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A New Approach to Styrenic Thermoplastic Elastomers: Synthesis and Characterization of Crystalline Styrene−Butadiene−Styrene Triblock Copolymers[†]

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ABSTRACT: Crystalline styrene−butadiene−styrene (SBS) triblock copolymers consisting of elastic *cis*-polybutadiene (*cis*-PB) chemically bonded with crystallizable syndiotactic polystyrene (*syn*-PS) were synthesized through a stereospecific sequential triblock copolymerization of S with B catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3$/trioctylaluminum ($Al(oct)_3$) under controllable polymerization conditions. The first polymerization step was conducted at −25 °C, yielding *syn*-PS with controllable molecular weight by changing the polymerization time. The second one was started with the addition of excess B to the progressing *syn*-PS polymerization at −40 °C, yielding *syn*-PS/*cis*-PB diblock copolymer with high block efficiencies. The third one was conducted at −25 °C just by removal of the unreacted B in order to enhance the reinsertion and propagation of the remained S, yielding crystalline SBS triblock copolymers with relatively high PS compositions. The livingness of the whole polymerization process was confirmed through a linear increase of the molecular weights of the polymer products obtained in each step against their polymer yields, while keeping the polydispersity values almost constant. The ^{13}C NMR analysis of the copolymer product proves that the PS blocks were highly syndiotactic ([rrrr] > 95%), and the PB block was primarily *cis*-1,4 structure (>70%). Cross-fractionation chromatography (CFC) was used to evaluate the contamination of the dead polymers in the crystalline SBS. Transmission electronic microscopy (TEM) was used to observe the phased separation morphology of the PS and PB blocks in the crystalline SBS. The existence of the *syn*-PS blocks in the crystalline SBS was further confirmed with the observation of a strong endothermic peak at 272 °C in their differential scanning calorimetry (DSC) curves. Preliminary results on the heat deformation stability as well as the chemical resistance property of this new material have also been evaluated in comparison with those of the corresponding anionic SBS materials.

Introduction

The styrene−butadiene−styrene (SBS) triblock copolymer, which has been commercially produced via a living anionic polymerization technology, is one of the most productive and important thermoplastic elastomers (TPE).[1,2] Despite many advantages on the precise control of the copolymer composition and functionality, the alkyllithium reagent in the anionic polymerization is still far less effective in controlling the stereoregularity of either polystyrene (PS) or polybutadiene (PB) blocks. Actually, the lack of stereoregular PS and PB in the anionic SBS material caused some defections on its chemical and mechanical properties. For instance, the tensile strength of the anionic SBS is remarkably decreased at elevated temperatures and loses completely at the glass transition temperature (T_g) of the PS (ca. 100 °C) because of the softening of the glassy PS domains, which serve as physical cross-linking sites in these materials.[3] Accordingly, the current application of the anionic SBS has been limited by the glass transition temperature of the PS blocks. To solve this problem, significant efforts have been paid to increase the glass transition temperature of the glassy PS domains in the anionic SBS using vinylaromatic monomers like poly(*tert*-butylstyrene) or poly(α-methylstyrene), which possess higher T_g values (130 and 165 °C, respectively), in place of PS.[4] On the other hand, a partial hydrogenation of the unsaturated unit in the PB block is also found to enhance their thermal stability as well as the oxidation resistance.[5]

A recent achievement on the stereospecific coordination polymerization of S and B with transition metal catalysts has offered unique possibilities to control the stereoregularity of the PS and the PB blocks in their copolymer products.[6] Zambelli and co-workers have recently reported that stereoregular styrene/butadiene (SB) copolymer consisting of *syn*-PS blocks and *cis*-PB blocks could be obtained with $CpTiX_3$ ($Cp = C_5H_5, C_5Me_5$; $X = Cl, F, Me$) activated with methylaluminoxane (MAO).[7a] This new material should exhibit more thermal stability, harder phase-separated styrenic domains, and improved mechanical and processing properties in comparison with that of copolymer with atactic PS (*ata*-PS) blocks.[7c] However, because of the lack of S and B livingness in these copolymerization systems, it was

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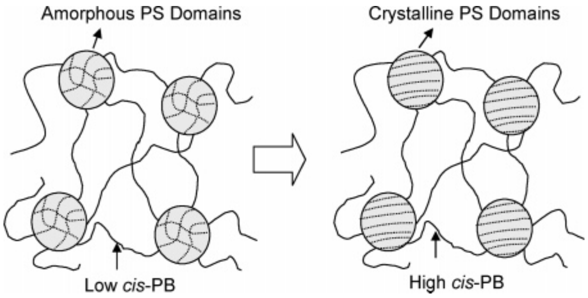
Scheme 1. A New Approach to the Styrenic Thermoplastic Elastomers: Introduction of Crystalline Phases to the Amorphous SBS Materials



difficult to control precisely the copolymer molecular weights as well as their sequence distributions.

We have considered that the introduction of the crystalline PS, i.e., *syn*-PS or isotactic-PS (*iso*-PS), and the elastic *cis*-PB blocks in place of the amorphous PS domains and the low *cis*-PB matrix in the anionic SBS material would strengthen its tensile strength and oil and chemical resistances even at elevated temperatures (Scheme 1).[8]

This new approach, however, cannot be realized unless we could develop a polymerization technique that is able to control spontaneously the stereoselectivity and the livingness of the S and B in their copolymerization systems. In fact, we have succeeded in the development of the stereospecific living polymerization of widely used vinyl monomers such as olefins, diolefins, and styrene with transition metal catalyses.[9] Recently, we have found that highly stereoregular S and B diblock copolymers consisting of crystalline *syn*-PS and elastic *cis*-PB blocks can be obtained with the half-titanocene catalysts under stereospecific and living polymerization conditions.[10] These achievements prompted us to expand the technique for the preparation of the stereoregular SBS triblock copolymer, which has not been available with the current polymerization technologies. This article thus reports our original method to prepare the crystalline SBS triblock copolymer consisting of elastic *cis*-PB block chemically bonded with crystalline *syn*-PS blocks through a stereospecific sequential triblock copolymerization of S with B catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3$/trioctylaluminum (Al(oct)$_3$). Detailed characterizations on the copolymerization products have been carried out by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), cross-fraction chromatography (CFC), transmission electronic microscopy (TEM), and polarized optical microscopy (POM). Attempts to evaluate the heat deformation stability and the chemical resistance property of this new material in comparison with those of the anionic SBS have also been discussed in detail.

Experiment

Materials. $C_5Me_5TiMe_3$ purchased from STREM Chemical Co., solution of $B(C_6F_5)_3$ (3% in Isopar-E), and Al(oct)$_3$ purchased from Tosoh-Finechem Corp., Japan, were used without further treatment. Styrene (S) from Kanto Chem. Co., Japan, was distilled over CaH_2 under a reduced pressure prior to use. 1,3-Butadiene (B) donated by Zeon Corp., Japan (>99.5% pure), was distilled from the container, dried by passing it through a column packed with molecular sieves, and distilled again over CaH_2 before use. Toluene (from Kanto Chem. Co., Japan) was refluxed over sodium/benzophenone for 12 h and distilled prior to use.

Polymerization Procedure. All the operations were conducted under a dried and high-grade argon atmosphere. The sequential triblock copolymerization of S with B was conducted in a 300 mL pressure-resistant glass ampule, equipped with a rubber septum, via three steps with toluene as solvent. A typical polymerization run was carried out as follows: measured amounts of toluene (200 mL), Al(oct)$_3$ (0.1 mmol), toluene solution of $C_5Me_5TiMe_3$ (0.1 mmol), and $B(C_6F_5)_3$ (0.1 mmol) were introduced into the ampule in this order at room temperature. The reaction mixture was aged at −25 °C for 1 h in the presence of 0.1 mmol of S. Polymerization was started by adding a toluene solution of S (17.2 mmol) equilibrated at −25 °C. After 1 h of polymerization, the ampule was transferred to a methanol bath that precooled at −40 °C, and a small amount of polymer solution was sampled out for characterizations (conversion, molecular weight, and its distribution). A toluene solution of B (90 mmol) precooled at −40 °C was rapidly added into the ampule. After 6 h of polymerization, a small amount of polymer solution was sampled out for characterizations (B conversion, molecular weight, and its distribution of the SB diblock copolymer), followed by a complete removal of the unreacted B via a vigorous bubbling of dried and high-grade argon into the polymer solution for 10 min. The copolymerization reaction was continued at −25 °C for an additional 8 h without adding any fresh S monomer. Polymerization was then terminated by the addition of a small amount of acidic methanol. The resulting polymer solution was precipitated into a large amount of the acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as an antioxidant reagent, followed by drying at 60 °C for 12 h under reduced pressure. The obtaining copolymer was then extracted with tetrahydrofuran (THF) at room temperature for 12 h to remove all the amorphous copolymer byproducts. Both the THF-soluble and -insoluble parts were brought into further characterizations.

Polymer Characterization. The weight-average molecular weights (M_w) and the molar mass distributions [MMD; weight-average molecular weight/number-average molecular weight (M_w/M_n)] of the polymer were determined by gel permeation chromatography (GPC) systems: (1) a Tosoh HLC-8120 operated at 40 °C in THF for the characterization of the amorphous polymers and (2) a Tosoh HLC-8121 operated at 135 °C in *o*-dichlorobenzene (*o*-DCB) for the characterization of the crystalline copolymer. Both systems used standard PS for calibration. The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA600 spectrometer operated at 600 MHz for ^1H and 150 MHz for ^{13}C at 50 °C in 1,1,2,2-$C_2D_2Cl_4$. The solvent peak appearing at 5.95 ppm was used as an internal reference. Melting temperature (T_m) and heat of fusion (ΔH) of the copolymer were measured by differential scanning calorimetry (DSC, Mac Science DSC-3200S) at the heating and cooling rates of 10 °C/min under a nitrogen atmosphere. The crystalline distribution of the copolymer was obtained by a cross-fractionation chromatograph (CFC T-150A Mitsubishi Petrochemical Co., Japan) operated at 140 °C with *o*-DCB as an extraction solvent. A polymer solution (0.38 wt %) in *o*-DCB was loaded onto a glass bead packed column at 140 °C. The column was then cooled to 0 °C at a slow cooling rate (8.4 °C/h), followed by stepwise elution from the column at 0, 10, 20, 30, 40, 50, 60, 70, 80, 85, 99, 100, 105, 110, 120, 130, and 140 °C at a flow rate of 1 mL/min. The polymer solution eluted at each temperature was automatically sent to a GPC section (Shodex AD-806NS, Showa Denko K.K., Japan) of the CFC system equipped with an infrared (RI) detector. Polarized light microscopy (Linkam L-600A, Linkam LTS-350) was used to monitor the surface deformation stability of the triblock copolymer against rising temperatures from 20 to 200 °C with a heating rate of 10 °C/min. Transmission electron microscopy (TEM, Hitachi H-7000, 75 kV) was used to image the morphology of the copolymer samples, which were prepared by a hot casting from its xylene solution (3 wt %) on Teflon sheets. The solvent was freely evaporated over 3 days, followed by vacuum-drying at 60 °C for a week. The amorphous PB phase of the ultrathin sections (ca. 50−70 nm thick) was selectively stained with osmium tetraoxide (OsO_4) prior to operation.

Results and Discussion

Synthesis of the Crystalline SBS Triblock Copolymers. Table 1 shows the result of the stereospecific sequential triblock

Table 1. Results of the Stereospecific Sequential Triblock Copolymerization of S with B Catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$

run[a]	F_{ST}[b] (mmol)	F_{BD}[c] (mmol)	polym temp (°C)	polym time (h)	yield[d] (wt %)	$10^{-4}M_n$[e]	M_w/M_n[e]
1_1	17.2		−25	1	14	18.9	1.41
1_2		90	−40	6	10	23.4	1.41
1_3			−25	8	12	29.1	1.38
2_1	9.6		−25	0.5	8	5.6	1.48
2_2		83	−40	3	7	14.4	1.45
2_3			−25	8	6	20.2	1.52

[a] Polymerization conditions: 300 mL pressure-resistant glass ampule, toluene = 200 mL. 1_1, 1_2, and 1_3 correspond to the first, second, and third polymerization steps. $[C_5Me_5TiMe_3] = [B(C_6F_5)_3] = [Al(oct)_3] = 0.1$ mmol. [b] F_{ST} = styrene content in feed. [c] F_{BD} = butadiene content in feed. [d] Yield corresponds to each polymerization step. [e] M_n and M_w/M_n values of THF-insoluble parts determined by GPC operated at 135 °C in *o*-dichlorobenzene and calibrated with polystyrene standards.

Table 2. Results of the S and B Copolymerization Catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$

run[a]	F_{ST}[b] (mol %)	F_{BD}[c] (mol %)	polym time (h)	yield[d] (wt %)	f_{ST}[e]	f_{BD}[f]
1	95	5	12	1.2	14	86
2	90	10	12	1.3	5	95
3	80	20	12	1.5	2	98
4	70	30	8	3.3	0.5	99.5
5	50	50	8	6.6	trace	100
6	25	75	8	8.9	0	100

[a] Polymerization conditions: 300 mL pressure-resistant glass ampule, toluene = 200 mL. $[C_5Me_5TiMe_3] = [B(C_6F_5)_3] = [Al(oct)_3] = 0.1$ mmol, $T_p = -25$ °C. [b] F_{ST} = styrene content in feed. [c] F_{BD} = butadiene content in feed. [d] Yield corresponds to styrene and butadiene monomer feeds. [e] f_{ST} = styrene content in copolymer determined by the ^{1}H NMR spectrum. [f] f_{BD} = butadiene content in copolymer determined by the ^{1}H NMR spectrum.

copolymerization of S with B catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$.

The first step was conducted at −25 °C, yielding *syn*-PS with controllable molecular weight and relatively narrow molar mass distribution ($M_w/M_n < 1.50$, runs1_1 and 2_1). Generally speaking, in a sequential monomer addition for preparation of the ABA-type triblock copolymer, B is added after the full conversion of A. However, we realized that the full conversion of S in the first polymerization step promptly led to the precipitation of the crystalline *syn*-PS, which in turn damages the homogeneity and the livingness of the whole polymerization system. In fact, *syn*-PS with broader molar mass distributions ($M_w/M_n > 1.8$) was produced if S is fully consumed. The second step was thus started with the addition of B to the progressing *syn*-PS polymerization at −40 °C to achieve the livingness of the cis-specific B copolymerization.[10b] Since we should confirm the efficiency of the B cross propagation reaction toward the styrenic-end active species, a series of S polymerizations were then carried out at −25 °C in the presence of various amounts of B under similar polymerization conditions (Table 2).

By characterization of the copolymer products with a ^{1}H NMR spectrometer, we found that the content of PS in the copolymer is rapidly decreased from 100 to 14 mol % with the addition of only 5 mol % B in the feed. When the content of B in the feed reaches to 75 mol %, only PB was produced regardless the existence of the S in the polymerization system. This result suggested that the addition of the excess B to the progressing S polymerization catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$ led to the selective propagation of the B from the styrenic-end active species, yielding *syn*-PS/*cis*-PB diblock copolymer with a high block efficiency.[10b]

It is well established that in order to synthesize the anionic SBS from its corresponding diblock precursor, one can use a coupling reagent or a further addition of the S monomer. However, these techniques show far less effective for the preparation of the crystalline SBS with titanium-based transition metal catalysts because of the weaker coordination and much slower cross-propagation of the S to the butadienic-end active species.[7a] However, we have found that the rate of the styrene cross-propagation reaction to the butadienic-end active species could be dramatically enhanced when all the unreacted B monomers are completely removed out of the system.[10a] Taking these factors into account, the third polymerization step was conducted at −25 °C without adding any fresh S, in conjunction with a complete removal of the remaining B via a vigorous babbling of dried and high-grade argon into the polymer solution. The copolymers thus obtained were then extracted with tetrahydrofuran (THF) at room temperature for separation of the amorphous and the crystalline parts. The weight of the THF-soluble (amorphous) parts, which might contain the stereoirregular S and B homo- or copolymers, varied from 10 to 20 wt % depending on the polymerization times. However, the ^{1}H and ^{13}C NMR analyses of the THF-soluble parts indicated that they contain only *cis*-PB, which might be formed in the second polymerization step as a byproduct. On the other hand, the THF-insoluble (crystalline) parts would contain the target crystalline SBS triblock copolymer and some dead polymers like *syn*-PS or *syn*-PS/*cis*-PB diblock copolymer and therefore need a further characterization.

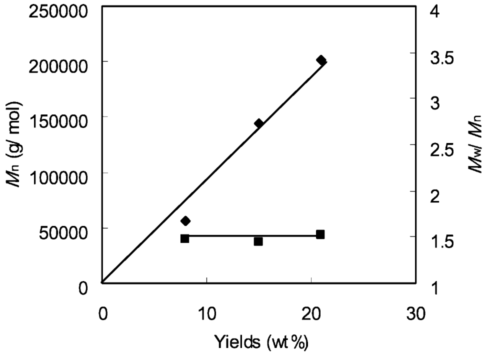


Figure 1. Plots of M_n and M_w/M_n vs polymer yields (run 2, Table 1).

To evaluate the livingness of this polymerization system, we plot the correlation between the number-average molecular weight (M_n) and the molar mass distribution (M_w/M_n) of the THF-insoluble samples obtained in each step (run 2, Table 1) vs their polymer yields.

It is apparent from Figure 1 that the M_n values increased proportionally with the polymer yields, while keeping the M_w/M_n values almost constant. In addition, the molar mass distribution (MMD) curves of these samples shifted to the higher molecular weight regions with an increase in the polymerization time while the unimodal shape was maintained, and no shoulder peak or no low molecular weight tail was detected during the course of the polymerization (Figure 2).

These results clearly indicated that the sequential triblock copolymerization of S with B catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$ proceeded with high block efficiencies, i.e.,

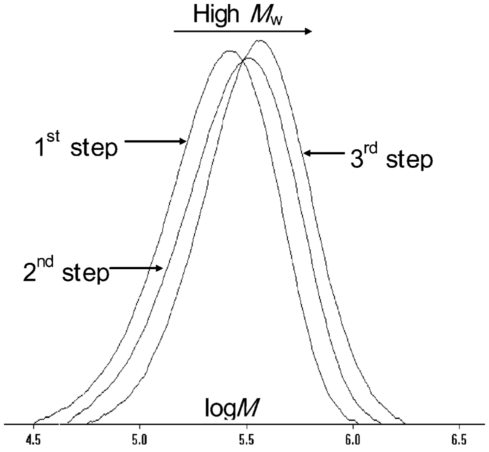


Figure 2. Representative molar mass distribution curves of the polymers obtained in the first, second, and third polymerization steps (run 2, Table 1).

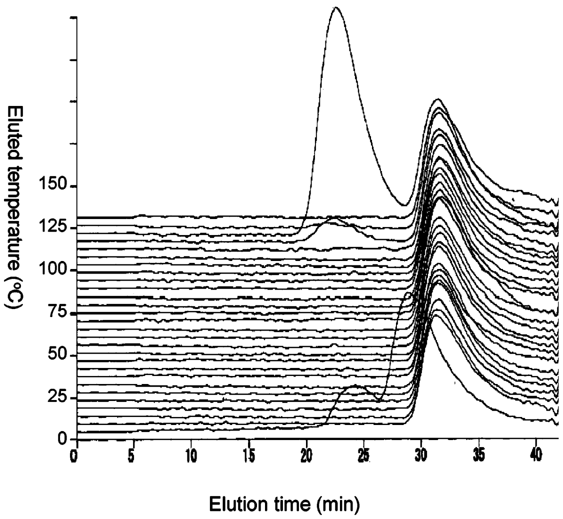


Figure 3. CFC curves of the THF-insoluble part (run 1, Table 1).

from S block to B block and B block to S block, under a living polymerization condition.

As mentioned above, it is necessary to confirm the contamination of the dead polymers, which might be contaminated in the crystalline SBS triblock copolymer. The THF-insoluble parts were, therefore, further fractionated with boiling toluene for 8 h. The result was, however, not sufficient because of both the main and the contaminated products show almost identical solubilities. In this case, cross-fractionation chromatography (CFC) seems to be the best method for the detection and the separation of the dead polymers from the target crystalline SBS triblock copolymer according to their differences in the crystalline distribution.[11]

In Figure 3 is shown a typical CFC curve of the THF-insoluble part obtained in run 1 (Table 1), which was recorded at various temperatures ranging from 0 to 140 °C. Judging from a narrow crystalline distribution of the CFC curve with a narrow molar mass distribution, we conclude that the contamination of the dead polymers in the crystalline SBS was negligible.

Polymer Microstructures and Chemical Compositions. The achievement of the S and B stereospecific living copolymerization with transition metal catalysts gave us unique possibilities to control not only the stereoregularity of either PS or PB blocks but also their block lengths and distributions. The THF-insoluble part obtained in run 2 (Table 1) was then selected for the detail characterization of the copolymer microstructure as well as its chemical composition. While the former can be estimated from the ^{13}C NMR analysis, the latter can be determined from the ^{1}H NMR characterization.

As shown in Figure 4, the peaks appearing at 6.5−7.1 ppm indicated the presence of phenyl protons in the S units. The peaks appearing at 4.9−5.6 ppm confirmed the presence of olefinic protons in the B units. Judging from the intensity ratio of the phenyl and the olefinic protons, we estimate that this sample contained about 84.5 mol % PS and 15.5 mol % PB. On the other hand, the ^{13}C NMR spectrum of the THF-insoluble part obtained in run 2 (Table 1) is shown in Figure 5. The strong and sharp peaks appearing at 27.5 and 145.6 ppm indicated that the stereoregularity of the PS blocks are highly syndiotactic ([rrrr] > 95%)[12] and the PB blocks primarily *cis*-1,4 structure (>70%).[13] Attempts to observe direct evidence for the linkage carbons between the *syn*-PS and the *cis*-PB have been tried out through a detail ^{13}C NMR characterization of the copolymer samples with various concentrations and acquisition times. Because of the relatively high molecular weights of these samples, such a carbon signal could not be observed.

Thermal Characteristics and Chemical Resistance Properties. The thermal property of the crystalline SBS was investigated by differential scanning calorimetry (DSC) analysis.

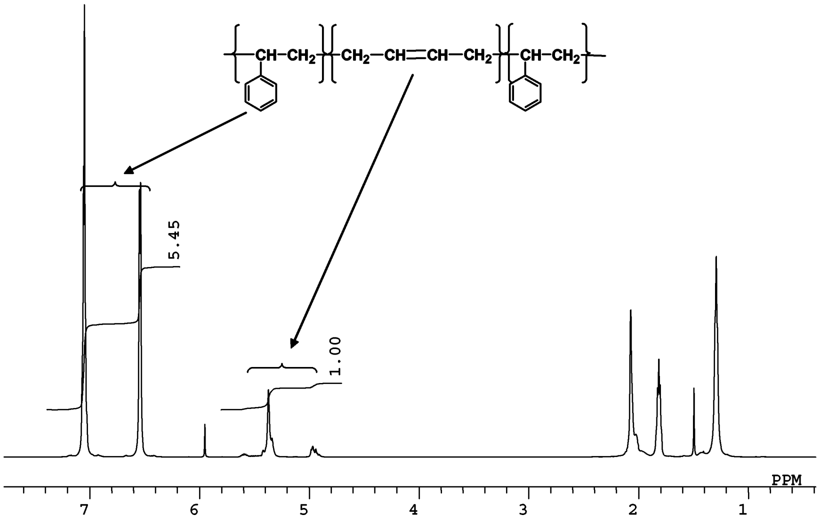


Figure 4. ^{1}H NMR spectrum (1,1,2,2-$C_2D_2Cl_4$) of the THF-insoluble part (run 2, Table 1).

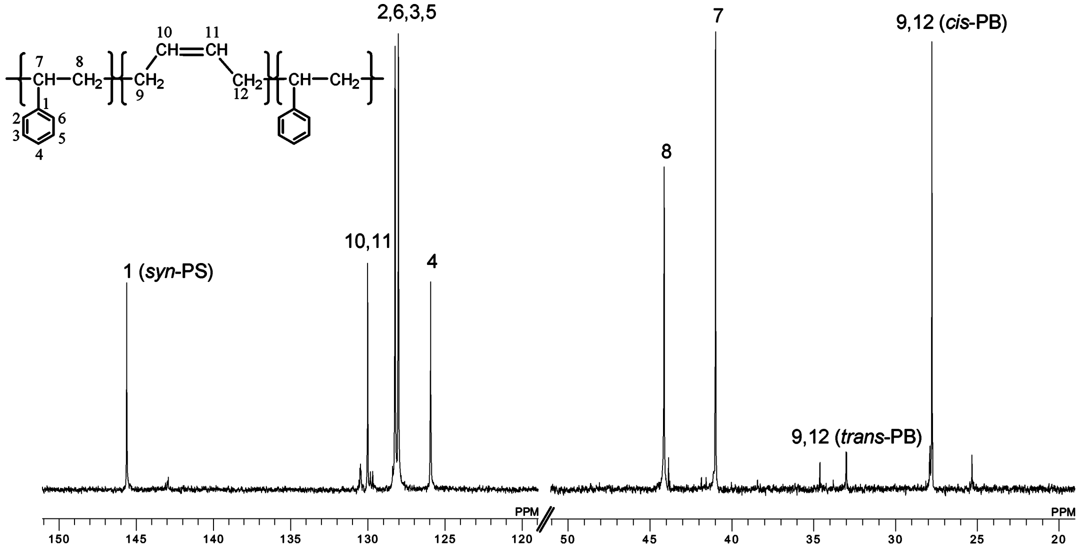


Figure 5. ^{13}C NMR spectrum (1,1,2,2-$C_2D_2Cl_4$) of the THF-insoluble part (run 2, Table 1).

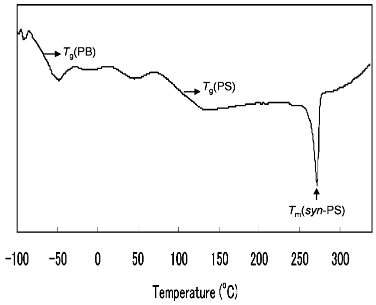


Figure 6. DSC curve of the THF-insoluble part (run 2, Table 1).

A typical DSC curve of the THF-insoluble sample obtained in run 2 (Table 1) is shown in Figure 6.

There are two separated glass transition temperatures T_{g-1} and T_{g-2} that appear clearly at −70 and 100 °C, which correspond to the T_gs of the PB and the PS blocks. The relatively high T_g value of the PB segments would be correlated with the high content of the 1,2-vinyl PB (ca. 20 mol %) obtained with this catalyst.[14] In addition, a strong exothermic peak appeared at 272 °C with a ΔH value about 3.48 kJ mol^{-1}, which should be attributed to the melting of the crystallizable *syn*-PS blocks.[15] According to the GPC, NMR, CFC, and DSC characterization results, we conclude that the THF-insoluble part obtaining in this S and B sequential triblock copolymerization was the target crystalline SBS triblock copolymer without contaminating of any detectable dead polymers.

In an attempt to evaluate the heat stability of the crystalline SBS, we monitor the deformation process of these samples against temperature rising from 20 to 200 °C with a heating rate 10 °C/min using a polarized optical microscopy (POM, Figure 7a). For comparison, the POM image of the anionic SBS that collected under similar conditions is also displayed (Figure 7b).

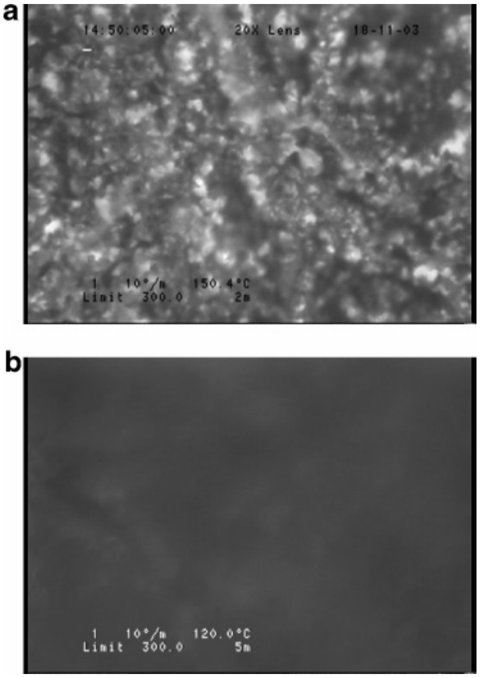


Figure 7. (a) POM picture of the crystalline SBS recorded at 150 °C. (b) POM picture of the anionic SBS recorded at 120 °C.

Contrary to the anionic SBS, where the transmitted light completely disappeared at 120 °C due to the softening of the glassy PS domains, the transmitted light of the crystalline SBS still remained visible up to 150 °C. This result indicated that the PS domains in the crystalline SBS are still stable even at temperatures higher than PS's T_g. In addition, the chemical resistance of the crystalline SBS was also examined with common organic solvents like toluene, chloroform, and THF. Contrary to the anionic SBS samples, which were promptly soluble in couple of minutes, the crystalline SBS ones are still stable even after 1 week of dipping them in those solvents. These results indicated that the existence of the *syn*-PS blocks in the crystalline SBS has remarkably improved not only its heat deformation stability but also the chemical resistance property in comparison with those of the anionic SBS materials.

Finally, the morphology of the crystalline SBS was characterized by transmission electron microscopy (TEM). The TEM sample was prepared by a hot casting from its xylene solution (3 wt %) on a Teflon sheet. The elastic PB phase of the ultrathin sections (ca. 50−70 nm thick) was selectively stained with osmium tetraoxide (OsO_4) prior to operation.

As shown in Figure 8, both the crystalline *syn*-PS (bright phase) and the elastic *cis*-PB (dark phase) were homogeneously observed. Because of the relatively high content of the *syn*-PS blocks (>80 mol %), the crystalline phases become continuous and the SBS triblock copolymer obtained in this work looks like a plastic rather than an elastomer. Since the morphology and the mechanical properties of the styrene/butadiene block

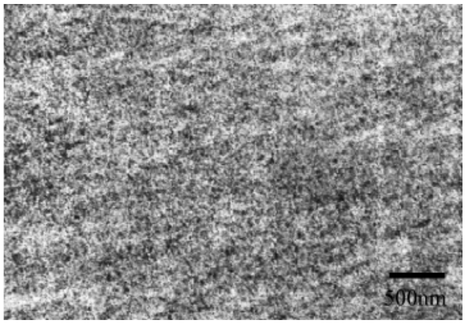


Figure 8. TEM image of the crystalline SBS (run 2, Table 1).

copolymer strongly depended on the length of each PS and PB blocks, we are preparing a series of block copolymers with different PS and PB block lengths and compositions, the results of which will be reported elsewhere.

In conclusion, crystalline SBS triblock copolymers consisting of elastic *cis*-PB blocks chemically bonded with crystallizable *syn*-PS blocks were prepared for the first time through a stereospecific sequential triblock copolymerization of S with B catalyzed by $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$. The GPC analysis of the copolymers indicated that the block copolymerizations between S and B proceeds effectively under a controllable polymerization condition, yielding the SBS triblock copolymers with high block efficiencies. The NMR results of the block copolymers proved that the stereoregularity of the PS blocks were highly syndiotactic ([rrrr] > 95%) and the PB block contained primarily *cis*-1,4 structure (>70%). The CFC result suggested that the crystalline SBS thus obtained was not contaminated any dead polymers like *syn*-PS or *syn*-PS/*cis*-PB diblock copolymer. The most distinguishing feature of the crystalline SBS is that it contains highly crystallizable *syn*-PS blocks, which exhibited extremely high melting temperatures (up to 272 °C) in comparison with that of the corresponding anionic SBS, which has no melting temperature. Accordingly, the crystalline SBS obtained with $C_5Me_5TiMe_3/B(C_6F_5)_3/Al(oct)_3$ catalyst exhibited superior heat deformation stability and the chemical resistance property than those of the anionic SBS materials.

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