

“One-Pot” Random Terpolymerization of Styrene, Isoprene and Butadiene with Nd-based Catalyst

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ABSTRACT: Random styrene-isoprene-butadiene rubber (SIBR) were achieved with the catalyst system composed of neodymium isopropoxide ($\text{Nd}(\text{O}^i\text{Pr})_3$), methylaluminoxane (MAO) and indene. This catalyst proved to be highly effective in cyclohexane even at low $[\text{Al}]/[\text{Nd}]$ ratio (ca. 50) to give styrene-rich terpolymer with high number-average molecular weight (M_n) and narrow molecular weight distribution (M_w/M_n). Indene was critical to improve the coordination of styrene. High temperature was beneficial to increase the yield. Aliphatic solvents (hexane and cyclohexane) achieved a higher M_n of polymer than toluene as a solvent. The glass transition temperature (T_g) and composition of SIBR can be controlled by tuning the feed ratio of monomers. All the products have been fully characterized by NMR spectroscopy, gel permeation chromatograph (GPC), and DSC. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: terpolymerization; SIBR; Nd-based catalyst; random

Received 15 November 2012; accepted 25 March 2013; Published online 00 Month 2013

DOI: 10.1002/app.39327

INTRODUCTION

The development of new generations of tire tread has been a long-standing research subject of both academic research and vehicle industrial application. Generally, rubber employed in tire tread should satisfy the requirements of elasticity, wet skid resistance and wear characteristics. However, the present elastomers based on butadiene, isoprene and styrene can not implement a good overall balance of these properties. To improve the toughness of single type product, physical blending was utilized in practice as an attempt, but subject to the disadvantage of microphase separation and unreliable repeatability.^{1,2} In 1984, Nordsiek reported a new integral rubber, styrene-isoprene-butadiene rubber (SIBR), incorporating high performance of homo/copolymer based on styrene, isoprene and butadiene monomers.³ To date, SIBR were synthesized by anionic polymerization with alkyl lithium catalyst.^{4–10} Owing to the limited control of initiator configuration, the *cis*–1,4 content of butadiene/isoprene units was low. High temperature or polar additive was used to obtain random distribution, which stimulated the formation of vinyl and *trans*–1,4 units. Recently, rare earth metal catalyst attracted considerable interest because of its excellent regio-/stereoselectivity (>99%) and high activity in the polymerization of conjugated diene.^{11–16} Ziegler-Natta catalyst based on rare earth metal, especially Nd-based catalyst, served

as a good catalyst in styrene-butadiene/isoprene copolymerization field.^{17–21} But the increased styrene content in the copolymer declined the *cis*–1,4 content of butadiene/isoprene sequence.^{22–28} The styrene-rich poly(syndiotactic styrene-*co*-butadiene/isoprene) with high *cis*–1,4 content were obtained by cationic cyclopentadienyl rare earth metal catalyst.^{29–35} The block distribution with highly syndiotactic styrene sequence (*rrrr* > 99%) resulted in high crystallinity and high melting point (270°C).³³ To our best knowledge, terpolymerization of styrene, isoprene and butadiene with rare earth metal catalyst giving block poly(syndiotactic styrene-isoprene-butadiene) was limited to two examples, such as $[(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]/[(\text{C}_5\text{H}_5)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{TIBA}$ ³⁴ and $(\text{C}_5\text{Me}_4\text{-C}_5\text{H}_4\text{N})\text{Lu}(\eta^3\text{-C}_3\text{H}_5)_2/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.³⁵ Therefore, it is still a challenge to prepare a material as tire tread aforesaid.

In this article, random SIBR with high styrene content were synthesized with neodymium isopropoxide ($\text{Nd}(\text{O}^i\text{Pr})_3$)-methylaluminoxane (MAO)-indene catalyst system. The yield, number-average molecular weight (M_n) and styrene content were effected by $[\text{Al}]/[\text{Nd}]$ and $[\text{indene}]/[\text{Nd}]$ molar ratio. The terpolymer composition was controllable by varying MAO, indene and feed ratios, resulting in a series SIBR having narrow molecular weight distribution (M_w/M_n) with various M_n and glass

transition temperature (T_g). The polymerization temperature and solvent were also examined to confirm the optimum reaction condition.

EXPERIMENTAL PROCEDURE

Materials

$\text{Nd}(\text{O}^i\text{Pr})_3$ (J&K, 99.9%) was used as toluene solution ($0.10 \text{ mmol mL}^{-1}$). MAO (Albemarle, 10 wt % in toluene) was used as received. Indene (90%, TCI) was used as cyclohexane solution (0.5 mmol mL^{-1}). Butadiene (Yanshan Petrochem, China, polymerization grade) was treated with a small amount of *n*-butyllithium to remove the moisture and inhibitor and then vaporized to keep water content below 10 ppm. Isoprene (Puyang Xinqu Petrochemical Industry, polymerization grade), was refluxed for about 1 h over CaH_2 , and then distilled and stored over molecular sieves (5 \AA) under highly purified nitrogen gas (N_2). Styrene (Beijing Yanshan Petrochemical, China, polymerization grade), was dried over CaCl_2 for 15 days, then refluxed over CaH_2 under N_2 and distilled under negative pressure before use. Cyclohexane, hexane, and toluene were refluxed over CaH_2 under N_2 and distilled under negative pressure before use.

Catalyst Preparation and Polymer Synthesis

All synthesis and polymerization were carried out in ampule tubes under an inert atmosphere via standard Schlenk techniques. A typical polymerization reaction was performed connected to the Schlenk line and equipped with an inert gas (N_2) inlet and a rubber septum. Before the reaction, the ampule tube was dried with three cycles of a flaming/ N_2 -purging/evacuating. Catalyst preparation and polymerization were carried out under a dry and oxygen-free nitrogen atmosphere. Then a variable amount of $\text{Nd}(\text{O}^i\text{Pr})_3$, indene and MAO were added in sequence, besides a little amount of isoprene, aging at 50°C for 2 h.

The polymerization runs were implemented in the following standard process. Solvent and monomers (styrene, butadiene, isoprene) were placed in the ampule. After the injection of preformed catalyst solution, the polymerizations were carried out for 6 h. The reactions were terminated by the addition of acidified ethanol (5 mL) containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as a stabilizer. The polymers were precipitated, repeatedly washed with ethanol, cut into small pieces and dried under vacuum at 40°C to a constant weight. The polymer yields were determined by gravimetry.

Characterization of SIBR

Gel permeation chromatograph (GPC). M_n and M_w/M_n of the polymers were measured by GPC with a Viscotek TDA-302 size exclusion chromatograph. Polystyrene sample with a stated peak molecular weight of $99,500 \text{ g mol}^{-1}$ and a M_w/M_n of 1.03 was used to calibrate the instrument. THF was used as the eluent at a flow rate of 1.0 mL min^{-1} at 30°C . The samples were dissolved in THF with the concentration of $1.0\text{--}5.0 \text{ mg mL}^{-1}$, depending on molecular weight of polymers.

NMR. The microstructure of the polymers were recorded by ^1H NMR and ^{13}C NMR spectroscopy with a Varian Inova (USA) or Bruker Avance (Switzerland) spectrometer (400 MHz for ^1H

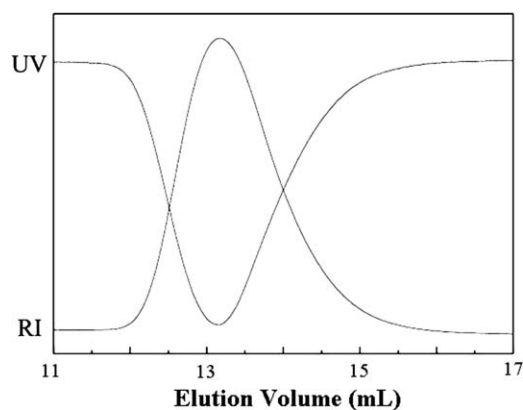


Figure 1. The representative GPC trace (RI and UV dual detectors) of SIBR.

NMR; 100 MHz for ^{13}C NMR) in CDCl_3 at room temperature, with the tetramethylsilane as an internal reference.

DSC. T_g of the polymers were measured by DSC with a NETZSCH DSC 204 instrument (Netzsch, Selb, Germany). The samples were dried under vacuum for 2 days, and each sample of 5–10 mg was sealed in an aluminum pan. Each sample was scanned in the range of -120 to 150°C at a heating rate of $10^\circ\text{C min}^{-1}$, and sample cooling was achieved with a stream of N_2 flowing from liquid nitrogen.

RESULTS AND DISCUSSION

Random SIBR were obtained in cyclohexane using $\text{Nd}(\text{O}^i\text{Pr})_3$ -MAO-indene catalyst system. The unimodal GPC traces of SIBR with RI and UV ($\lambda = 254 \text{ nm}$) dual detectors are shown in Figure 1. UV detector is sensitive to styrene units, while RI detector is sensitive to butadiene, isoprene and styrene units. The UV and RI traces of the terpolymers in this study are all in harmony with each other, with the M_w/M_n in the range of 1.5–2.2. This result illustrates that each terpolymer is not a mixture.³⁶

Effect of $[\text{Al}]/[\text{Nd}]$ Molar Ratio

The effect of the molar ratios of MAO toward $\text{Nd}(\text{O}^i\text{Pr})_3$ on SIBR terpolymerization was examined. As shown in Table I, SIBR with high content of 1,4-butadiene and 1,4-isoprene incorporations were achieved within the $[\text{Al}]/[\text{Nd}]$ molar ratio varied from 30 to 200. The polymer yield increased obviously with a growth of the $[\text{Al}]/[\text{Nd}]$ molar ratio from 30 to 50. When the $[\text{Al}]/[\text{Nd}]$ molar ratio further increased up to 200, the yield did not change apparently from the case of $[\text{Al}]/[\text{Nd}] = 50$. Excess amount of MAO ($[\text{Al}]/[\text{Nd}] > 50$) caused the decrease of M_n , due to its chain transfer effect besides the cocatalyst. Comparing with the previous Nd-based catalyst with MAO ($[\text{Al}]/[\text{Nd}] > 100$),^{37,38} $\text{Nd}(\text{O}^i\text{Pr})_3$ -MAO-indene catalyst system provided the highest conversion at $[\text{Al}]/[\text{Nd}]$ molar ratio of 50. This ratio was also utilized in further investigation. The terpolymers also possessed high M_n and narrow M_w/M_n (1.5–1.9). In addition, it is unique that the microstructure of butadiene/isoprene units in SIBR changed little with the increasing styrene content in the terpolymers.

Table I. Effect of [Al]/[Nd] Molar Ratio on Styrene/Isoprene/Butadiene Terpolymerization^a

Run	[Al]/[Nd] (mol mol ⁻¹)	Yield (%)	$M_n \times 10^{-4b}$	M_w/M_n^b	S//I/B ^c (mol %)	1,4-B ^d (mol %)	1,2-B ^d (mol %)	1,4-I (cis/trans) ^e (mol %)	3, 4-I ^e (mol %)
1	30	13.9	2.2	1.9	9.3/49.3/41.4	94.3	5.7	61.7/13.2	25.1
2	50	51.0	3.0	1.6	18.5/40.9/40.6	89.1	10.9	56.2/22.4	21.4
3	100	50.8	1.4	1.6	18.3/40.1/41.6	82.2	17.8	59.0/21.9	19.1
4	150	46.0	1.0	1.5	18.9/46.2/34.9	77.2	22.8	55.7/27.7	16.6
5	200	45.1	0.8	1.5	18.9/46.0/35.1	77.3	22.7	57.6/28.0	14.4

^aCatalyzed by Nd(OⁱPr)₃-MAO-indene catalyst, conditions: polymerization in cyclohexane at 70°C for 6 h; [Nd]/[monomers] = 6×10^{-4} ; [indene]/[Nd] = 0.5; monomer concentration: [butadiene] = [isoprene] = 1 mol L⁻¹, [styrene] = 2 mol L⁻¹, ^bDetermined by GPC (in THF, Polystyrene calibration), ^cS//I/B: proportions of styrene/isoprene/butadiene in SIBR, determined by ¹H NMR, ^d1,4-B, 1,2-B: 1,4 units and 1,2 units of butadiene sequence in SIBR, the microstructure was determined by ¹H NMR, ^e1,4-I (cis/trans), 3,4-I: 1,4 (cis/trans) units and 3,4 units of isoprene sequence in SIBR, the microstructure was determined by ¹³C NMR.

Table II. Effect of [indene]/[Nd] on Styrene/Isoprene/Butadiene Terpolymerization^a

Run	[Indene]/[Nd] (mol mol ⁻¹)	Yield (%)	$M_n \times 10^{-4b}$	M_w/M_n^b	S//I/B ^c (mol %)	1,4-B ^d (mol %)	1,2-B ^d (mol %)	1,4-I (cis/trans) ^e (mol %)	3, 4-I ^e (mol %)
1	0	35.9	2.0	2.2	12.6/44.7/42.7	88.9	11.1	82.3/12.6	5.1
2	0.3	40.5	1.8	1.7	10.3/44.6/45.1	93.0	7.0	55.7/20.3	24.0
3	0.5	51.0	3.0	1.6	18.5/40.9/40.6	89.2	10.8	56.2/22.4	21.4
4	1.0	33.1	1.5	1.6	11.9/50.4/37.7	84.3	15.7	66.6/12.0	21.4
5	2.0	8.9	1.1	1.6	8.1/50.3/41.6	82.7	17.3	66.5/10.2	23.3

^aCatalyzed by Nd(OⁱPr)₃-MAO-indene catalyst, conditions: polymerization in cyclohexane at 70°C for 6 h; [Nd]/[monomers] = 6×10^{-4} ; [Al]/[Nd] = 50; monomer concentration: [butadiene] = [isoprene] = 1 mol L⁻¹, [styrene] = 2 mol L⁻¹, ^bDetermined by GPC (in THF, polystyrene calibration), ^cS//I/B: proportions of styrene/isoprene/butadiene in SIBR, determined by ¹H NMR, ^d1,4-B, 1,2-B: 1,4 units and 1,2 units of butadiene sequence in SIBR, the microstructure was determined by ¹H NMR, ^e1,4-I (cis/trans), 3,4-I: 1,4 (cis/trans) units and 3,4 units of isoprene sequence in SIBR, the microstructure was determined by ¹³C NMR.

Effect of [indene]/[Nd] Molar Ratio

With Nd(OⁱPr)₃-MAO-indene catalyst system, random SIBR were obtained within the [indene]/[Nd] molar ratio varied from 0.3 to 2.0, on the basis of [Al]/[Nd] molar ratio at 50. Table II summarizes the effect of indene molar ratio toward Nd(OⁱPr)₃ in the terpolymerization. SIBR with high content of 1,4-butadiene and 1,4-isoprene incorporations were achieved. When [indene]/[Nd] increased from 0.3 to 0.5, the yield, M_n and styrene

content rose while M_w/M_n was in a narrow range (1.6–1.7). When [indene]/[Nd] further raised from 0.5 to 2.0, the M_w/M_n had little change while the yield, M_n and styrene content in SIBR decreased, possibly due to the steric hindrance effect induced by the increased coordination of indene. So the most favorable molar ratio of [indene]/[Nd] was 0.5. Compared with this condition, the polymer obtained without indene (Table II, Run 1) possessed low yield and broad M_w/M_n . Similar as the

Table III. Effect of Styrene Feed Molar Ratio on Styrene/Isoprene/Butadiene Terpolymerization^a

Run	St% ^b (mol %)	Yield (%)	$M_n \times 10^{-4c}$	M_w/M_n^c	S//I/B ^d (mol %)	1,4-B ^e (mol %)	1,2-B ^e (mol %)	1,4-I (cis/trans) ^f (mol %)	3, 4-I ^f (mol %)
1	0	99.9	5.4	1.9	0/49.6/50.4	92.5	7.5	58.0/19.3	22.7
2	20	77.2	3.9	1.8	8.3/48.0/43.7	92.5	7.5	57.8/18.8	23.4
3	40	61.2	3.1	1.7	17.0/41.2/41.8	90.1	9.9	56.1/22.1	21.8
4	60	38.1	2.6	1.6	23.0/42.8/34.2	88.1	11.9	56.1/24.2	19.7
5	80	18.4	2.5	1.7	30.4/35.1/34.5	85.6	14.4	54.7/26.7	18.6

^aCatalyzed by Nd(OⁱPr)₃-MAO-indene catalyst, conditions: polymerization in cyclohexane at 70°C for 6 h; [Nd]/[monomers] = 6×10^{-4} ; [Al]/[Nd] = 50; [indene]/[Nd] = 0.5; monomer concentration: [monomers] = 4 mol L⁻¹, [butadiene]:[isoprene] = 1 : 1 (molar ratio), ^bSt %: styrene feed molar ratio, ^cDetermined by GPC (in THF, Polystyrene calibration), ^dS//I/B: proportions of styrene/isoprene/butadiene in SIBR, determined by ¹H NMR, ^e1,4-B, 1,2-B: 1,4 units and 1,2 units of butadiene sequence in SIBR, the microstructure was determined by ¹H NMR, ^f1,4-I (cis/trans), 3,4-I: 1,4 (cis/trans) units and 3,4 units of isoprene sequence in SIBR, the microstructure was determined by ¹³C NMR.

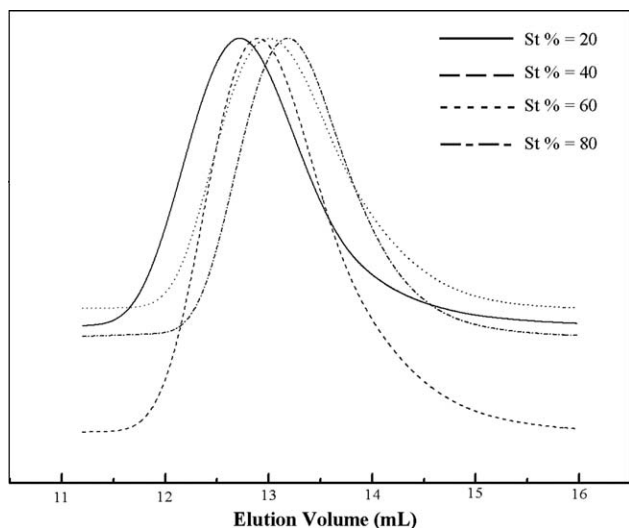


Figure 2. GPC elusive curves of SIBR, St %: styrene feed molar ratio.

NdV-based catalyst system,³⁹ it was plausible that a proton of indene was snatched by the impression of MAO, generating cyclopentadienyl-type anions coordinated to the active Nd site. NMR results exhibited that the variation in the amount of indene did not show an obvious influence on the microstructure of butadiene and isoprene sequences.

Effect of Styrene Feed Ratio

As summarized in Table III, on the basis of $[Al]/[Nd]$ molar ratio at 50 and $[indene]/[Nd]$ molar ratio at 0.5, terpolymers with a wide range of styrene molar fractions ($\sim 30.4\%$) can be produced using $Nd(O^iPr)_3$ -MAO-indene catalyst system in cyclohexane at $70^\circ C$ for 6 h. SIBR with high content of 1,4-butadiene and 1,4-isoprene incorporations were achieved within the styrene in feed molar ratio of 0.2–0.8. The catalyst system is more active in the copolymerization of butadiene and isoprene. As is shown in Figure 2, the M_n reduced dramatically with an increase in styrene concentration in the monomer feed, indicating that the coordination of conjugated dienes to the active species was preferred to styrene. The styrene content of SIBR was controllable by tuning the styrene concentration in feed ratio, which was demonstrated by 1H NMR spectrum, as shown in Figure 3. Interestingly, it was also found that the increase of styrene incorporation in SIBR rarely effected the microstructure of butadiene and isoprene units.

Effect of Temperature and Solvent in Terpolymerization

Table IV describes the effect of polymerization temperature and solvent on the terpolymerization. Raising the temperature remarkably accelerated the conversation of monomers. The catalyst system showed no activity in cyclohexane at $30^\circ C$ after 6 h, whereas the yield increased from 22.9 to 51.0% when the solutions were heated from 50 to $70^\circ C$ for 6 h. As the temperature

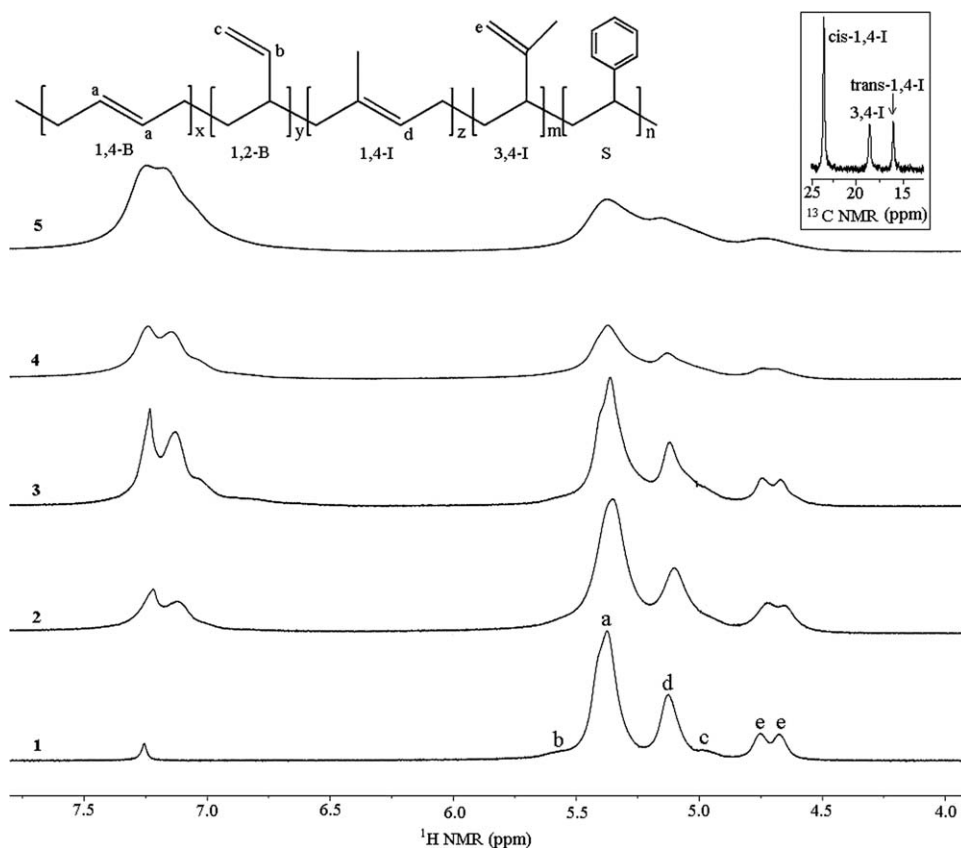


Figure 3. 1H NMR and ^{13}C NMR spectrum of SIBR. 1H NMR spectrum: low-field resonance field. Samples: 1-Table III, Run 1; 2-Table III, Run 2; 3-Table III, Run 3; 4-Table III, Run 4; 5-Table III, Run 5. ^{13}C NMR spectrum: high-field resonance field. Signals for *cis*-1,4-I/*trans*-1,4-I/3,4-I.

Table IV. Effect of Terpolymerization Conditions on Styrene/Isoprene/Butadiene Terpolymerization^a

Run	T (°C)	Solvent	Yield (%)	$M_n \times 10^{-4b}$	M_w/M_n^b	S/I/B ^c (mol %)	1,4-B ^d (mol %)	1,2-B ^d (mol %)	1,4-I (cis/trans) ^e (mol %)	3, 4-I ^e (mol %)
1	30	cyclohexane	0	-	-	-	-	-	-	-
2	50	cyclohexane	22.9	2.5	2.2	7.6/46.8/45.6	92.7	7.3	64.0/11.7	24.3
3	70	cyclohexane	51.0	3.0	1.6	18.5/40.9/40.6	89.2	10.8	56.2/22.3	21.5
4	70	Hexane	47.1	2.9	2.0	14.8/43.5/41.7	89.7	10.3	59.5/18.9	21.6
5	70	Toluene	47.5	1.5	1.7	19.8/44.7/35.5	81.6	18.4	57.6/23.6	18.8

^aCatalyzed by Nd(OⁱPr)₃-MAO-indene catalyst, conditions: [Nd]/[monomers] = 6×10^{-4} ; [Al]/[Nd] = 50; [indene]/[Nd] = 0.5; monomer concentration: [butadiene] = [isoprene] = 1 mol L⁻¹, [styrene] = 2 mol L⁻¹, ^bDetermined by GPC (in THF, Polystyrene calibration), ^cS/I/B: proportions of styrene/isoprene/butadiene in SIBR, determined by ¹H NMR, ^d1,4-B, 1,2-B: 1,4 units and 1,2 units of butadiene sequence in SIBR, the microstructure was determined by ¹H NMR, ^e1,4-I (cis/trans), 3,4-I: 1,4 (cis/trans) units and 3,4 units of isoprene sequence in SIBR, the microstructure was determined by ¹³C NMR.

rising, the M_n and styrene content in SIBR increased while M_w/M_n fell down.

Regarding the polymerization solvent, as is shown in Table IV, the M_n of SIBR prepared in cyclohexane and hexane were higher than that in toluene. The reduced M_n of polymer in toluene was due to a competitive coordination between the aromatic hydrocarbon and the monomer to the Nd active center.⁴⁰ The terpolymers were completely dissolved in these solvents, and the GPC curves remained unimodal with M_w/M_n range of 1.6–2.0. Comparing with the terpolymer afforded in hexane, SIBR synthesized in cyclohexane had narrower M_w/M_n , because of the better solubility in cyclohexane to improve the chain propagation.

Microstructure of SIBR

The microstructure of SIBR samples initiated by Nd(OⁱPr)₃-MAO-indene catalyst were examined by ¹H NMR and ¹³C NMR. The composition of the terpolymers were determined by comparing the integrals of the H resonances of ¹H NMR

spectrum in the following regions, as illustrated in Figure 3 (δ in ppm, CDCl₃, room temperature): 7.20–6.20 (m, 5H, CH₂CH(C₆H₅), S (styrene)), 5.60 (m, 1H, CH₂CH(CH=CH₂), 1, 2-B (butadiene)), 5.35 (m, 2H, CH₂CH=CHCH₂, 1, 4-B), 5.12 (m, 1H, CH₂(CH₃)C=CHCH₂, 1,4-I (isoprene)), 4.95 (m, 2H, CH₂CH(CH=CH₂), 1,2-B), 4.70 (m, 2H, CHCH₂(CH₃)C=CH₂, 3,4-I).^{7,41,42} The absent peaks at 5.82 ppm (m, 1H, CHC(CH₃)CH=CH₂, 1,2-I) indicated no 1,2-I units in the terpolymers. Generally, the signals of styrene units in ¹H NMR are located at the region of 6.20–6.85 and 6.85–7.40 ppm with area ratio of 2/3, and the peaks are assigned to be block and random distribution in styrene sequence, respectively⁴³ (Figure 3). It can be concluded that the styrene units in the resultant SIBR samples are distributed randomly. According to ¹³C NMR, isoprene units composition was calculated based on the relative peaks intensity of the methyl carbon atoms at 23.7, 16.3, and 18.9 ppm, which represented to *cis*-1,4-I, *trans*-1,4-I and 3,4-I units, respectively.⁴⁴ It is worth noting that the 1,4 content of the butadiene and isoprene units decreased little with increasing styrene content in terpolymerization. As is shown in Figure 3, the relative area ratio of peaks a and d, assigning to the methyne protons in the 1,4-B and 1,4-I units, are nearly constant with increasing styrene content in SIBR. This suggested the stability of selectivity of the catalyst system, which is practically useful and important in further application.

Thermodynamic Results Analysis

The thermal properties of SIBR synthesized in the presence of Nd(OⁱPr)₃-MAO-indene catalyst were analyzed by DSC. As is shown in Figure 4, the T_g of the polymers rose significantly with the increase of styrene content in products. The melting point (270°C) for syndiotactic styrene units was not observed in the terpolymers. With the random distribution, The terpolymer possessed only one T_g . In contrast, SIBR prepared by anionic polymerization exhibited more than one T_g , owing to the block configuration.^{4,7,8}

CONCLUSION

The Nd(OⁱPr)₃-MAO-indene catalyst system showed a high activity for the terpolymerization of styrene, isoprene and

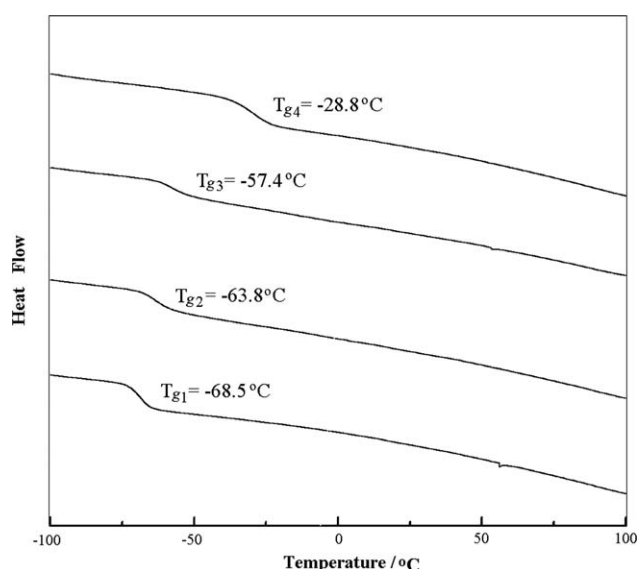


Figure 4. DSC curves of the SIBR. T_{g1} : Table III, Run 2; T_{g2} : Table III, Run 3; T_{g3} : Table III, Run 4; T_{g4} : Table III, Run 5.

butadiene to give SIBR with high 1,4 content of butadiene and isoprene units. Random SIBR with high content of styrene units initiated with rare earth metal catalyst was realized without formation of each homo/copolymers. The MAO and indene were essential components in the terpolymerization. In this study, the optimum terpolymerization condition can be concluded as: [Al]/[Nd] = 50, [indene]/[Nd] = 0.5, in cyclohexane at 70°C for 6 h. The variation of reaction conditions showed little effect toward the microstructure of butadiene and isoprene sequences in final terpolymers, indicating the fairly stability of selectivity of the catalyst. The composition and T_g of the terpolymer were well controlled by feed ratios, with narrow M_w/M_n . Further works will focus on the study of physical properties of these terpolymers to explore their characteristics as a tire tread. The low T_g , chain microstructure and random distribution of the SIBR herein is expected to exhibit outstanding properties as an “integral rubber” of low-temperature performance, high elasticity and skid resistance.

ACKNOWLEDGEMENTS

This work was financially supported by The National Nature Science Foundation of China for project Nos. 21034001 and 21174021.

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