

Styrene–Butadiene Block Copolymer with High *cis*-1,4 Microstructure

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ABSTRACT: The sequential block copolymerization of styrene (St) and butadiene (Bd) was carried out with an activated rare earth catalyst composed of catalyst neodymium tricarboxylate (Nd), cocatalyst Al(*i*-Bu)₃ (Al), and chlorinating agent (Cl). The microstructure, composition, and morphology of the copolymer were characterized by FTIR, ¹H NMR, ¹³C NMR, and TEM. The results show that styrene–butadiene diblock copolymer with high *cis*-1,4 microstructure of butadiene units (~97 mol %) was synthesized. The *cis*-selectivity for Bd units was almost independent on the

content of styrene units in the copolymer ranging from 18.1 mol % to 29.8 mol %. The phase-separated morphology of polystyrene (PS) domains of about 40 nm tethered by the elastomeric polybutadiene (PB) segments is observed. The PS-*b-cis*-PB copolymer could be used as an effective compatibilizer for noncompatibilized binary PS/*cis*-PB blends. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 103–109, 2007

Key words: block copolymer; polybutadiene; polystyrene; stereospecific polymerization

INTRODUCTION

Block copolymers are one of the most widely used materials because they combine different macromolecular segments by chemical bond. A variety of elastomers such as styrene–butadiene diblock (SB) and triblock (SBS) copolymers are manufactured industrially by anionic polymerization. Generally, the SB and SBS copolymers contain Bd homosequence with only 35–40 mol % of *cis*-1,4 configuration. It is difficult to increase *cis*-1,4 content of Bd units in anionic polymerization. Ziegler–Natta catalysts offer a better control over microstructure and stereospecificity of the polymer.¹ Rare earth catalysts are well known as excellent catalysts for the stereospecific polymerization of conjugated dienes, such as butadiene and isoprene.^{2–4} The copolymerization of butadiene and styrene with rare earth catalyst has attracted considerable interest in the last decade and a random copolymer of Bd and St has been obtained. However, both the *cis*-1,4 content of Bd units in the

copolymer and molecular weight of the copolymer decreased significantly with an increase in St content in the copolymer obtained by the rare earth catalysts.^{5–15}

The block copolymers of poly(syndiotactic styrene-*co*-butadiene) with high *cis*-1,4 content were achieved by using CpTiX₃ (Cp = C₅H₅, X = Cl, F; Cp = C₅Me₅, X = Me) and TiX_{*n*} (*n* = 3, X = acetylacetonate(acac); *n* = 4, X = *o*-*tert*-Bu) activated with methylaluminumoxane as a catalyst.^{16,17} However, copolymerization activity was low (24–36 kg mol⁻¹ of cat. h⁻¹) and only block like copolymers *syn*-PS-*b-cis*-PB were obtained under specific polymerization conditions because of lack of livingness in this polymerization system. The *syn*-PS-*b-cis*-PB copolymers could be prepared through a stereospecific sequential block copolymerization of St and Bd with a C₅Me₅TiMe₃/B(C₆F₅)₃/Al(oct)₃ catalyst.^{18,19} However, *cis*-1,4 Bd units in the copolymer were relatively low (more than 70 mol %).

The styrene–butadiene copolymers contained 10–15 mol % St units and 85–90 mol % Bd units, with 90–96 mol % *cis*-1,4 configuration were obtained under appropriate conditions in our previous research work.⁵ In this article, styrene–butadiene block copolymers with high *cis*-1,4 content were synthesized with a Nd/Al/Cl catalyst by sequential addition of styrene and butadiene. The microstructure, composition and its distribution, sequence, and morphology of the copolymer that was insoluble in both methyl ethyl ketone and hexane, respectively, were characterized.

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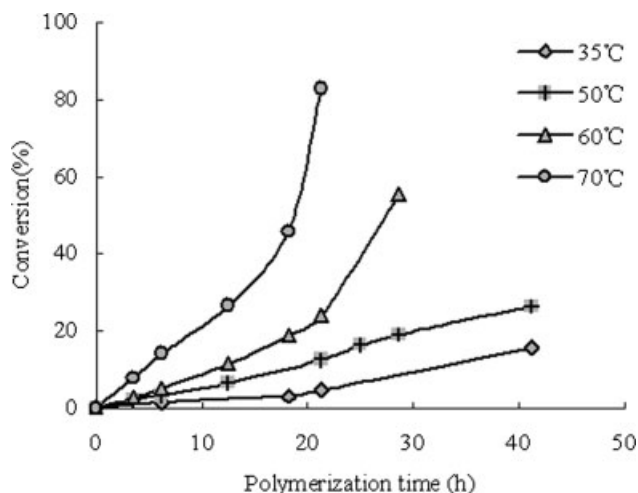


Figure 1 Effect of Polymerization temperature on styrene conversion. Cl/Nd = 35, Al/Nd = 17, Nd/St = 3.0×10^{-3} , [St] = 4 mol L⁻¹, solvent: CHX.

EXPERIMENTAL

Materials

Styrene (St), provided by Beijing Yansan Petrochemical Company was purified by distillation at reduced pressure over calcium hydride and stored at -14°C . Butadiene (purity: 99.5%) and triisobutyl aluminum in heptane ($[\text{Al}(\text{i-Bu})_3] = 0.74 \text{ mol L}^{-1}$) from Beijing Yansan Petrochemical Company were used as received. Hexane (Hex) and cyclohexane (CHX) (Beijing Yansan Petrochemical Company) were purified by distillation over calcium hydride before used.

Polymerization

All the operations were conducted under an atmosphere of dry nitrogen. First, styrene and cyclohexane were introduced into a vessel and the Nd/Al/Cl catalyst system was added to start the St polymerization at a definite temperature for a definite time. Then butadiene solution in cyclohexane or in hexane/cyclohexane mixture was dropped into the above St polymerization system and the copolymerization was conducted for an extra definite time. The copolymerization was terminated by addition of a methanol-H₂O-NaOH mixture containing 2,6-di-*t*-butyl-4-methylphenol. The polymerization mixture was poured into a large quantity of ethanol/H₂O containing a small amount of hydrochloric acid. The precipitated polymer was further washed by ethanol and water until neutral. The polymer product was dried under vacuum at 45°C until a constant weight was obtained. The polymer product was extracted by methyl ethyl ketone (MEK) (Yili Chemical Company, Beijing, China) and hexane, respectively. The copolymer was obtained from that was insoluble in MEK and hexane, respectively.

Copolymer characterization

The film of the copolymer was prepared by spreading a small amount of tetrahydrofuran (THF) solution of the copolymer on the slice of KBr after the evaporation of THF. The copolymer was characterized on a Nexus 670 FTIR spectrophotometer (Nicolet, Madison, WI).

The copolymer sample was dissolved in THF with the concentration of 1 mg/mL. M_n , M_w , and MWD of the copolymer were determined at 25°C by a Waters 515-2410 GPC System equipped with Waters 996 PAD, RI 2410 and UV detectors and three Waters styragel HT3-5-6E columns (Milford, MA). THF was used as eluent with a flow rate of 1.0 mL/min. The calibration was established with polystyrene (PS) standards.

The copolymer sample was dissolved in CDCl₃ in a 5 mm (o.d.) NMR tube and analyzed at room temperature (25°C) with a Bruker AV600 spectrometer (Bruker, Bremen, Germany) (600 MHz for ¹H NMR and 150 MHz for ¹³C NMR). Chemical shifts were referenced to tetramethylsilane as internal standard and calculated by using the residual isotopic impurities of the deuterated solvents. All NMR chemical shifts are reported in ppm. The following parameters were used to acquire the ¹H NMR spectra: relaxation time = 2 s; acquisition time = 2.73 s; flip angle = $\pi/4$; number of transients = 16. The following parameters were used to acquire the ¹³C NMR spectra: relaxation time = 2 s; acquisition time = 0.54 s; flip angle = $\pi/4$; number of transients = 22 K.

The copolymer sample (20 mg) was dissolved in toluene (10 mL), and the copolymer film was formed

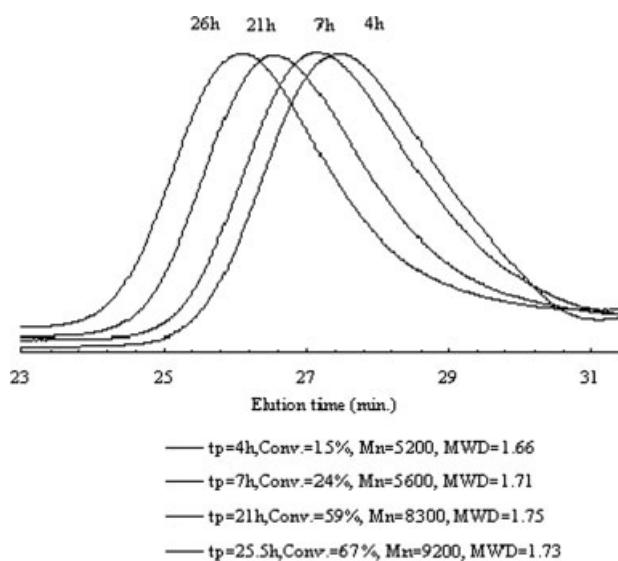


Figure 2 GPC traces of polystyrenes obtained at different polymerization time. Cl/Nd = 35, Al/Nd = 16, Nd/St = 3.0×10^{-3} , [St] = 4 mol L⁻¹, solvent: CHX, polymerization temperature: 70°C .

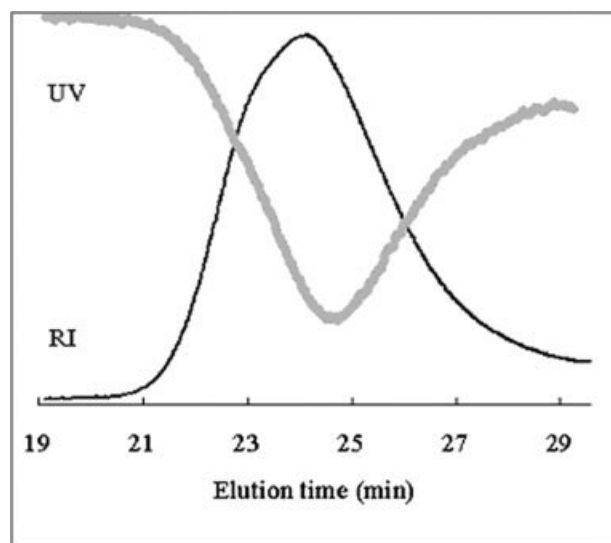


Figure 3 GPC traces (RI and UV detectors) of the copolymer synthesized in cyclohexane. Cl/Nd = 35, Al/Nd = 16, Nd/Bd = 1.0×10^{-3} , [St] = 8.7 mol L^{-1} , St/Bd = 0.3 (molar ratio).

after the evaporation of toluene, supported on 3 mm copper grids, and stained with osmium tetroxide. The sample was then examined with a HITACHI - 800 transmission electron microscope (Hitachi, Tokyo, Japan) operating at 150 KV.

RESULTS AND DISCUSSION

The catalyst of neodymium carboxylate combined with triisobutyl aluminum and chlorinating agent was used to initiate the polymerization of styrene then the polymerization of butadiene. The catalyst exhibited much higher activity for butadiene polymerization than for styrene polymerization. As shown in Figure 1, the styrene conversion increased gradually with increases in polymerization temperature and time. So, the polymerization of styrene should be conducted at high temperature such as 70°C . It can be seen from Figure 2 that all the GPC traces of PS obtained at different polymerization time exhibited unimodal distribution and the num-

ber-average molecular weight (M_n) of PS increased almost linearly with monomer conversion and polydispersity index (M_w/M_n) kept around 1.7. Normally, butadiene solution in cyclohexane or in hexane/cyclohexane mixture was introduced after styrene polymerization reached high conversion and then copolymerization with butadiene was conducted at relatively low temperature (40°C) to prepare the poly(styrene-*b*-butadiene) diblock copolymer.

When butadiene solution in cyclohexane was dropped into the styrene polymerization system, the copolymerization system was a homogenous solution with high viscosity since cyclohexane is a good solvent for PS, polybutadiene (PB), and their block copolymer (SB). The copolymer was obtained by two steps of extraction with hexane and MEK to remove the homopolymers PB and PS formed during the copolymerization, respectively. The unimodal GPC traces of the copolymer with RI and UV ($\lambda = 254 \text{ nm}$) dual detectors are given in Figure 3. The GPC curve recorded by UV detector which is only sensitive to St units was consistent with the GPC curve recorded by RI detector which is sensitive to both Bd and St units. It can be observed that the GPC curves by RI and UV detector almost coincide with each other, indicating that no homopolymers (PB and PS) existed in the copolymer. It also reflects that the copolymer with lower molecular weight contains more St units. The molecular weight (M_n) of the copolymer was $2.9 \times 10^4 \text{ g mol}^{-1}$.

Interestingly, it was found that the copolymerization system was a homogenous solution initially and then turned gradually to be a heterogenous system like "mini-emulsion" in organic medium with relatively low viscosity when butadiene solution in hexane/cyclohexane mixture was dropped into the above styrene polymerization system. Cyclohexane is a good solvent for both PS and PB segments while hexane is a good solvent for PB segment but nonsolvent for PS segment. The phenomenon of "mini-emulsion" indicates the formation of diblock copolymer of PS-*b*-PB. The content of original polymer obtained at different molar ratios of St/Bd are listed Table I. The content of PS ranged from 26 to

TABLE I
SB Block Copolymers Prepared by Sequential Polymerization

Run no.	St (mmol)	Bd (mmol)	Original polymer content (wt %)			Molecular weight and its distribution of copolymers	
			PS (soluble in MEK)	PB (soluble in Hex)	SB (insoluble in MEK and Hex)	M_n	M_w/M_n
03-4-1-4-Z2-Y4	228	380	43.0	3.6	53.4	39200	4.46
03-4-1-5-Z2-Y4	304	380	26.0	6.7	67.3	38000	3.27
03-4-1-6-Z2-Y4	380	380	31.9	9.8	58.3	38800	3.02

Cl/Nd = 34.8, Al/Nd = 15.9, Nd/Bd = 1.8×10^{-3} , [St] = 4 mol L^{-1} , [Bd] = 1.64 mol L^{-1} , Hex/CHX = 1.0(v/v).

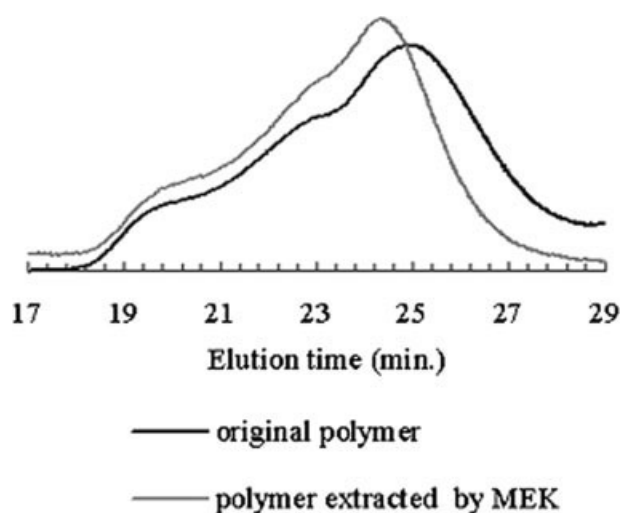


Figure 4 The comparison of GPC traces of original polymer and polymer extracted by MEK (03-4-1-4-Z2-Y4).

43% in weight while the content of PB was less than 10% in weight and the copolymer content was around 60% in weight.

The representative GPC traces of the original polymers and those extracted by MEK and then hexane are given in Figures 4 and 5. Polymer product contained homopolymer PB in its higher molecular weight region and homopolymer PS in its lower molecular weight region. As shown in Figure 6, the copolymer could be obtained after extraction by MEK and Hex exhibited unimodal molecular weight distribution and the GPC curve by RI detector was almost in harmony with the curve by UV detector, reflecting that homopolymers (PB and PS) did hardly exist in the copolymer. The polymer with higher molecular weight consists of relatively long PB seg-

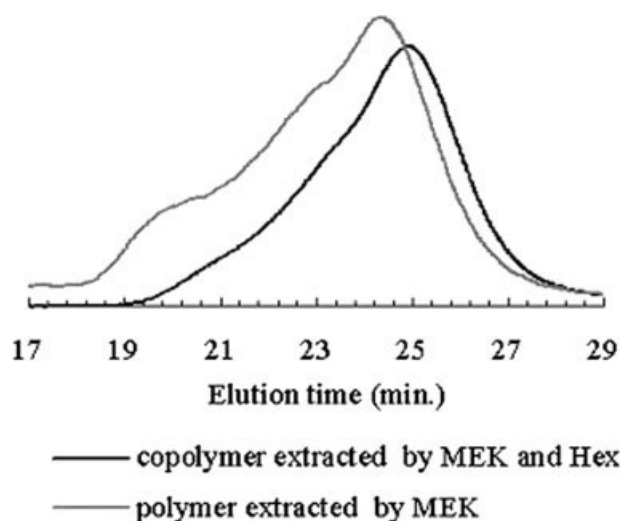


Figure 5 The comparison of GPC traces of polymer extracted by MEK and copolymer (03-4-1-4-Z2-Y4).

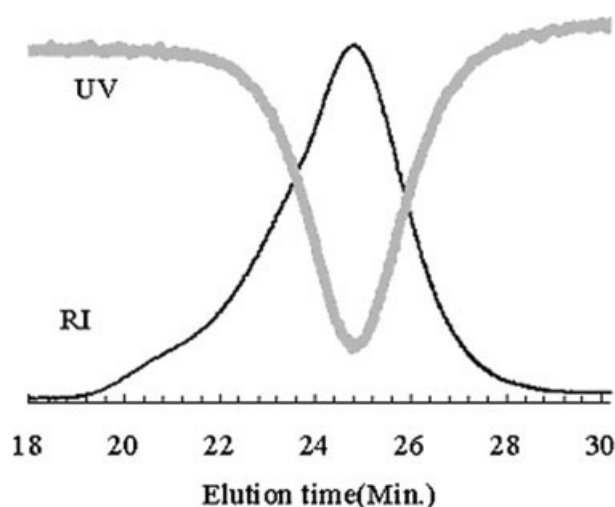


Figure 6 The representative GPC trace (RI and UV) of the copolymer (03-4-1-4-Z2-Y4).

ment and short PS segment. The molecular weight (M_n) of the copolymer was around 3.9×10^4 g mol⁻¹, as listed in Table I. The molecular weight distribution narrowed with an increase in molar ratio of St/Bd in monomer feed and polydispersity index (M_w/M_n) decreased from 4.5 to 3.0.

The representative FTIR spectrum of the styrene-butadiene copolymer recorded from 2000 cm⁻¹ to 500 cm⁻¹ is presented in Figure 7. The absorption band at 1657 cm⁻¹ is assigned to the stretching vibration of double bond in Bd units. The bands at 746 cm⁻¹, 969 cm⁻¹, and 910 cm⁻¹ are assigned to the *cis*-1,4, *trans*-1,4, and vinyl configuration of Bd units, respectively. The fact that strong absorption at 746 cm⁻¹ and weak absorptions at 969 cm⁻¹ and 910 cm⁻¹ indicates that there exist primarily *cis*-1,4 Bd units in the copolymer. On the other hand, a series of bands at 1603 cm⁻¹, 1494 cm⁻¹, 1451 cm⁻¹, and 1405 cm⁻¹ are attributed to the stretching vibration of phenyl group in St units. FTIR characterization shows preliminarily that the copolymer contains St units and Bd units with high *cis*-1,4 configuration.

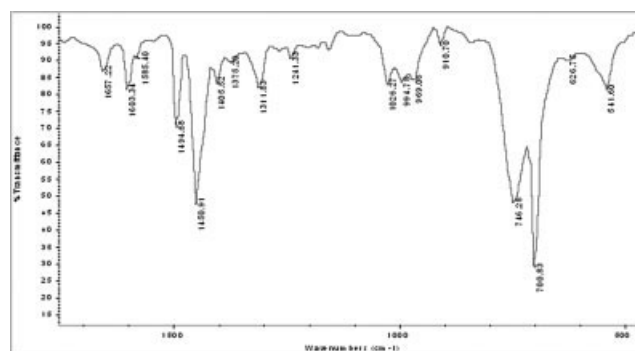


Figure 7 The representative FTIR spectrum of the copolymer (03-4-1-6-Z2-Y4).

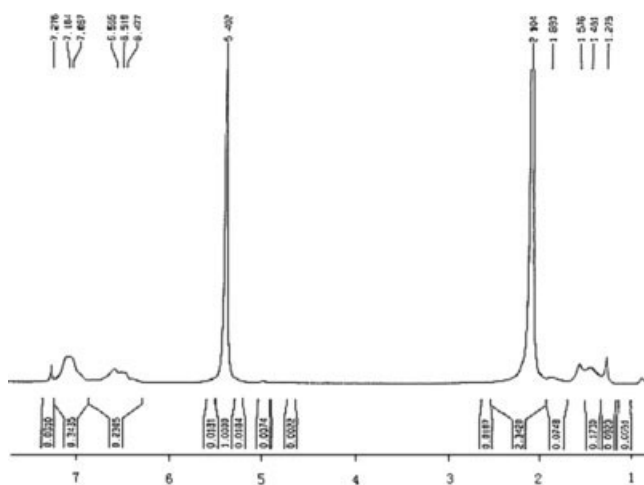


Figure 8 ^1H NMR spectrum of SB copolymer.

The microstructure and the composition of the SB copolymer were investigated by the ^1H NMR and ^{13}C NMR spectrum, as shown in Figures 8 and 9. The microstructure of the copolymer are presented by four monomer units, namely, butadiene units with *cis*-1,4(C), *trans*-1,4(T), vinyl (V) configurations, and styrene units (S). The very strong signal at 5.39 ppm, which assigned to the proton of CH in the *cis*-1,4 configuration, indicates that the copolymer contained primarily high *cis*-1,4 butadiene units. This result is supported by the undetectable signal at 5.43 ppm and the very weak signal at 4.98 ppm, which attributed to the proton of CH in the *trans*-1,4 and of CH_2 in vinyl configurations, respectively. The observed signals at 7.07 ppm and 6.56 ppm (3:2 integral) reflect the occurrence of vicinal effect between *o*-proton in neighboring phenyl groups in styrene units. Therefore, there exist PB sequences with high *cis*-1,4 content and PS sequences in the SB copolymer.

The chemical shifts of the ^{13}C NMR signals of the different monomer triads and diads are listed in Table II for the aliphatic region. The very strong signal at 27.43 ppm, assigned to the CC_1C and CC_4C car-

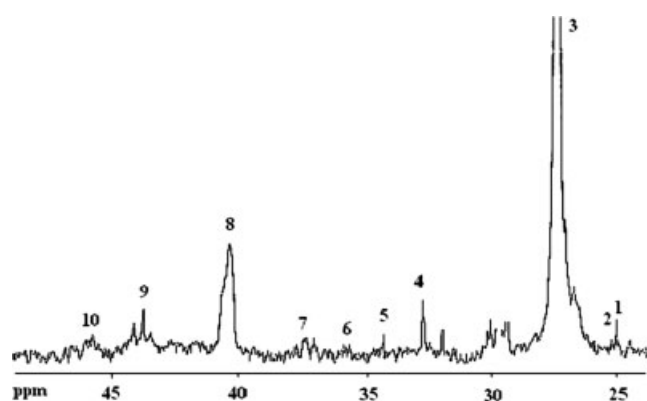


Figure 9 ^{13}C NMR spectrum of the SB copolymer.

TABLE II
Signal Assignment of the Aliphatic Carbons in the SB Copolymer

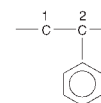
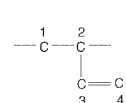
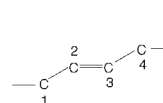
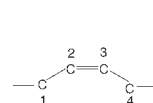
Line	Sequence	Exptl. chemical shifts (ppm)	Ref.	
			17	13
1	$\text{C}_1^*\text{-V}$	25.00	24.95	24.92
2	$\text{C}_1^*\text{-S}$	25.21	25.17	25.12
3	$\text{C(T)-C}_1^*\text{-C(T)}$	27.43	27.38	27.34
4	$\text{C(T)-T}_1^*\text{-C(T)}$	32.71	32.5	32.64
5	$\text{C-V}_1^*, \text{T-V}_1^*$	34.31	34.26	34.22
6	$\text{S-C}_1^*, \text{C}_1^*\text{-S}^*$	35.72	35.7	35.62
7	CV_1^*T	38.15	38.2	
8	$\text{S}_2^*\text{-S}, \text{V}_2^*\text{-S}, \text{S}_2^*\text{-V}$	40.35	40.6	40.17-40.47
9	$\text{V}_2^*\text{-C}, \text{V}_2^*\text{-T}$	43.69	43.7	43.7
10	$\text{S}_2^*\text{-C}, \text{S}_2^*\text{-T}$	45.70	45.7	45.69

Scheme: C

T

V

S



*: noticed unit

bons, suggests that the primary *cis*-1,4 configuration is presented in Bd units. Small fraction of V and T unit occasionally distribute among the polymer chain. The presence of the diads CT_1 and T_4C at 32.7 ppm and the triad CVT at 38.2 ppm suggests that the T units are followed by V and C units. The presence of the diads C_1S at 25.21 ppm, 35.72 ppm, and 45.70 ppm indicates that the S units connect mainly to C units. No signals of *St-trans*-1,4 Bd sequence (30.51 ppm and 39.83 ppm)²⁰ and of *St-vinyl* Bd linkage (32.33 ppm and 42.93 ppm) are observed in the spectrum.

The microstructure content of Bd and St units were calculated on the basis of ^1H NMR and ^{13}C NMR analysis.²⁰⁻²² The content of 1,4-configuration, vinyl configuration, and St units were calculated by the intensities of peaks C, T, V, S. It is difficult to calculate the molar ratio of *cis*-1,4 and *trans*-1,4 from ^1H NMR spectrum because of contiguous chemical shifts. The contents of microstructure and composition of the copolymers were listed in Table III. As shown in Table III, *cis*-1,4 content of Bd unit in the

TABLE III
Microstructure and Composition of the Copolymers

Run no.	Styrene content (mol %) (by ^1H NMR)	Microstructure of butadiene unit (mol %) (by ^{13}C NMR)		
		<i>cis</i> -1,4	<i>trans</i> -1,4	1,2-
02-12-18-Z6-Y4	18.1	97.7	1.0	1.3
03-4-1-4-Z2-Y4	29.8	96.1	3.0	1.9
03-4-1-5-Z2-Y4	21.8	97.0	1.4	1.6
03-4-1-6-Z2-Y4	23.3	97.6	1.2	1.2

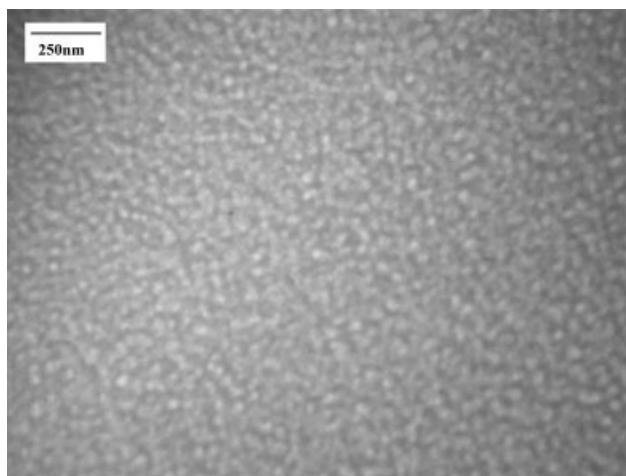


Figure 10 TEM image of the SB copolymer.

copolymer ≥ 97.0 mol % when styrene content in the copolymers was less than 23.3 mol %. It is interestingly found that *cis*-1,4 content in Bd units was 96.1 mol % when styrene content in the copolymer was 29.8 mol %. It is unique that the *cis*-1,4 microstructure of the Bd unit of the copolymer decreased very little with the increase in the styrene content of the copolymer. The diblock copolymer of butadiene–styrene with high *cis*-1,4 content and relatively high styrene content could be obtained using Nd/Al/Cl catalyst system.

To provide further experimental evidence for the SB block copolymers, the representative TEM image is presented in Figure 10. The TEM image indicates that the SB block copolymer form a homogeneous separated-phase morphology with PS domains (light phase) of ~ 40 nm in size tethered by PB segments (dark continuous phase).

It is well known that block copolymers can be used as effective compatilizers for immiscible poly-

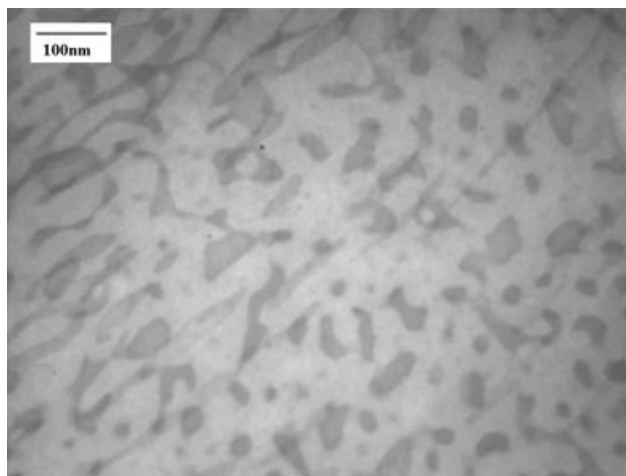


Figure 11 TEM images of binary PS/*cis*-PB (75/17 wt %) blend with the addition of PS-*b-cis*-PB copolymer (8 wt %).

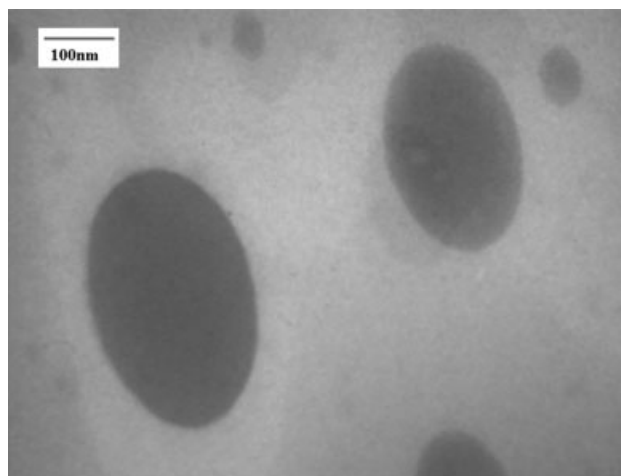


Figure 12 TEM images of binary PS/*cis*-PB (90/10 wt %) blend without the addition of PS-*b-cis*-PB copolymer.

mer blends. To investigate the potential use of the SB block copolymer, a typical binary PS/*cis*-PB blend sample was prepared as follows. A mixture of 75 wt % PS and 17 wt % *cis*-PB was dissolved in toluene, followed by 8 wt % PS-*b-cis*-PB copolymer. Polymer mixture film cast from the solution was used as sample for TEM. A TEM image of the binary PS/*cis*-PB with the addition of PS-*b-cis*-PB copolymer is presented in Figure 11. A TEM image of the binary PS/*cis*-PB is presented for comparison in Figure 12. It can be seen that the oval *cis*-PB domains with size of 100–300 nm and with clear borderline distributed in PS matrix due to the immiscibility of PS and *cis*-PB. Interestingly, it was observed that *cis*-PB domains with size of 10–50 nm and with blurry borderline distributed homogeneously in PS matrix even at higher *cis*-PB content. Therefore, PS-*b-cis*-PB copolymer could be used as an effective compatilizer for noncompatilized binary PS/*cis*-PB blends.

CONCLUSIONS

Novel styrene–butadiene block copolymers PS-*b-cis*-PB consisting of high *cis*-1,4-content of around 97 mol % in Bd units and St content ranging from 18.1 mol % to 29.8 mol % were synthesized by sequential copolymerization of styrene and butadiene with Nd/Al/Cl catalyst system. The *cis*-1,4 microstructure of the Bd units of the copolymer decreased very slightly with the increase in the styrene content of the copolymer. Small fraction of vinyl and *trans*-1,4 of Bd units occasionally distributed among PB sequences. Styrene units connect mainly with *cis*-1,4 butadiene units. PS-*b-cis*-PB copolymer could be used as an effective compatilizer for noncompatilized binary PS/*cis*-PB blends.

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