1,3-Cyclohexadiene Polymers. 2. Near-Monodisperse Star and Star-Block Polymers Based on Poly(1,3-cyclohexadiene)

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ABSTRACT: The synthesis of well-defined, near-monodisperse, three-arm star and star-block copolymers based on poly(1,3-cyclohexadiene) (PCHD) is described. The stars were prepared by the reaction of living anionic chain ends of PCHD, poly(styrene−1,3-cyclohexadiene) (PS-PCHD), and poly(1,3-cyclohexadiene−styrene) (PCHD-PS) with CH_3SiCl_3 in benzene. 1,4-Diazabicyclo[2.2.2]octane (DABCO) was used to control the anionic polymerization of 1,3-CHD; it also acted as a promoter during the linking reaction. The star polymers were fractionated to remove excess arm material and thoroughly characterized by size exclusion chromatography, matrix-assisted laser desorption ionization time-of-flight mass spectrometry, and light scattering.

Introduction

Constituting the simplest form of branching, star polymers are ideal for investigation into the structure−property relationships of branched polymers.[1] The first star polymers were synthesized in 1948 through condensation chemistry.[2] Since then, virtually all polymerization methods have been used to make various star polymers; however, all of these methods are variations of two more general methodologies.[3,4] The first method involves the polymerization of a monomer "*out of*" a multifunctional initiator. This can be an experimentally expedient and clean approach, but common practical difficulties with this method involve synthesis of an appropriate initiator and adequately promoting its efficiency. (To obtain narrow molecular weight distribution materials, all initiating sites must react quickly.) The second general method for making stars involves linking prepolymerized living polymer chains "*into*" a coupling reagent. This is by far the more extensively studied procedure. This latter approach provides the opportunity to sample and thus characterize the "arm" material before forming the star polymer and often allows mixed arm incorporation.[5,6] Divinylbenzene (DVB) and chlorosilanes are the most popular linking agents used. Chlorosilanes have become the classic linking agents for the synthesis of star polymers using anionic polymerization because of the clean and quantitative nature of the linking reaction (assuming steric effects are adequately considered). On the other hand, DVB provides robust but relatively less well-defined branched materials, since precise control over the number of arms is not possible and stars produced by this method are always mixtures of materials having different numbers of arms.

Compared to the number of publications on the synthesis and properties of star homopolymers, the number of studies published on star-block copolymers, which have block copolymer arms, is quite small. Price et al.[7] synthesized three- and four-armed star-block copolymers of styrene and isoprene (with styrene as the outer block) using chlorosilanes as linking agents. The styrene volume fractions of their samples were fixed at about 0.24. Even though about 25% excess of living arms was used, significant amounts of three-arm (for $SiCl_4$) and two-arm (for CH_3SiCl_3) species were formed. Bi and Fetters[8] synthesized six- and nine-armed DVB-linked polystyrene−polyisoprene stars containing ∼25 vol % polystyrene. This was achieved by adding a predetermined amount of DVB compounds to a solution of living diblock chains. Later, a variety of star-block copolymers with different kind of blocks have been synthesized with this method.[9,10] Extending their work, Bi and Fetters[11] synthesized and studied two series of chlorosilane and DVB linked styrene−butadiene and styrene−isoprene star-block copolymers containing up to 29 arms and having approximately 27−40 vol % polystyrene (outer block). They found that the synthesis of four-armed star-block copolymers was facilitated by adding several units of butadiene to the polyisoprenyllithium chain ends prior to the addition of tetrachlorosilane. The linking of the diblock chains by DVB proceeded to virtual completion in benzene without a polar promoter or end-capping. Thomas, Fetters, and co-workers[12−14] studied a family of polystyrene−polyisoprene star-block copolymers (having up to 18 arms) made from the reaction of living diblock arms with chlorosilane linking agents. A new equilibrium microdomain morphology, thought to be ordered bicontinuous double-diamond (OBDD), was found in certain cases. Even though the nature of the morphology was subsequently reevaluated,[15] the salient morphological features of star-block copolymers had been clearly demonstrated by this group. Inverse star-block copolymers, $(AB)_2Si(BA)_2$, with A = polystyrene and B = polyisoprene, were prepared by the chlorosilane method using $SiCl_4$.[16] In these materials, two arms were connected to the central silicon by their PS ends, and the other two arms were connected via their PI ends. The linking agent $SiCl_4$ was titrated with living (PI-*b*-PS)Li solution until two arms were linked to $SiCl_4$, as determined by size exclusion chromatography (SEC). The difunctional macromolecular linking agent was then treated with a small excess of the living (PS-*b*-PI)Li solution to prepare the inverse star-block copolymer. The order of the addition was dictated by steric factors. Tsiang[17] synthesized several four-armed stars with three polybutadiene arms and one polystyrene-*block*-

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polybutadiene arm, (PS-*b*-PB)Si(PB)$_3$. The key step for this method is the successful synthesis of the pure (PB)$_3$SiCl intermediate, which is obviously demanding. Molenberg and co-workers[18] synthesized four-armed polybutadiene-*b*-poly(diethylsiloxane) (PB-*b*-PDES) star-block copolymers by the reaction of living PB-*b*-PDES chains with 1,4-dimethyl-1,1,4,4-tetrachloro-1,2-disilyethane. The star-block copolymers were cross-linked by hydrosilylation of the PB double bonds with chlorodimethylsilane followed by condensation of the chlorosilane groups with water. The resulting rubbers showed elastomeric behavior in tension and stress induced mesophase formation. All of the studies of star-block copolymer noted above focused on well-behaved monomers, mostly styrene, butadiene, and isoprene.

1,3-Cyclohexadiene (1,3-CHD)-based polymers are a structurally interesting class of material. With six-member alicyclic units in the main chain, a dramatic improvement of stabilities (thermal, chemical) and strength is expected in PCHD-based polymers. Through subsequent post-polymerization chemistry, such as aromatization or hydrogenation, PCHD can be converted to other novel materials. Marvel and Hartzell polymerized 1,3-CHD using a Ziegler−Natta catalyst system and subsequently aromatized the polymer in 1959.[19] Since then, essentially all the conventional polymerization methods have been used to polymerize 1,3-CHD.[20] However, the best molecular weight and conversions obtained were via anionic polymerization in hydrocarbon solvent.[21−28] Copolymerization of 1,3-CHD with other monomers (styrene, isoprene, or butadiene) under various anionic conditions has also been investigated.[29−37] Kara et al.[38] very recently presented preliminary results of the synthesis of PCHD stars having up to 19 arms. To produce these materials, they synthesized PCHD anions using *n*-BuLi/*N*,*N*,*N*′*N*′-tetramethylethylenediamine (TMEDA) and linked them using DVB.

In this work, we report the synthesis of new three-arm star polymers having PCHD, polystyrene-*block*-poly(1,3-cyclohexadiene) (PS-*b*-PCHD), or poly(1,3-cyclohexadiene)-*block*-polystyrene (PCHD-*b*-PS) arms using methyltrichlorosilane as linking agent. These near-monodisperse star and star-block materials were rigorously characterized.

Experimental Section

Materials. All materials were purified to anionic polymerization standards as reported in the literature,[39,40] and brief procedures were described as follows. Benzene (Fisher, >99%) and hexanes (Fisher, ≥99.9%) were purified by stirring over concentrated sulfuric acid for 2 weeks followed by drying over grounded calcium hydride (CaH$_2$) in a vacuum line overnight. After degassing several times, they were distilled into calibrated cylinders containing *n*-BuLi (Aldrich, 1.6 M in hexanes) and a few drops of styrene. The persistence of the bright orange color (polystyryllithium) indicated the purity of the solvents. Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a round flask containing sodium dispersions under argon. This flask was then connected to the vacuum line; the solvent was degassed and distilled into a flask with sodium/potassium alloy. After stirring for some time, the bright blue color showed that the THF was free from impurities deleterious to anionic polymerizations. 1,3-Butadiene (1,3-BD, Aldrich, ≥99%) was condensed in a flask containing freshly grounded CaH$_2$ at −78 °C and connected to high-vacuum line. After stirring at −10 °C for 2 h, the monomer was distilled into another flask containing sodium chunks and stirred for 30 min at −10 °C. The monomer was then exposed to *n*-BuLi for 30 min at −10 °C, collecting the desired amount into calibrated ampules, and diluted with purified hexanes. Styrene (Aldrich, 99%) was dried over CaH$_2$ and finally distilled from dibutylmagnesium (MgBu$_2$) and collected in ampules using short-path distillation apparatus. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and then diluted in benzene or cyclohexane. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH$_2$, sodium mirror (three times), and finally *n*-BuLi or MgBu$_2$, and the details was described elsewhere.[28] *sec*-Butyllithium (*sec*-BuLi), prepared from the reaction of *sec*-butyl chloride (Aldrich, ≥99%) with lithium powder in hexane, was used as the initiator. Methyltrichlorosilane (CH$_3$SiCl$_3$, United Chemical Technologies, Inc., ≥99.9%) was stirred over CaH$_2$ overnight, followed by fractional distillation on the vacuum line (collecting the middle $^1/_3$ fraction) and then subdivided into ampules. It was diluted to the desired concentration with purified hexane.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors with *sec*-BuLi/DABCO (1/2) as the initiating system and benzene as the solvent. Detailed procedures are outlined in the literature.[40] PCHD-PS and PS-PCHD arms were made by sequential addition of monomers. Following the completion of each polymerization stage, an aliquot was taken for characterization. In a typical experiment, about 90 mL of purified benzene was distilled into a high-vacuum evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line after degassing. Then 3.8 mL of *sec*-BuLi (1.23×10^{-4} mol/mL in hexanes) and 2.5 mL of DABCO (2.8×10^{-4} mol/mL in benzene) in ampules were introduced into the reactor through break-seals. After stirring about 5 min at room temperature, 4.6 g (0.058 mol) of 1,3-CHD was added. The polymerization started right away (golden yellow color) and was allowed to continue for about 6 h. An aliquot (~1 mL) was taken, and SEC results indicated the MW of the arm was 13.6 kg/mol (calibrated with polystyrene standard) with MWD = 1.05. After end-capping the PCHD living chains with about 0.2 mL of butadiene, the linking reaction started by adding 2.9 mL of CH$_3$SiCl$_3$ (4.6×10^{-5} mol/mL in hexanes). The linking process was monitored by taking aliquots on a scheduled basis and checking with SEC. After the linking reaction was completed, degassed methanol was added to terminate the excess arm. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added. The final polymer was filtered and dried under high vacuum. After fractionation, the M_w of the three-arm PCHD star from the polymerization described above is 41.2 kg/mol with a MWD of 1.06 as determined by SEC equipped with a multiangle laser light scattering (MALLS) detector.

Solvent/nonsolvent (toluene/methanol) fractionation was used at room temperature to remove the excess unreacted arm material. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was heated gently to eliminate turbidity while stirring. It was then transferred to a warm separatory funnel. This system was left undisturbed overnight to allow phase separation. This procedure was repeated as necessary.

Characterization. SEC experiments in THF were carried out at 30 °C using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5Å). SEC experiments in chloroform (CHCl$_3$, flow rate 0.3 mL/min) were done at 30 °C on a Waters 2690 system with Waters 2410 refractive index and Waters 996 photodiode detectors. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. This system was also connected to a Wyatt DAWN DSP MALLS detectors equipped with 5 mW linearly polarized He−Ne laser (wavelength = 632.8 nm). The MALLS unit has 18 detectors with fixed detector angles from 22° to 147°. To calculate the absolute MW, d*n*/d*c* values of the samples are required. The refractive index increments (d*n*/d*c*) for PCHD and PS in CHCl$_3$ were measured

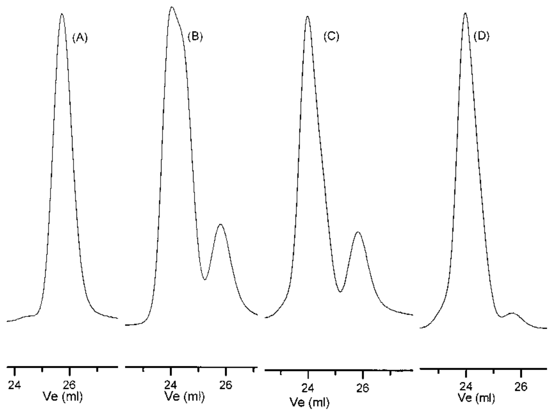
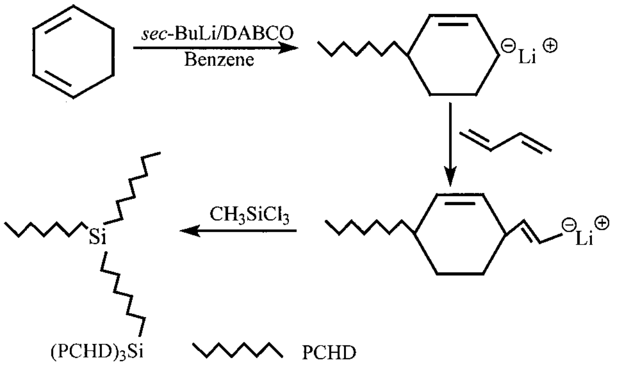


Figure 1. SEC chromatograms from the synthesis of three-armed PCHD star: (A) PCHD arm, (B) first sampling (120 min), (C) unfractionated three-armed PCHD star, (D) fractionated three-armed PCHD star.

Scheme 1



with a Brice-Phoenix differential refractometer, operating at 632.8 nm and calibrated with aqueous potassium chloride solutions ($\mathrm{d}n/\mathrm{d}c_{\mathrm{PS}} = 0.172$ mL/g and $\mathrm{d}n/\mathrm{d}c_{\mathrm{PCHD}} = 0.125$ mL/g). The $\mathrm{d}n/\mathrm{d}c$ for the star-block polymers were calculated from the weighted average $\mathrm{d}n/\mathrm{d}c_{\mathrm{star}} = x_{\mathrm{PS}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PS}} + (1 - x_{\mathrm{PS}})(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PCHD}}$, where x_{PS} is the PS weight fractions determined by ^{1}H NMR. The ^{1}H NMR experiment was carried out in CDCl$_3$ at 30 °C using a Bruker ARX 300 instrument.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. 20 kV acceleration was used with delayed extraction. The spectra were collected by summing 250 shots by using a nitrogen laser (337 nm, 3 ns pulse width) operated at 5 Hz. Samples were prepared by mixing matrix (dithranol, ~10 mg/mL) and ionizing salt (silver trifluoroacetate, ~1 mg/mL) with polymer species (~1 mg/mL) in a ratio of 20/20/1 (v/v). CHCl$_3$ was the solvent. Approximately 0.5 μL of the sample solution was applied to the sample plate. All spectra were baseline corrected and smoothed. Peptide standards were used to calibrate the instrument externally.

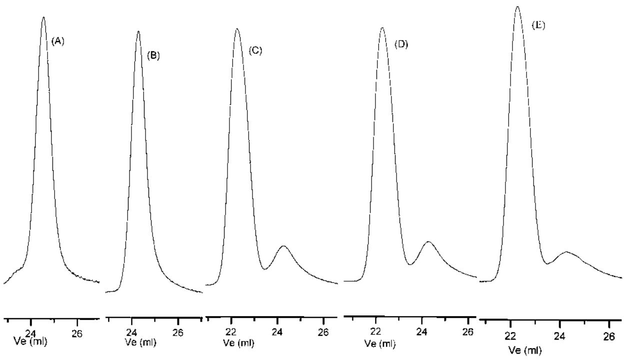


Figure 2. SEC chromatograms from the synthesis of three-armed PCHD star with end-capping: (A) PCHD arm, (B) 1,3-butadiene end-capped PCHD arm, (C) first sampling (60 min), (D) unfractionated three-arm PCHD star, (E) fractionated three-armed PCHD star.

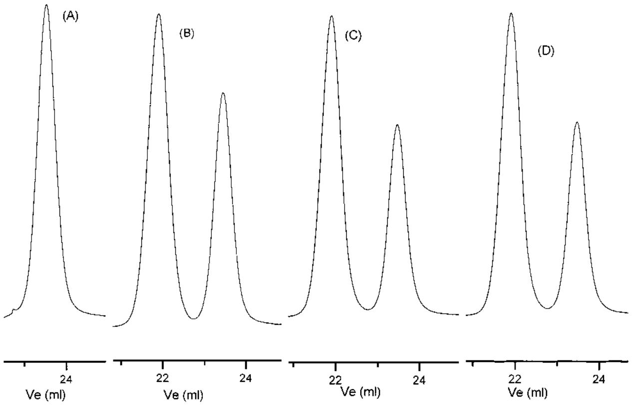


Figure 3. SEC chromatograms from the synthesis of three-armed polybutadiene star: (A) PBD arm, (B) first sampling (15 min), (C) second sampling (60 min), (D) unfractionated three-arm PBD star.

Results and Discussion

The synthesis of the 3-arm PCHD homo-star polymers was performed according to Scheme 1. The key step of this synthetic route was the linking procedure. We anticipated that the PCHDLi chain end, without end-capping with 1,3-BD, was sufficiently bulky that steric hindrance would prohibit its complete reaction with the linking agent, CH$_3$SiCl$_3$. To our surprise this reaction did yield three-arm star, although it required long reaction times (up to 2 weeks) as shown in Figure 1. The two-armed intermediate is clearly seen in the SEC trace of the first sampling. We cannot exclude the possibility that some coupled material remains in the final product due to the limitations of SEC separation; however, the star peak is quite symmetrical. When we capped the PCHDLi anions with several 1,3-BD units, the chain ends became much less bulky and the linking reaction took place much faster, as shown in Figure 2. The linking reaction was so fast under our reaction conditions that we could not detect the two-arm intermediate after only 15 min of reaction. One possible reason for this very rapid linking reaction is that the additive, DABCO, also functions as a promoter. To check this hypothesis, we polymerized 1,3-BD using *sec*-BuLi in benzene and linked the resulting anions with CH$_3$SiCl$_3$ in the presence of DABCO. The condensation reaction proceeded quickly; no two-arm material was detected even at the first sampling (after 15 min of reaction), as shown in Figure 3. Even though the linking reaction was allowed to continue, it was virtually finished in 1 h, as can be seen by comparing the SEC traces at 1 h and 1 day (Figure 3c,d). Tsiang[17] found that the linking efficiency of (PB)$_3$SiCl with PS−PBLi was promoted from ~30% without a polar additive to >90% with a polar additive in 10 min, which is consistent with our results. The large arm peak was from the large excess of arm anions used in this experiment. The molecular characteristics of the resulting star polymers are summarized in Table 1. The measured molecular weights of the arms (weight-average molecular weight) are higher than those of the predicted (number-average molecular weight) probably

Table 1. Characterization of Three-Armed PCHD Stars

	PCHD arm			3-armed star			
run	$M_{th}{}^{a}$ $\times 10^{-3}$	$M_{w}{}^{b}$ $\times 10^{-3}$	$M_w/M_n{}^{c}$	$M_{th}{}^{a}$ $\times 10^{-3}$	$M_{w}{}^{b}$ $\times 10^{-3}$	$M_w/M_n{}^{c}$	$M_w/M_n{}^{b}$
1	4.9	5.8	1.07	14.7	18.3	1.05	1.09
2	5.9	7.3	1.04	17.7	21.4	1.06	1.08
3	9.8	13.6	1.05	29.4	41.2	1.06	1.09

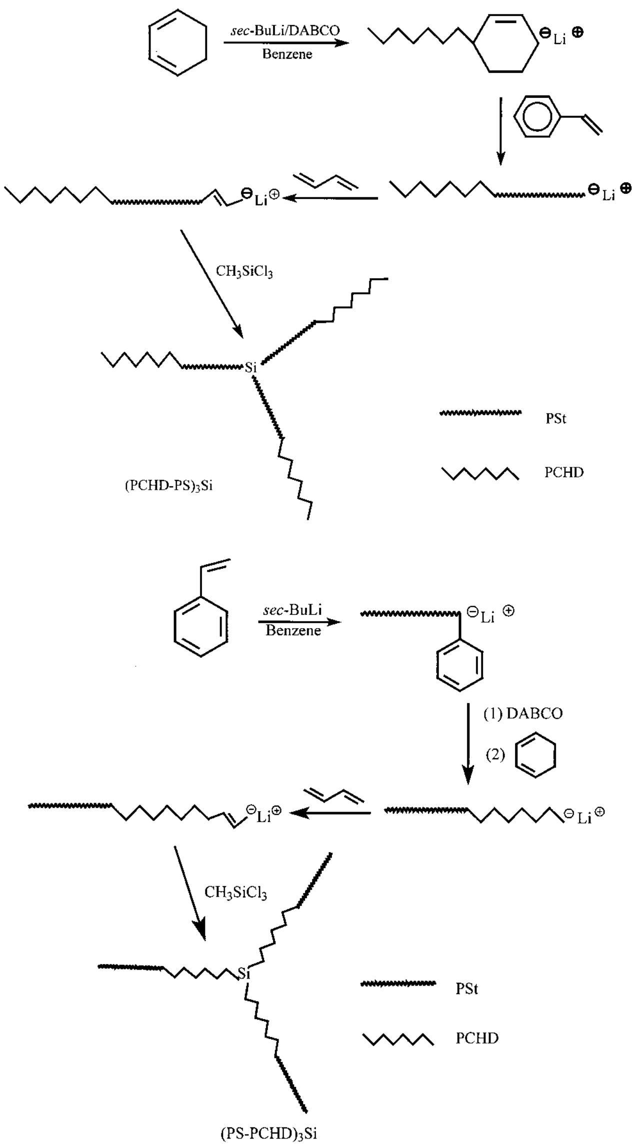
[a] For the arm, calculated from [monomer](g)/[initiator](mol); for the star, calculated from $3 \times M_{\text{theory,arm}}$. [b] From SEC with MALLS detectors. [c] From SEC with RI detector.

because some initiators were killed by some impurities in the reactor. From Table 1 we can see that both arms and fractionated stars had very narrow molecular weight distributions ($M_w/M_n < 1.1$), indicating that the final star material is homogeneous.

Solvent (toluene)/nonsolvent (methanol) fractionation was used to remove the extra arm from the final three-armed PCHD star, and this proved to be difficult as shown in Figure 2E (also Figure 1D). This may arise from the modest molecular weights of the PCHD materials investigated. The polymer precipitate and solution phase separation of a polymer in the solvent/nonsolvent system depend on its molecular weight.[41] The higher the molecular weight, the easier the phase separations and hence the higher the fractionation efficiency. However, there was one factor that prevented us from pursuing PCHD star homopolymers with higher molecular weight: polymers of 1,3-CHD are difficult to dissolve in common organic solvents if the molecular weight is high (>30 000 g/mol). A block-copolymer arm composed in part of polystyrene should improve the solubility. Thus, we were motivated to synthesize PS/PCHD star-block copolymers. The star-block copolymers were synthesized as shown in Scheme 2.

Several star-block copolymers with both PS and PCHD as the outer blocks were synthesized, and the molecular characteristics of those polymers are summarized in Table 2. Molecular weights determined by light scattering and by MALDI-TOF-MS are in excellent agreement with one another if one considers that the former value is a weight-average and the latter a number-average molecular weight. Both SEC and the absolute methods confirm very narrow molecular weight distributions for the star-block materials. The initial steps for these syntheses involved the preparation of living block copolymers that could be linked to make the desired star-block copolymers. For the arms with PS as the outer block, the polymerization of 1,3-CHD using the living polystyrene chain as initiator has proven to be feasible. It has been reported that the polymerization rate of 1,3-CHD initiated by PSLi is faster than that by BuLi.[42] The progress of the synthesis for one (PS-PCHD)$_3$SiCH$_3$, as monitored by SEC, is shown in Figure 4. The monomodal nature of the PS block and PS-PCHD arm indicates their homogeneity. The small amount of coupled product seen in the chromatogram of the PS-PCHD arm is due to termination of the sample with methanol containing air. The linking reactions are very similar to these of PCHD three-arm star as discussed above. Excess arm can be removed by solvent/nonsolvent fractionation. However, if the targeted PCHD composition was too high, the monomer (1,3-CHD) was not consumed quickly. Over time, a small portion of 1,3-CHD molecules may isomerize to its 1,4-isomer, which can terminate some of the living chains (PS-*b*-PCHDLi). Such “dead polymer” can be removed easily by solvent/nonsolvent fractionation.

Scheme 2



The key to the synthesis of stars with PCHD as the outer block, (PCHD-PS)$_3$SiCH$_3$, is an efficient crossover reaction from PCHDLi to styrene. This reaction was previously demonstrated to be possible.[43] We also found that[44] the *sec*-BuLi initiated polymerization of 1,3-CHD and styrene simultaneously resulted in random copolymers, which indicated the comparable cross reaction rate. Francois and co-workers also reported the quasi-alternate nature of the synchronized polymerization of styrene and 1,3-CHD using BuLi.[45] Figure 5 shows the SEC chromatograms of one of the (PCHD-PS)$_3$SiCH$_3$ (run 5 in Table 2). The PCHD block shows a symmetric peak, but the PCHD-PS arm has a small peak at the low molecular weight end, which corresponds to the PCHD block as shown in Figure 5. There is no such problem when the molecular weight of the PCHD block is low (<10 000 g/mol). This indicates that the crossover reaction from PCHDLi to styrene is not 100% complete when the PCHD block is very long. In this case, the 1,3-CHD polymerization takes longer to attain high molecular weight PCHD, and during this time some PCHDLi can be terminated or undergo chain transfer. These transferred species are not reactive enough to initiate styrene. Moreover, it is very difficult to remove this small peak by fractionation using toluene/methanol as

Table 2. Star-Block Copolymer Characteristics

	first block		block copolymer				star-block copolymer			
polymer	$M_n{}^a \times 10^{-3}$	$M_w/M_n{}^b$	$M_n{}^a \times 10^{-3}$	$M_w{}^c \times 10^{-3}$	$M_w/M_n{}^b$	wt % PCHD^d	$M_w{}^c \times 10^{-3}$	dn/dc^e	$M_w/M_n{}^b$	$M_w/M_n{}^c$
				Polystyrene as Outer Block						
1	9.8	1.02	14.8	15.7	1.03	26.8	46.2	0.160	1.04	1.07
2	5.6	1.04	13.9	15.3	1.06	54.0	43.9	0.148	1.05	1.09
3	2.3	1.08	15.5	15.7	1.08	80.4	47.3	0.136	1.04	1.08
				Poly(1,3-cyclohexadiene) as Outer Block						
4	4.7	1.10	14.2	15.3	1.06	31.2	45.1	0.158	1.05	1.07
5	14.2	1.08	24.9	27.1	1.09	56.3	74.9	0.147	1.07	1.10
6	13.4	1.07	16.6	18.1	1.08	74.1	49.4	0.139	1.06	1.09

[a] From MALDI-TOF-MS. [b] Via SEC. [c] From SEC-MALLS. [d] Via ^{1}H NMR. [e] In mL/g and calculated from the weight composition and the dn/dc data for PS and PCHD in $CHCl_3$ (0.172 and 0.125 mL/g, respectively).

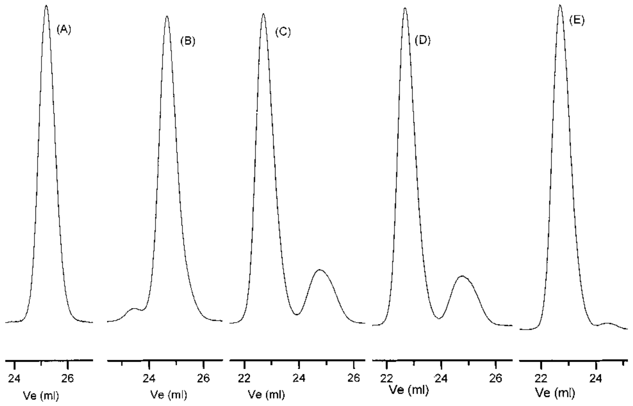


Figure 4. SEC chromatograms from the synthesis of PS-PCHD three-arm star-block copolymer: (A) PS segment of the diblock arm, (B) PS-PCHD diblock arm, (C) first sampling (60 min), (D) unfractionated PS-PCHD three-arm star-block copolymer, (E) fractionated PS-PCHD three-arm star-block copolymer (once).

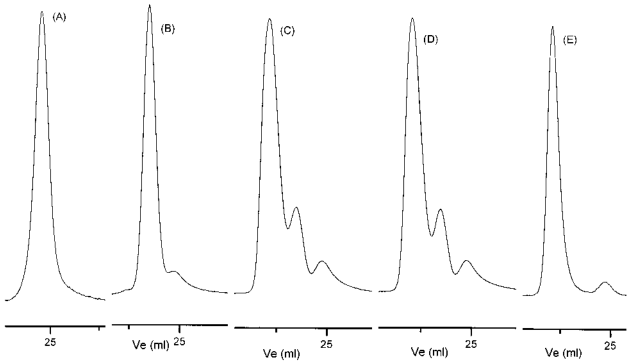


Figure 5. SEC chromatograms from the synthesis of PCHD-PS three-arm star-block copolymer: (A) PCHD segment of the diblock arm, (B) PCHD-PS diblock arm, (C) first sampling (60 min), (D) unfractionated PCHD-PS three-arm star-block copolymer, (E) fractionated PCHD-PS three-arm star-block copolymer four times.

the solvent/nonsolvent. This may be because toluene is not a good solvent for PCHD of high molecular weight. Under careful experimental condition, the unwanted lower molecular weight components can be fractionated away by using chloroform (as solvent) and hexane (nonsolvent). Our preliminary results indicate that the PCHD chains are stiff.[46] Thus, these star-block copolymers are expected to have interesting morphological properties since they have both architectural asymmetries (star architecture) and conformational asymmetry (stiff chain). These morphological properties will be explored in future work.

Conclusions

In conclusion, we have synthesized near-monodisperse three-arm PCHD, PCHD-PS, and PS-PCHD stars by linking the corresponding living chains with methyltrichlorosilane. The excess arm material, used to force the linking reaction to completion, can be readily removed by solvent/nonsolvent fractionation for PS-PCHD stars and PCHD-PS stars with low PCHD content. Fractionation of the star PCHD homopolymers is difficult using the toluene/methanol system.

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References and Notes

(1) Grest, G.; Fetters, L. J.; Huang, J. S.; Richter, D. In *Advances Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; Vol. XCIV, p 67.
(2) Schaefgen, J. R.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2709.
(3) Pispas, S.; Pitsikalis, M.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.
(4) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerizations, Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(5) Hadjichristidis, N. *J. Polym. Sci., Polym. Chem. Ed.* **1999**, *37*, 857.
(6) Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. *Adv. Polym. Sci.* **1999**, *142*, 72.
(7) Price, C.; Watson, A. G.; Chow, M. T. *Polymer* **1972**, *13*, 333.
(8) Bi, L. K.; Fetters, L. J. *Macromolecules* **1975**, *8*, 90.
(9) Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 1051.
(10) Rein, D.; Lamps, J. P.; Rempp, P.; Lutz, P.; Papanagopoulos, D.; Tsitsilianis, C. *Acta Polym.* **1993**, *44*, 225.
(11) Bi, L. K.; Fetters, L. J. *Macromolecules* **1976**, *9*, 732.
(12) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, C. D.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197.
(13) Alward, D. B.; Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1986**, *19*, 215.
(14) Kinning, D. J.; Alward, D. B.; Thomas, E. L.; Fetters, L. J.; Handlin, D. L., Jr. *Macromolecules* **1986**, *19*, 1288.
(15) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1995**, *28*, 2570.
(16) Tselikas, Y.; Hadjichristidis, N.; Lescanec, R. L.; Honeker, C. C.; Wohlgemuth, M.; Thomas, E. L. *Macromolecules* **1996**, *29*, 3390.
(17) Tsiang, R. C. C. *Macromolecules* **1994**, *27*, 4399.
(18) Molenberg, A.; Moller, M.; Soden, W. *Acta Polym.* **1998**, *49*, 45.
(19) Marvel, C. S.; Hartzell, G. E. *J. Am. Chem. Soc.* **1959**, *81*, 448.
(20) Hong, K. Ph.D. Dissertation, The University of Alabama at Birmingham, 2000.
(21) Lefebvre, G.; Dawans, F. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1964**, *2*, 3277.

(22) Cassidy, P. E.; Marvel, C. S.; Ray, S. J. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1965**, *3*, 1553.
(23) Lussi, H.; Braman, J. *Helv. Chim. Acta* **1967**, *50*, 1233.
(24) Mango, L. A.; Lenz, R. W. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, *12*, 402.
(25) Sharaby, Z.; Jagur-Grodzinski, J.; Martan, M.; Vofsi, D. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 901.
(26) Natori, I. *Macromolecules* **1997**, *30*, 3696.
(27) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31* 4687.
(28) Hong, K.; Mays, J. W. *Macromolecules* **2001**, *34*, 782.
(29) Hsieh, H. L. US Patent 4020251, 1977 (Application # 559197, 1975).
(30) Hsieh, H. L. US Patent 4,127,710, 1978 (Application # 511561, 1974).
(31) Hsieh, H. L. US Patent 4,138,536, 1979 (Application # 851649, 1977).
(32) Hsieh, H. L. US Patent 4,237,246, 1980 (Application # 705481, 1976).
(33) Zhong, X. F.; Francois, B. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 411.
(34) Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743.
(35) Zhong, X. F.; Francois, B. *Makromol. Chem.* **1991**, *192*, 2277.
(36) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982.
(37) David, J. L.; Gido, S. P.; Hong, K.; Zhou, J.; Mays, J. W.; Beck Tan, N. *Macromolecules* **1999**, *32*, 3216.
(38) Kara, S.; Pasquale, A. J.; Long, T. E. *Polym. Prepr.* **2000**, *41* (1), 8.
(39) Morton, M.; Fetters, L. *Rubber Chem. Technol.* **1975**, *48*, 359.
(40) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Polym. Chem. Ed.* **2000**, *38*, 3211.
(41) Francuskiewicz, F. *Polymer Fractionation*; Springer Lab Manual, Berlin, 1994; Chapter 3.
(42) Zhong, X. F.; Francois, B. *Makromol. Chem.* **1990**, *191*, 2735.
(43) Francois, B.; Izzilllo, S.; Iratcabal, P. *Synth. Met.* **1999**, *102*, 1211.
(44) Hong, K.; Mays, J. W. *Macromolecules*, submitted.
(45) Francois, B.; Lartigau, C.; Da Cunha, L. *J. Chim. Phys.* **1998**, *95*, 1226.
(46) Hong, K.; Mays, J. W.; Guenoun, P., results to be published.

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