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Copolymerization of styrene with butadiene and isoprene using a rare earth catalyst[*]

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In the copolymerization of styrene–butadiene and styrene–isoprene, a novel rare earth catalyst system $(CF_3CO_2)_3Ln/R_{3-n}AlH_n/(CH_3)_3CCH_2Br$ (Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; R = Me–, Et–, i-Bu–, and Oct–; $n = 0$ and 1) has been studied. The 1, 4 unit contents in the copolymers obtained are found to range from 64.4 to 99.6% with St contents of 5.2 to 59.9%, and intrinsic viscosities of 0.1 to 0.5 dl g^{-1} measured by i.r., ^{1}H n.m.r. and ^{13}C n.m.r. spectra. From the calculated data of linked ratios, a change in the microstructure is induced by the styrene unit, probably adjacent to the butadiene or isoprene unit. An interesting result is that the ratios of styrene unit linked with 1, 2 or 3,4 units in the copolymers are far higher than in copolymers obtained with the nickel catalyst. The experimental results are discussed in terms of rare earth π–allyl coordination and back-biting mechanism.

(Keywords: rare earth catalyst; copolymerization; styrene)

Introduction

The subject of introducing rare earth compounds as a main component into catalyst systems in the copolymerization of styrene (St) with conjugated dienes was followed with interest soon after the rare earth coordination catalyst appeared in the early 1960s. The main reason is that the catalyst has been demonstrated to have fairly high stereoselectivity and high activity; the resulting polymer was characterized and found to have very high molecular weight and high linearity in the homopolymerizations of butadiene (Bd) and isoprene (Ip)[1].

Early trials indicate that either the rare earth catalyst does not allow significant copolymerization of St and Bd[2] or the catalyst has very poor activity for copolymerization of St and Ip[3]. Some catalysts that are more active for copolymerization have been presented in the literature[4–7].

This communication reports significant results arising from a new rare earth catalyst system $(CF_3CO_2)_3Ln/R_{3-n}AlH_n/(CH_3)_3CCH_2Br$.

Experimental

Materials. The synthesis of $(CF_3CO_2)_3Ln$ and the methods for purifying St, Bd, Ip and toluene as solvent were carried out according to ref. 4. Various $R_{3-n}AlH_n$ (Fluka Pure except R = Oct–, Merck, 90%) were used without further purification. 1-Bromo-2, 2-dimethylpropane, $(CH_3)_3CCH_2Br$ (Fluka, 97%), was stored over active Al_2O_3 (Shanghai Molecular Sieve Factory) under 99.999% pure argon.

Polymerization. All operations were conducted under argon. Polymerization was carried out as before[4]. Polymerization conditions are noted in the captions of *Tables 1* and *2*. The reactivity ratios of monomers were calculated by the integral method[8] on the basis of the data in *Table 2*.

Copolymer characterization. ^{1}H and ^{13}C n.m.r. spectra were recorded on the FX-100 and Unity-400 spectrometers in $CDCl_3$ at 19°C using tetramethylsilane as internal standard. The relative intensities were measured via the peak heights. The composition of St–Bd copolymer and the microstructure of Bd structured unit in St–Bd copolymer were measured by i.r. spectrophotometry according to the method of Anzai *et al.*[9] after extraction of homopolystyrene[10]. The spectra were taken on a Perkin–Elmer 580B i.r. grating spectrophotometer, using film on KBr discs. The composition of St–Ip copolymer and the microstructure of Ip structured unit in the St–Bd copolymer were measured by ^{1}H n.m.r. spectroscopy after extraction of homopolystyrene[10]. Intrinsic viscosities were determined in toluene at 30°C using an NC-Z Viscometer.

Results and discussion

The effects of various alkyl aluminiums as cocatalyst component on copolymerizations of St–Bd and St–Ip are listed in *Table 1*. It follows that the highest polymerization activity appeared when $(Oct)_3Al$ was used as cocatalyst in St–Bd copolymerization, but in St–Ip copolymerization the highest activity appeared when Me_3Al was used. On the contrary, both the cocatalysts were shown to have very poor activities in the homopolymerization[12] of Bd or Ip. The effects of six kinds of alkyl aluminiums on the activities of both

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Table 1 Effects of various $R_{3-n}AlH_n$ on two copolymerizations of St–Bd and St–Ip. Polymerization conditions: [Nd] = 3×10^{-2} mol l^{-1}, [St] = [Bd] = [Ip] = 100 g l^{-1}, Al/Nd = 15 (17), molar ratio, Br/Nd = 3 molar ratio, polymerization for 7 (8) h at 50°C[a]

		Copolymer microstructure (%)					St incorporated	
$R_{2-n}AlH_n$	Conversion (%)	*cis*-1,4	*trans*-1,4	Total 1,4	1,2	3,4	(mol%)	η (dl g^{-1})
M_3Al	43.7	81.7	13.6	95.3	4.7	–	–	0.12
	(100.0)	(5.3)	(92.5)	(97.8)	–	(2.2)	(31.4)	(0.12)
Et_3Al	37.5	–	–	–	–	–	–	–
	(37.5)	–	–	(95.3)	–	(4.7)	(35.6)	(0.12)
$(i–Bu)_3Al$	68.8	97.8	1.8	99.6	0.4	–	32.4	0.19
	(62.5)	–	–	(97.5)	–	–	(32.7)	(0.23)
$(Oct)_3Al$	82.5	77.4	17.0	94.4	5.6	–	–	0.20
	(98.5)	–	–	(98.1)	–	(1.9)	(28.9)	(0.46)
$(i–Bu)_2AlH$	31.5	63.2	30.3	92.5	6.5	–	–	0.05
	(50.0)	–	–	(89.3)	–	(10.7)	(18.7)	(0.17)
Et_2AlH	(82.5)	–	–	(88.5)	–	(11.5)	(21.2)	(0.12)

[a] Data in parentheses show the corresponding results and polymerization conditions of St–Ip copolymerization

Table 2 Effects of monomer composition in the feed on both copolymerizations. Polymerization conditions: Al/Nd = 10 (5) molar ratio, Al represents $(i–Bu)_3Al$, the others are identical with *Table 1*[a]

			Copolymer microstructure (%)				
St/St + Bd(IP) (mol%)	Conversion (%)	St incorporated (mol%)	*cis*-1,4	*trans*-1,4	Total 1,4	1,2	3,4
0	95.0	0	83.4	16.0	99.4	0.6	–
	(94.4)	(0)	–	–	(97.2)	–	(2.8)
10	85.5	5.2	–	–	–	–	–
	(81.3)	(8.0)	–	–	(95.8)	–	(4.2)
20	82.5	5.3	82.9	16.0	98.9	1.1	–
	(68.8)	(9.3)	–	–	(94.4)	–	(5.6)
30	46.3	–	–	–	–	–	–
	(65.8)	(16.0)	–	–	(91.5)	–	(8.5)
40	36.0	25.1	80.4	18.2	98.6	1.4	–
	(63.8)	(25.3)	–	–	(90.1)	–	(9.9)
60	33.8	34.9	–	–	-	–	–
	(55.0)	(37.2)	–	–	(85.8)	–	(14.2)
80	40.0	50.0	71.4	25.0	96.4	3.6	–
	(37.5)	(59.9)	–	–	(64.4)	–	(35.6)
100	87.5	100.0	–	–	–	–	–
	(86.5)	(100.0)					

[a] Data in parentheses show the corresponding results and polymerization conditions of St–Ip copolymerization

copolymerizations are in the following order: for St–Bd copolymerization, $(Oct)_3Al > (i–Bu)_3Al > M_3Al > Et_3Al > (i–Bu)_2AlH$; for St–Ip copolymerization, $M_3Al > (Oct)_3Al > Et_2AlH > (i–Bu)_3Al > (i–Bu)_2AlH > Et_3Al$.

Using these alkyl aluminiums a high content of 1, 4 units was observed in all the copolymers. It is of interest that a St–Ip copolymer with a high content of *trans*-1, 4 units (92.5%) is obtained from the Me_3Al. In these alkyl aluminiums, the $(i–Bu)_3Al$, whether in St–Bd or in St–Ip copolymerization, results in the formation of copolymers with a higher content of 1, 4 units.

It is evident from *Figure 1* that although the $(CF_3CO_2)_3Ln$ used as a main catalyst component are very similar to each other in general chemical properties, they show quite a different catalytic activity towards the copolymerizations. The activities for the St–Bd copolymerization decreased in the following order: Nd > Pr ~ Ce ~ Gd > Tb > Dy > Yb ~ Y > Tm > Er > Ho > Sm > La > Lu ~ Eu. For the St–Ip copolymerization catalyst activities decreased in the following order: Nd > Gd > Pr > Ce > Tb > Dy > Ho > Y > La ~ Er > Tm > Sm > Yb > Eu. $(CF_3CO_2)_3Nd$ showed the highest activity, while $(CF_3CO_2)_3Eu$ showed very low activity in both copolymerizations. Overall, the two curves of a relationship between the activities and the atomic numbers of Ln have an inverted 'W' pattern. The pity is that the universal and significant W pattern or 'double-peak regularity', which was first observed in the homopolymerizations of Bd and Ip in 1973 (work published in 1980[13]), has not been convincingly explained so far.

Table 2 gives an indication of a relation between copolymer compositions and monomer compositions in the feed for the copolymerizations of St–Bd and St–Ip. For both St–Bd and St–Ip copolymerization, with increasing the St amounts in the feed the catalytic activities and the 1, 4 contents in Bd and Ip units are

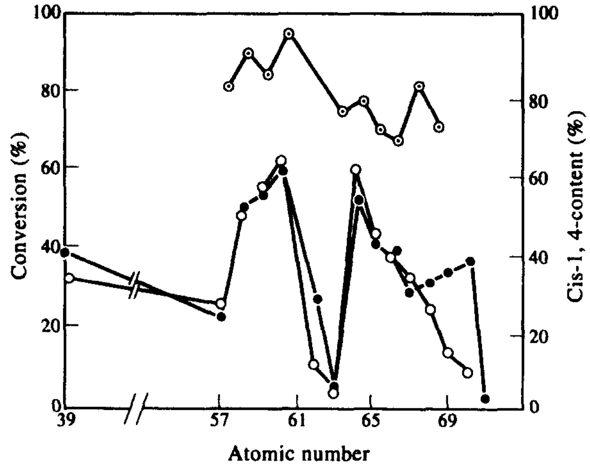


Figure 1 Catalytic activity of various $(CF_3CO_2)_3Ln$ and *cis*-1,4-content. Polymerization conditions: Al/Nd = 10 molar ratio, Al represents $(i\text{-}Bu)_3Al$, polymerization for 7 h, other conditions are identical with Table 1. ● and ⊙ denote, respectively, the conversions and *cis*-1,4-contents in St–Bd copolymerization and copolymer, and ○ denotes the conversions in St–Ip copolymerization

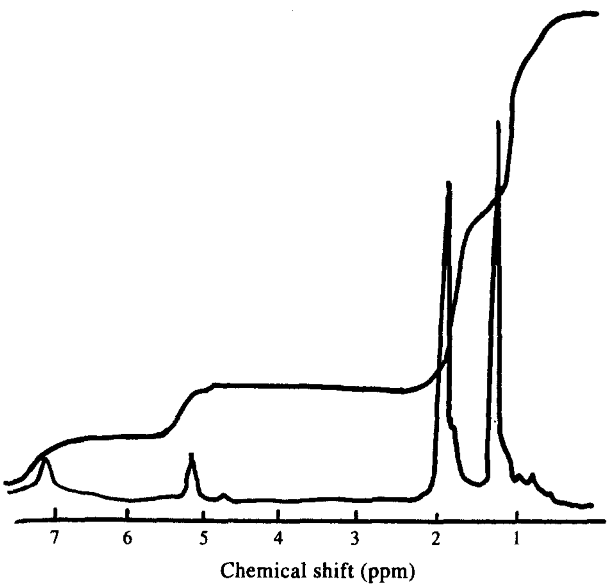


Figure 2 ^1H n.m.r. spectrum of St–Ip copolymer

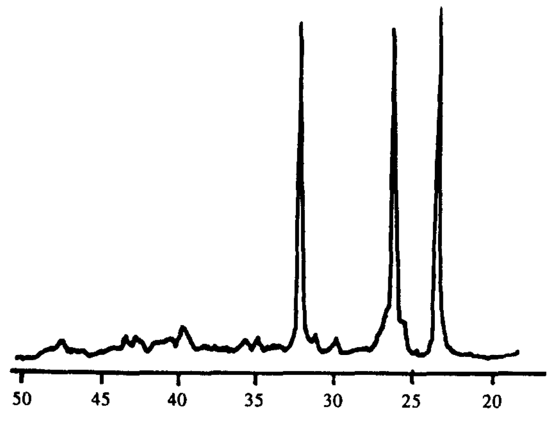
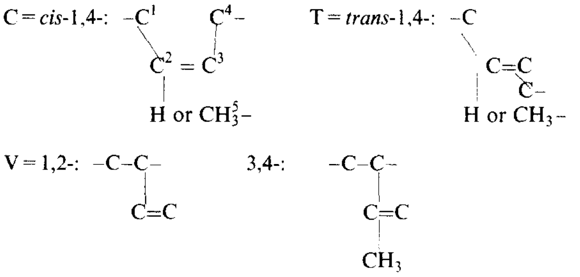


Figure 3 ^{13}C n.m.r. spectrum of St–Ip copolymer

decreased, and the contents of St and other units are increased simultaneously in the corresponding copolymerizations.

Table 3 Peak intensity and its ratio of the two copolymers

Sample	Sequence[a]	Chem. shift (ppm)	Relative peak intensity	Ratio of peak intensity (%)
1	S–C*[b]	35.76	117	28 [SB(C)][c]
	C*–S	25.24	103	
	S–T*	39.57	96	30 [SB(T)]
	T*–S	30.44	139	
	S–V*	41.42	170	42 [SB(V)]
	V*–S	39.37	152	
	(Ct)–C*–C(T)	27.38	18261	84 [BB(C)]
	V–C*	33.72	171	
	C*–V	24.94	90	
	(CT)–T*–C(T)	32.64	2447	13 [BB(T)]
	V–T*	39.18	128	
	T*–V	24.33	221	
	C–V*, T–V*	34.50	118	3 [BB(V)]
	C–V*, T–V*	34.79	149	
	V–V*	41.81	183	
2	C_4^*–S	25.29	36	46 [SI(C)]
	T_4^*–S	25.82	35	45 [SI(T)]
	V_1^*–S	38.30	7	9 [SI(V)]
	C_4^*–C	26.36	318	87 [II(C)]
	C_4^*–T	26.90	41	11 [II(T)]
	C_4^*–V	25.29	7	2 [II(V)]

[a]


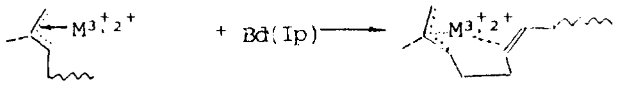
[b] Asterisk represents noticed unit

[c] SB(C), SB(T) and SB(V) means a fraction of the St unit linked with Bd unit of C, T and V unit, respectively. The others are analogous to this

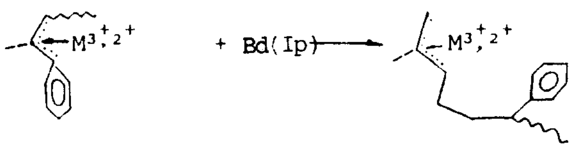
Two samples were selected for i.r. and n.m.r. analyses. One was the copolymer containing 27.5% St obtained from St–Bd copolymerization (sample 1); the other copolymer (sample 2) contained 28.1% St from St–Ip copolymerization.

The i.r. spectrum of sample 2 indicates that in addition to the main absorption peaks, such as 760 and 700 cm^{-1} (νCH on the phenyl group), 840 cm^{-1} (γ=CH on the *cis*-1, 4 unit), 845 cm^{-1} (γ=CH on the *trans*-1, 4 unit) and 890 cm^{-1} (γ=CH on the 3, 4 unit), the absorption peak considered as a characteristic peak of St–Ip copolymer[14] appeared at 540 cm^{-1} (δCH on the phenyl group).

As shown in *Figure 2*, the chemical shifts at 7.18 ppm (the hydrogens, H, on the phenyl group), 5.12 ppm (H on the double bond in 1, 4 unit), 4.75 ppm (H on the double bond in 3, 4 unit), 2.02 ppm (H on the CH_2- in 1, 4 unit), 1.67 ppm (H on the CH_3- in 1, 4 unit), 1.59 ppm (H on the CH_3- in 3, 4 unit) and 1.0–3.0 ppm (H on the $-CH_2-CH-$ at St), appeared in the ^1H n.m.r. spectrum. Inter alia, the chemical shifts of St linked with Bd or Ip unit have been assigned for samples 1 and 2 by ^{13}C n.m.r. spectra. Similar results in i.r. and ^1H n.m.r. spectra were obtained from sample 1. From the above experimental results, samples 1 and 2 are identified to be a kind of copolymer, not a mixture of two homopolymers. Such an example has seldom been found in the literature, where copolymerizations of both St–Bd and St–Ip took place



Scheme 1



Scheme 2

simultaneously yielding copolymers with high 1, 4 unit content using a kind of catalyst system.

The ^{13}C n.m.r. spectrum of sample 2 is shown in *Figure 3*. The assignments of the chemical shifts of the spectra of samples 1 and 2 according to the methods of refs 15–17 and the ratios of the structural units linked to each other based on relative peak intensities are summarized in *Table 3*. The ratios indicate that SB (C) is 28% but BB (C) is 84% in St–Bd copolymer chains; that is, in such a chain the incorporation of the St unit adjacent to the Bd unit diminishes the *cis*-control of the rare earth catalyst. A similar result also occurs in sample 2 (see *Table 3*). It is of interest to note that the ratio of SB(V) is relatively high (42%); however, the ratio is only 24% in the same copolymer obtained with the nickel catalyst[18]. A question is whether the above feature in the sequence structure will be advantageous to the improvement of copolymer properties, e.g. wet skid resistance and degradation, etc.

As illustrated in *Table 2*, both homopolymerization activities of Bd and Ip are higher than that of St. The data of these monomer reactivity ratios $(r)^8$–r_{st} $(0.71 \pm 0.05) < r_{\mathrm{Bd}}$ (1.25 ± 0.05) in St–Bd copolymerization; $r_{\mathrm{St}}(0.50 \pm 0.05) < r_{\mathrm{Ip}}$ (1.05 ± 0.05) in St–Ip copolymerization–further justify the above result. Thus, it can be comprehended why the block peak is observed in the i.r. spectra. Moreover, in copolymerization reactions, only the colours of the catalytic systems of Sm, Eu, Tm and Yb, liable to change from three-valence-state to two-valence-state elements, were varied by addition of monomers. For example, the Yb system varied from colourless to yellowish-green, characteristic of the two-valence state. But its activity is not less than that of the La or Y, universally regarded as typical three-valence-state elements (see *Figure 1*), and therefore the two-valence state cannot be ruled out in an investigation of the valence state of an active centre in the catalyst.

In view of the aforementioned results and according to the rare earth π-allyl coordination polymerization mechanism[19], the monomer, Bd or Ip, is first coordinated on the active centre, $\mathrm{Ln}^{3+,2+}$, and π-allyl terminal of Bd or Ip polymer is formed. In the case of back-biting coordination[20] of a penultimate Bd (or Ip) unit on the $\mathrm{Ln}^{3+,2+}$, the Bd (or Ip) unit becomes favourable to the formation of *cis*-1, 4 unit (*Scheme 1*). In the case of the St unit as the penultimate unit, the back-biting coordination is subjected to steric hindrance of the bigger phenyl group and in consequence the *cis*-1, 4 unit contents are decreased and both contents of *trans*-1, 4 and 1,2 (or 3,4) units are increased (*Scheme 2*). A more clear and unambiguous explanation remains to be discussed.

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