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Copolymerization of Butadiene with Styrene by Nd(vers)₃–Al(i-Bu)₃–CHCl₃ Catalyst System

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ABSTRACT

Copolymerization of butadiene (Bd) with styrene (St) was carried out by a catalytic system composed of Nd(versate)₃ (Nd(vers)₃), Al(i-Bu)₃, and chloroform. The catalyst system exhibited a high catalytic activity and high stereospecificity of Bd in the copolymerization. The effects of Al/Nd molar ratio, Cl/Nd molar ratio, polymerization time, and monomer feed ratio on the copolymerization were thoroughly studied. It is found that the *cis*-selectivity for Bd units of this catalyst was disturbed slightly by incorporating St unit in the copolymers, quite different from some other rare earth catalysts, and this is supposed to be related with monomer reactivity ratio of St (r_{St}) in the copolymerization system.

Key Words: Butadiene; Styrene; Rare earth catalyst; Copolymerization.

INTRODUCTION

Styrene–butadiene rubber (SBR), the random copolymer of butadiene (Bd) and styrene (St) containing about 18–25% St unit, is industrially produced through radical or anionic polymerization. Unlike Bd or isoprene rubber, the *cis*-1,4 content of diene units in

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such a copolymer is less than 40%. In order to synthesize a stereoregular SBR, a number of Bd with St copolymerization studies have been carried out by transition metal catalysts since the 1960s.^[1–15] These investigations are not only of preparative interest but also important for understanding the mechanism. Despite several proposals of the mechanism have been suggested for the *cis*-1,4 polymerization by transition metal catalysts, such as monomer coordination mode of bidentate or unidentate,^[16,17] *syn-anti* π -allylisomerization,^[18,19] and back-biting coordination,^[20–22] the *cis*-1,4 polymerization mechanism of diene especially the *cis*-1,4 selectivity of Bd unit in copolymerization of Bd and St is still obscure.

Being one type of the most important transition metal catalysts, rare earth catalysts are well known as excellent catalysts for the diene polymerization. Butadiene–styrene copolymerization with rare earth catalysts has attracted considerable interest in the last decade.^[7–15] However, one problem of the copolymers obtained by almost all rare earth catalysts is that the *cis*-1,4 content of Bd units decreases significantly with increasing St content. Here, we report a new rare earth catalyst system of Nd(vers)₃–Al(*i*-Bu)₃–CHCl₃ which exhibited high activity and high stereospecificity of Bd unit even at high St contents in the copolymer. Furthermore, it is interesting to find that the stereoselectivity difference between Nd(vers)₃–Al(*i*-Bu)₃–CHCl₃ and other rare earth catalysts is related to the reactivity ratio of St.

EXPERIMENTAL

Materials

Butadiene, styrene, and toluene were purified the same as in the previous article.^[14] Neodymium compounds were prepared from Nd₂O₃ (Shanghai Yuelong Plant, 99.95%) according to Ref.^[23] Al(*i*-Bu)₃ containing 15% Al(*i*-Bu)₂H was used as received from Shanghai Gaoqiao Petrochemical Company. The chloroform used as a third component was an analytical reagent.

Polymerization

The catalyst was prepared by aging the Nd compound and Al(*i*-Bu)₃ for 40 min under an atmosphere of dry argon at 50°C, then adding chloroform and aging 4 h. Butadiene, styrene, and catalyst were introduced into a vessel and polymerized at 50°C for a definite time. The polymerization mixture was poured into a large quantity of ethanol containing a small amount of hydrochloric acid (5%). The precipitated copolymer was washed by ethanol and then dried in vacuum at 40°C for 24 h.

Measurements

The copolymer composition and the microstructure of Bd units were calculated according to the method of Binder^[24] and Morero^[25] by IR spectra taken on a Perkin-Elmer 983 IR spectrophotometer, using film on KBr disc. Parts of the copolymer



composition used to determine monomer-reactivity ratios were also measured by ^1H -NMR spectra. ^1H and ^{13}C -NMR spectra were recorded on an Avance DMX 500 NMR in CDCl_3 using tetramethylsilane as an internal standard. The intrinsic viscosities of the copolymer were measured in toluene with an Ubbelohde viscosimeter at 30°C . The molecular weight and the molecular weight distribution (MWD) were determined by a Waters 150C GPC with UV (Waters 486UV) and RI (R401) detectors using THF as eluent and polystyrene as a standard at 30°C .

RESULTS AND DISCUSSION

We have found that the rare earth catalysts using CHCl_3 or CCl_4 as a third component are effective for St polymerization.^[26] Based on this result, various neodymium compounds (listed in Table 1) combined with $\text{Al}(\text{i-Bu})_3$ and CHCl_3 were used to initiate the copolymerization of Bd with St. All catalysts were found to give copolymers containing St unit, and the catalysts based on $\text{Nd}(\text{vers})_3$ and $\text{Nd}(\text{P}_{507})_3$ showed the highest activity for the copolymerization. Comparing to the $\text{Nd}(\text{P}_{507})_3$ system, $\text{Nd}(\text{vers})_3$ system obtained the copolymer with higher molecular weight and *cis*-1,4 content of Bd unit, so it was selected for the following studies.

The features of the Bd and St copolymerization with $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$ system are illustrated in Figs. 1–5. Figures 1 and 2 indicate that an appropriate Cl/Nd molar ratio should be larger than 6. Too small Cl/Nd molar ratio leads to not only the poor catalyst activity and stereospecificity, but also a small molecular weight and St content. There are no upper limit exists in the Cl/Nd molar ratio, because CHCl_3 can even use as solvent in this copolymerization. The data of the Figs. 3 and 4 show that Al/Nd molar ratio of 10–12 is the most favorable ratio. When Al/Nd molar ratio is higher than 12, the yield, molecular weight, St content, and the *cis*-1,4 content of Bd unit of the copolymer decrease with the increasing Al/Nd molar ratio. As show in Fig. 5, the copolymer yield and the St

Table 1. Effect of ligand on copolymerization with $\text{NdL}_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$.

NdL_3^a	Yield (%)	$[\eta]$ (dL/g)	St content (mol%)	Microstructure of Bd (%)		
				<i>cis</i>	<i>trans</i>	Vinyl
$\text{Nd}(\text{vers})_3$	43.8	0.64	18.9	93.1	6.4	0.6
$\text{Nd}(\text{P}_{204})_3$	33.8	0.52	10.6	89.2	8.2	2.6
$\text{Nd}(\text{P}_{507})_3$	45.7	0.44	20.5	88.5	9.9	1.6
$\text{Nd}(\text{naph})_3$	38.3	0.46	13.3	92.6	6.5	1.0
$\text{Nd}(\text{iPrO})_3$	36.3	0.65	11.7	90.5	7.5	2.0

Note: $[\text{Bd}] = [\text{St}] = 1.5 \text{ mol/L}$, $[\text{Nd}] = 3.0 \times 10^{-3} \text{ mol/L}$, $\text{Al/Nd} = 20$, $\text{Cl/Nd} = 10$, copolymerized in toluene at 50°C for 18 h.

^a $\text{Nd}(\text{naph})_3$, Neodymium naphthenate; $\text{Nd}(\text{P}_{204})_3$, Neodymium *bis*(2-ethyl hexyl phosphonate); $\text{Nd}(\text{P}_{507})_3$, Neodymium 2-ethyl hexyl-(2-ethyl hexyl phosphonate); $\text{Nd}(\text{vers})_3$, Neodymium versatate.



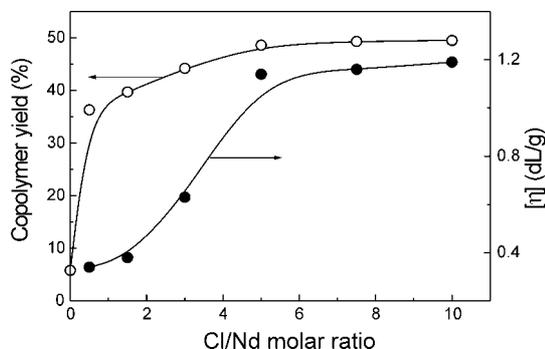


Figure 1. Effect of Cl/Nd on copolymer yield and $[\eta]$. [Copolymerized by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$, other conditions are the same as Table 1.]

content in the copolymer increased with the increasing polymerization time, but the molecular weight of the copolymer obtained decreased as the St content increased.

The copolymer obtained with Al/Nd molar ratio of 10 and 20 were measured by GPC with RI and UV ($\lambda = 254 \text{ nm}$) detectors, shown in Fig. 6. It is well known that RI detector is sensitive to both Bd and St unit, while UV detector is only sensitive to St unit. The MWD of the copolymer prepared at Al/Nd molar ratio of 10 is relatively narrow ($M_w/M_n = 3.5$), and its GPC curve detected by RI detector is almost in harmony with the curve by UV detector, indicated no both homopolymers existed. However, the copolymer obtained at Al/Nd molar ratio of 20 has broader MWD ($M_w/M_n = 5.8$), and has contained polybutadiene in its higher molecular weight region, as reflected by its GPC curves in Fig. 6. Thus, it is reasonable to suppose that a change of active site was occurred in the latter case, which might also contain active site for polymerization of Bd only.

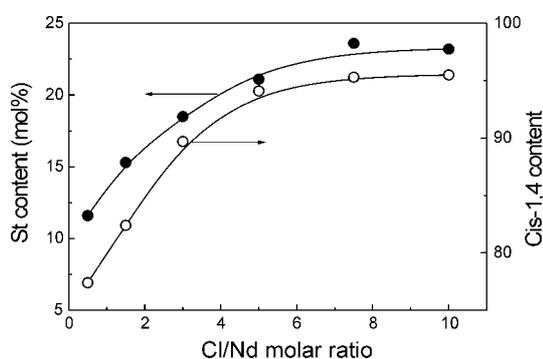


Figure 2. Effect of Cl/Nd on St content and *cis*-1,4 content. [Copolymerized by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$, other conditions are the same as Table 1.]



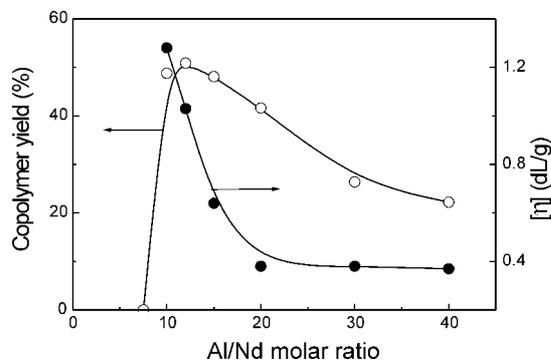


Figure 3. Effect of Al/Nd on copolymer yield and $[\eta]$. [Copolymerized by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$, other conditions are the same as Table 1.]

As shown in Fig. 6, though the copolymer has a unimodal MWD curve in the case of $\text{Al/Nd} = 10$, the GPC curve by RI detector and the curve by UV detector do not coincide with each other perfectly. It shows that the copolymer with the higher molecular weight contains fewer St units, while the copolymer with lower molecular weight contains more St units. This phenomenon is caused by the complex composition of the copolymer obtained. Figure 5 depicts the plots of the yield, $[\eta]$ and St content of the copolymer vs. the polymerization time. The copolymer with a low St content and high molecular weight was achieved at the beginning stage of the copolymerization. Since the catalyst is much more active to the Bd monomer than to the St monomer, the Bd monomer was consumed faster than St in the copolymerization. Thus, the monomer ratio of St to Bd became progressively higher in the continued copolymerization, where the copolymer with the higher St unit content and lower molecular weight was achieved. The St content in the copolymer increases if the reaction time is prolonged, but the composition of the copolymer becomes more uneven.

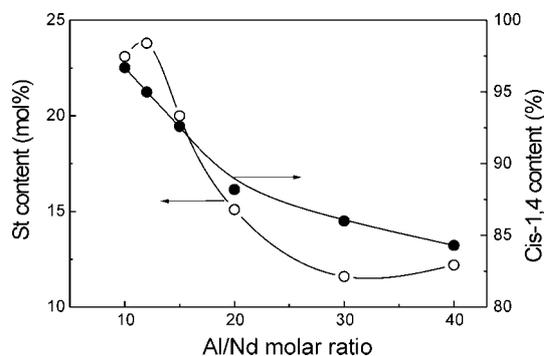


Figure 4. Effect of Al/Nd on St content and *cis*-1,4 content. [Copolymerized by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$, other conditions are the same as Table 1.]



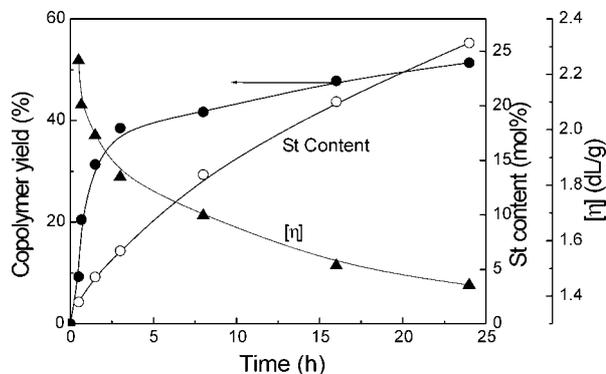


Figure 5. Effect of time on copolymer yield and St content. ($Al/Nd = 10$, other conditions are the same as Fig. 3.)

The copolymerization of Bd with St was carried out at various monomer-feeding ratios, as shown in Table 2. The monomer reactivity ratios were evaluated to be $r_{Bd} = 45$ and $r_{St} = 0.11$ by the Fineman–Ross method.^[27] The Table 2 data reveals that the most unique point of this new rare earth system is that the *cis*-1,4 microstructure of the Bd unit of the copolymer decreases very little with the increasing St content of the copolymer. This is also verified by the ¹³C-NMR spectrum shown in Fig. 7. The spectrum of the 34.6 mol% St copolymer only shows strong signals of St-*cis*-1,4 Bd linkage [25.33 ppm (A) and 35.85 ppm (B)],^[28] but weak signals of St-*trans*-1,4 Bd sequences [30.51 ppm (C) and 39.83 ppm (D)] and the St-vinyl Bd linkage [32.33 ppm (E) and 42.93 ppm (F)].

In order to understand this unique phenomenon of the new catalyst system, we have collected and summarized the references' data of various rare earth systems, as shown in Fig. 8. It is interestingly found that this phenomenon is related with the r_{St} of various

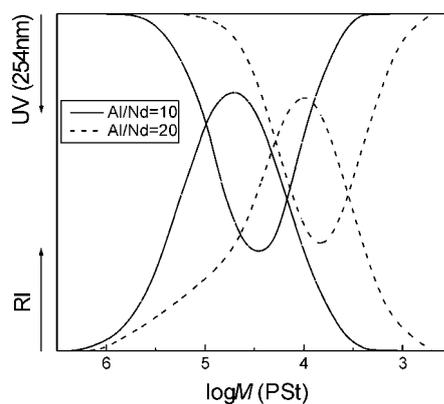


Figure 6. GPC curves of Bd–St copolymers obtained by $Nd(vers)_3-Al(i-Bu)_3-CHCl_3$ catalyst with different Al/Nd . (Polymerization conditions are the same as Fig. 1.)



Table 2. Effect of St feed ratio on the copolymerization by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$.

St in feed (mol%)	Yield (%)	$[\eta]$ (dL/g)	St content (mol%)	Microstructure of Bd (%)		
				<i>cis</i>	<i>trans</i>	Vinyl
0	72.5	2.98	—	97.7	2.0	0.3
50.0	24.9	2.08	2.5	97.0	2.6	0.4
67.5	13.7	1.61	5.0	96.4	3.3	0.3
80.0	6.7	1.21	10.0	94.9	4.6	0.5
85.8	5.2	0.91	16.7	93.8	5.5	0.7
92.6	1.4	0.30	34.6	91.0	7.9	1.1
100	0.9	0.21	100.0	—	—	—

Note: $[\text{Bd}] + [\text{St}] = 3.0 \text{ mol/L}$, $[\text{Nd}] = 5.0 \times 10^{-3} \text{ mol/L}$, polymerized for 1 h, others are the same as Table 1.

systems. That is systems having smaller r_{St} will give higher *cis*-1,4 content of Bd unit of the Bd–St copolymer.

CONCLUSION

The $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$ catalyst system showed high activity for the copolymerization of Bd with St to give copolymers with high *cis*-1,4 content of Bd unit. The copolymer composition seems to be affected significantly by the Cl/Nd molar ratio

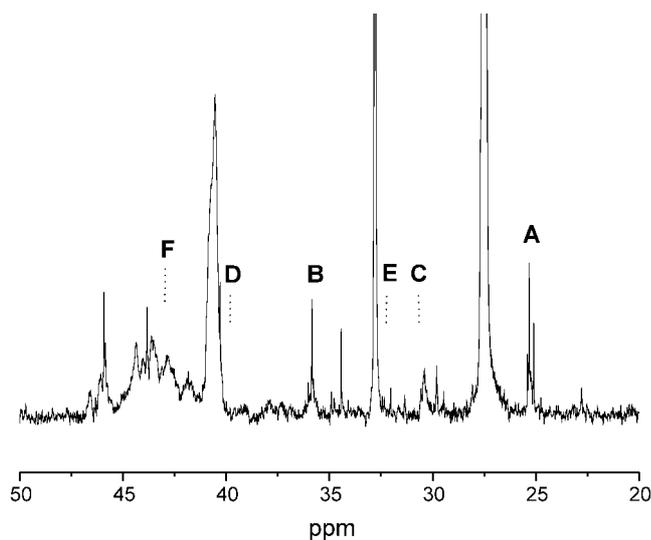


Figure 7. ^{13}C -NMR spectrum of the Bd–St copolymer obtained by $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$ catalyst (St content in copolymer: 34.6 mol). (Copolymerization conditions are given in Table 2.)



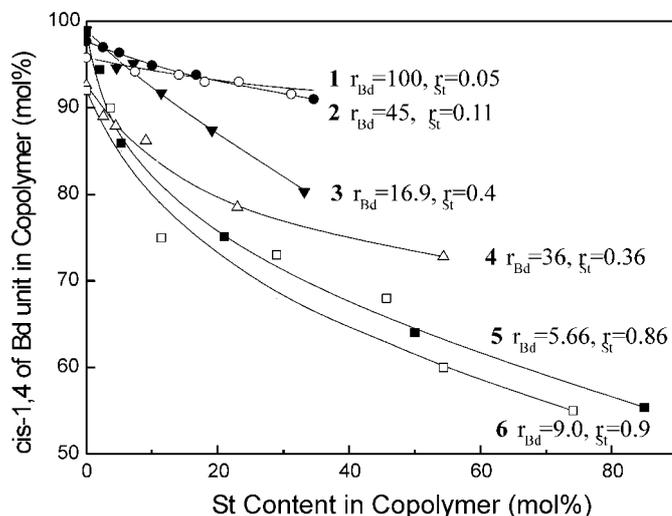


Figure 8. Relationship between the St content and the microstructure of the Bd unit in copolymers with various rare earth catalysts. *Key:* 1, $\text{Nd}(\text{naph})_3\text{-Al}(\text{i-Bu})_3\text{-Al}(\text{i-Bu})_2\text{Cl}^{15}$; 2, $\text{Nd}(\text{vers})_3\text{-Al}(\text{i-Bu})_3\text{-CHCl}_3$; 3, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-Me})_2\text{AlMe-Al}(\text{i-Bu})_3\text{-[Ph}_3\text{C][B}(\text{C}_6\text{F}_5)_4]^{13}$; 4, $\text{Nd}(\text{P}_{507})_3\text{-Mg}(n\text{-Bu})_2\text{-CHCl}_3^{14}$; 5, $\text{Nd}(\text{OCOCl}_3)_3\text{-Al}(\text{i-Bu})_3\text{-AlEt}_2\text{Cl}^{12}$; 6, $\text{Gd}(\text{OCOCl}_3)_3\text{-Al}(\text{i-Bu})_3\text{-AlEt}_2\text{Cl}^{10}$.

and Al/Nd molar ratio of the catalyst system. In the case of Cl/Nd > 6 and Al/Nd = 10, a random Bd–St copolymer without each homopolymer could be obtained. Different from some other rare earth catalysts, the *cis*-selectivity for Bd units of this catalyst decreased slightly by increasing the St unit in the copolymers

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