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(Star PS)-*block*-(Linear PI)-*block*-(Star PS) Triblock Copolymers – Thermoplastic Elastomers with Complex Branched Architectures

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Summary: Polystyrene-*block*-polyisoprene-*block*-polystyrene triblock copolymers were synthesized with star-shaped branching in the polystyrene phase. The block copolymers were formed through sequential anionic polymerization by first synthesizing linear polystyrene, followed by star coupling using 4-(chlorodimethylsilyl)styrene, then the polymerization of isoprene, followed by difunctional coupling with dichlorodimethylsilane. The polymerization was followed by gel permeation chromatography and the resulting copolymers were characterized by ^{1}H NMR spectroscopy to examine the polyisoprene microstructure.

Keywords: anionic polymerization; branched; copolymerization; elastomers; star polymers

Introduction

Polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymers where the inner polyisoprene block is the major component are well known thermoplastic elastomers.[1,2] The triblock copolymers are phase separated at room temperature and the hard and rigid polystyrene domains that are distributed in the polyisoprene matrix act as thermally reversible multi-functional junction points to give a physically crosslinked elastomeric network.[1,3,4] The block copolymers are also soluble in many solvents (such as toluene, THF, dichloromethane, etc.), but can regain their phase-separated morphology and mechanical properties when the solvent is evaporated. These thermoplastic elastomers are therefore reprocessible by heating or solvent casting, but their morphology and resulting mechanical properties are influenced by their process history.[5,6]

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SIS triblock copolymers have been synthesized by living anionic polymerization initiated by organolithium compounds in a hydrocarbon solvent (see references in review articles[2,7-9]). Three basic methods have been described for the synthesis of these triblock copolymers: the sequential addition of monomers to an alkyllithium initiator, the sequential addition of monomers to a di-functional initiator, and the sequential addition of monomers to an alkyllithium initiator followed by coupling reactions.

We have been investigating a one-pot convergent living anionic polymerization procedure for introducing star-branching into polystyrene.[10-12] Star-shaped polystyrene with a living site at the core can be synthesized by slowly introducing a dual functional coupling agent to living polystyryllithium.[10-12] The resulting living star can initiate the polymerization of styrene monomer to obtain a star-*block*-linear diblock polystyrene.[13-15] The living diblock polystyrene can be coupled by adding a difunctional coupling agent to obtain star-*block*-linear-*block*-star triblock (pom-pom) polystyrene,[14,16] or it can be coupled with a multifunctional coupling agent to yield a more complex architecture.[17]

Star-branching can also be introduced into the polystyrene block of SIS triblock copolymers by this convergent living anionic polymerization technique. The resulting SIS triblock copolymer with the pom-pom structure can be used as a model sample to study the influence of the structural modification on the morphology, mechanical properties, and processibility of SIS thermoplastic elastomers. While other researchers have begun investigation of thermoplastic elastomers with other types of complex architectures through controlled, multistep syntheses,[18-20] our synthetic method can potentially yield unique structures in a single reaction container.

Experimental details

Materials Styrene (99%, inhibited with ~ 10 - 15 ppm 4-*tert*-butylcatechol), *p*-chlorostyrene (97%, inhibited with ~ 500 ppm 4-*tert*-butylcatechol), 1,2-dibromoethane(99%), dichlorodimethylsilane (99%) and trichloromethylsilane (99%) were obtained from Aldrich Chemical Company. Reagents were dried over calcium hydride and distilled under argon or under reduced pressure immediately prior to use. Isoprene (99%, inhibited with ~ 100 ppm 4-*tert*-butylcatechol) was distilled twice over calcium hydride and distilled once over a dibutylmagnesium solution (1.0 M in heptane, Aldrich Chemical Co.) just prior to use. *sec*-Butyllithium in a mixture of cyclohexane and heptane was kindly donated by FMC, Lithium

Division. The effective molarity of the solution was determined to be 1.10 M by repeated initiation and polymerization of styrene and the subsequent analysis of the molecular weights by GPC-MALLS. HPLC grade tetrahydrofuran (99.9+%) was obtained from Fisher Scientific, dried over sodium metal, and distilled from sodium benzophenone ketyl under argon immediately prior to use. HPLC grade cyclohexane (99%) from Fisher Scientific was purified by repeated washings with H_2SO_4 and water and distilled from sodium metal. 4-(Chlorodimethylsilyl)styrene (CDMSS) was synthesized as reported,[11] and was distilled from calcium hydride under reduced pressure immediately prior to use. All glassware, glass syringes, and needles were oven dried at 150 °C for at least 24 hours, and cooled under argon. The glassware was further flame dried under an argon purge after assembly. Gastight syringes were prepared by washing with a dilute *sec*-butyllithium solution followed by washing with dry cyclohexane.

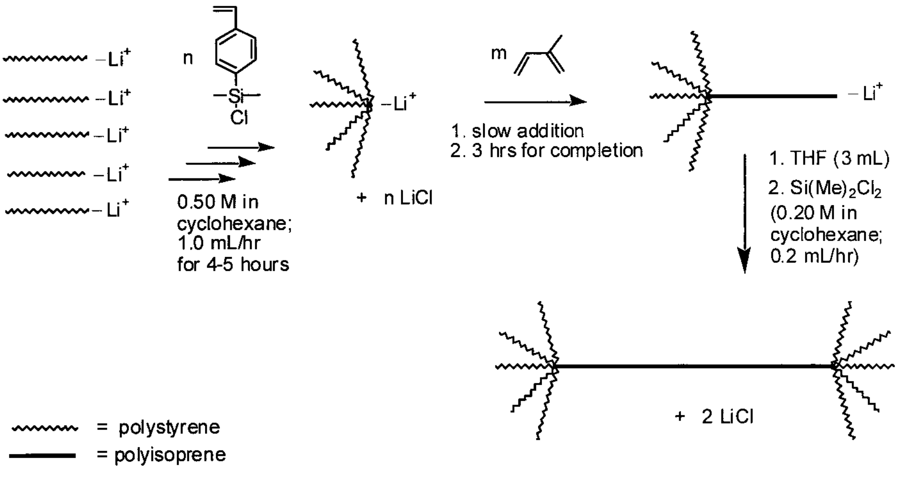
Polymerization Polymerizations were conducted at room temperature. A typical polymerization procedure is as follows (Experiment 1): Styrene (2.5 mL, 21.8 mmol) was charged to 100 mL of cyclohexane in a 250 mL round bottom flask sealed with a rubber septum under an argon atmosphere. *sec*-BuLi was added dropwise to titrate impurities until a pale yellow color indicative of the polystyryllithium was observed. The calculated charge of *sec*-BuLi initiator (2.5 mL, 2.75 mmol) was then added. After two hours, an aliquot was removed and precipitated into argon-purged methanol. A solution of CDMSS in cyclohexane (approximately 0.50 M) was slowly added by using a gastight syringe with the addition rate controlled by a syringe pump. The addition rate of the CDMSS solution was 1.0 mL/hour over a course of 4.2 hours to introduce a total of 4.2 mL (2.10 mmol) of the CDMSS solution. Thirty minutes after the complete addition, an aliquot (5 mL) was removed and precipitated in argon-purged methanol. Isoprene (6.0 mL, 60 mmol) was then added to the solution from a syringe, and the solution was allowed to stir for three hours at room temperature. An aliquot (5 mL) was removed and THF (3 mL) was added to the solution. A dichlorodimethylsilane mixture in cyclohexane (0.20 M) was added slowly into the living anion solution using a gastight syringe. The addition rate was controlled to a rate of 0.20 mL/hour by a syringe pump and the addition was continued until the reaction solution turned colorless. The reaction mixture was then precipitated into methanol, filtered, washed with methanol, and dried to a constant weight at room temperature in a vacuum oven. 2,6-di-*tert*-butyl-4-methylphenol (0.02 wt %) was added to the methanol to prevent the oxidation of the polyisoprene block. The reaction yield was quantitative after considering the sampled aliquots.

Characterization

Molecular weights and molecular weight distributions were characterized by gel permeation chromatography (GPC) performed on a Hewlett-Packard model 1084B liquid chromatograph equipped with two Hewlett-Packard Plgel 5μ Mixed-D columns (linear molecular weight range: 200 – 400,000 g/mol), a calibrated RI (Waters R401) detector, and a Wyatt Technology miniDAWN multi-angle laser light scattering (MALLS) detector (λ = 690 nm, three detector angles: 45^o, 90^o and 135^o), using Astra 1.5.0b2 molecular weight characterization software. Elutions were carried out at an ambient temperature with THF as the solvent and a flow rate of 0.70 mL/min. The refractive index increment (d*n*/d*c*) used for the polystyrene samples was 0.193 mL/g, which was obtained for the polystyrene stars[11] and which also corresponds to linear polystyrene in THF.[21] The d*n*/d*c* of polyisoprene was determined to be 0.117 mL/g in THF at room temperature by using an Abbe Refractometer (Bausch & Lomb). The refractive index increments of the SIS copolymers were calculated based on the summation of the products of the d*n*/d*c* of each block times its weight fraction.[22] ^{1}H NMR spectroscopy was performed on samples dissolved in deuterated chloroform on a Chemagnetics CMX Infinity 400 instrument.

Results and Discussion

Synthesis Method The synthesis of (star PS)-*block*-(linear PI)-*block*-(star PS) triblock is depicted in Scheme 1. Living star-shaped polystyrene anions were synthesized via the convergent living anionic polymerization method by introducing a less than stoichiometric amount of CDMSS to living polystyrene anions in a procedure similar to that previously described.[16,17] Isoprene monomer was added into the living star-shaped polystyrene anions to make a (star PS)-*block*-(linear PI) living diblock. The syntheses of the living star and the (star PS)-*block*-(linear PI) were performed in cyclohexane without any added polar modifiers to maintain the predominately *cis*-1,4 structure of the polyisoprene block, which is important for the formation of thermoplastic elastomers.[1,2] To the living diblocks was added the difunctional coupling agent dichlorodimethylsilane (DCDMS) to obtain the (star PS)-*block*-(linear PI)-*block*-(star PS) triblock. A small amount of THF was added into the solution before the addition of DCDMS to increase the coupling reaction rate.[16] The addition of reactants was conducted using syringe transfer techniques, and the rate of addition was controlled by using a syringe pump.



Scheme 1. Reaction sequence for the synthesis of (star PS)-*block*-(linear PI)-*block*-(star PS) triblock copolymer.

The structural variations, such as the length of the initial chain and the average number of arms, can be readily controlled by the molar ratio of styrene monomer to *sec*-BuLi and the amount of CDMSS added, respectively.[16] The molecular weight of the linear polyisoprene block can also be controlled by varying the amount of isoprene monomer relative to the star-shaped macroinitiator.

Synthesis of Living Stars In the convergent process, CDMSS is slowly introduced to the living polystyrene solution using a gastight syringe, with the addition rate controlled by a syringe pump. The CDMSS reacts with the living polymer by first terminating one chain through the substitution of the silyl chloride in the formation of a macromonomer, and then another living chain quickly adds to the vinyl group of the macromonomer to form a polymer with two coupled chains and a living site at the junction point. The series of reactions are repeated as more CDMSS is added, and a star-shaped polymer with a hyperbranched core is finally obtained.[11]

We have studied this convergent process in cyclohexane solutions with different amounts of added THF.[11,16] The THF was added because the rates of both the substitution reaction and addition reaction can be increased.[23,24] The maximum number of arms of star-shaped polystyrene under given reaction conditions, and the relationship between the desired number of arms of a living star and the amount of CDMSS added, have been reported.[16] In this work, it was desired to synthesize living star-shaped polystyrenes in a hydrocarbon solvent without any added THF. An experiment was designed to compare star-shaped polystyrene after stoichiometric CDMSS addition, synthesized with and without added THF. The results are compared in Figure 1. Convergent living anionic polymerization was determined to proceed favorably in cyclohexane to synthesize star-shaped polystyrenes

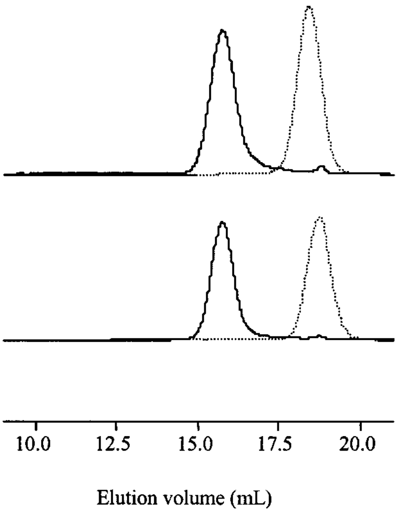


Figure 1. GPC chromatograms of star-shaped polystyrenes (... initial linear polystyrene, — star-shaped polystyrene). (a) Synthesized in cyclohexane only; linear polystyrene (M_n = 1210 g/mole), star-shaped polystyrene (M_n = 12,900, PDI = 1.16, no. of arms = 9.5) (b) synthesized in cyclohexane with 3% v/v THF; linear polystyrene (M_n = 940 g/mole), star-shaped polystyrene (M_n = 12,100, PDI = 1.14, no. of arms = 11).

The number of coupled arms in the living star is related to the stoichiometric amount of CDMSS added. To obtain an *f*-armed star, (1-1/*f*) of the stoichiometric amount of CDMSS is needed and the resulting living anion concentration is 1/*f* of the initial concentration of living anions.[16] This relationship was used to control the number of arms of living polystyrene stars in this work.

Living polystyrene chains were prepared in cyclohexane by initiating styrene monomers with *sec*-BuLi. An aliquot of the reaction solution was sampled and subsequently characterized by

GPC-MALLS. The desired amount of CDMSS was then added slowly by using a gastight syringe with the addition rate controlled by a syringe pump. After complete addition, an aliquot of the living star-shaped polystyrene solution was removed and isolated by precipitating in argon-purged methanol, then characterized by GPC-MALLS. Using the molecular weights of the living star and the initial living chains, the number of arms, *f*, can be readily calculated based on Equation 1 as previously reported,[11,16,17]

$$G = \frac{\log(M_{star} + M_{branch}) - \log(M_{initial} + M_{branch})}{\log 2}; \qquad f = 2^G \qquad \text{Eq. 1}$$

where G equals the number of generations of growth, M_{star} equals the number average molecular weight of the star-shaped polystyrene, M_{branch} equals the number average molecular weight of the residue from the coupling agent, and $M_{initial}$ equals the number average molecular weight of the initial linear polystyrene chain. The molecular weight characterization results of living polystyrene chains and stars from aliquots removed during the experiments are shown in Table 1. In this work, different arm lengths of the living polystyrene star, from ~ 1,000 g/mol to ~ 6,300 g/mol were used. The average number of arms of the living star was determined to be around 5 (4.4 – 5.3) by controlling the amount of CDMSS added.

Table 1. Synthesis and characterization for initial chains and stars

Exp.	St/BuLi (mmol/ mmol)	^aM_n of initial chain (g/mol)/PDI	Addition rate of CDMSS(mmol/hr) /BuLi(mmol)	^{a}Mn of PS star (g/mol)/PDI	^{b}*f*: Avg. no. of arms
1	8.0	1, 060/1.05	0.50/2.75	6,260/1.35	5.3
2	20	2,210/1.04	0.50/2.75	11,700/1.30	5.0
3	50	5,530/1.01	0.02/1.10	28,600/1.27	4.7
4	30	3,470/1.04	0.50/2.08	18,400/1.27	5.1
5	55	6,300/1.02	0.25/1.16	28,200/1.22	4.4
6	30	3,130/1.02	0.50/2.08	15,300/1.24	4.7

All reactions were done at room temperature in cyclohexane and the addition of CDMSS (approximately 0.50M in cyclohexane) was completed in the time range of 4-5 hours. ^{a}Determined by GPC-MALLS; ^{b}Determined by Eq. 1, the number of arms $f = 2^G$.

Synthesis of Triblock Copolymers The star-shaped polystyrene contains a living chain end at the focal point of the hyperbranched core; thus, it can be used as a macroinitiator to polymerize sequentially added isoprene monomer. In a hydrocarbon solvent, the crossover rate of the polystyryllithium to the polyisoprenyllithium is approximately 150 times faster than the polymerization rate of isoprene.[25] The initiation rate of the living polystyrene star should therefore be fast despite any steric hindrance at the living site.

Experiments were performed to polymerize isoprene from the polystyrene star initiator. Based on the expected quantitative initiation and subsequent propagation of living anionic polymerization, the length of the linear polyisoprene block was controlled by the stoichiometric amount of isoprene monomer to the living polystyrene star. The mass ratio of the polystyrene block to the polyisoprene block was fixed at 35/65 by controlled monomer feed ratios.

Table 2. Synthesis and characterization for (star PS)-*block-* (linear PI) diblock and SIS triblock copolymers

Exp.	^{a}Mass ratio PS/PI	^{b}M$_n$ of diblock (g/mol)/PDI	Addition rate of DCDMS (mmol/hr)	^{b,c}M$_n$ of product (g/mol)/PDI	^{d}Diblock content (wt %)
1	35/65	16,000/1.12	0.04	26,400/1.12	21
2	35/65	31,200/1.08	0.04	54,000/1.05	15
3	35/65	79,900/1.08	0.02	131,000/1.05	22
4	35/65	42,400/1.07	0.04	74,400/1.06	14
5	35/65	62,900/1.05	0.02	107,000/1.05	18
6	35/65	34,100/1.07	0.04	58,200/1.07	17

All reactions were done at room temperature in cyclohexane with 3% v/v THF added prior to the addition of DCDMS (approximately 0.20 M in cyclohexane). ^{a}By feed ratio; ^{b}Determined by GPC-MALLS with d*n*/d*c* = 0.144 mL/g; ^{c}Before fractionation, peak includes residual diblock; ^{d}Calculated based on the theoretical molecular weight of triblock (i.e., 2 x M$_n$ of diblock); wt% diblock = 100 x (2 x M$_n$ of diblock – M$_n$ of product)/(M$_n$ of product).

After sampling for GPC-MALLS characterization, the living (star PS)-*block*-(linear PI) diblocks with a 35/65 mass ratio were coupled with dichlorodimethylsilane (DCDMS) to form the triblock. To increase the coupling efficiency, 3% v/v THF was added before the addition of DCDMS.[16,24] A dilute solution of DCDMS in cyclohexane (0.20 M) was added at a slow rate to the living diblock anions. The slow addition technique maintains a deficiency of coupling agent to allow the diblock anions to couple efficiently.[16,26]

The molecular weights and molecular weight distributions for the diblock and triblock samples were characterized by GPC-MALLS. The refractive index increments (d*n*/d*c*) used for the (star PS)-*block*-(linear PI) diblock and the (star PS)-*block*-(linear PI)-*block*-(star PS) triblock, were calculated based on the summation of the products of the d*n*/d*c* of each block multiplied by its weight fraction.[22] The d*n*/d*c* of the polyisoprene block was determined to be 0.117 mL/g in THF at room temperature by using an Abbe Refractometer (Bausch & Lomb), and the d*n*/d*c* of the polystyrene block was 0.193 mL/g.[11,21] The d*n*/d*c* is calculated to be 0.144 mL/g for the diblock and triblock with a polystyrene to polyisoprene mass ratio of 35/65.

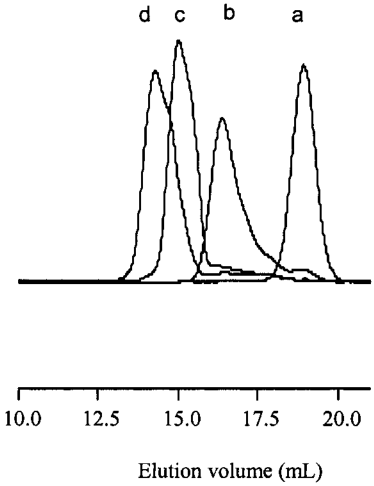


Figure 2. GPC chromatograms for Experiment 1. (a) Initial chain; (b) star; (c) (star PS)-*block*-(linear PI) diblock; (d) (star PS)-*block*-(linear PI)-*block*-(star PS) triblock copolymer.

The progression of the molecular weight of samples during the synthesis is demonstrated by the representative GPC-MALLS chromatograms of Experiment 1 (Figure 2). From high elution volume to low elution volume, the corresponding initial linear chains, the polystyrene star, the (star PS)-*block*-(linear PI) diblock, and the (star PS)-*block*-(linear PI)-*block*-(star PS) triblock are observed as relatively narrow peaks.

The GPC results for the (star PS)-*block*-(linear PI) diblock and the (star PS)-*block*-(linear PI)-*block*-(star PS) triblock are presented in Table 2. The molecular weight of the diblock was controlled from 16,000 g/mol to 79,900 g/mol. The molecular weight of the final product containing the triblock is not exactly twice that of the corresponding diblock because of the co-existence of diblock residue. The weight percentage of residual diblock was calculated based on the difference in average molecular weight of the final sample (diblock plus triblock) and the theoretical triblock molecular weight (twice the molecular weight of the diblock),[16,27] and is presented in Table 2. The amount of diblock in each sample varies from 14 to 22 wt% by the calculation. It is reported that the commercial Kraton SIS triblock copolymers possess bimodal molecular weight distributions with 15 to 20 wt % of apparently diblock copolymers with one-half of the molecular weight of the triblock copolymers.[28] The diblock residue has been demonstrated to lower the mechanical properties of the final products.[29,30]

Microstructure Characterization The (star PS)-*block*-(linear PI)-*block*-(star PS) triblock samples were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the triblock copolymer from Experiment 1 is shown in Figure 3. Signals from the linear polyisoprene block and the star-shaped polystyrene block are observed. The peaks are readily identified by comparison with ^{1}H NMR spectra of polystyrene and polyisoprene.[31-34]. The small peak at 0.1 ppm represents the silyl methyl groups from the CDMSS residue in the polystyrene star block. The small peaks at 0.6-0.8 are due to the residue of the intiator (*sec*-butyl group). The peaks at chemical shifts from 1.3 ppm to 2.3 ppm, are attributed to signals from the residue of the initiator and from the polymerized vinyl groups of polyisoprene and polystyrene, together with the typical signals from the methylene groups at 2.1 ppm and the methyl group from the 1,4-structures of polyisoprene (1.7 ppm for the *cis*-1,4-structure and 1.6 ppm for the *trans*-1,4-structure). The double peak at 4.7 ppm represents the two olefinic protons from the 3,4-structure of polyisoprene and the single peak at 5.1 ppm represents the olefinic proton from the 1,4-structure of polyisoprene. The peaks with a chemical shift of 6.4 ppm to 7.2 ppm are signals from the aromatic ring of the polystyrene block.

The microstructure of the polyisoprene block can be analyzed based on this spectrum. The ratio of the peaks at 4.7 ppm (two olefinic protons from the 3,4-structure) and 5.1 ppm (one olefinic proton from 1,4-structure) is approximately 1:9 by integration, which indicates that there is only a small amount of polyisoprene units with the 3,4-structure co-existing with the polyisoprene units with1,4-structure. The ratio of the *cis*-1,4-structure relative to the *trans*-

1,4-structure can be estimated based on the peak intensity at 1.7 ppm and 1.6 ppm. The precise ratio is hard to obtain because these two peaks are mixed with signals from polymerized vinyl groups of the polystyrene block, but it is easy to tell that the *cis*-1,4-structure is the predominant microstructure.

Preliminary property characterization Films have been made by solution casting from toluene for all of the triblock samples. The films are transparent and demonstrate the typical mechanical properties of thermoplastic elastomers. Complete examination of the morphology, melt viscosity, and tensile properties, which should be influenced by introduction of branching, is being done and more detailed results will be forthcoming. Other samples are also being produced to better control the extent of branching, composition, and the efficiency of coupling.

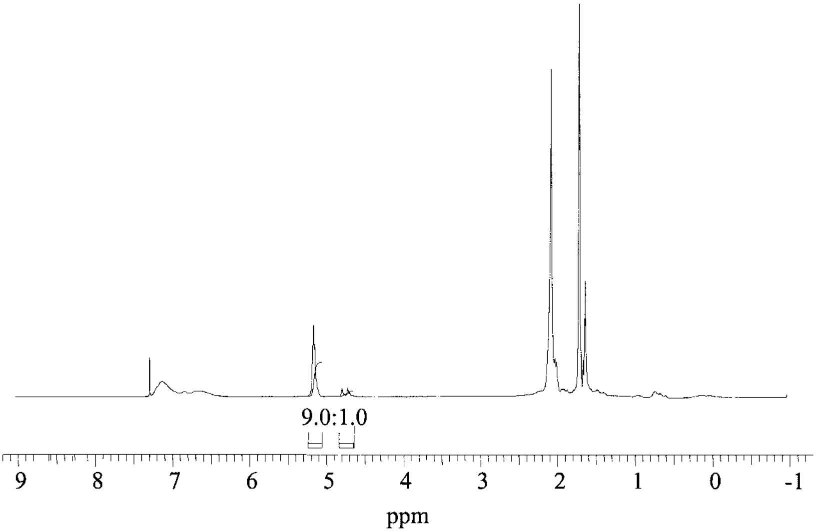


Figure 3. ^{1}H NMR spectrum for (star PS)-*block*-(linear PI)-*block*-(star PS) triblock copolymer (Experiment 1). Solvent: $CDCl_3$.

Conclusions

Styrene based thermoplastic elastomers with a novel structure, (star PS)-*block*-(linear PI)-*block*-(star PS) triblock copolymers, were synthesized by the sequential addition of isoprene monomer and DCDMS to living polystyrene stars obtained by convergent living anionic polymerization. GPC-MALLS characterization demonstrated the progression of the molecular weight during the synthesis. Samples with controllable arm lengths, numbers of arms, molecular weights of the diblock, and polystyrene to polyisoprene mass ratios were obtained. The microstructure of the resulting copolymers was characterized by ^{1}H NMR spectroscopy. Preliminary mechanical property tests demonstrate that these copolymers possess elastomeric properties as expected based on their phase separated morphologies.

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