Macromolecules **1994,** *27,* 4397–4398 **4397**

Notes

A Rare-Earth Catalyst Capable of Modulating the Stereocontrol of Isoprene Polymerization[†]

Yingtai Jin,* Fengfu Li, Fengkui Pei,
Fosong Wang, and Yufang Sun

Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022,
People's Republic of China

Received December 12, 1993
Revised Manuscript Received April 11, 1994

Introduction

From the polymericular structure point of view, there are two problems to be solved in an investigation on a conjugated diene (here in point of isoprene and butadiene) polymerization with rare-earth catalysts. One problem is that it is not easy to change the stereoregularity of these polymers; either high cis-1,4[1] or high trans-1,4[2] polymer was obtained in the polymerization. Another is the difficulty in getting a polymer of low molecular weight[3] or narrow molecular weight distribution.[3] Attempts to change for stereoregularity were somewhat unsuccessful using various methods in the literature. One of the more effective examples is the polyisoprene containing 51.0% trans-1,4, 47.5% 3,4, and 1.5% 1,2 structure units with a $(C_6H_5CNd)_2 \cdot n$THF catalyst reported by Chigir et al.[4] Another example is the polybutadiene containing 80.2% 1,2, 15.0% trans-1,4, and 5.0% cis-1,4 structure units with LiCe(π-allyl)$_4$·5TMED by Mazzei.[5] However, under usual polymerization conditions, such a rare-earth catalyst, which markedly varied the stereoregularity of the polymer, has not been found in the literature.

In this work, effects of the usual polymerization conditions, such as polymerization temperature, solvent, and Al/Ln molar ratio, etc., on the stereoregularity and molecular weight of polyisoprene as well as the catalytic activity in isoprene polymerization are reported with a new (β-CH_3-π-allyl)$_2$LnCl$_5$Mg$_2$·2TMED(Ln)/R$_3$Al(Al) (Ln = Nd, Ce, and La, TMED = *N,N,N',N'*-tetramethylethylenediamine, R = Me-, Et-, i-Bu-, and Oct-) catalyst.

Experimental Section

The synthetic method and characterization of the Ln-π-allyl complexes have been described elsewhere.[6] Various R$_3$Al (Fluka, pure except R = Oct-, Merck, 90%) were used without further purification. *n*-Hexane, toluene, and *o*-xylene used as polymerization solvents were purified by refluxing with an Na–K alloy and benzophenone for over 8 h and then distilled and stored over active aluminas (Shanghai Molecular Sieve Factory). Chlorobenzene, purified over calcium hydride and distilled and stored over the aluminas, was also used as a solvent. Isoprene (solution polymerization grade, Institute of Chemical Engineering, Jilin, China) was freed of inhibitor by distillation and dried over the aluminas prior to use. The polymerization procedure was the same as before.[7] Polymer microstructures were determined according to the ^{13}C-NMR method[8] with an FX-100 spectrometer. All operations of purifying solvents and polymerization procedure were carried out under 99.999% pure argon free from moisture and oxygen.

Results and Discussion

The effects of three kinds of Ln-π-allyl complexes on isoprene polymerization are listed in Table 1. Among the complexes the neodymium complex showed the best activity under the same polymerization conditions. A significant result is that a lower molecular weight polyisoprene was obtained by using any one of the complexes. Even when smaller amounts of the complex were added to the polymerization system, the [η] values of the formed polymers were lower than 0.5 dL/g (Figure 1), and near-equibinary *cis*-1,4-/*trans*-1,4-isoprene polymers were obtained as shown in Table 1.

The effects of four kinds of alkylaluminums on the polymerization activity and stereoregularity of the polymers are evident from Table 2. The order of their activities is as follows: (i-Bu)$_3$Al > Et$_3$Al > Me$_3$Al > (Oct)$_3$Al. Me$_3$Al was capable of forming higher cis-1,4 polymer. Whichever alkylaluminum, the [η] value was lower than 0.5 dL/g. We have proven that the insertion reaction of isoprene occurs between Ce^{3+} and the π-allyl group instead of between Ce^{3+} and the –CH$_2$CH(CH$_3$)$_2$ group in the isoprene polymerization with the (π-allyl)$_2$CeCl$_5$Mg$_2$·2TMED/(i-Bu)$_3$Al catalyst.[9] This implies that (i-Bu)$_3$Al plays a role in decreasing the electron density of the active center Ce^{3+} as a Lewis acid although weak, and the result conduces to the coordination of the monomer and further increases in the polymerization activity. If other alkylaluminums also play the same role as above, the active order of the first three alkylaluminums corresponds with a dissociation power, big or small, because the order of their capabilities to associate is as follows:[10] Me$_3$Al > Et$_3$Al > (i-Bu)$_3$Al. In the case of (Oct)$_3$Al, the reason is the decreasing role rather than the probable bigger steric hindrance.

The above effects of catalyst varieties are presented, and the following effects of three usual polymerization conditions will be discussed.

Table 3 shows the effects of Al/Ln molar ratios on isoprene polymerization. The highest activity appeared at Al/Ln = 6 (molar ratio), and with an increase in the Al/Ln molar ratios, the [η] values somewhat decreased. It is worthy to emphasize that the best activity appeared at such a low Al/Ln molar ratio, and when the Al/Ln values were increased from 2 to 20, the cis-1,4 structure unit contents rose from 18.6 to 46.5% and the 3,4 contents were rather low and hardly changed in the polymers. To the best of our knowledge, a result similar to that above has not been obtained. The unusual low Al/Ln molar ratio may be relevant to the π-allyl complex, which functioned as the only active species in isoprene polymerization although with low activity (Table 3, footnote *b*). Thereby, provided that the electron density is decreased somewhat just as mentioned before, the polymerization activity rapidly increased even if a very small amount of the alkylaluminum is added.

The stereoregularity was also influenced significantly by various solvents (Table 4). Under the same conditions, when *n*-hexane was used as the solvent, the cis-1,4 content

---

[†] The project was supported by the National Natural Science Foundation of China.

* To whom correspondence should be addressed.

0024-9297/94/2227-4397$04.50/0

Table 1. Effect of Different Ln-π-Allyl Complexes in Isoprene Polymerization[a]

complex	conversion, %	[η], dL/g	cis-1,4, %	trans-1,4, %	3,4, %
Nd	74.0	0.29	49.3	48.0	2.7
Ce	62.8	0.31	48.2	51.8	0
La	51.2	0.28	50.7	46.5	3.8

[a] All polymerization conditions: [Ln] = 1.25×10^{-2} mol/L, Et_3Al/Ln = 4 molar ratio, [isoprene] = 200 g/L, in toluene as a solvent at 50 °C for 1 h.

Table 2. Effect of Various Alkylaluminums on Isoprene Polymerization[a]

R_3Al	convn, %	[η], dL/g	cis-1,4, %	trans-1,4, %	3,4, %
Me_3Al	36.7	0.45	82.6	17.4	0
Et_3Al	62.8	0.31	48.2	51.8	0
$(i\text{-}Bu)_3Al$	76.5	0.34	58.6	41.4	0
$(Oct)_3Al$	29.4	0.41	67.6	32.4	0

[a] All polymerization conditions: [Ce] = 1.25×10^{-2} mol/L, Al/Ce = 4 molar ratio, others identical with those in Table 1.

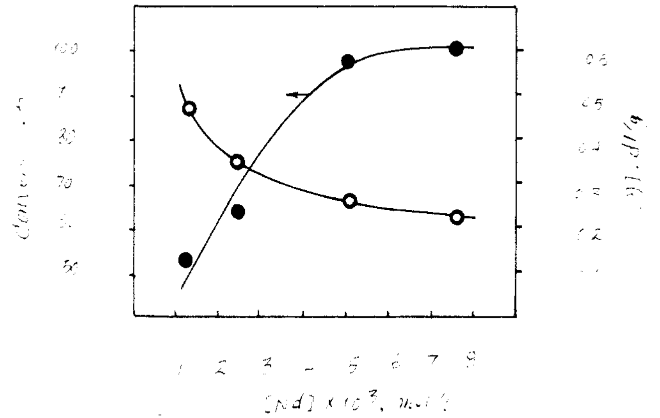


Figure 1. Relationship between the concentration of the Nd complex and conversion or [η] of polyisoprene (polymerization conditions were identical with those in Table 1).

Table 3. Effect of Al/Ce (molar ratios) on Isoprene Polymerization[a]

Al/Ce molar ratio	convn, %	[η], dL/g	cis-1,4, %	trans-1,4, %	3,4, %
0[b]	2.5		45.0	50.7	4.3
0.5	0				
2.0	10.8		18.6	77.9	3.5
6.0	99.0	0.19	40.1	57.4	2.5
15.0	100.0	0.18	43.4	53.9	2.7
20.0	100.0	0.16	46.5	53.5	0

[a] All polymerization conditions except *b*: Al represents Et_3Al, polymerization time 4 h, others identical with those in Table 2. [b] [Ce] = 7.85×10^{-2} mol/L, [isoprene] = 680 g/L, at 70 °C for 15 h.

Table 4. Effect of Different Solvents on Isoprene Polymerization[a]

solvent	dielectric constant ε	convn, %	[η], dL/g	cis-1,4, %	trans-1,4, %	3,4, %
n-hexane	1.90	7.4	0.30	75.0	25.0	0
o-xylene	2.43	64.2	0.40	50.5	49.5	0
toluene	2.40	81.6	0.45	47.2	52.8	0
chlorobenzene	5.62	94.6	0.46	54.0	46.0	0

[a] All polymerization conditions: [Ce] = 5.0×10^{-3} mol/L, for 2 h, others identical with those in Table 3.

in the polymer amounted to 75%, but when toluene was used as the solvent, it amounted to only 47%. We had reported[11] the effects of nine kinds of solvents (ε = 1.00–10.20) on conjugated diene polymerization. Therein, the cis-1,4 contents in polyisoprene only ranged from 93 to 96% with a typical homogeneous rare-earth catalyst.

Table 5. Influence of Polymerization Temperature and Time on Isoprene Polymerization[a]

polym temp, °C	polymn time, h	convn, %	cis-1,4, %	trans-1,4, %	3,4, %
25	3	69.9	48.5	51.5	0
0	24	24.8	57.0	43.0	0
−30	72	12.3	79.3	20.7	0

[a] All polymerization conditions: Et_3Al as cocatalyst, other identical with those in Table 2.

From Table 5 a remarkable change of the stereoregularity resulted from different polymerization temperatures and/or polymerization times, while in typical rare-earth catalysts the change was extremely small.[12] In general, it is unreasonable to change the stereoregularity of the polymer with the varying time. The main parameter is probably due to the temperature.

The π-allyl complexes can be considered as a better model compound for the active species of a rare-earth catalyst;[13] nevertheless a very low activity was shown with the complex alone. The reason probably is in connection with its coordinate saturation.

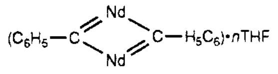
References and Notes

(1) Jin, Y.; Li, F.; Wang, P.; Wu, Y. *Chin. Polym. Bull.* **1992**, *4*, 211.

(2) Jin, Y. *Chin. Elastomerics* **1993**, *1*, 44.

(3) Sen, Z. *Collected Papers on Synthetic Rubber Prepared with Lanthanide Catalyst*; Science Press: Beijing, 1980; pp 40, 150, and 250.

(4) Chigir, N. N.; Guzman, I. Sh.; Sharaev, O. K.; Tinyakova, E. I.; Dolgoplosk, B. A. *Dokl. Acad. Nauk SSSR* **1982**, *263*, 375. A probable structure of the complex was characterized by Guzman et al. (*Dokl. Acad. Nauk SSSR* **1979**, *249*, 860) as follows:



(5) Mazzei, A. *Makromol. Chem. Suppl.* **1981**, *4*, 61.

(6) Li, F.; Jin, Y.; Pei, F.; Wang, F. *Chin. J. Appl. Chem.* **1992**, *9*, 107.

(7) Jin, Y.; Li, X.; Sun, Y. *Chin. Polym. Commun.* **1984**, *5*, 351; *Chem. Abstr.* **1985**, *102*, 185561z.

(8) Randall, J. C. *Polymer Sequence Determination Carbon-13 NMR Method*; Academic Press: New York, 1977; p 94.

(9) Li, F.; Jin, Y.; Pei, F.; Wang, F.; Wu, W. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 273.

(10) Müller, E. *Methoden der Organichen Chemie*, 4th ed.; Georg Thieme Verlag Stuttgart: 1970; Vol. 13, Book Four, Chapter 1.

(11) (a) Jin, Y.; Zhang, X.; Pei, F.; Wu, Y. *J. Chin. Rare Earth Soc.* **1990**, *1*, 79; *Chem. Abstr. 113*, 232090j. (b) Sun, Y.; Li, X.; Zhang, Q.; Chen, Y.; Jin, Y. *Chin. J. Rare Earth* **1993**, *2*, 43. The ε expresses dielectric constants of different solvents.

(12) Jin, Y.; Sun, Y.; Liu, X. *Chin. J. Mol. Sci.* **1984**, *2*, 247; *Chem. Abstr.* **1984**, *101*, 131149g.

(13) (a) Jin, Y.; Zhang, X.; Pei, F.; Wu, Y. *Chin. J. Polym. Sci. (Eng.)* **1990**, *2*, 121; *Chem. Abstr.* **1991**, *114*, 164870g. (b) See ref 9.