Synthesis and Characterization of ABC-type Star and Linear Block Copolymers of Styrene, Isoprene, and 1,3-Cyclohexadiene

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ABSTRACT: Mikto three-arm, ABC-type star copolymers of styrene, isoprene, and 1,3-cyclohexadiene were synthesized by anionic polymerization using 1,3-bis(1-phenylvinyl)benzene (MDDPE) as linking precursor. A polystyrene macromonomer was prepared by monoaddition of polystyryllithium toward MDDPE. The resulting macromonomer was coupled with polyisoprenyllithium through the remaining double bond in MDDPE moiety, forming a diblock copolymer of styrene and isoprene. The diblock copolymer possessed a living center of diphenylethyllithium, which subsequently initiated the polymerization of a small amount of isoprene (“seeding”) and 1,3-cyclohexadiene. It was found that, without the “seeding” process, diphenylethyllithium was not able to initiate the polymerization of 1,3-cyclohexadiene. The resulting macromonomer and star polymers were characterized by gel permeation chromatography, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, and ^{1}H NMR spectroscopy. In addition, linear ABC-type triblock copolymers of the corresponding monomers with different sequences were also synthesized. Microphase separation of the linear and star copolymers was investigated by differential scanning calorimetry and transmission electron microscopy.

Introduction

Polycyclohexadiene (PCHD) and its hydrogenated products possess the highest glass transition temperature among nonconjugated hydrocarbon polymers due to the alicyclic enchainment in the backbones. Since Natori[1] and Mays[2] reported the synthesis of narrow disperse PCHD with large molecular weight by anionic polymerization of 1,3-cyclohexadiene (CHD) in the presence of polydentate chelates such as *N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) and 1,4-diazobicyclo[2.2.2]octane (DABCO), a number of works have concerned the effects of reaction condition on polymerization[2−5] and the microstructure[6] of the resulting PCHD. The protocol was employed in the synthesis of block and star copolymers containing PCHD segments.[2b,4b,6b,7−14] The block copolymers were synthesized through sequential polymerizations of different monomers. Core−shell cylindrical structure[15] was observed for diblock copolymers of styrene and CHD. Star-shaped homo PCHD and star-block copolymers of CHD and isoprene/styrene were synthesized by end-linking using divinylbenzene[10,11] and chlorosilane[12] as linking agents. Miktoarm A_2B, A_3B-type star copolymers containing PCHD segments, and the subsequent hydrogenation products were also reported by Hadjichristidis and co-workers using stepwise chlorosilane linking process.[13]

On the other hand, ABC-type linear block and miktoarm star copolymers have attracted much attention due to the diversity of their morphologies.[16] Many of these copolymers were synthesized by anionic polymerization.[17] Focusing on star copolymers, the linking of different arms was accomplished by chlorosilane and 1,1-diphenylethylene (DPE) derivatives. For instance, Hadjichristidis and co-workers synthesized (PS)(PI)(PB),[18] (PI)(PS)(PDMS),[19] (PS)(PI)(P2VP),[20] and (PS)(PI)(PMMA),[21] in which PB, PDMS, P2VP, and PMMA represent polybutadiene, poly(dimethylsiloxane), poly(2-vinylpyridine), and poly(methyl methacrylate), respectively, using a stepwise chlorosilane coupling technique. Hashimoto and co-workers[22] used DPE derivative **1** to prepare PDMS macromonomers after the hydroxyl group was titrated with 1,1-diphenylhexyllithium. The macromonomer was then coupled with polystyryllithium (PSLi) by anionic addition to the DPE double bond to form diphenylhexyllithium, which subsequently initiated polymerization of *tert*-butyl methacrylate (*t*BMA) to prepare miktoarm star copolymer (PDMS)(PS)(P*t*BMA). Quirk and co-workers[23] prepared poly(ethylene oxide) (PEO) macromonomer with DPE terminus using DPE derivative with propanol functionality, **2**, treated with triphenylmethylpotassium as initiator. Star copolymers of (PEO)(PS)(P*t*BMA) were synthesized after coupling with PSLi followed by anionic polymerization of *t*BMA. Abetz and co-workers[24,25] prepared PS and PB macromonomer by coupling polymer anion with the bromomethyl group in DPE derivative **3**. Star copolymers of (PS)(PB)(P2VP) and (PS)(PB)(PMMA) were synthesized after coupling with corresponding polymer anion and polymerization of 2-vinylpyridiene and MMA. Dumas et al.[26] synthesized a series of ABC-type amphiphilic star copolymers using DPE derivative **4**.

Most recently, ABCD-type miktoarm star copolymers of styrene, α-methylstyrene, 4-methylstyrene, and MMA, as well as copolymers of isoprene, 4-methoxystyrene, styrene, and 4-trimethylsilylstyrene were synthesized using DPE derivatives **4** and **5**, respectively, by Hirao and co-workers.[27] In another example, Hadjichristidis and co-workers[28] synthesized 4-miktoarm star copolymer (PI)(PDMS)(PS)(P2VP) using compound **6** as the linking core.

Bifunctional DPE derivatives, such as 1,3-bis(1-phenylvinyl)benzene (MDDPE, **7**) and its 1,4-isomers, were used as precursors for dilithium initiators many years ago.[29] Quirk proposed the synthesis of heteroarm star copolymers using **7** and its 1,4-isomer as the linking precursor.[30] Although the process worked well, the heteroarm stars synthesized by the same authors were homopolystyrene with different arm lengths. The synthesis of ABC-type miktoarm star copolymer through MDDPE route was not yet reported in a peer-reviewed scientific journal. In this

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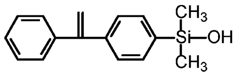
paper, we first report the synthesis of ABC-type miktoarm star copolymers of styrene, isoprene, and CHD, coded as (PS)(PI)(PCHD), employing the MDDPE route. Our purpose is to introduce a contrast of flexibility among different arms, since PCHD is unlike flexible coil polymers,[31] which may cause interesting properties of the tertiary copolymers.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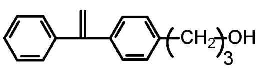
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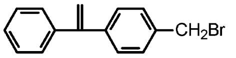
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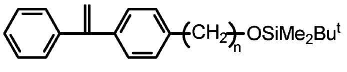
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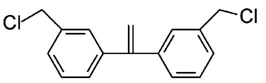
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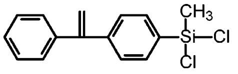
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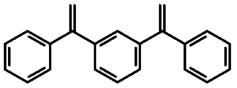
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Experimental Section

Materials. CHD (Fluka, 97%) and isoprene (Fluka, ≥98%) were stirred over CaH_2, vacuum distilled, and stored under nitrogen atmosphere at 4 °C. These monomers were freshly redistilled on polystyryllithium (PSLi) before polymerization. Styrene (China National Pharmaceutical, ≥99%) was stirred over CaH_2 for one night and then distilled, stored in nitrogen atmosphere at 4 °C, and distilled over di-*n*-butylmagnesium ($MgBu_2$) (Aldrich, 1.0 M in heptane) prior to use. Cyclohexane (Shanghai Feida, 99.5%) and tetrahydrofuran (THF) (Shanghai Feida, 99.5%) were refluxed over sodium (Na) in the presence of benzophenone until a brightly deep purple color was attained. These solvents were redistilled from 1,1-diphenylhexyllithium (DPELi, adduct of *n*-BuLi or *s*-BuLi and DPE) or PSLi in a vacuum line before use. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) (Aldrich, >99%) was purified by distilling from PSLi in a vacuum line and diluted with dry cyclohexane. *sec*-Butyllithium (*s*-BuLi) (Acros, solution in cyclohexane/heptane) and methyllithium (Acros, 1.6 M solution in diethyl ether) were used as received. The concentration of *s*-BuLi was analyzed by double titration. Methyltriphenylphosphonium bromide (Lancaster, >98%) and 1,3-dibenzoylbenzene (Aldrich, 98%) were vacuum-dried at 50 °C for 12 h. MDDPE (**7**) was synthesized from 1,3-dibenzoylbenzene via the Wittig reaction of methyltriphenylphosphonium bromide and methyllithium in ether according to the method of Schulz and Höcker[32] to yield a clear oil in 40% yield (purity 98.2% by HPLC). ^1H NMR ($CDCl_3$): δ (ppm) = 7.36 (m, 14 H, aromatic), 5.47 (m, 4 H, $=C\mathbf{H}_2$). GC−MS: 99.1%, *m*/*e* = 282. Anal. Calcd for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.0; H, 6.5. FT-IR (NaCl): $\nu = 3080$ cm^{-1} ($=CH_2$), 1610 and 1493 cm^{-1} (aromatic ring). UV−vis (cyclohexane): λ_{max} (by second derivative) = 223, 234, 252, 258, 264, 267, 271, 284, 292 nm.

Synthesis of Miktoarm Star Copolymers. All of the reactions were performed in round-bottom flasks connected to the vacuum line and equipped with an inert gas (Ar or N_2) inlet and a rubber septum. The glass apparatus was dried by three cycles of flaming/N_2-purging/evacuating and rinsed with a dilute solution of *s*-BuLi in cyclohexane and then purified cyclohexane several times before polymerization. All reactions were conducted in inert atmosphere.

Synthesis of PS Macromonomer. Cyclohexane (30 mL) and styrene (2.73 g, 0.03 mol) were distilled over PSLi and $MgBu_2$, respectively, into the reaction flask. *s*-BuLi (0.39 mmol, 0.30 mL of cyclohexane/heptane solution) was injected to the system using a syringe. Upon the addition of initiator the color of the solution turned light orange, indicating that the polymerization started. The mixture was thermostated at 40 °C, polymerized completely in 2 h. Then an aliquot of the reaction mixture was taken for characterization. GPC: $M_{n,GPC} = 6.4 \times 10^3$ g/mol, $M_w/M_n = 1.09$. ^1H NMR: $M_{n,NMR} = 8.1 \times 10^3$ g/mol.

The resulting polystyryllithium solution was slowly dropped into a solution of **7** (0.44 g, 1.56 mmol) in THF (90 mL) with vigorously stirring at −78 °C (dry ice/acetone bath). The solution immediately became dark red in color, indicating the addition of polystyryllithium to **7**. After 5 h the reaction was deactivated by 0.5 mL of degassed methanol. The reaction mixture was dropped into large amounts of methanol and then filtered. The process was repeated three times to remove unreacted **7**. The precipitate was filtered and dried in a vacuum at 55 °C for 48 h. Yield: 99.6%

Coupling of PS Macromonomer and Polyisoprenyllithium. The PS macromonomer (2.72 g, 0.34 mmol) was dissolved in 50 mL of cyclohexane and titrated with dilute DPELi solution until a light yellow color was sustained. The titrated solution was mixed with a solution of polyisoprenyllithium (GPC: $M_n = 1.5 \times 10^4$ g/mol, $M_w/M_n = 1.10$) in cyclohexane, which was prepared from isoprene (4.10 g, 0.06 mol) polymerization initiated by *s*-BuLi (0.39 mmol, 0.30 mL of cyclohexane/heptane solution) in cyclohexane at 35 °C. THF (1 mL, [THF]/[Li] = 32) was added and the mixture became immediately deep red in color, indicative of the addition of polyisoprenyl anion to the DPE double bond of the PS macromonomer. The mixture was stirred at 30 °C for 4−5 h. GPC: $M_n = 2.2 \times 10^4$ g/mol, $M_w/M_n = 1.24$.

Polymerization of CHD. The resulting polymeric 1,1-diphenylethyl anion in the coupling reaction was "seeded" with a small amount of isoprene. Thus, a total of 0.40 g of isoprene was added into the reactor in three batches and the polymerization proceeded for 40 min at 5−10 °C. Then TMEDA (0.48 mmol, 1 mL × 0.48 M cyclohexane solution) was injected into the flask and the reaction mixture was stirred for 40 min before CHD (3.36 g, 0.04 mol) was added. The polymerization proceeded for 14 h at 5−10 °C and was terminated by 0.5 mL of degassed methanol.

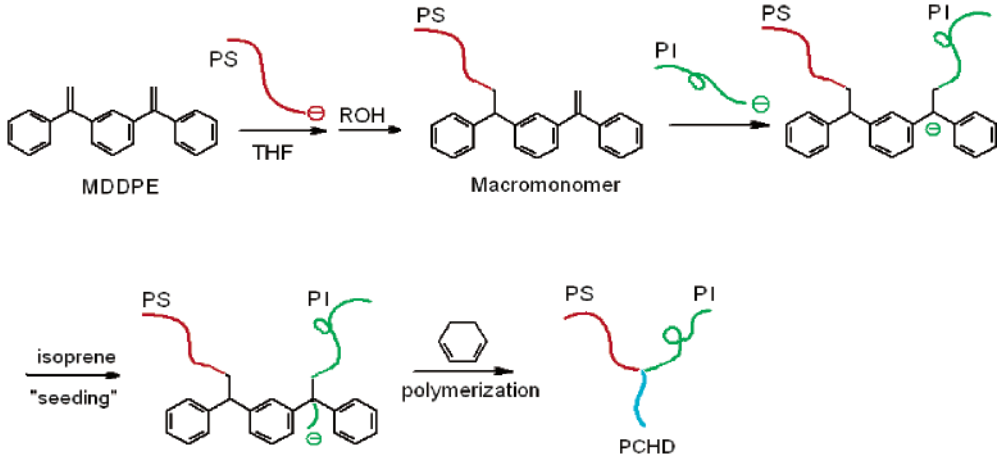
The product was precipitated in a 10-fold excess of methanol containing ~0.1% w/v 2,6-di-*tert*-butyl-4-methylphenol (BHT, stabilizer), filtered, and dried under vacuum at 55 °C to constant weight. GPC: $M_n = 3.2 \times 10^4$ g/mol, $M_w/M_n = 1.29$.

Model Polymerization of CHD Initiated by DPELi and Polyisoprenyllithium (PI−Li). DPELi (0.18 mmol, 5 mL × 0.04 M solution in cyclohexane, addition products of *s*-BuLi and DPE) and TMEDA (0.23 mmol, 0.48 M solution in cyclohexane) were added to 25 mL of dry cyclohexane. The solution was slowly warmed to 60 °C, stirred for 10 min, and then cooled to room temperature for 30 min. CHD (1.70 g, 0.02 mol) was added and the mixture was stirred in N_2 atmosphere at room temperature. No polymer was detected by GPC after 24 h of reaction.

DPELi (0.56 mmol, solution in cyclohexane, addition products of *s*-BuLi and DPE) was added in 25 mL of cyclohexane. Then isoprene (0.14 g, 2.05 mmol) was added with rigorous stirring, and the solution color changed into yellow immediately. After reaction for 40 min at 35 °C, TMEDA (0.55 mmol, 0.48 M solution in cyclohexane) was injected and the mixture was stirred for 0.5 h. CHD (0.053 mol, 4.20 g) was added and polymerized for 2 h at 40 °C. The polymerization was quenched by injecting 0.5 mL of methanol into the reaction system. GPC: $M_n = 1.50 \times 10^4$ g/mol, $M_w/M_n = 1.60$.

Synthesis of Linear Triblock Copolymers of Styrene, Isoprene, and CHD with Different Sequences. Linear triblock copolymers were prepared by sequential polymerization of the monomers, in which TMEDA was used as additive for CHD polymerization. One example of PI-*b*-PCHD-*b*-PS was described below. Polyisoprenyllithium with calculated molecular weight $M_{n,theo.} = 1.8 \times 10^4$ g/mol was synthesized by polymerization of isoprene (4.80 g, 0.071 mol) initiated by *s*-BuLi (0.26 mmol, 1.30 M in cyclohexane) in 140 mL of cyclohexane at 35 °C. An aliquot was withdrawn and terminated with methanol for GPC characterization. TMEDA (0.32 mmol, 0.67 mL × 0.48 M cyclohexane

Scheme 1



solution) was injected into the reaction system and the reaction mixture was stirred for 40 min at 40 °C. Then CHD (2.1 g, 0.03 mol) was added to the reaction vessel and the reaction stood for 4 h at 25 °C, followed by polymerization of styrene (4.1 g, 0.04 mol) for 3.5 h at 30 °C. The polymerization was terminated by injecting 0.5 mL of degassed methanol. The final product was precipitated in a 10-fold excess of methanol containing ~0.1% w/v 2,6-di-*tert*-butyl-4-methylphenol (BHT, stabilizer) and dried in a vacuum at 55 °C. GPC: PI, $M_n = 2.56 \times 10^4$ g/mol, $M_w/M_n = 1.11$; diblock PI-*b*-PCHD, $M_n = 4.04 \times 10^4$ g/mol, $M_w/M_n = 1.24$; triblock of PI-*b*-PCHD-*b*-PS, $M_n = 5.15 \times 10^4$ g/mol, $M_w/M_n = 1.29$.

Characterization. High performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters 515 pump, a C-18 column (SymmetryShieldP RP-18, 5.0 μm, 4.6 × 250 mm), and a UV-detector (254 nm). Acetonitrile/water (83/17, v/v) was used as eluent (1.0 mL·min^{-1}) at 40 °C. ^{1}H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using $CDCl_3$ as the solvent and tetramethylsilane as the reference. Gas chromatography/mass spectroscopy (GC−MS) was performed on a Finnigan Voyager instrument in electrospray ionization mode (70 eV). Fourier transform infrared spectroscopy (FT-IR) was performed on a Magna-550 instrument (sodium chloride pellet). The ultraviolet adsorption of MDDPE in cyclohexane was recorded by a Perkin-Elmer Lambda 35 UV−vis spectroscope at 25 ± 0.1 °C with wavelength from 190 to 600 nm.

The number-average molecular weight, M_n, and polydispersity index, M_w/M_n, of all samples were measured by gel permeation chromatography (GPC) through three Waters Styragel columns (pore size 10^2, 10^3, and 10^4 Å) in series calibrated by narrow polystyrene standard with molecular weight ranging from 2.2×10^3 to 5.15×10^5 g/mol. THF was used as the eluent at a flow rate of 1.0 mL·min^{-1} at 40 °C. The elution of the sample was detected by a Waters 410 RI detector. Elemental analysis was carried out on an Elementar Vario EL Instrument.

The mass spectrum was acquired using a Voyager DE-STR matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF MS) mass spectrometer equipped with a 337-nm nitrogen laser. Samples, dithranol (matrix), and silver trifluoroacetate were dissolved in THF with the concentrations of 10, 20, and 10 mg/mL, respectively. These solutions were mixed in the volume ratio of matrix/polymer/salt = 10/2/1. A volume of 0.5 μL of the mixed solution was placed on a copper plate and air-dried at ambient temperature. Mass spectra were acquired in positive linear mode using an acceleration voltage of 25 kV. External mass calibration was performed using a standard peptide mixture (insulin, thioredoxin). Spectra were obtained by setting the laser power close to the threshold of ionization, and generally 700 pulses were acquired and averaged.

Differential scanning calorimetry (DSC) was measured on a Thermal Analysis Q 100 instrument calibrated with indium and tin. The samples (10−20 mg) were heated to 180 °C at a rate of 20 K·min^{-1} and then cooled to −90 °C and heated to 250 °C for the second heating process. The glass transition temperature (T_g) was attained at the second heating process.

Transmission electron microscopy (TEM) was performed on film specimen microtomed at −100 °C that were cast from the polymer solutions of toluene (10%, w/v) and annealed at 120 °C in high vacuum for 1 week. Slices with thickness of about 80 nm were collected with copper grids and stained in OsO_4 vapor for 40 min. The measurement was conducted on a Hitachi-800 instrument at an accelerating voltage of 200 kV.

Results and Discussion

Synthesis of Miktoarm Star Copolymer (PS)(PI)(PCHD). The synthesis of the star copolymer through the MDDPE route is outlined in Scheme 1. It is similar to that used by Quirk[30] to prepare star polystyrene with three arms of different lengths. The procedure involved the preparation of polystyrene macromonomer by the monoaddition reaction of polystyryllithium with MDDPE. To minimize the chain transfer effect of CHD,[2,3] this monomer was polymerized as the final step in all cases.

Synthesis and Characterization of PS Macromonomer. The key factor to the success of macromonomer synthesis is exclusive formation monoadduct (free of diadduct) between polystyryllithium and MDDPE. It was reported[29,33−36] that the two double bonds in MDDPE had equivalent reactivity toward anionic addition, since the first anion could not be delocalized to the second double bond. However, it was also found that the addition reaction behavior depended on the solvent, i.e., sole monoadduct in THF[37,38] and remarkable diadduct in cyclohexane,[33,34] even in an excess of MDDPE. Therefore, we performed the addition reaction in THF at −78 °C with 2−4-fold excess of MDDPE.

Figure 1 is the GPC chromatograms of the polystyrene precursor and the macromonomer. The same molecular weight and the unimodal distribution demonstrate that only monoadduct was formed. Figure 2 shows the ^{1}H NMR spectrum of the macromonomer purified by three cycles of dissolving (THF)/precipitating(methanol) process and dried in a vacuum. The signals of vinylic protons are clearly visible at a chemical shift 5.40 and 5.32 ppm, while that of the methine proton appeared at 3.46 ppm. The functionality of the PS macromonomer was nearly 100%, as estimated from the integration of vinyl protons relative to that of methyl protons derived from the *s*-BuLi fragment at 0.5−0.78 ppm.

The high functionality is not only a consequence of selective addition reaction but also, technically, a consequence of the high purity of MDDPE. Since MDDPE is not easy to purify by distillation due to its high boiling point, we used a dilute solution of DPELi to titrate the solution of MDDPE to eliminate any

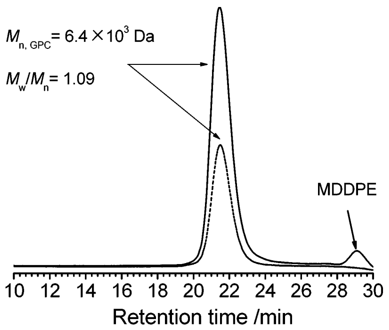


Figure 1. Gel permeation chromatograms (GPC) of polystyrenes before (dashed line) and after (solid line) addition toward 1,3-bis(1-phenylvinyl)benzene (MDDPE). Reaction conditions: styrene, 2.73 g (0.03 mol); *s*-BuLi, 0.39 mmol; MDDPE, 0.44 g (1.56 mmol); [MDDPE]/[PSLi] = 4 (molar ratio); temperature, −78 °C. The polymerization was conducted in cyclohexane, and the addition reaction in a mixture of tetrahydrofuran and cyclohexane (3/1, v/v).

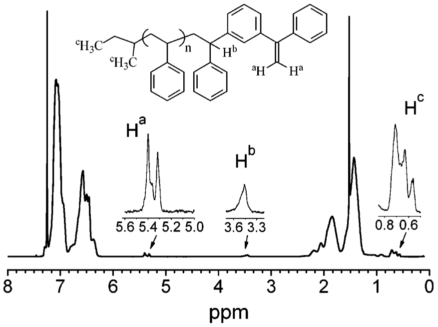


Figure 2. ^{1}H NMR spectrum of polystyrene macromonomer. The preparation conditions of macromonomer are identical with those in Figure 1.

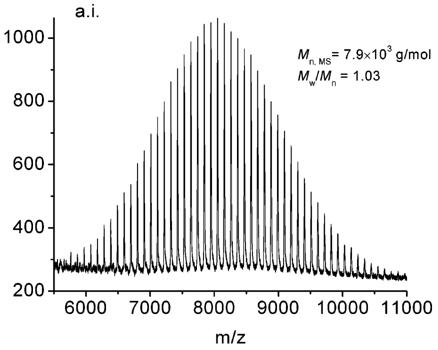


Figure 3. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (linear mode) of polystyrene macromonomer. The preparation conditions of macromonomer are identical with those in Figure 1.

impurities, until a slight red color was sustained. The presence of trace amounts of residual DPELi did not cause any side reaction.

The resulting PS macromonomer was further analyzed by MALDI-TOF MS. Figure 3 shows a monomodal MS spectrum, with the enlargement shown in Figure 4. The interval between two main peaks is 104.2, equal to the molecular weight of styrene. The observed mass of the peaks, for example, 8052.5 Da in Figure 4, corresponds to those polymer chains with 74 styrenic repeating units plus silver ion, e.g., $C_4H_9(C_8H_8)_{74}C_{14}H_{11}\cdot Ag^+$, calcd mass = 8051.5 Da, within the range of system error, ±1.5‰, of the linear mode. Besides, the enlargement of the spectrum in Figure 4 shows that the sample is quite pure, indicative of a high functionality of the macromonomer.

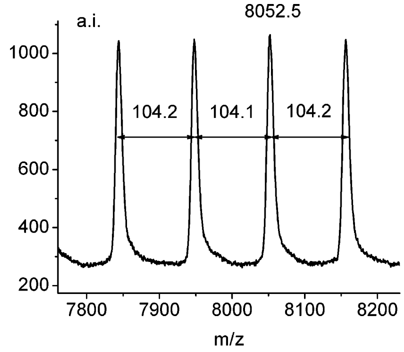


Figure 4. Enlargement of matrix-assisted laser desorption/ionization time-of-flight mass spectrum (linear mode) of polystyrene macromonomer shown in Figure 3.

Table 1. Synthesis and Characterization of Polystyrene Macromonomer

sample no.	[MDDPE]/[anion]	$M_{n, GPC}$ × 10^{-3} (Da)	$M_{n,NMR}$ × 10^{-3} (Da)	$M_{n,CAL.}$ × 10^{-3} (Da)	M_w/M_n (GPC)	functionality (NMR)
1	2	11.1	16.4	15.0	1.19	1.00
2	2	16.9	22.7	21.0	1.14	0.91
3	4	6.4	8.1	7.0	1.09	0.95

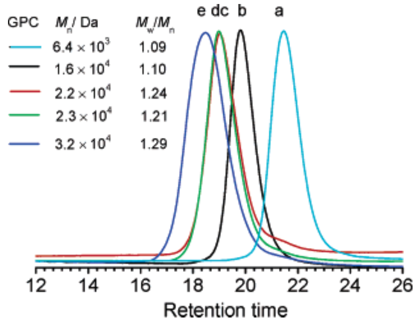


Figure 5. Gel permeation chromatograms monitoring the synthesis of 3-miktoarm star terpolymer of styrene, isoprene, and 1,3-cyclohexadiene (no. 5, Table 2). (a) Polystyrene macromonomer: styrene, 2.73 g (0.03 mol); *s*-BuLi, 0.39 mmol; 1,3-bis(1-phenylvinyl)benzene, 0.44 g (1.56 mmol); temperature, −78 °C; in mixture of tetrahydrofuran and cyclohexane (3/1, v/v). (b) Polyisoprenyllithium (PILi): isoprene, 4.10 g (0.06 mol); *s*-BuLi, 0.39 mmol; at 35 °C in cyclohexane for 2 h. (c) Diblock copolymer after coupling of macromonomer and PILi, in the presence of THF ([THF]/[PILi] = 32), at 30 °C for 4−5 h. (d) Diblock after "seeding" with isoprene (0.40 g, 6 mmol). (e) Star copolymer (PS)(PI)(PCHD): CHD, 3.36 g (0.04 mol); tetramethylethylenediamine (TMEDA), [TMEDA]/[Li] = 5/4; temperature, 5−10 °C; 14 h.

The characterization of macromonomers is summarized in Table 1. It is noted that the number-average molecular weights measured by NMR are closer to theoretical values than those measured by GPC, possibly due to the drift of GPC columns.

Coupling of PS Macromonomer and Polyisoprenyllithium. The obtained PS macromonomer was dissolved in cyclohexane and was coupled with polyisoprenyllithium through the addition of living anion to the remaining double bond of MDDPE terminus. Again, the solution of the macromonomer was purified by titration with DPELi until a slight red color appeared. It was reported[39] that the addition reaction of DPE with polyisoprenyllithium was very slow in nonpolar solvent such as cyclohexane, i.e., that even after 4 days the yield of adduct was lower than 60% at 50 °C. In the presence of Lewis base such as THF, the addition reaction became very fast and was completed within 1−4 h.[39] In this work, we used THF with a molar amount of 32-fold of anion species and 1/170 v/v of cyclohexane. The

Table 2. Polymerization Results of Star and Linear Polymers of Styrene, Isoprene, and CHD

	PS macromonomer		polyisoprenyllithium		PCHD	diblock after "seeding"		star	
star no.	$M_{n,NMR}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)	$M_{n,NMR}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)	$M_{n,NMR}$ $\times 10^{-3}$ Da	$M_{n,GPC}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)	$M_{n,GPC}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)
1	9.6	1.10	13.3	1.14	1.5			22.6	1.21
2	13.4	1.18	10.6	1.13	3.8	22.1	1.32	25.0	1.47
3	16.4	1.20	6.5	1.06	6.4	30.6	1.19	42.4	1.29
4	22.7	1.14	23.7	1.13	4.5	51.6	1.26	61.6	1.29
5	8.1	1.09	12.5	1.10	6.6	23.7	1.21	32.0	1.29
6[a]	12.8	1.15	14.2[b]	1.13		21.2[c]	1.24	40.1	1.27

		first block		diblock		triblock	
linear		$M_{n,GPC}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)	$M_{n,GPC}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)	$M_{n,GPC}$ $\times 10^{-3}$ Da	M_w/M_n (GPC)
7	PS-*b*-PI-*b*-PCHD	20.3	1.12	52.0	1.16	62.4	1.18
8	PI-*b*-PCHD-*b*-PS	25.7	1.11	40.4	1.24	51.5	1.29
9	PI-*b*-PS-*b*-PCHD	27.5	1.13	46.5	1.20	112.0	1.24

[a] Three-arm star homopolystyrene. [b] Polystyrenyllithium, measured by GPC. [c] Coupling product of PS macromonomer and polystyrenyllithium, without "seeding".

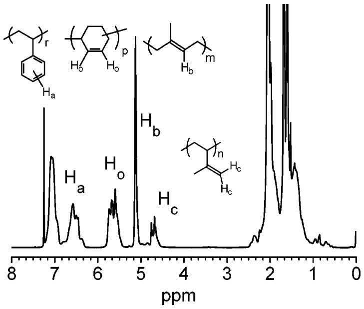


Figure 6. ^{1}H NMR spectrum of star polymer of isoprene, styrene, 1,3-cyclohexadiene (no. 5, Table 2). The preparation conditions of star polymer are identical to those of Figure 5.

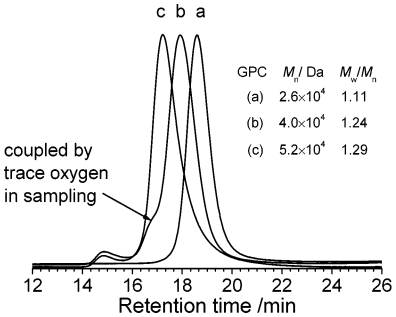


Figure 7. Gel permeation chromatography monitoring the synthesis of linear triblock copolymer (no. 8, Table 2). (a) Polyisoprenyllithium (PILi): isoprene, 4.8 g (0.07 mol); *s*-BuLi, 0.26 mmol; cyclohexane, 140 mL; 35 °C, 4 h. (b) PI-*b*-PCHD diblock: TMEDA, 0.32 mmol; CHD, 2.1 g (0.03 mol); 25 °C; 4−5 h. (c) PI-*b*-PCHD-*b*-PS triblock: styrene, 4.1 g (0.04 mol); 30 °C; 3.5 h.

initial solution of polyisoprenyllithium and macromonomer in cyclohexane was pale yellow in color at 30 °C. Upon addition of THF, the solution became deep red in color immediately, indicative of the addition reaction of polyisoprenyllithium toward PS macromonomer. The dramatic effect of Lewis base on the rate of addition was explained in terms of its effect on aggregation of the organolithium chain ends.[34] In the presence of THF, these chain ends tended to disaggregate, thus improving the reactivity of anions.[40]

The coupling reaction was completed within 4−5 h. GPC monitoring in Figure 5 shows that the peaks for PS macromonomer (line a, cyan) and polyisoprenyllithium (line b, black) disappeared, while a new peak (line c, red) appeared with negligible residual precursors. This demonstrated that the coupling reaction was nearly quantitative.

Polymerization of CHD. The final step of the miktoarm star synthesis was the polymerization of CHD. This was designed by regarding the chain transfer[2,3] to CHD monomer and the possible difficulty of addition of PCHD anion to DPE double bond. CHD was polymerized in the presence of TMEDA according to Natori's protocol,[1] with initiation by the resulting DPE anion formed in the coupling reaction. However, the GPC results showed no polymerization after 24 h. Therefore, we carried out the model reaction in which DPELi, an adduct of *s*-BuLi and DPE, was used as initiator. The result showed indeed that no polymer formed even in the presence of TMEDA. This implies that DPE anion could not initiate the polymerization of CHD, possibly due to steric hindrance of both the anion and the monomer.

Thus, it is necessary to change the 1,1-diphenylalkyllithium to an anion that can initiate the polymerization of CHD. We transformed 1,1-diphenylalkyllithium into polyisoprenyllithium by a "seeding" technique,[9] which was widely used in the preparation of dilithium initiator, using isoprene as the monomer. To achieve high "seeding" efficiency, we distilled a total small amount of isoprene in three batches into the reaction system after the coupling reaction. The "seeding" polymerization was evidenced by the change in color, from deep red to orange, of the reaction solution. As expected, the polymerization product contained only a very short polyisoprene segment, approximately 10−15 repeating units, as shown by the little shift of the GPC peak in Figure 5 (lines c, d).

In the above experiment, THF was introduced to ensure a fast coupling reaction. TMEDA had a similar effect but retarded the "seeding" process at the molar ratio of TMEDA/anion = 5/4. The same result was found for a model system of DPELi/TMEDA/isoprene. Thus DPELi was not able to initiate the polymerization of isoprene in the presence of TMEDA. This is quite surprising, since DPELi works very well in the initiation of isoprene and butadiene in cyclohexane.[39] The reason is unclear presently.

In this regard, TMEDA had to be introduced only after the THF-aided "seeding" polymerization. CHD was then polymerized steadily for a long time. The GPC chromatogram in Figure 5 (line e) shows negligible remaining diblocks and "seeding" products, illustrating the high efficiency of "seeding" and the preparation of the star copolymers.

A number of ABC-type miktoarm star copolymers with varying arm length were synthesized according to the above process. The results are summarized in Table 2 (no. 1−6), together with the synthesis of ABC triblock copolymers. It is

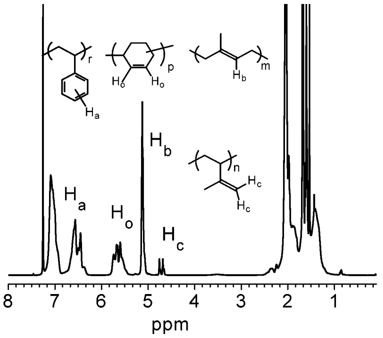


Figure 8. ^{1}H NMR of the PI-*b*-PCHD-*b*-PS triblock copolymer (no. 8, Table 2). The preparation conditions of linear triblock copolymer are identical to those of Figure 7.

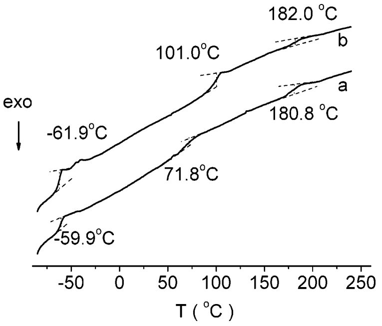


Figure 9. DSC of star and linear triblock copolymers: (a) star polymer, no. 5 in Table 2, $(PS)_{78}(PI)_{184}(PCHD)_{83}$; (b) linear polymer, no. 8 in Table 2, $PI_{270}PCHD_{102}PS_{172}$. The samples were annealed for 7 days at 120 °C, heated from −90 to 180 °C, and quenched before characterization. The measurements were performed from −90 to 250 °C at a rate of 20 K·min^{-1}.

noted that the measured percentage of 1,3-CHD units in the star terpolymer was always lower than the feed. The difference is a consequence of chain transfer reactions that lead to an incomplete conversion of CHD. Figure 6 shows a typical ^{1}H NMR of the miktoarm star copolymer (sample no. 5 in Table 2). The percent of 1,4-enchainment in polyisoprene block is as high as 84.5% because the polyisoprene arm was prepared in cyclohexane and the "seeding" reaction was conducted in the presence of THF.

Synthesis of Linear Triblock Copolymer of Isoprene, Styrene, 1,3-Cyclohexadiene with Different Sequences. One of the motives of this work is to synthesize a series of ABC-type tertiary block and star copolymers with different sequences in the former. Although the linear diblock and multiblock copolymers have been synthesized previously,[2b,7,9,12,14] ABC-type triblock copolymers with a central PCHD block have never been reported, possibly due to the chain transfer reaction caused by residual CHD monomer. Hadjichristidis mentioned in ref 7 the synthesis of ABCD-type block copolymer with PCHD as the C block. However, detailed characterization of the product was not disclosed. In the present work, we found that ABC triblock copolymers with PCHD as the central block can be synthesized using simple sequential polymerization, in which TMEDA was always introduced before polymerization of CHD. Nevertheless, attention should be paid to ensure a high conversion of CHD so that the following polymerization of the third block was free of CHD. This was done by prolonging polymerization time and lowering the reaction temperature (25 °C) to reduce the chain transfer reaction. It was quite successful, since ^{1}HNMR showed no notable differences of CHD composition between diblock and triblock copolymers. In addition, polyisoprene was prepared as the first block to ensure high 1,4-enchainment in the absence of TMEDA.

As an example, Figure 7 shows GPC results of synthesis of a triblock copolymer PI-*b*-PCHD-*b*-PS. Stepwise increase in molecular weight is observed. Notably, a new peak appeared at very high molecular weight, ~500 000 Da, for both diblock and triblock copolymers. A similar result[7,9] was reported previously and was attributed to micelle formation in THF, the eluent of GPC measurement. However, we are not assured of the explanation because a similar high molecular weight species was also reported,[9] and observed in our laboratory, in the homopolymerization of CHD with an initiating system of TMEDA/*s*-BuLi. Figure 8 shows the ^{1}H NMR spectrum of the triblock product (sample 8, in Table 2). The percent of 1,4-enchainment in polyisoprene block is as high as 94.4%, because isoprene was polymerized in cyclohexane.

The synthesized triblock copolymers with different sequences, PS-*b*-PI-*b*-PCHD, PI-*b*-PCHD-*b*-PS, and PI-*b*-PS-*b*-PCHD, are listed in Table 2 (no. 7−9).

Microphase Separation of the Block and Star Copolymers: Preliminary Results. Numerous papers reported the microphase separation of block and star copolymers with dissimilar blocks. The formation of domains of individual blocks affords the possibility to observe the corresponding glass transition temperature (T_g). The blocks of PS, PI, and PCHD in

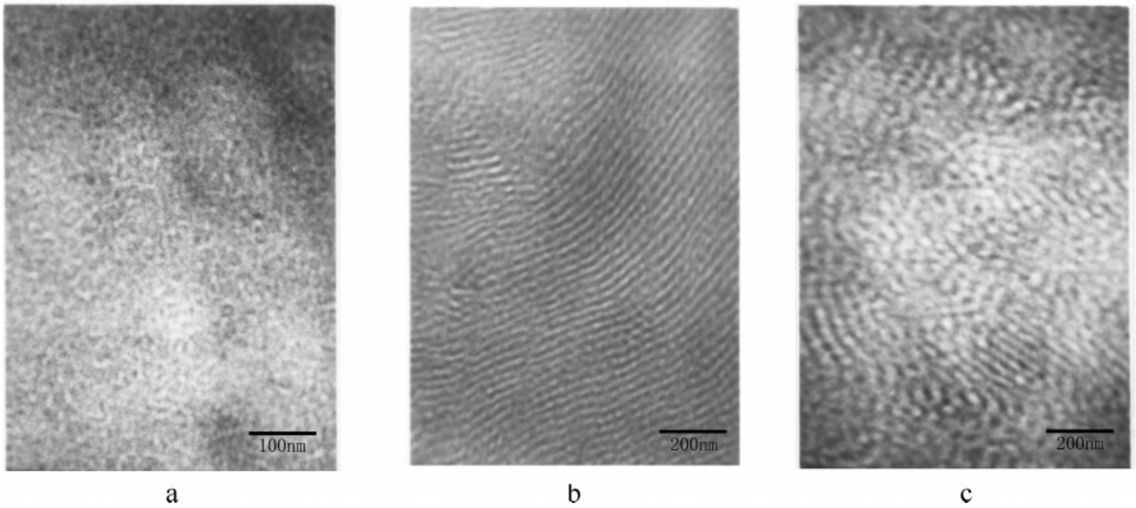


Figure 10. TEM morphologies of star and linear triblock copolymers: (a) Star polymer, no. 3 in Table 2, $(PS)_{158}(PI)_{96}(PCHD)_{80}$; (b) star polymer, no. 4 in Table 2, $(PS)_{218}(PI)_{349}(PCHD)_{56}$; (c) linear polymer, no. 8 in Table 2, PI_{270}-*b*-$PCHD_{102}$-*b*-PS_{172}.

this work are quite different in modulus and should undergo microphase separation in bulk material. Figure 9 shows DSC curves of a linear block and a miktoarm star copolymers. The samples were annealed at 120 °C for 7 days. The T_g values for PI, PS, and PCHD blocks are clearly visible at about −60, 70/100, and 180 °C, respectively. Regarding the block length of PCHD, the measured T_g values are notably higher than those in the literature of approximately 150 °C[5,6b,9,11,14] (Natori[6b] reported the highest T_g = 176 °C for, however, very large molecular weight PCHD homopolymer). This may be due to more 1,2-enchainment of CHD caused by the remaining THF in addition to TMEDA. The initiating species, polyisoprenyllithium, could also have effects on microstructure. Indeed, Natori reported that the microstructure depended on the initiating system, such as BuLi/TMEDA and PSLi/TMEDA.[3]

The morphologies of star polymers and linear triblock copolymers observed by TEM are shown in Figure 10. For star polymer $(PS)_{158}(PI)_{96}(PCHD)_{80}$, in which polyisoprene has significantly shorter block length, sphere-like morphology was observed (a). In samples with higher PI content, lamellar patterns were observed for either star (b) or linear triblock (c) copolymers. The presence of PCHD domains was evidenced by the periodic substructure of the polydiene lamella. Nevertheless, the contrast between PI and PCHD domains was not enough. Systematic work will be done on morphology observation in relation to the molecular structure, annealing process, and staining conditions.

Summary

ABC-type three-arm star copolymers of styrene, isoprene, and CHD with different arm lengths were synthesized by anionic polymerization through the MDDPE route. The synthesis was complexed by the initiation and polymerization of CHD. Specifically, the latter cannot be initiated directly by DPELi formed in the second stage of the preparation, i.e., the coupling of polystyrene macromonomer and polyisoprenyllithium, due to the steric hindrance of both DPE anion and CHD monomer. It is necessary to use a “seeding” procedure to activate the anion toward CHD monomer. Besides, linear block copolymers of styrene, isoprene, and CHD, including those with PCHD central blocks, were synthesized by simple sequential polymerization of the monomers.

The precursor macromonomer and star and block copolymers were characterized by GPC, MALDI-TOF MS, ^1H NMR, and DSC. Spherelike and lamellar morphologies of the microphase-separated samples were observed by TEM.

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