

Synthesis and characterization of symmetrical triblock copolymers containing crystallizable high-*trans*-1,4-polybutadiene

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Abstract A series of symmetrical triblock copolymers containing crystallizable high-*trans*-1,4-polybutadiene (HTPB) were synthesized by sequential anionic polymerization of 1,3-butadiene (Bd) with isoprene (Ip) (or styrene (St)) using barium salt of di(ethylene glycol) ethyl ether/triisobutylaluminium/dilithium (BaDEGEE/TIBA/DLi) as initiation system. The microstructures of the symmetrical triblock copolymers were determined by IR, ^1H NMR, and ^{13}C NMR. The results indicated that polyisoprene-*block*-high-*trans*-1,4-polybutadiene-*block*-polyisoprene (IBI) contained HTPB segments and medium 3,4-polyisoprene (PI) segments, and polystyrene-*block*-HTPB-*block*-polystyrene (SBS) contained HTPB and *atactic*-polystyrene (PS) segments. The DSC analysis revealed that SBS tended to phase separate but IBI did not. The cold crystallization was observed in IBI but not in SBS.

Keywords Symmetrical triblock copolymers · High-*trans*-1,4-Polybutadiene · Cold crystallization · Styrene · Isoprene

Introduction

Block copolymers often exhibit unique and useful properties in solution and in solid states as a consequence of the general thermodynamic incompatibility of blocks which results in microphase separation into domains [1, 2].

Block copolymers containing polybutadiene (PB) segments are among the most important rubbery materials and are industrial produced by emulsion [3] and

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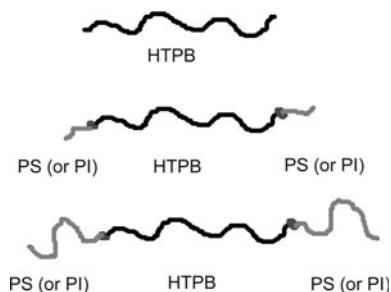
solution polymerizations [4]. Due to the development of the catalysts which are effective in controlling the stereoregularity of PB, polystyrene (PS), or polyisoprene (PI) segments, it is possible to synthesize stereoregular block copolymers containing PB segments. Recent achievements in the stereospecific copolymerization of St and Bd with transition-metal catalysts have controlled the *cis*-1,4 selectivity of PB segments [5–10]. However, none of these catalysts are able to effectively control the stereoregularity of PS segments. Further more, copolymers with both *cis*-1,4-PB segments and *syn*-PS segments were achieved by Naga [11] and Zambelli [12], who used CpTiCl₃/methylaluminoxane (MAO; Cp = cyclopentadienyl, indenyl, or pentamethylcyclopentadienyl) as catalysts. Nevertheless, because of the lack of livingness in these systems, no true block products were obtained. In fact, *syn*-PS-*b*-*cis*-1,4-PB copolymers were achieved by Ban et al. [13], who used C₅Me₅TiMe₃/B(C₆F₅)₃/Al(oct)₃ as catalyst, and Caprio et al. [14], who used CpTiX₃ (Cp = C₅H₅, X = Cl, F; Cp = C₅Me₅, X = Me) and TiX_n (*n* = 3, X = acetylacetonate (acac); *n* = 4, X = *t*-BuO) activated by MAO.

To sum up, because of the industrial importance [15], many studies have been devoted to *cis*-1,4-PB while *trans*-1,4-PB has received rather limited attention [16, 17]. More recently, late transition metal based catalysts have been achieved for the synthesis of *trans*-1,4-PB with high selectivity (>95%) and narrow molecular weight distributions [16, 18]. The discovery of such single-site catalysts has renewed the interest in synthesis and use of *trans*-1,4 selective catalysts also for their outstanding performances in the copolymerization of Bd with olefins [19–21]. For example, high *trans*-1,4-Bd/Ip copolymers were synthesized with a TiCl₄/MgCl₂-Al(*i*-Bu)₃ catalyst system [22]. *Iso*-PS-co-*trans*-1,4-PB with an unprecedented architecture, covering a wide range of compositions (*x*_S = 0.15–0.97), were also obtained with octahedral Titanium catalyst [23]. However, because of the lack of livingness, only block-like or multiblock copolymers were obtained under specific polymerization conditions.

Our strategy for synthesizing block copolymers containing high-*trans*-1,4-PB (HTPB) segments is derived from the development of a new living anionic polymerization initiation system that is able to polymerize Bd to HTPB [24]. The initiation system is comprised of (a) an organolithium compound, (b) a group IIA metal salt, (c) an organoaluminium compound, and (d) an amine compound.

In this study, symmetrical triblock copolymers were first prepared by sequential anionic polymerization of Bd with Ip or St (Scheme 1) using barium salt of

Scheme 1 Symmetrical triblock copolymers



di(ethylene glycol) ethyl ether/triisobutylaluminium/dilithium (BaDEGEE/TIBA/DLi) as initiation system. The copolymers contained crystallizable HTPB segments and hard segments (PS) or soft segments (PI). The microstructures and macromolecular architectures were determined by IR, NMR, and size exclusion chromatography (SEC). The thermal behaviors were recorded by differential scanning calorimetry (DSC).

Experimental

Materials

1,3-Butadiene (Bd, polymerization grade, Beijing Yanshan Petrochemical Co., China) was purified with a small amount of *sec*-butyllithium (*s*-BuLi) and then vaporized to keep the water content below 10 ppm.

Styrene (St, polymerization grade, Beijing Yanshan Petrochemical Co., China) was dried over CaH₂ for 12 h and distilled under reduced pressure before use.

Isoprene (Ip, polymerization grade, Puyang Xinyu Petrochemical Industry Co., Ltd., China) was refluxed for about 1 h over CaH₂, and then distilled and stored over molecular sieves (5Å) under highly purified nitrogen (N₂).

s-BuLi (1.3 M solution in cyclohexane/hexane (92/8), Acros Organics Co., Geel, Belgium) and triisobutylaluminium (TIBA, 1.1 M solution in toluene, Acros Organics Co., Geel, Belgium) were diluted in dry cyclohexane under highly purified N₂, respectively. The concentration of *s*-BuLi was calibrated by Gilman double titration method [25]. The concentration of TIBA was calibrated by EDTA complexation titration method [26].

Cyclohexane (analytical reagent, Liaoyang Petrochemical Co., China) was dried and kept over molecular sieves (5Å) to keep water content below 5 ppm, and then it was purged with highly purified N₂ for more than 15 min prior to use to keep oxygen content below 10 ppm.

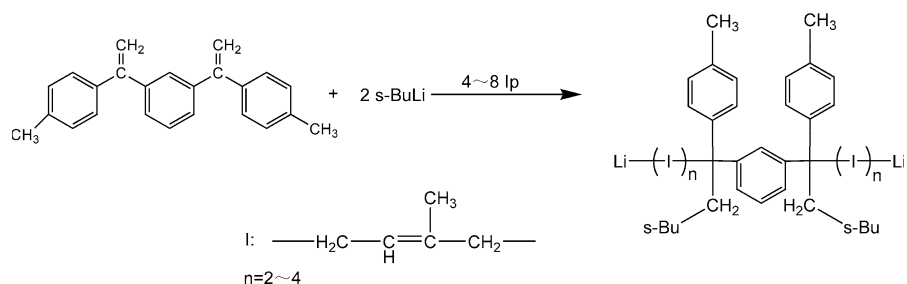
Barium salt of di(ethylene glycol) ethyl ether (BaDEGEE) was synthesized according to the literature procedure [27].

Synthesis of dilithium

The synthesis of dilithium was described in the literatures [28, 29]. Further more, several Ip units were added to C–Li⁺ bond to enhance the solubility of the dilithium in cyclohexane (as shown in Scheme 2). The dilithium we adopted in the polymerization was simplified as DLi. The concentration of DLi was approximately 0.05 mol/L determined by the double titration method of Gilman.

Polymerization procedure

All the operations were conducted under highly purified N₂ atmosphere. A typical anionic polymerization reaction was performed in a glass reactor connected to the Schlenk line and equipped with an inert gas (N₂) inlet and a rubber septum. The



Scheme 2 Synthesis of dilithium

glass assembly was dried with 3 cycles of a flaming/ N_2 -purging/evacuating, before adding all the reagents.

The *trans*-specific living polymerization of Bd was conducted in a 300 mL, press-resistant glass reactor at 50 °C with cyclohexane as solvent. The sequential block copolymerization of Bd with St (or Ip) was conducted in a 300 mL, pressure-resistant glass reactor at 50 °C for the first step and at 70 °C for the second step with cyclohexane as solvent. A typical Bd and St (or Ip) sequential block polymerization was carried out as follows. A measured amount of Bd (10.4 g) in cyclohexane (200 mL) was introduced into the reactor, the polymerization was started by the addition of BaDEGEE (0.52 mmol), TIBA (2.08 mmol), and DLi (2.08 mmol) in that order at 50 °C. After 3 h of polymerization, a small amount of the polymer solution was taken out for the evaluation of microstructures and molecular weights of the corresponding polymers. Then the polymerization temperature was lowered to 20 ± 1 °C and 10.0 g of St (or Ip), which had been purified by *s*-BuLi, was added to the reactor. The polymerization proceeded for another 3 h at 70 °C. After finishing the polymerization, the symmetrical triblock polymers were terminated by a small amount of degassed isopropanol containing 2.5% w/v 2,6,4-antioxidant, precipitated by the addition of an excess amount of neat ethanol, and then dried in a vacuum oven at 40 °C.

Characterizations

IR. Infrared (IR) spectra of the polymers were recorded on a Nicolet FTIR spectrophotometer (USA) with films on NaCl discs.

DSC. The differential scanning calorimetry (DSC) measurements were conducted with a NETZSCH DSC 204 instrument (Germany). The calorimeter was calibrated with indium standard. About 8–10 mg samples were used at a heating rate of 10 °C min^{-1} under a flow of N_2 (20 mL min^{-1}).

SEC. The molecular weight (M_n) and molecular weight distribution (PDI) of the samples were measured by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 30 °C. The measurements were performed using a Viscotek TDA-302 SEC (Viscotek Co., Houston, TX, USA), equipped with tetra detectors [refractive index (RI), UV, viscosity (VISC), and two-angle laser light scattering (7° and 90° , laser wavelength, $\lambda = 670$ nm)]. And the molecular weight was determined by light

scattering. PS sample (Viscotek Co.) with a stated peak molecular weight of 99,500 g mol⁻¹ and a PDI of 1.03 was used to calibrate the instrument. The value of dn/dc and intrinsic viscosity of this standard are 0.185 and 0.477 dL g⁻¹, respectively. Two Viscogel-mixed bed columns (GMMXL, GMLXL, with a linear range of molecular weights from 10³ to 10⁷ g mol⁻¹) were employed; THF was used as the mobile phase at a flow rate of 1.0 mL min⁻¹, and the column temperature was 30 °C. The samples were dissolved in THF with the sample concentrations of 2.0–3.0 mg mL⁻¹, and 100 μ L of such solution was injected to start data collection. The data obtained were analyzed using OmniSEC software version 4.5 (Viscotek Co.).

NMR. The polymers were analyzed by ¹H NMR and ¹³C NMR spectroscopy on a Varian Inova (USA) 400 MHz NMR spectrometer in CDCl₃ at ambient temperature at a concentration of 4% w/v (for ¹H NMR) and 15% w/v (for ¹³C NMR), respectively. The chemical shifts were recorded as δ values (ppm) relative to internal tetramethylsilane (TMS) in CDCl₃.

Results and discussion

The synthesis of the symmetrical triblock copolymers

Polyisoprene-*block*-high-*trans*-1,4-polybutadiene-*block*-polyisoprene (PI-*b*-HTPB -*b*-PI, simplified as IBI) with different PI mass fractions (x_I) was synthesized. The results are shown in Table 1. Polystyrene-*block*-high-*trans*-1,4-polybutadiene-*block*-polystyrene (PS-*b*-HTPB-*b*-PS, simplified as SBS) with different PS mass fractions (x_S) was synthesized. The results are shown in Table 2.

Figure 1 shows the SEC traces of HTPB-1, IBI-5, HTPB-2, and SBS-5. From Fig. 1, we can conclude that well-defined symmetrical triblock copolymers were obtained.

The x_I was designed at 10, 20, 30, 40, and 50 wt%, and the value was determined by ¹H NMR [22] and SEC, respectively. The x_S was designed at 10, 20, 30, 40, and

Table 1 Characterization of symmetrical triblock copolymers IBI

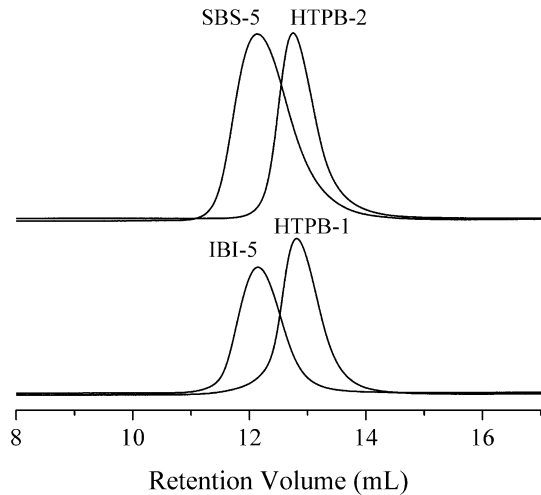
Sample	x_I/x_B (%/%) ^a	$M_n/10^4$	$M_w/10^4$	PDI	Microstructures of Bd units (%) ^b			Microstructures of Ip units (%) ^b	
					<i>trans</i> -1,4	1,2-	<i>cis</i> -1,4	1,4-	3,4-
HTPB-1	0/100	5.6	7.0	1.25	82.2	6.9	10.9	–	–
IBI-1	12/88	6.1	8.1	1.32	83.1	7.2	9.7	77.7	22.3
IBI-2	19/81	6.7	9.1	1.36	79.2	6.9	13.9	75.7	24.3
IBI-3	30/70	7.8	11.2	1.44	77.8	9.8	12.4	80.2	19.8
IBI-4	42/58	8.9	13.9	1.56	81.3	7.8	10.9	72.8	27.2
IBI-5	51/49	11.2	18.5	1.65	79.8	8.2	12.0	73.2	26.8

^a Determined by ¹H NMR

^b Determined by IR

Table 2 Characterization of symmetrical triblock copolymers SBS

Sample	x_S/x_B (%/%) ^a	$M_n/10^4$	$M_w/10^4$	PDI	Microstructures of Bd units (%) ^b		
					<i>trans</i> -1,4	1,2-	<i>cis</i> -1,4
HTPB-2	0/100	5.4	7.0	1.30	82.1	7.6	10.3
SBS-1	11/89	5.9	8.0	1.36	79.2	8.1	12.7
SBS-2	21/79	6.9	9.8	1.42	80.0	7.9	12.1
SBS-3	29/71	8.1	12.2	1.50	76.5	8.2	15.3
SBS-4	39/61	9.3	15.4	1.66	79.2	9.2	11.6
SBS-5	48/52	11.9	20.9	1.76	77.3	10.2	12.5

^a Determined by IR^b Determined by IR**Fig. 1** SEC traces of HTPB-1, IBI-5, HTPB-2, and SBS-5

50 wt%, and the value was determined by IR [30] and SEC, respectively. According to Canto [30], the value determined by SEC was calculated based on Eq. 1.

$$x_S = \frac{M_n^{\text{SBS}} - M_n^{\text{HTPB}}}{M_n^{\text{SBS}}} \times 100\%$$

$$x_I = \frac{M_n^{\text{IBI}} - M_n^{\text{HTPB}}}{M_n^{\text{IBI}}} \times 100\%$$
(1)

Figure 2 shows the comparison of the values of x_I (or x_S) determined by ¹H NMR (or IR for x_S) and SEC. The values of x_I determined by ¹H NMR are bigger than that determined by SEC, but the values of the two methods agree well with each other. The values of x_S (except sample SBS-1) determined by IR are smaller than that determined by SEC; however, the values of the two methods coincide well with each other.

The IR spectra of typical IBI and SBS, as well as that of the starting homopolymer HTPB are presented in Fig. 3. The absorption peaks in copolymers

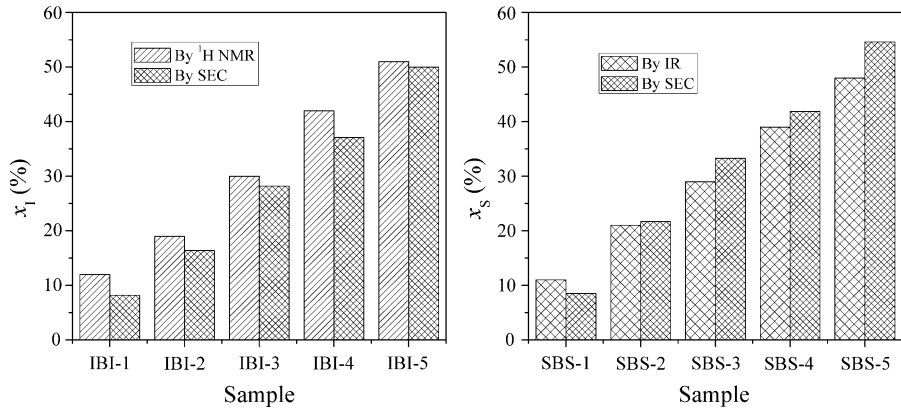


Fig. 2 Comparison of the values of x_1 (or x_s) determined by $^1\text{H NMR}$ (or IR for x_s) and SEC

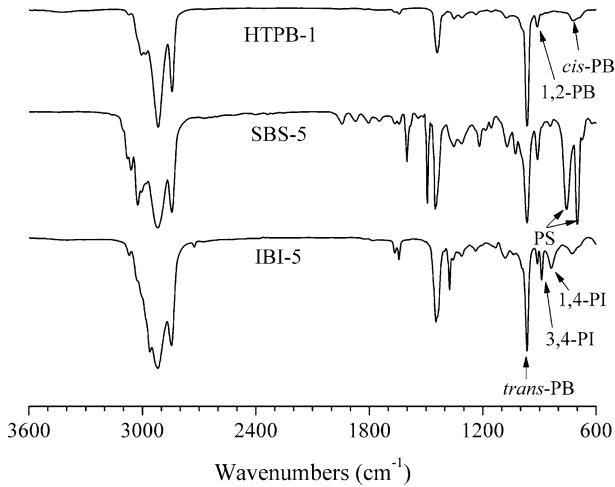


Fig. 3 IR spectra of HTPB-1, SBS-5, and IBI-5

spectra are the combination of those of the two corresponding components in them. As marked in Fig. 3, the bands at 740, 911, and 966 cm^{-1} represent *cis*-1,4, 1,2, and *trans*-1,4 of Bd units, respectively, the bands at 840 and 889 cm^{-1} represent 1,4 and 3,4 of Ip units, respectively, and the bands at 699 and 750 cm^{-1} represent St units. As shown in Fig. 3, the relative peak intensity of *trans*-PB is high in all polymers, which indicates high content of *trans*-PB. As in SBS, the absorption at 966 cm^{-1} could be used to analyze x_s because the contents of *trans*-PB of different types of SBS are very close [30] (Table 2).

The $^1\text{H NMR}$ spectra of typical IBI and SBS as well as that of the starting homopolymer HTPB are presented in Fig. 4. As shown in Fig. 4, the peaks

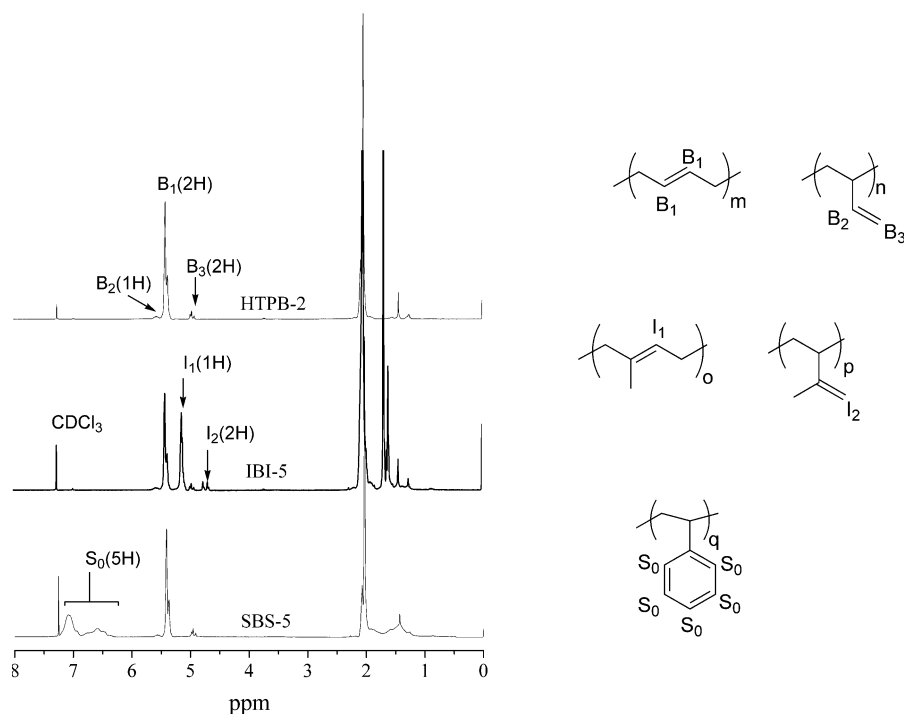


Fig. 4 ^1H NMR spectra of HTPB-2, SBS-5, and IBI-5

appearing at 4.85–4.98 ppm indicate the few content of 1,2-Bd units, and the peaks appearing at 5.35–5.41 ppm indicate the high content of 1,4-Bd units. The chemical composition of IBI was determined by ^1H NMR. The absent peak at 5.70 ppm which represent 1,2-*I*_p units indicates that IBI dose not contain any 1,2-*I*_p units. The peaks at 4.60–4.80 and 5.00–5.20 ppm represent 3,4-*I*_p and 1,4-*I*_p units, respectively. Judging from the intensity ratio of the olefinic protons, we estimated that the sample IBI-5 contained about 51 wt% *I*_p units and 49 wt% Bd units. It can conclude from Fig. 4 that the appearance of the peaks at 6.50 and 7.10 ppm indicates the block nature of SBS [31].

The ^{13}C NMR spectrum (olefinic region) of typical SBS is presented in Fig. 5. The observation of the weak peaks at 114.6 and 143.0 ppm indicates that the polymer contains low 1,2-Bd units [32, 33]. However, the peaks (at 129.5 and 130.2 ppm) assigned to *cis*-PB and *trans*-PB are predominantly observed, and the intensity of *trans*-PB is much larger than that of *cis*-PB, which represents high *trans*-1,4 content. The pentad aromatic carbon derived from the aromatic ring is an asymmetric carbon and is sensitive to the monomer insertion in the macromolecular chains. Three main peaks with small peaks and shoulders are seen in Fig. 5. The assignments of the pentad sequences as shown in Fig. 5 very nearly obey Bernoullian statistics [34]. It is clear to identify the sample SBS-5 as an *atactic* PS (*ata*-PS) according to Fig. 5.

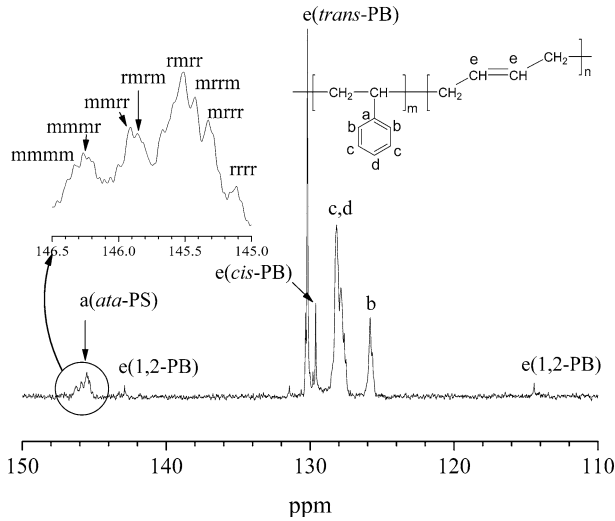


Fig. 5 ¹³C NMR spectrum (olefinic region) of SBS-5

Basic thermal behavior

The thermal behaviors of IBI block copolymers and corresponding homopolymer HTPB are shown in Fig. 6 and Table 3. The molecular mobility can be well characterized by the position of glass transition temperature (T_g) of the components. It is obvious that a significant shift of T_g of IBI toward higher temperature occurs in the order IBI-1 → IBI-2 → IBI-3 → IBI-3 → IBI-5. Generally, the main factors affecting the values of T_g are molecular weight and polymer structure [35]. In our

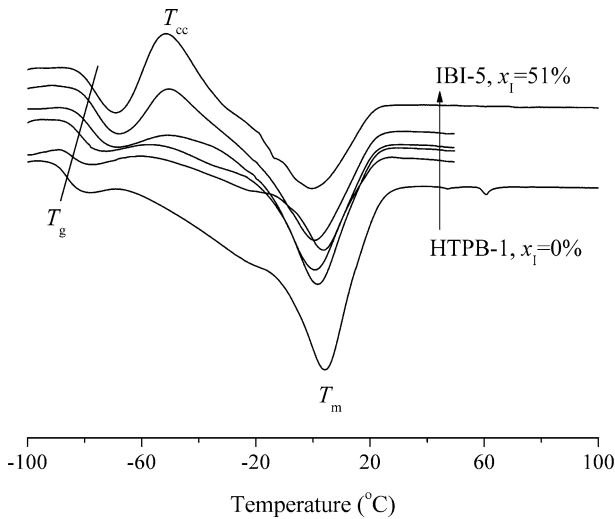


Fig. 6 DSC curves of IBI block copolymers

Table 3 DSC results of IBI block copolymers

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)
HTPB-1	-85.2	-	3.0
IBI-1	-83.7	-	6.0
IBI-2	-81.2	-	2.9
IBI-3	-79.5	Ambiguous	2.9
IBI-4	-77.2	-49.8	2.7
IBI-5	-75.5	-50.0	2.7

case, the molecular weight of IBI is far above $10,000 \text{ g mol}^{-1}$ where the molecular weight has only a negligible influence on the position of T_g . Therefore, the clarification of the shifting of T_g should be found in the difference of interfacial structures. The components tend to phase miscible because of the thermodynamic compatibility (solubility parameter $\delta_{PB} = 8.38$ and $\delta_{PI} = 8.35 \text{ (cal cm}^{-3})^{0.5}$) [36]. Due to the irregular structures at the interface, a part of PB segments is seriously restricted in mobility and hence as flexible components only at elevated temperatures. The shift of the glass transition should be explained by an increased amount of PI segments (higher T_g than that of PB segments) that are 'dissolved' in the PB matrix [37].

The melting temperature (T_m) of HTPB-1 is observed at about $3 \text{ }^\circ\text{C}$, which indicates the crystallization of the polymer. An exothermic peak corresponding to cold crystallization (T_{cc}) is observed above T_g when x_1 is bigger enough. It has been reported that high *cis*-PB (more than 95% *cis*-1,4 content) exhibited cold crystallization [38, 39]. Crystallization of a polymer in its melt state involves transport and rearrangement of entangled chains in the vicinity of the crystal front. The strong tendency of induced nucleation might be related to the strain of entangled chains at the crystal front in a manner similar to strain-induced crystallization of cross-linked rubber [38]. Therefore, the cold crystallization peaks are introduced by the entanglement of crystallizable HTPB segments and soft PI segments. When the sample is quenched, there is not enough time for the crystallizable chain to reorganize. After being heated above T_g , the sample exhibits rubbery and the frozen chains become free. The crystallizable HTPB segments become crystal because of being induced by soft PI (with x_1 bigger enough) to reorganize into regular structure. The soft PI segments promote the segmental motion of crystallizable HTPB segments.

The thermal behaviors of SBS block copolymers and corresponding homopolymer HTPB are shown in Fig. 7 and Table 4. As shown in Fig. 7, the glass transition temperature of PB phase ($T_{g,B}$) remains unchanged, while it appears ambiguous as the x_S increased. It is obvious that the glass transition temperature of PS phase ($T_{g,S}$) appears when x_S is bigger than 29% (sample SBS-3, SBS-4, and SBS-5). A significant shift of $T_{g,S}$ toward higher temperature occurs in the sequence SBS-3 \rightarrow SBS-4 \rightarrow SBS-5. The components tend to phase separate because of the thermodynamic incompatibility (solubility parameter $\delta_{PB} = 8.38$ and $\delta_{PS} = 9.10 \text{ (cal cm}^{-3})^{0.5}$) [36]. The shift of $T_{g,S}$ toward lower temperature is due to the increasing intermixing of soft PB segments into the PS domains.

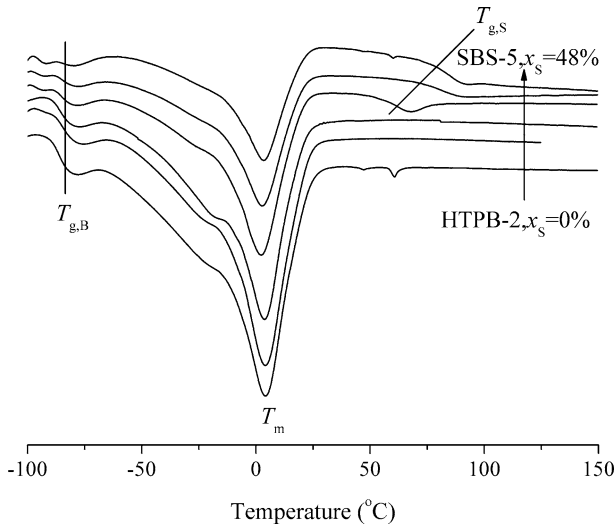


Fig. 7 DSC curves of SBS block copolymers

Table 4 DSC results of SBS block copolymers

Sample	$T_{g,B}$ (°C)	$T_{g,S}$ (°C)	T_m (°C)
HTPB-2	-84.9	–	4.6
SBS-1	-83.7	–	4.5
SBS-2	-85.4	–	4.7
SBS-3	-85.1	62.0	4.2
SBS-4	-84.7	75.2	4.5
SBS-5	-85.0	84.1	4.4

In addition, no cold crystallization is observed in SBS in Fig. 7. The absence of cold crystallization in SBS can be explained as the reason for the formation of cold crystallization in IBI. When the hard PS segments are used instead of soft PI segments, the crystallizable HTPB segments are seriously restricted in mobility and hence can not reorganize to regular structure.

Conclusion

The sequential anionic copolymerization of Bd and Ip (or St) was achieved with ternary initiation system BaDEGEE/TIBA/DLi to give *trans*-1,4-Bd units, medium 3,4-*Ip* units, and *ata*-PS units. Since soft PI segments could promote the mobility of crystallizable *trans*-PB segments, the cold crystallization was observed in IBI. However, there was no cold crystallization in SBS because the hard PS segments could not induce the *trans*-PB segments to crystallize. The thermodynamic incompatibility of PB and PS segments made SBS tend to phase separate. In

contrary, the thermodynamic compatibility of PB and PI segments made IBI tend to phase miscible.

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