Nanocrystallization-locked Network of Poly(styrene-b-isobutylene-b-styrene)-g-Polytetrahydrofuran Block Graft Copolymer

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ABSTRACT

Poly(styrene-b-isobutylene-b-styrene) triblock copolymer (SIBS), a kind of thermoplastic elastomer with biocompatibility and biostability containing fully saturated soft segments, could be synthesized via living cationic copolymerization. A novel poly[(styrene-co-methylstyrene)-b-isobutylene-b-(styrene-co-methylstyrene)]-g-polytetrahydrofuran (M-SIBS-g-PTHF) block graft copolymer was prepared to increase the polarity and service temperature of SIBS by grafting polar PTHF segments onto SIBS. A series of the above block graft copolymers with average grafting numbers from 2 to 6 and molecular weights of PTHF branches ranging from 200 g mol⁻¹ to 4200 g mol⁻¹ were successfully synthesized via living cationic ring-opening polymerization of tetrahydrofuran (THF) coinitiated by AgClO₄⁻. The introduction of PTHF branches led to an obvious microphase separation due to thermodynamic incompatibility among the three kinds of segments of polyisobutylene (PIB), polystyrene (PS) and PTHF. Moreover, the microphase separation promotes the rearrangement of PTHF branches to form the nanocrystallization-locked physically cross-linked network after storage at room temperature for 2 months, leading to insolubility of the copolymers even in good solvents. The melting temperature and enthalpy of PTHF nanocrystallization locked in hard domains of M-SIBS-g-PTHF block graft copolymer increased remarkably up to 153 °C and 117.0 J·g⁻¹ by 23 °C and 11.6 J·g⁻¹ respectively after storage for long time. Storage modulus (G') of M-SIBS-g-PTHF block graft copolymer at temperatures ranging from 100 °C to 180 °C, which is much higher than those of the SIBS triblock copolymer. To the best of our knowledge, this is the first example of high performance M-SIBS-g-PTHF block graft copolymers containing segments of PIB, PS and PTHF with nanocrystallization-locked architecture.

KEYWORDS

Poly(styrene-b-isobutylene-b-styrene); Polytetrahydrofuran; Living cationic polymerization; Block graft copolymers; Nanocrystallization-locked network

INTRODUCTION

Poly(styrene-b-isobutylene-b-styrene) triblock copolymer (SIBS), a kind of thermoplastic elastomer (TPE), composed of polyisobutylene (PIB) as soft segments (SSs) and polystyrene (PS) as hard segments (HSs), could be synthesized via living cationic sequential block copolymerization of isobutylene (IB) and styrene (St).⁻¹ It has been widely used in biomedical field including endovascular devices, drug carriers, coronary stent, microshunt to treat glaucoma, and stick-to-skin pressure sensor owing to its outstanding biocompatibility and biostability.⁻²⁻⁷ However, thrombosis and infection might occur due to its hydrophobicity on SIBS surface.⁻⁸ Moreover, some specific applications of SIBS, such as permeselective barrier elastomers with enhanced moisture transmission capabilities, were restricted due to weak polarity and lack of functional group.⁻⁹ The service temperature was limited by the glass transition temperature of HSs (TgHSs).⁻¹⁰ It was essential to develop functionalized SIBS to improve its hydrophilicity, polarity and TgHSs.⁻¹¹⁻¹²

Three approaches have been used for the synthesis of modified SIBS so far. Polar SIBS could be synthesized via living cationic sequential block copolymerization of IB with polar St derivative monomer, such as p-tert-butyl(dimethyl)silyloxy)styrene (TBDMS), p-tert-butoxyxystyrene (tBuOS), and 4-[2-(tert-butyldimethylsiloxy)ethyl]styrene (TBDMES).⁻¹⁰⁻¹² Phenolic hydroxyl functionalized SIBS, e.g. poly(hydroxyisobutylene-b-isobutylene-b-hydroxy styrene), was prepared by the hydrolysis of poly(TBDMS-b-IB-b-TBDMS) or poly(tBuOS-b-IB-b-tBuOS) triblock copolymer. Furthermore, acetylated derivative of SIBS was further synthesized via quantitative acetylation of the phenolic hydroxyl functionalized SIBS.⁻¹⁰⁻¹² Both phenolic hydroxyl functionalized and acetylated SIBS could be used as polymer drug carrier for paclitaxel-eluting coronary stent and improved drug-polymer miscibility, relative to SIBS.⁻¹⁰ Phenolic hydroxyl functionalized random copolymers of IB with vinyl phenol, prepared via cationic co-

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polymerization of IB with polar comonomers (4-acetoxy styrene or 4-tert-butoxy styrene), exhibit an excellent self-healing property. This kind of PIB with phenol side groups could be used as a good matrix for the homogeneous dispersion of silica nanoparticles.[13]

Chemical modification is a common method for introducing polar functional groups.[14−19] Sulfonated SIBS membranes at high sulfonation levels possessed a complex three-dimensional network and high ion exchange capacity, which is potentially used for fuel cell.[14,15] Cross-linked quaternized SIBS (QSIBS) synthesized by chloromethylated SIBS reacting with amine could be used for composite anion exchange membranes.[17−19] Cationic carboxybetaine ester-modified styrenic thermoplastic elastomers were synthesized by chloromethylated SIBS reacting with methyl 3-(dimethylamino) propionate and exhibit efficient bactericidal ability. Meanwhile, antifoiling surface against protein, platelets, erythrocytes, and bacteria could be obtained via hydrolysis of carboxybetaine esters into zwitterionic groups.[16]

Copolymerization with another monomer to synthesize block or graft copolymer based on SIBS is a common method for introducing new functionalized segments.[8,9,20−26] SIBS with sec-benzyl chloride end groups prepared via living cationic sequential triblock polymerization of IB and St could be used as macroinitiator for atom transfer radical polymerization (ATRP).[9,20−25] 2,5-Bis[(4-methoxyphenyl)oxycarbonyl] styrene (MPCS) was block-copolymerized from sec-benzyl chloride terminated SIBS with low PS content to generate PMPCS-b-PiB-b-PMPCS triblock copolymers, which formed lamellar structures at moderate fractions and hexagonal coil cylinders at high fractions of rod-like PMPCS blocks.[22,23] SIBS-based pentablock terpolymers containing polyacrylate segments could be synthesized by ATRP of methyl acrylate, n-butyl acrylate, tert-butyl acrylate (iBA), and methyl methacrylate initiated by sec-benzyl chloride terminated SIBS.[22,23] Amphiphilic poly(acrylic acid-b-styrene-b-isobutylene-b-styrene-b-acrylic acid) (PAAP−b-PS−b-PiB−b-PS−b-PAAP) block copolymers could be synthesized via deprotection of the tert-butyl groups using trifluoroacetic acid or simple heat treatment without dissolving the polymer or further sample cleaning from PtBA-b-PS-b-PiB-b-PS-b-PtBA.[22,24] (PAAP-b-PS-b-PiB)2-star-PAAP and (PS-b-PiB)2-star-PAAP star terpolymers also could be obtained by the above similar method and represented different microdomain structures containing highly ordered cylinders, lower ordered spheres, and gyroid structures with an increase in PAA content.[9,25] A biocompatible and nontoxic slippery surface could be fabricated via combination of photografting polymerization of 1H,1H,2H,2H-perfluorooctyl methacrylate (FMA) on the SIBS matrixes to generate a coarse morphology and then infusing with fluorocarbon liquid. Moreover, compared to SIBS, this slippery surface of fluorocarbon liquid-infused SIBS-g-PFMA brushes can effectively reduce thrombosis and bacterial infection against E. coli and S. aureus.[26] SIBS-g-polycarboxylate graft copolymers acted as intermediate to create nuclease-modified SIBS via reaction with deoxyribonuclease and ribonuclease, which could availabley hinder bacterial adhesion and biofilm formation.[26]

Polytetrahydrofuran (PTHF), an aliphatic saturated polyether, could be synthesized via living cationic ring-opening polymerization (CROP) of THF. PTHF has been widely applied due to some advantages such as favorable biological inertness, biocompatibility, breathability, moisture resistance, elasticity at low temperature, flexibility, impact resistance, chemical resistance, and hydrolytic stability.[27,28] PTHF is also commonly introduced into commercially available TPEs for high mechanical properties.[29−31] It can also be used in gene and drug delivery therapy.[32−36] PTHF grafted copolymers displaying obvious microphase separation between macromolecular backbone and PTHF side chains had been synthesized via combination of living CROP and grafting-onto method and reported in our previous works.[31−42] Compared to the unconfined free PTHF segments, the crystallization of PTHF branches in PTHF-grafted copolymers was confined, and the crystallization degree and spherulitic growth rate of PTHF branches decreased with an increase in grafting density or an increase in the molecular weight of PTHF segments in branches. The melting temperature and enthalpy of PTHF crystallization improved with an increase in the molecular weight of PTHF segments.

The aim of this work is to introduce polar PTHF chains into SIBS backbone and to provide a means of developing novel polar SIBS-based copolymers with polyether. A series of poly(styrene-co-methylstyrene)-b-isobutylene-b-(styrene-co-methylstyrene)-g-PTHF (M-SIBS-g-PTHF) block graft copolymers with different PTHF lengths (Mn,PTHF) and grafting numbers (GN) in every M-SIBS backbone were synthesized for the first time via sequential living cationic block polymerization of IB, St and p-methylstyrene (p-MSt), nucleophilic substitution and living CROP of THF by using brominated M-SIBS (BM-SIBS) as a macroinitiator and silver perchlorate (AgClO4) as a coinitiator. The microphase separation improved after grafted with PTHF polymer. The degree of microphase separation improved with decreases in Mn,PTHF and GN. Compared to M-SIBS, nanocrystallization-locked network endowed M-SIBS-g-PTHF block graft copolymers with an increased glass transition of HSs (Tg,HSs) and melting temperature of PTHF crystallization (Tm,PTHF), which is meaningful for improving service temperature of SIBS TPE materials.

**EXPERIMENTAL**

**Materials and Reagents**

Isobutylene (IB, 99.9%, Beijing Yanshan Petroleum Chemical Co.), styrene (St, 99.9%, Beijing Yanshan Petroleum Chemical Co.), p-methylstyrene (p-MSt, 98%, Acros), anhydrous ferric chloride (FeCl3, 99%, Acros, packaging under nitrogen), isopropanol (iPrOH, AR, Beijing Chemical Works), bromine (Br2, 99.9%, Aladdin), 2,2′-azobisisoheptonitrile (ABVN, 98%, Macklin), sodium hydroxide (NaOH, AR, Beijing Chemical Works), ethanol (AR, Beijing Chemical Works), silver perchlorate (AgClO4, 99%, anhydrous grade, Alfa Aesar), toluene (AR, Beijing Chemical Works), and cyclohexane (AR, Beijing Chemical Works) were used as received. Dichloromethane (CH2Cl2, AR, Beijing Yili Fine Chemicals) and n-hexane (n-Hex, AR, Beijing Yili Fine Chemicals) were further purified by distillation with calcium hydride (CaH2, J&K Scientific Ltd.) for several hours before use. Di(2-chloro-2-propyl) benzene (DCC) was prepared by passing dry gaseous HCl through a 30% solution of 1,4-diisopropylbenzene (AR, TCI Co.) in dried CH2Cl2 at 0 °C for 12 h.[43] The solvent was removed and the crude product was purified by recrystallization from n-Hex at −60 °C. Tetrahydrofuran (THF, AR, Beijing Chemical Works)
was distilled with sodium wire (Na, Aladdin) under nitrogen atmosphere till the system becomes bright blue by adding diphenylmethane as an indicator prior to use.

**Synthesis of M-SIBS Triblock Copolymer**

Living cationic block copolymerizations were performed at −80 °C under a dry nitrogen atmosphere in a three-necked round-bottom Schlenk bottle equipped with a mechanical stirrer. The M-SIBS triblock copolymers were produced by sequential addition of the monomers from a small molecular initiator of DCC starting with IB followed by the addition of a prechilled monomer mixture of p-MSt and St. Specially, a 2 L flask was charged with 0.60 mol of IB, 3.45×10⁻³ mol of DCC, and 550 mL of n-Hex/CH₂Cl₂ (60/40, V/V) solvent mixtures. 1.13×10⁻² mol of FeCl₃ with 1.58×10⁻² mol of iPrOH were added into the reaction mixture to start IB polymerization under stirring. After the polymerization of IB for 5–10 min, 60 mL of a prechilled solution containing 0.0355 mol of St and 0.073 mol of p-MSt in n-Hex/CH₂Cl₂ (60/40, V/V) was added into reaction flask. After the process of block copolymerization for 40 min, polymerizations were terminated by prechilled ethanol. The triblock copolymers were in ethanol and then washed with ethanol for three times. The copolymer products were dried in a vacuum oven at 40 °C to a constant weight, expressed as M-SIBS.

**Synthesis of BM-SIBS Macroinitiator**

Bromination was carried out in a 1 L closed glass reactor by a teflon plug seal and two ground-in glass stoppers equipped with a mechanical stirrer. The sample of M-SIBS triblock copolymer was dissolved in distilled n-Hex to get a 10 wt% solution. This solution was poured into the three-necked reaction flask in ice-water bath, followed by injecting 0.5 mL of bromine per 10 g of polymer. The flask was transferred to oil bath at 65 °C and the reaction was started by ABVN addition. After 1 h of reaction time, the reaction was terminated by adding a 4.8 wt% NaOH solution, washed with ethanol for three times and stirred for 10 min. The polymer was precipitated in excess ethanol and dried in a vacuum oven at 40 °C to a constant weight, expressed as BM-SIBS.

**Synthesis of M-SIBS-g-PTHF Block Graft Copolymer**

M-SIBS-g-PTHF was synthesized via living CROP of THF with BM-SIBS (Mn=16100 g·mol⁻¹, PD1=1.22, H5 mol%19%/AgClO₄ initiating system. Specially, 3.8 g of BM-SIBS and 500 mg of AgClO₄ were added into a prechilled mixture of CH₂Cl₂ (120 mL) and THF (120 mL) under nitrogen atmosphere. The living CROP of THF was conducted for 3 h at 0 °C under magnetic stirring for synthesis of M-SIBS-g-PTHF living chains and then terminated by H₂O molecules. After 3 h of nucleophilic substitution between M-SIBS-g-PTHF living chains and H₂O, reaction mixture was centrifuged by a TG16G table-top high-speed centrifuge at 3000 r·min⁻¹ for 10 min, and then supernatant liquid was precipitated with ethanol and deposited at room temperature until supernatant liquid turned into clarified liquid. Then, supernatant liquid was removed. The precipitate was rinsed with n-Hex to remove unreacted BM-SIBS macroinitiator, followed by drying in a vacuum at 40 °C to a constant weight repeatedly until the weight of product was nondecreasing.

**Characterization**

The ¹H-NMR spectra of all the copolymers solution were recorded on a Bruker 400 MHz NMR spectrometer AVANCE III. The copolymers of M-SIBS, BM-SIBS and M-SIBS-g-PTHF were dissolved in deuterated chloroform (CDCl₃, 40 mg·mL⁻¹) with tetramethylsilane (TMS) as an internal standard at 25 °C. The calculation method of structural composition, such as molar content of hard segments containing 5t and p-MSt units (HS mol%), molar content of p-MSt in hard segments (M mol%), number of Br (N₄) along polymer chain, average grafting number (G₄) and average molecular weight (M₄) of PTHF branches and content of PTHF (W₄) are shown in the electronic supplementary information (ESI).

Number-average molecular weight (Mₙ) and polydispersity index (PDI, Mₙ/Mₘ) of M-SIBS triblock copolymers were determined by a chromatographic system (Waters) using a Waters 1515 isocratic HPLC pump connected to four Waters Strylagel HT2, HT3, HT4 and HT6 columns and equipped with a refractive index detector (RI, Waters 2414) and a ultraviolet-visible light detector (UV, Waters 2489, absorption wavelength was 254 nm) double detectors at 30 °C. M-SIBS triblock copolymers were dissolved in THF (2 mg·mL⁻¹) and THF was used as the mobile phase at a flow rate of 1.0 mL·min⁻¹. The columns were calibrated against the standard polystyrene (PS) samples.

The FTIR spectra of M-SIBS, BM-SIBS and M-SIBS-g-PTHF copolymers were recorded on a FTIR analyzer (Nicolet6700, Nicolet Co., USA) in the wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹ with 32 scans and 4 cm⁻¹ resolution at ambient temperature. The solutions of the above-mentioned copolymers in CH₂Cl₂ (12 mg·mL⁻¹) were dropped onto a pre-dried potassium bromide wafer and the spectra were collected after solvent evaporation.

The dn/dc values of samples were used for calculating the absolute weight-average molecular weight (Mₖ) measured by gel permeation chromatography coupled with multiangle light scattering detector coupled with multiangle light scattering (GPC-MALS). The dn/dc values of M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers were determined by a refractive index detector (RI, Optilab T-rEx), which was used for calculating the corresponding absolute weight-average molecular weight. The copolymers of M-SIBS and M-SIBS-g-PTHF were dissolved in THF with a series of concentrations (0.25, 0.5, 0.75, 1, 1.25, and 1.5 mg·mL⁻¹) and THF was used as the mobile phase at a flow rate of 0.5 mL·min⁻¹. The slopes of obtained fitting curves were dn/dc values. The results demonstrate tiny difference in dn/dc values between M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymer due to small G₄ of PTHF branches.

The absolute Mn of the copolymers was determined by a chromatographic system (Wyatt Technology) using a LabAlliance series 1500 isocratic HPLC pump connected to four MZ Gel Styragek 100 Å, 10 Å, 10 Å, and 10 Å columns in series and equipped with a refractive index detector (RI, Optilab T-rEx), four bridge capillary viscometer (VIS, Wyatt ViscoStar-II) and multiangle laser light scattering (MALS, DAWN HELEOS-II, laser wavelength was 658 nm) triple detectors at 35 °C. The MALS signals were calibrated against the narrow polystyrene standard with Mn of 3.0×10⁴ g·mol⁻¹ and dn/dc value of 0.1845 mL·g⁻¹ was used for PS standards. Diluted THF was used as the mobile phase at a flow rate of 1.0 mL·min⁻¹. The copolymers of M-SIBS and M-SIBS-g-PTHF were dissolved in filtrated THF (2 mg·mL⁻¹) and sample solution of 100 µL
was injected. The absolute $M_w$ of copolymers was calculated by using $dn/dc$ value of 0.14 mLg$^{-1}$. The content of PTHF ($W_{PTHF,GPC}$) could be calculated according to Eq. (1):

$$W_{PTHF,GPC} = \frac{M_{w2} - M_{w1}}{M_{w2}} \times 100\% \quad (1)$$

where $M_{w1}$ stands for the absolute weight-average molecular weight of M-SIBS triblock copolymer and $M_{w2}$ stands for the absolute weight-average molecular weight of M-SIBS-g-PTHF block graft copolymers.

The dilute solution of M-SIBS triblock copolymers and M-SIBS-g-PTHF block graft copolymers in toluene with a concentration of 0.2 mg·mL$^{-1}$ was dropped onto a copper grid with carbon film by pipette. After complete volatilization of solvent, the copper grid with loaded samples was placed in oven at 50 °C for 8 h, followed by being annealed to room temperature. Then it was dyed with ruthenium tetroxide (RuO$_4$) for 20 min at room temperature. The flat surfaces of M-SIBS-g-PTHF block graft copolymers were prepared at −80 °C by using the cryomicrotome (Leica EM UC7, Germany). The micromorphology of copolymers was observed by a transmission electron microscope (TEM, Hitachi HT-7700) at an acceleration voltage of 100 kV. The micromorphology of crystallization in M-SIBS-g-PTHF block graft copolymers was observed by a high-resolution transmission electron microscope (HRTEM, JEOL JEM-3010) at an acceleration voltage of 300 kV.

The dilute solution of M-SIBS triblock copolymers and M-SIBS-g-PTHF block graft copolymers in toluene with a concentration of 0.2 mg·mL$^{-1}$ was dropped onto a silicon wafer to form film by KW4A spin coater (Beijing SETCAS Electronics Co., Ltd) at 3000 r·min$^{-1}$ concentration of 0.2 mg·mL$^{-1}$. The silicon wafer with loaded samples was put in oven annealed at 50 °C for 8 h, followed by being annealed to room temperature. Then it was observed in tapping mode by Bruker DI ultra-fast probe atomic force microscope (AFM) under N$_2$ atmosphere.

M-SIBS-g-PTHF block graft copolymers were soaked in cyclohexane for 2 weeks, followed by vacuum freeze drying at −80 °C for 12 h. Then, the surfaces and cross sections of freeze-dried samples were sputter-coated with gold and were observed with a field emission scanning electron microscope (SEM, Hitachi S-4700) at an acceleration voltage of 20 kV and a working current of 10 $\mu$A.

Differential scanning calorimeter (DSC) thermograms on M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers were collected by Q200 thermoanalyzer system (TA Co., USA) with 10 °C·min$^{-1}$ heating and cooling rate under N$_2$ atmosphere. Samples were cut into many pieces with weights of 5−10 mg for DSC testing.

The rheological behavior of M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymer was examined using a TA Instruments DHR-2 rheometer with an environmental test chamber (ETC). Dynamic isothermal frequency sweeps were performed using 8 mm diameter parallel geometry plates at different temperatures, at a frequency that ranged from 0.1 Hz to 100 Hz. Dynamic temperature ramps were performed at a frequency of 1 Hz while heated at 3 °C·min$^{-1}$.

**RESULTS AND DISCUSSION**

The synthetic strategy for poly[(styrene-co-methylstyrene)-b-isobutylene-b-(styrene-co-methylstyrene)]-g-polytetrahydrofuran (M-SIBS-g-PTHF) block graft copolymers to modify M-SIBS backbone by introducing PTHF segments is shown in **Scheme 1**. The synthetic routes include three steps: (1) synthesis of M-SIBS triblock copolymer by living cationic block copolymerization of IB with St and p-MSt; (2) synthesis of BMSIBS macroinitiator by nucleophile substitution of molecular bromine with benzyl groups on M-SIBS triblock copolymer; (3) synthesis of M-SIBS-g-PTHF block graft copolymers via living CROP of THF using BM-SIBS/AgClO$_4$ as an initiating system.

**Scheme 1** Schematic illustration for the synthesis process of M-SIBS-g-PTHF block graft copolymers.

**Synthesis and Characterization of M-SIBS Triblock Copolymer**

The schematic illustration for M-SIBS triblock copolymers is shown in **Scheme 1**. Living cationic polymerization of IB with DCC/FeCl$_3$发起 system could be achieved in n-Hex/CH$_2$Cl$_2$ mixed solvents at −80 °C. Subsequently, the fresh mixed solution of St and p-MSt was added for block copoly-
merization after almost quantitative consumption of IB, leading to the formation of M-SIBS triblock copolymer. M-SIBS triblock copolymer was finally synthesized.

\(^1H\) NMR characterization was performed on M-SIBS triblock copolymers to analyze the detailed chemical structure. The \(^1H\) NMR spectra of M-SIBS triblock copolymers are shown in Fig. 1. The characteristic resonance at 0.78 ppm is assigned to the corresponding protons in the dicumyl unit (a, \(-\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_4\text{C}(\text{CH}_3)_2\text{C}-\), PIB) introduced by DCC initiator. The characteristic resonances at 1.41 ppm (d, \(-\text{CH}_2\text{CH}_{2}\text{CH}_3\), PIB) and 1.11 ppm (c, \(2\times-\text{CH}_2\text{PIB}\)) are assigned to the corresponding protons along PIB segments. Besides the characteristic signals of PIB segments, the characteristic resonances of PS segments are detected at 1.70–1.96 ppm (f, \(-\text{CH}_2\text{H}_2\text{C}_2\text{H}_2\), St) and 2.28 ppm (j, \(-\text{C}_2\text{H}_4\text{CH}_3\), p-MSt units). The presence of proton signal at \(\delta=2.28\) ppm attributed to the formation of M-SIBS triblock copolymer. M-SIBS triblock copolymers were determined to be 18%, 40% and 69%, respectively.

The different amounts and proportions of fresh mixed solution of St and p-MSt were added in the block copolymerization with DCC\text{FeCl}_3/\text{PrOH} initiating system after almost quantitative consumption of IB in the living cationic polymerization system, leading to formation of M-SIBS triblock copolymers with different molecular weights (M_n=14.0–16.1 kg mol\(^{-1}\)) and copolymer compositions (HS mol\%=7%–20%, M mol\%=52%–98%). The GPC traces of triblock copolymers with RI/UV double detectors are shown in Fig. S1 (in ESI). All structural units were reflected in RI detector, while only phenyl groups of styrene and p-MSt units in the copolymer chains could be detected in UV detector. All GPC traces of M-SIBS triblock copolymers by RI/UV double detectors were consistent with each other, which demonstrates that styrene and p-MSt units were introduced to PIB chain ends to form M-SIBS triblock copolymers. All GPC traces of M-SIBS triblock copolymers possessing different structural compositions with RI detector present symmetrical and unimodal molecular weight distribution. Characterization results for M-SIBS triblock copolymers are summarized in Table S1 (in ESI).

**Bromination of M-SIBS Triblock Copolymer**

Brominated M-SIBS triblock copolymer (BM-SIBS) was prepared by using molecular bromine as bromine source, as shown in Scheme 1. The nucleophilic substitution of molecular bromine with benzyl groups was conducted in the presence of ABVN in \(n\)-Hex at 65 °C. The reaction is fast due to direct generation of a mass of bromine radicals. The degree of bromination of four BM-SIBS triblock copolymers were determined to be 18%, 40%, 42% and 69%, respectively.

The representative FTIR spectra of M-SIBS triblock copolymer and BM-SIBS macroinitiator are shown in Fig. S2 (in ESI). It can be observed that a new characteristic absorbance at 608 cm\(^{-1}\) generated, which is attributed to the stretching vibration of \(-\text{C}^-\text{Br}\) in benzyl bromide (p-BMSt) groups after bromination. The result preliminarily proved that bromine atom could be successfully introduced to M-SIBS.

![Fig. 1](https://doi.org/10.1007/s10118-021-2536-9)

**Fig. 1** \(^1H\) NMR spectra of M-SIBS triblock copolymers in CDCl\(_3\), M-SIBS1#: M-SIBS-16.5k0792; M-SIBS2#: M-SIBS-18.5k1198; M-SIBS3#: M-SIBS-19.7k1955; M-SIBS4#: M-SIBS-18.7k2052.
The $^1$H-NMR spectra of BM-SIBS triblock copolymers are shown in Fig. 2. The characteristic resonances at 0.78 ppm (a, $-\text{CH}(\text{CH}_3)_2$), 1.37–1.42 ppm (b, $-\text{CH}_2\text{CH}_2$), 1.63–1.70 ppm (c, $-\text{CH}2\text{CH}$), 4.51 ppm (d, $-\text{OH}$), 5.09 ppm (e, $-\text{CH}_2\text{CH}_2$), and 7.00 ppm (f, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PIB backbone and at 2.04 ppm (g, $-\text{CH}_2\text{CH}$), 2.37–2.44 ppm (h, $-\text{CH}_2\text{CH}$), 2.73–2.81 ppm (i, $-\text{CH}_2\text{CH}$), and 3.69–3.76 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PIB backbone and at 4.28 ppm (k, $-\text{CH}_2\text{CH}$), 5.07 ppm (l, $-\text{CH}_2\text{CH}$), 5.53 ppm (m, $-\text{CH}_2\text{CH}$), and 7.00 ppm (n, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PIB backbone.

Synthesis and Characterization of M-SIBS-g-PTHF Block Graft Copolymers

As shown in Scheme 1, terminal hydroxyl functionalized M-SIBS-g-PTHF block graft copolymers were successfully synthesized in CH$_2$Cl$_2$ by using the BM-SIBS with multifunctional benzyl bromine side functional groups as macrorinitiators to initiate living CROP of THF in the presence of AgClO$_4$ at 0 °C to create living M-SIBS-g-PTHF chains, which were terminated by H$_2$O via nucleophilic substitution.

The representative FTIR spectra of BM-SIBS macroinitiator and M-SIBS-g-PTHF block graft copolymer are shown in Fig. S3 (in ESI). A new characteristic absorbance at 1100 cm$^{-1}$ is assigned to the stretching vibration of the C–O–C groups in PTHF branches. The characteristic band at 820 cm$^{-1}$ is attributed to the bending vibration from the benzene rings of PS segments, which are located by the restriction arising from PTHF branches linking the p-MSt units. The broad and weak characteristic band at 3445 cm$^{-1}$ is attributed to the stretching vibration from the terminal –OH groups of PTHF branches could be observed in FTIR spectrum of the M-SIBS-g-PTHF chains. It suggests that M-SIBS-g-PTHF block graft copolymers could be successfully synthesized.

The $^1$H-NMR characterization was further performed on a representative M-SIBS-g-PTHF block graft copolymer to evaluate the chemical structure, as shown in Fig. 3. The characteristic resonances at 0.78 ppm (a, $-\text{CH}(\text{CH}_3)_2$), 1.37–1.42 ppm (b, $-\text{CH}_2\text{CH}_2$), 1.63–1.70 ppm (c, $-\text{CH}2\text{CH}$), 4.51 ppm (d, $-\text{OH}$), 5.09 ppm (e, $-\text{CH}_2\text{CH}_2$), and 7.00 ppm (f, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist. The characteristic resonance at 4.41 ppm is assigned to the corresponding protons in the benzyl bromine groups (k, $-\text{CH}_2\text{CH}_2$), 1.41 ppm (d, $-\text{CH}_2\text{CH}$), 2.28 ppm (i, $-\text{CH}_2\text{CH}$), and 2.82 ppm (j, $-\text{CH}_2\text{CH}$) are attributed to the corresponding protons along PS segments still exist.
copolymerization of THF. The absolute weight-average molecular weight of M-SIBS-g-PTHF block graft copolymers increased from 15.6 kg·mol\(^{-1}\) of M-SIBS triblock copolymer to 17.3–29.4 kg·mol\(^{-1}\). The content of PTHF in M-SIBS-g-PTHF block graft copolymers measured by \(^1\)H-NMR and gel permeation chromatography coupled with multiangle light scattering (GPC-MALS) were calculated according to Eq. S(6) (in ESI) and Eq. (1), respectively. It can be seen from Fig. S5 (in ESI) that the content of THF calculated by \(^1\)H-NMR \((W_{\text{THF,NMR}})\) is relatively close to the result calculated by GPC-MALS \((W_{\text{THF,GPC}})\). Characterization results for M-SIBS-g-PTHF block graft copolymers are summarized in Table S1 (in ESI).

**Effect of \(G_N\) and \(M_n,\text{PTHF}\) on Aggregation Structure of M-SIBS-g-PTHF Block Graft Copolymers**

Thermodynamic incompatibility from different segments in copolymers results in microphase separation. Transmission electron microscopy (TEM) was performed on M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymer dyed with RuO\(_4\) to characterize microphase separation structure in copolymers, as shown in Fig. 4. The light gray phases are attributed to the PIB segments. The size of hard domains increased after being grafted with PTHF polymer due to visible dyed PS and associated crystallizable PTHF segments (dark black phase). In contrast, M-SIBS-g-PTHF block graft copolymer was invisible without dyeing, as shown in Fig. S6(a) (in ESI). The TEM image of blank copper grid is shown in Fig. 4(c) and Fig. S6(b) (in ESI) for comparison.

To investigate the micromorphology of PTHF domains, HRTEM was applied to observe thin film formed from dilute solution of M-SIBS-g-PTHF block graft copolymer. The HRTEM images at different magnifications and fast Fourier transform (FFT) image are shown in Fig. 5. Clear microphase separation phenomenon at the nanoscale could be observed at relatively low magnification (Fig. 5a), which was different from foregoing TEM image dyed with RuO\(_4\) (Fig. 4b) due to invisible PS segments without dyeing. Regular lattice diffraction lines with lattice diffraction spacing of 0.222 nm appeared at relatively high magnification (Fig. 5b), demonstrating that PTHF nanocrystallization indeed existed. Moreover, diffraction points from PTHF nanocrystallization and dispersion ring from amorphous PIB and PS segments could be simultaneously observed in FFT image (Fig. 5c) of M-SIBS-g-PTHF block graft copolymer. These results proved the existence of PTHF.
nanocrystallization in bulk of M-SIBS-g-PTHF block graft copolymers.

The phase images of surfaces in M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers were obtained by AFM to further study microphase separation structure. As shown in Fig. S7 (in ESI), clear microphase separation phenomenon at the nanoscale could be observed. The phase images by AFM can be used for calculating the separated size of domains. The phase profiles of the topographs were presented in Fig. S7 (in ESI). After grafted with PTHF segments, strong separated peaks translated into weak multiplet due to introduction of tertiary component. Four sizes of separated domains formed on the surfaces of M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers; from a to d, they were 167, 67, 83, and 103 nm, respectively. The separated size of domain structure is related to structural composition of copolymers. The relationship between separated size of domain structure and $G_N$, $M_n,PTHF$ is shown in Fig. 6. The separated size significantly decreases after grafted with PTHF polymer, indicating that microphase separation degree was promoted by grafting PTHF segments. The separated size increases with increases in $G_N$ and $M_n,PTHF$, indicating that the size of domains containing PTHF and PS increases due to more PTHF branches incorporated into the SIBS backbone.

The height sensor images of surfaces in M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers obtained by AFM were used to investigate the influence of $G_N$ and $M_n,PTHF$ on the flatness of surfaces. As shown in Fig. 7, the height difference ($\Delta H$) significantly decreased after grafted with PTHF polymer. The roughness ($R_s$) of surfaces in M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers are shown in Fig. 8. All the $R_s$ values were less than 1.5 nm before and after grafted with PTHF polymer due to small $G_N$ of 2–6 and $M_n,PTHF$ of 200–4200 g·mol$^{-1}$. There was a tiny decrease in $R_s$ with increases in $G_N$ and $M_n,PTHF$.

### Nanocrystallization-locked Network in M-SIBS-g-PTHF Block Graft Copolymers

The samples of M-SIBS-g-PTHF block graft copolymers after storage at room temperature for 2 months became insoluble. It can be seen from Fig. 9(a) that M-SIBS-g-PTHF block graft copolymer is insoluble in cyclohexane. Compact physically cross-linked network was supposed to exist in M-SIBS-g-PTHF block graft copolymers due to PTHF crystallization locked in hard domains. To prove this hypothesis, M-SIBS-g-PTHF block graft copolymers were soaked in cyclohexane for 2 weeks, followed by freeze drying. The surfaces and cross sections after swelling of M-SIBS-g-PTHF block graft copolymers with different PTHF contents were observed by SEM, as shown in Figs. 9(b)−9(d) and Figs. S8(a)−S8(c) (in ESI). A lot of holes appeared on the surfaces of M-SIBS-g-PTHF block graft copolymers (Fig. 9d and Fig. S8c in ESI). The tightness and integrity of physically cross-linked network in the surfaces decreased with a decrease in PTHF content. Moreover, it is clear from cross section after swelling that only surface with certain depth was immersed and no change happened inside, indicating the formation of compact physically cross-linked network due to PTHF nanocrystallization locked in M-SIBS-g-PTHF block graft copolymers.

To prove the existence of PTHF nanocrystallization in M-SIBS-g-PTHF block graft copolymers, ultrathin sections without dyeing were observed by TEM. As shown in Fig. 10, clear microphase separation could be observed in M-SIBS-g-PTHF block graft copolymers due to PTHF nanocrystallization (dark black), which was clearly different from Fig. S6(a) (in ESI). When $M_n,PTHF$ decreased from 3.2k to 1.4k, the size of PTHF nanocrystallization decreased due to the short PTHF segments against crystallization. Therefore, the PTHF nanocrystallization in M-SIBS-g$_2$-PTHF-1.1k became more conspicuous due to the lower $M_n,PTHF$ compared with M-SIBS-g$_2$-PTHF-1.4k. Moreover, PTHF nanocrystallization in M-SIBS-g-g-PTHF block graft copolymer was also observed by HRTEM. The HRTEM images of ultrathin section without dyeing are shown in Figs. 11(a) and 11(b). Clear microphase separation phenomenon at the nanoscale and regular lattice diffraction lines still existed, but the lattice diffraction spacing increased to 0.241 nm. Diffraction points and dispersion ring also could be simultaneously observed in FFT image (Fig. 11c), indicating that PTHF nanocrystallization was stable in M-SIBS-g-PTHF.
The schematic diagram of the formation of nanocrystal-lization-locked physically cross-linked network was proposed on the basis of above results, as shown in Fig. 12. Nanocrystallization created and locked in hard microphase domains due to crystallisable PTHF branches embedded in the hard PS domains.

DSC was applied to investigate the transformation of HSs after grafted with PTHF polymer, as shown in Fig. 13(a). Two glass transition temperatures appeared during heating, suggesting phase separation behavior between SSs and HSs. No glass transition temperature of PS in HSs ($T_{g,HSs}$) was observed after grafted with PTHF polymer, which may be attributed to crystallisable PTHF segments in cross-linked network confining segmental mobility of PS segments. A broad endothermic peak was observed during heating, which was attributed to the melting temperature of PTHF ($T_{m,PTHF}$) in cross-linked network. The $T_{m,PTHF}$ shifted to higher temperature with increases in $G_N$ and $M_n,PTHF$, which was consistent with other PTHF-grafted copolymers,\[32,33,40\] as shown in Fig. 13(b). The $T_{m,PTHF}$ and melting enthalpy increased from 23 °C and 11.6 J·g$^{-1}$ in original soluble M-SIBS-g$_4$-PTHF-1.1k block graft polymer (Fig. S9 in ESI) to 153 °C and 117 J·g$^{-1}$, respectively, in nanocrystallization-locked M-SIBS-g$_4$-PTHF-1.1k block graft polymer network. Compared to the $T_{m,PTHF}$ of 7.0−43.2 °C in neat PTHF and PTHF-based block or graft copolymers,\[28,31,37,38,42\] the $T_{m,PTHF}$ in M-SIBS-g-PTHF block graft copolymer networks increased to above 140 °C due to PTHF nanocrystallization locked in cross-linked network containing hard PS domains.

Fig. 7 Representative two-dimensional phase images and three-dimensional height sensor images of (a) M-SIBS and (b) M-SIBS-g$_4$-PTHF-1.4k.

Fig. 8 The relationship between roughness ($R_a$) of M-SIBS-g-PTHF block graft copolymers and $G_N$, $M_n,PTHF$.

Fig. 9 (a) Photograph of insoluble nanocrystallization-locked M-SIBS-g$_4$-PTHF-3.2k block graft copolymer in cyclohexane and (b–d) SEM images of M-SIBS-g$_4$-PTHF-3.2k block graft copolymer after swelling in cyclohexane for 2 weeks and freeze drying to remove solvent.
In order to confirm the formation of physically cross-linked network in M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymer, the rheological behavior was measured by rheometer. The temperature ramp of M-SIBS triblock copolymer at a frequency of 1 Hz is shown in Fig. 14(a). The physically cross-linked network formed by microphase separation began to dissociate at 67 °C, corresponding to $T_{g,HS}$(Fig. 13a). Viscous transition appeared at 130 °C when the network completely dissociated.

If the $G''$ versus $G'$ plots measured at different temperatures are superimposable, the material exhibits no structural change in the examined temperature range. Obvious structural change occurred at the range from 110 °C to 130 °C, further verifying the disappearance of network. The temperature ramp of M-SIBS-g-PTHF block graft copolymer at a frequency of 1 Hz is shown in Fig. 14(c). When the temperature increased from 100 °C to 170 °C, $G'$ slightly decreased.

Fig. 10 TEM images of ultrathin sections without dyeing: (a) M-SIBS-g$_4$-PTHF-3.2k, (b) M-SIBS-g$_4$-PTHF-1.4k, and (c) M-SIBS-g$_5$-PTHF-1.1k.

Fig. 11 (a, b) HRTEM images and (c) FFT image of M-SIBS-g$_5$-PTHF-1.1k ultrathin section without dyeing.

Fig. 12 Schematic diagram of nanocrystallization-locked physically cross-linked network formed in M-SIBS-g-PTHF block graft copolymers containing crystallizable PTHF segments.

Fig. 13 (a) DSC thermograms recorded during heating for M-SIBS triblock copolymer and M-SIBS-g-PTHF block graft copolymers. (b) Ashby plot of $T_{m,PTHF}$ in M-SIBS-g-PTHF block graft copolymers and other PTHF-grafted copolymers reported in literature.[32,33,40]
while $G'$ sharply decreased. $G'$ is higher than $G''$ in the range from 100 °C to 170 °C, indicating that the integrity of network was maintained. $G''$ versus $G'$ plots for M-SIBS-g-PTHF-1.1k block graft copolymer by frequency sweeps at various temperatures but at the same frequency are shown in Fig. 14(d). The differences between $G'$ and $G''$ broaden with an increase in temperature. Therefore, no obvious structural change occurred at 100 °C and 150 °C, while structural change occurred at 180 °C due to the melt of PTHF crystallization.

CONCLUSIONS

A series of M-SIBS-g-PTHF block graft copolymers with various average grafting numbers ($G_N$) and molecular weights of branches ($M_{n,PTHF}$) were synthesized via combination of living cationic block copolymerization of IB, St and p-MSt, nucleophile substitution of M-SIBS with molecular bromine, and living CROP of THF. M-SIBS-g-PTHF block graft copolymers displayed clear microphase separation. The microphase separation improved after grafted with PTHF segments. The size of HSs increased and the separated size of microphase in M-SIBS-g-PTHF block graft copolymers decreased after grafted with PTHF segments. The separated size of microphase slightly increased with increases in $G_N$ and $M_{n,PTHF}$ due to PTHF. The roughness ($R_a$) decreased after grafted with PTHF segments and exhibited a gradually dropping trend with increased $G_N$ and $M_{n,PTHF}$. PTHF branches rearranged due to microphase separation to form nanocrystallization locked in network after storage at room temperature for 2 months. The melting temperature and enthalpy of PTHF nanocrystallization locked in hard domains of M-SIBS-g-PTHF-1.1k block graft copolymer increased remarkably upto 153 °C and 117.0 J·g$^{-1}$ by 130 °C and 106 J·g$^{-1}$ respectively after storage for long time. The movement of PS segments was confined by PTHF nanocrystallization locked in network, which could effectively improve the service temperature of SIBS TPE materials.

Electronic Supplementary Information

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