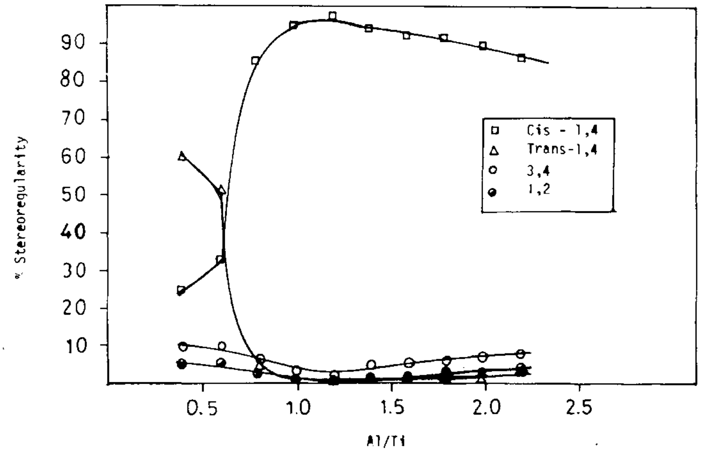

Fig. 3. Effect of the molar ratio Al/Ti of 0.50 g catalyst system on the stereoregularity of polyisoprene in a 1-L batch reactor at 30 ± 0.1°C and 1 atm pressure, 180 min reaction time, and 1/4 (v/v) monomer/solvent ratio.

increasing the ratio of Al/Ti. Narrow MWD in general was obtained at Al/Ti ratio < 1.2 reaching narrow MWD at Al/Ti < 0.8; on the contrary, a relatively broad MWD was obtained at Al/Ti ratio of 2.2.

DISCUSSION

One of the difficulties with Ziegler–Natta catalyst system is that the structure of the active species are not known with certainty. Stereoregular polymer can be obtained via anionic, cationic, or coordination mechanisms. Catalysts based on an insoluble transition metal compound provide little conclusive evidence as to the structure of the active species or the nature of the intermediates in the stereospecific polymerization.

TABLE I
Effect of Al/Ti Molar Ratio on the Molecular Weights of Polyisoprene Using 0.45 g Catalyst in *n*-Heptane at 30°C and 180 min Reaction Time

Sample no.	Al/Ti molar ratio	Yield (%)	$\overline{M}_n$	$\overline{M}_v$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	0.4	15	7009	7650	7869	8350	1.12
2	0.6	26	13,050	15,600	15,059	17,350	1.15
3	0.8	40	36,000	39,000	42,699	59,600	1.18
4	1.0	63	121,500	187,000	189,500	283,500	1.56
5	1.2	59	192,000	294,000	299,500	512,900	1.56
6	1.4	43	114,500	191,650	199,500	390,500	1.74
7	1.6	17	51,900	85,650	96,900	191,500	1.86
8	1.8	10	13,500	25,050	25,800	37,000	1.90
9	2.0	3	4950	15,150	15,150	20,100	3.14
10	2.2	1.5	1850	8100	8200	14,350	4.43

TABLE II
Effect of Al/Ti Molar Ratio on the molecular Weights of Polyisoprene Using 0.50 g Catalyst in *n*-Heptane at 30°C and 180 min Reaction Time

Sample no.	Al/Ti molar ratio	Yield (%)	$\overline{M}_n$	$\overline{M}_v$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	0.4	15	6800	7150	7700	9000	1.13
2	0.6	28	12,500	14,550	14,850	16,900	1.18
3	0.8	43	35,500	38,800	42,500	58,500	1.20
4	1.0	65	170,000	176,000	199,500	242,000	1.17
5	1.2	60	185,000	232,500	293,000	435,100	1.58
6	1.4	45	100,590	171,750	179,600	260,500	1.78
7	1.6	20	48,200	82,500	93,300	188,500	1.935
8	1.8	12	11,050	22,200	23,950	30,900	2.17
9	2.0	6	3200	14,350	15,950	18,200	4.98
10	2.2	3	1050	7420	7450	12,750	7.09

Ziegler thought of the aluminum alkyl as the catalyst and attributed a somewhat undefined role as cocatalyst to the transition metal component. For many years, several schools of thought maintained the firm belief that chain growth takes place at a base metal–carbon bond. However, it became more and more obvious that the transition metal, with its *d*-orbitals available for σ and π bonding, is more likely to be the true catalyst center.[18]

In this work the catalyst complex was prepared prior to polymerization; $AlEt_3$ was added to $TiCl_4$. This sequence of addition gives more active catalyst complex, which produces less gel and could also be the reason for such rather narrow MWD in general. It was reported that the excess of $AlEt_3$ may adsorb and block the active polymerization site of $TiCl_4$ or even reduce it to $TiCl_2$, which is inactive in isoprene polymerization.[2] Moreover, the high activity and selectivity of the catalyst complex were only achieved when a reddish-brown coordination complex was formed at 0°C. The marked increase in catalyst activity and selectivity at low temperature could be attributed to the formation of a catalyst complex with very small particle size and hence a high surface area. This results in the formation of a greater number of reactive polymerization sites, thus enabling more propagating chains of polyisoprenes to grow to high molecular weights. Also a greater number of reactive sites could indirectly contribute to the narrow MWD obtained in this work. The increase of the monomer percent conversion to polyisoprene with increase of Al/Ti ratio up to 1 and further increase in this ratio leading to decrease in conversion gives indirect evidence that the catalyst forms a complex in which Al and Ti atoms are joined by electron-deficient bonds. Furthermore, it also means that the complex alone without excess of $TiCl_4$ or $AlEt_3$ gives the highest conversion. Stereoregularity analyses of Figures 1 and 2 reveals that the presence of free $TiCl_4$ at a molar ratio of Al/Ti < 1 enhanced the *trans*-1,4 formation due probably to cationic polymerization. However, the narrow MWD obtained at Al/Ti < 1 could have been caused by a change in the nature of the propagating active center of isoprene growing macromolecules. It is possible that the coordination complex nature of the catalyst becomes more ionic due to the excess titanium cations. Further work on the kinetic analyses of these results and the reason for low values of polydispersity observed in this work will be the subject of a future communication from this laboratory.

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