

Preliminary investigations on polymerization catalysts composed of lanthanocene and methylaluminoxane *

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Summary

The polymerization of butadiene(Bd), isoprene(Ip) and styrene(St) has been examined using the six catalyst systems composed of lanthanocene, $(C_5H_9Cp)_2NdCl(I)$, $(C_5H_9Cp)_2SmCl(II)$, $(MeCp)_2SmOAr'(III)$, $(Ind)_2NdCl(IV)$, $Me_2Si(Ind)_2NdCl(V)$ and $(Flu)_2NdCl(VI)$, and methylaluminoxane(MAO) respectively.

All of them can be used to form the polyisoprene with molecular weights of 1 to 10 thousand and cis-1,4-unit contents of 41 to 47%. (I), (II) and (III) of them can be also used to form the polybutadiene with molecular weights of 10 to 20 thousand and cis-1,4-unit contents of 62 to 78%. In addition, the catalysts from (II) to (V) are still active for St polymerization and (II) of them gives a syndio -rich random polystyrene. It is noteworthy that (II) and (III) are active for homopolymerization of Bd, Ip and St in the same polymerization condition.

(**Keywords:** lanthanocene; methylaluminoxane; polymerization; butadiene; isoprene; styrene.)

Introduction

In recent years, metallocene polymerization catalysts have developed with great rapidity, some of which have been realized commercially. The study on these catalysts was mainly focused on the late transition metals of group of IVB and VB. However, the study on the early transition metals of IIIB group was laid emphasis on either noncyclopentadienyl rare earth compound/methylaluminoxane (MAO) systems [1] or cyclopentadienyl rare earth compound/non-MAO systems [2] or cyclopentadienyl rare earth compound only[3]. Recently, some papers [4] and patents [4] have published the findings of olefin polymerization with lanthanocene and MAO system. But the results of conjugated diene polymerization and styrene have not been reported with lanthanocene/MAO systems.

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In this work, effects of valence state, Ln/Al molar ratio and polymerization temperature on the catalytic activity, molecular weight, and stereoregularity in the homopolymerizations of butadiene (Bd), isoprene (Ip), and styrene (St) are reported with six new catalyst systems composed of six lanthanocenes and MAO respectively.

Experimental

Materials

The methods for purifying Bd (Beijing Yanshan Petroleum Chemical Company, CP), Ip (Research Institute of Jilin Chemical Company, CP) and St (Beijing 25952 Chemical Plant, AR) were carried out according to ref [5]. The methods for purifying toluene (Beijing Chemical Plant, AR) and tetrahydrofuran (Beijing Yili Fine Chemical limited company, AR) were the same as before [6]. The major agents of trimethylaluminum (Aldrich Chemical Co. Inc., > 97%), bicyclopentadiene (Merck-Schuchardt Co., 93%), indene (Fluka Chemi AG, 90-95%), fluorene (Fluka Chemi AG, > 99%) were purified in accordance with following concerned reference before use.

Synthesis of MAO and lanthanocene

MAO, $(C_5H_9Cp)_2LnCl$ [bis(cyclopentylcyclopentadienyl)lanthanide chloride, Ln= Nd(I) and Sm(II), C_5H_9 = cyclopentyl, Cp= cyclopentadienyl], $(MeCP)_2Sm$ Oar'(III) [bis(methylcyclopentadienyl)-2,6-tert-butyl-4-methyl-phenoxy. samarium], $(Ind)_2NdCl$ (IV) [bis(indyl)neodymium chloride] and $Me_2Si(Ind)_2NdCl$ (V) [ansa-dimethylsilyl-bis(indyl)neodymium chloride] were synthesized according to ref. [7], [8], [9], [10] and [11] respectively. Synthesis method of $(Flu)_2NdCl$ (VI) [bis(fluorenyl)neodymium chloride] will be presented in other paper.

Polymerization

All operations were conducted under argon (99.999%). Polymerization were carried out as ref. [12].

Measurements

Intrinsic viscosities of PBd (polybutadiene), PIp (polyisoprene) and PSt (polystyrene) were determined in toluene at 30°C using an NC-Z viscometer and molecular weight of the polymers was calculated by following formula:

$$PBd: [\eta] = 3.24 \times 10^{-4} [\bar{M}_w]^{0.70}$$

$$PIp: [\eta] = 1.93 \times 10^{-4} [\bar{M}_w]^{0.97}$$

$$PSt: [\eta] = 1.20 \times 10^{-4} [\bar{M}_w]^{0.71}$$

The microstructure of PBd was determined on BIO-RAD FTS-7 type IR spectrophotometer, using film on KBr discs [6]. The microstructure of PIp was determined with a unty-400 spectrometer. Chemical shifts of the polymer were referenced to tetramethylsilane added as the interior standard using chloroform- d_1 as solvent [12]. Besides NMR spectra, the tacticity of PSt was recorded using differential scanning calorimetry (Perkin-Elmer TAS-7 type) [6].

Results and discussion

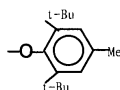
Bd polymerization with lanthanocene/MAO as catalyst

The findings of Bd Polymerization with three catalyst systems composed of lanthanocenes (I, II and III) and MAO respectively are listed in Tab 1. All three appeared considerable polymerization activity. Higher polymerization temperature and Al/Ln molar ratio is necessary to obtain higher activities as zirconocene/MAO system. It is noteworthy that using two-valence lanthanocene (III) as catalysts can also produce predominantly cis-1,4- unit structure polymer. Another significant result is that molecular structure of the polymer had very clear changes after cyclopentadienyl ligand was introduced to rare earth compound. The three systems-contained MAO as cocatalyst can be used to form the PBd with molecular weight of only 10 to 20 thousand and cis-1,4-unit contents of 62 to 78%. When the systems contained R_3Al as cocatalyst, either polymers were hardly soluble in toluene or no polymer was obtained. But the PBd arised from $(C_7H_{15}CO_2)_3Nd/MAO$ system contained cis-1,4-unit contents of 95% and molecular weight of 140 thousand [1]. The reason of the decrease in cis-1,4-unit contents is probably the bigger steric hindrance of substitutionary cyclopentadienyl than that of $C_7H_{15}CO_2-$, because at least one of the three $C_7H_{15}CO_2-$ groups in the former is alkylated and any one of the cyclopentadienyl groups in the later can not be alkylated by the MAO according to general conception, so it is unfavourable to 1,3-inserting of Bd monomer[13~15].

Table 1 Results of butadiene polymerization with some lanthanocene catalysts

Lanthanocene compd.	Cocatalyst		Temp., °C	Activity in g PBd/g Ln	$10^{-4} \bar{M}_n$	Microstructure, %			
	Type	Al/Ln ^a				cis-1,4	trans-1,4	1,2-	gel,%
$(C_5H_9Cp)_2NdCl(I)$	Me_3Al^b	30	50	347	-	-	-	-	98.5
	Me_3Al^b	100	50	555	-	-	-	-	94.5
	MAO	53	20	0	-	-	-	-	-
	MAO	1000	50	277	1.73	75.3	22.0	2.7	1.1
$(C_5H_9Cp)_2SmCl(II)$	MAO	1000	80	832	1.81	72.9	22.9	5.1	3.2
	Me_3Al^b	30	50	332	-	-	-	-	96.9
	MAO	38	20	0	-	-	-	-	-
	MAO	1000	50	306	1.49	72.6	16.8	10.6	3.7
$(MeCp)_2Sm OAr^c(III)$	R_3Al^c	30	50	0	-	-	-	-	-
	MAO	1000	50	492	1.41	78.4	17.6	4.0	1.4
	MAO	200	80	0	-	-	-	-	-
	MAO	500	80	120	1.81	61.6	25.6	12.8	3.9
MAO	1000	80	638	0.77	71.9	18.0	10.1	5.1	

Polymerization condition: $[Bd]=1.85M$, $[Ln]=2.54 \times 10^{-4} M$, polymerization time:20 h, ^a in molar ratio, ^b $[Ln]=5.0 \times 10^{-3} M$, ^c $[Sm]=5.0 \times 10^{-4} M$, R=Me,Et and i-Bu, C_5H_9 =cyclopentyl, Cp=cyclopentadienyl, OAr^c=



Ip polymerization

The six catalyst systems composed of lanthanocenes from I to IV and MAO respectively had polymerization activity as listed in Tab 2. The influence of polymerization temperature and Al/Ln molar ratio on activity are analogous to the results of Bd polymerization. In the same polymerization condition the increasing

order of the catalyst activities of latter three systems was VI<IV<V. Because of lacking structure data of some lanthanocenes, further discussion is not made. Two-valence lanthanocene(III) had also considerable activity. Compared with above-mentioned molecular structure of PBd, molecular weight is much smaller(1 to 10 thousands) and cis- 1,4- unit contents much lower(41 to 47%). The reason that cis-1,4-unit contents of PIp are much lower than that of PBd is possibly steric hindrance of methyl group in Ip molecule which results in much unfavour for 1,3-inserting.

St polymerization

Tab 3 gives an indication that (MeCp)₂Sm OAr'(III) or MAO alone has no activity, while III and MAO together has activity for St polymerization. It indicated that rare earth compound and MAO formed active center together. The catalyst activities of latter three systems decreased in the following order: VI>IV>V which tuned out contrary to Ip polymerization results with these systems.

Table 2 Results of isoprene polymerization with some lanthanocene catalysts

Lanthanocene compound	Cocatalyst		Temp., °C	Activity in g PIP /g Ln	Microstructure, %			
	Type	Al/Ln			10 ⁻³ · \bar{M}_n	cis-1,4-	trans-1,4-	3,4-
(C ₅ H ₉ Cp) ₂ NdCl(I)	Me ₃ Al ^a	100	20	0	-	-	-	-
	Et ₃ Al ^a	10	50	0	-	-	-	-
	MAO	360	20	0	-	-	-	-
	MAO	360	50	92	-	-	-	-
	MAO	1000	50	265	1.48	46.9	35.9	17.2
	MAO	200	80	0	-	-	-	-
(C ₅ H ₉ Cp) ₂ SmCl(II)	MAO	1000	80	402	2.02	-	-	-
	Et ₃ Al ^a	10	50	0	-	-	-	-
	MAO	100	20	0	-	-	-	-
	MAO	1000	50	78	10.20	40.8	42.8	15.0
	MAO	200	80	0	-	-	-	-
	MAO	1000	80	59	1.55	-	-	-
(MeCp) ₂ Sm-OAr'(III)	Et ₃ Al ^a	10	50	0	-	-	-	-
	MAO	1000	50	311	2.22	44.6	31.0	24.4
	MAO	1000	80	492	1.08	42.7	34.5	22.8
	MAO ^b	1000	50	62	-	-	-	-
(Ind) ₂ NdCl(IV)	MAO ^b	1000	50	143	-	-	-	-
Me ₂ Si(Ind) ₂ NdCl(V)	MAO ^b	1000	50	143	-	-	-	-
(Flu) ₂ NdCl(VI)	MAO ^b	1000	50	8	-	-	-	-

Polymerization condition: [Ip]=1.5 M, polym. time:20h,^a [Ln]=5.0x10⁻³ M, ^b [Nd]=2.8x10⁻⁴ M

Table 3 Results of styrene polymerization with some lanthanocene catalysts

Catalyst component	Al/Ln, molar ratio	Temp., °C	Activity in g PSt/g Ln	10 ⁻⁴ · \bar{M}_n
(MeCp) ₂ Sm-OAr' ^a	-	50	0	-
MAO	-	50	0	-
(MeCp) ₂ Sm-OAr' ^a /MAO	400	50	67	12.5
(MeCp) ₂ Sm-OAr' ^a /MAO	800	50	111	9.2
(MeCp) ₂ Sm-OAr' ^a /MAO	1000	80	1554	22.2
(C ₅ H ₉ Cp) ₂ SmCl ^b /MAO	1000	80	708	20.9
(Ind) ₂ NdCl ^c /MAO	1000	50	125	-
Me ₂ Si(Ind) ₂ NdCl ^c /MAO	1000	50	11	-
(Flu) ₂ NdCl ^c /MAO	1000	50	155	-

Polymerization condition: [St]=2.8 M, polym. time:20h, ^a [Sm]=9.0x10⁻⁴ M, ^b [Sm]=2.0x10⁻⁴ M, ^c [Nd]=2.8x10⁻⁴ M

A sample with the highest polymerization activity in Tab 3 and random PSt were selected for DSC analyses (Figure 1). The former had two absorptions of heat peak at 86.3 °C and 262.0°C, but the latter only had one peak at 84°C. Generally

considering, melting points of isotactic and syndiotactic PSt were 240°C and 270°C respectively. The melting point of sample selected approached that of syndiotactic PSt. To further prove this, ^{13}C -NMR analysis was used to determine the chemical shifts of $\alpha\text{-C}_1$ on aromatic group [16]. As shown in Fig 2, the chemical shifts at 145.6ppm (rrrr), 146.5ppm(mmmm) etc. appeared in the ^{13}C -NMR spectrum. So this sample was considered a syndio-rich random polystyrene. It is noteworthy that lanthanocene of II or III initiated homopolymerizations of Bd, Ip and St under the same polymerization condition. Because the copolymerizations of these monomers each other are probable of realization.

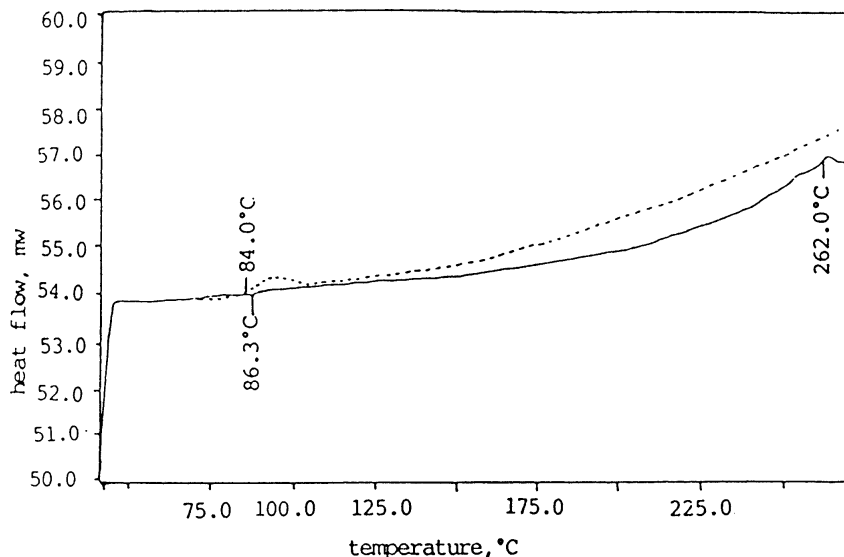


Fig.1 Curves of DSC for a-PSt(----) and sample(—)

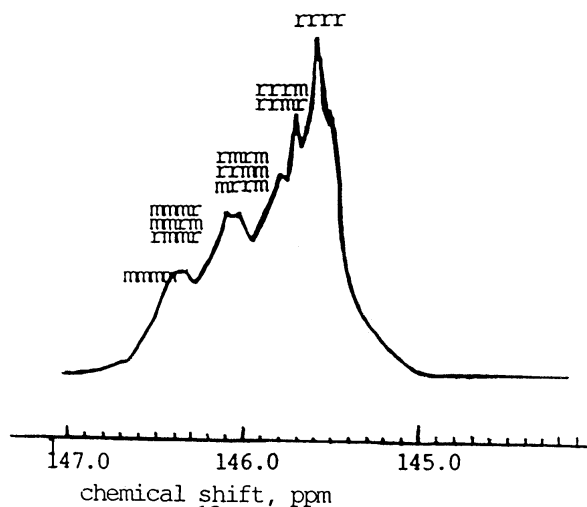


Fig.2 Enlarged ^{13}C NMR spectrum of the alpha-carbon in PSt

Conclusion

The catalyst systems of cyclopentadienyl group and MAO introduced is a significant work in rare earth coordination polymerization domain. The catalyst systems composed of lanthanocene I, II, III, and MAO respectively can be used to form the polybutadiene with molecular weights of 10 to 20 thousand and cis-1,4-unit contents of 62 to 78%, six lanthanocenes from I to IV with MAO respectively to form the polyisoprene with molecular weights of 1 to 10 thousand and cis-1,4-unit contents of 41 to 47% and lanthanocenes from II to V were still active for St polymerization and gave a syndio-rich random polystyrene. Lanthanocenes II and III can polymerize Bd, Ip and St under the same polymerization conditions.

Despite some findings had been obtained through the intensive investigation, further work in the domain is still needed in order to better understand the mechanistic features, increase the catalyst efficiency and realize copolymerization of St/Bd or St/Bd/Ip.

References

1. Ricci G, Italia S, comitani C, Porri L (1991) *Polym Commun* 32:514
2. Guan J-W, Shen Q, and Hu J-Y (1994) *Chin J Appl Chem* 11:99
3. Yasuda H, and Ihara E (1997) *Adv Polym Sci* 133:55
4. Jin J-Z, Uozumi T, Soka K (1995) *Macromol Rapid commun* 16:317; US Patents: 5,456,906;342,984
5. Jin Y-T, Wang P-X (1996) *Polym commun* 37:349
6. Li FF, Jin Y-T (1993) *J Appl Polym Sci* 50:2017
7. Kaminsky W, Spiehi R (1989) *Macromol chem* 190:515
8. Jin J-Z, Jin Z-S (1992) *Chin J Chem* 10:405
9. Evans W, Hanusa T P, Levan K (1985) *Inorg Chem acta*, 110:191
10. Chen W-Q, Wang X-Y (1985) *Acta Chemica sinica*, 43, 295
11. Akhonoukh T, Muller J, Qao k (1991) *J Organomet Chem*, 408:447
12. Li F-F, Jin Y-T (1994) *J Macromol Sci-pure App Chem*, A3(2):273
13. Furukawa J (1979) *Polymer(Jap)* 28:885
14. Jin Y-T, Zhang X-T, Pei F -K, and Wu Y (1990) *Chin J Polym Sci* 8:121
15. Hsieh H L, and Yeh H C (1986) *Ind Eng Chem Prod Res Dev* 25:456
16. Matsuzaki K, Uryu T, Seki T (1975) *Makromol Chem* 176:3051