1,3-Cyclohexadiene Polymers. 3. Synthesis and Characterization of Poly(1,3-cyclohexadiene-*block*-styrene)

Kunlun Hong and Jimmy W. Mays*

Department of Chemistry, The University of Alabama at Birmingham, Birmingham, Alabama 35294

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ABSTRACT: The synthesis of block copolymers of 1,3-cyclohexadiene (1,3-CHD) and styrene under various conditions is reported. *sec*-Butyllithium alone can initiate the polymerization of 1,3-CHD but does not yield a living process due to chain transfer and termination reactions. However, certain additives such as tetramethylethylenediamine, dimethoxyethane, and 1,4-diazabicyclo[2.2.2]octane, combined with the suitable butyllithium isomer, can be used to improve control of the polymerization of 1,3-CHD. Using these initiator systems, well-defined poly(styrene-*block*-1,3-cyclohexadiene)s with a wide range of compositions were synthesized and thoroughly characterized. In addition, the rate of crossover reactions during block copolymer formation and the "random" copolymerization of 1,3-CHD and styrene were investigated.

Introduction

Block copolymers, composed of thermodynamically incompatible blocks covalently bonded together, can self-assemble into well-ordered nanodomains because of the mutual repulsions between unlike chain segments and the constraints imposed by the connectivity of the blocks.[1] In the strong segregation limit, even the simplest linear AB diblock copolymers consisting of two flexible chains can exhibit a rich variety of morphologies depending on their volume fractions.[2] However, it is highly desirable to be able to control the microphase morphology and the composition separately in actual applications. Consequently, this dependence of morphology on composition limits flexibility in designing new materials for specific usage. For example, if a certain purpose requires a material with a cylindrical morphology in which the component comprising cylindrical domains makes up over 50 vol % of the material, traditional neat block copolymers would not be useful. In this composition range only lamellar equilibrium morphologies will form for typical diblock copolymers.

Two approaches have been used to uncouple this strict dependence of block copolymer morphology on volume fraction.[3] One approach is to introduce architectural asymmetry into the block copolymer (i.e., change the connectivity of the different blocks).[4] Nonlinear architectures, such as miktoarm stars and grafted block copolymers, have been demonstrated both theoretically and experimentally to allow control of morphology independent of the familiar composition windows found in linear AB diblock morphologies.[5−8] For instance, PI (PI = polyisoprene) in a 3-miktoarm star of $(PI)_2PS$ (PS = polystyrene) with about 0.81 volume fraction of PS formed randomly oriented wormlike micelles dispersed in a continuous PS matrix.[8] Moreover, this morphology was demonstrated to be the equilibrium state of the system. This unusual morphology is presumably due to the graft architecture of the molecule and the relationship between the particular volume fraction and the concavity of the PS/PI interface on which the two PI chains per molecule must reside. For comparison, at the same volume fraction and molecular weight, a linear PS−PI diblock would have PI spheres distributed in PS matrix. Also, for a regularly spaced, tetrafunctional multigrafted block copolymer (PI backbone with double PS grafts) with ∼9 vol % PS, instead of producing PS sphere/PS cylindrical structure as predicted by Milner's theory,[5] an unusual new morphology was formed.[6] The morphology can be described as a microphase-separated mesh of PS struts or wormlike domains in a PI matrix. These results clearly demonstrate the effectiveness of varying molecular architecture in "decoupling" the dependence between composition and morphology for block copolymers.

The alternate approach of introducing conformational asymmetry into the diblock copolymer has also attracted considerable interest recently.[3] In a sense, common block copolymers can be best considered as flexible−semiflexible block copolymers due to conformational asymmetry reflecting differences in the statistical segment length (chain stiffness) of the blocks. Conformational asymmetry can shift the volume fraction range over which various morphologies are observed because of different space filling characteristics of the two blocks.[9] AB diblock copolymers consisting of a flexible coil and a rigid rod block (so-called rod−coil block copolymers) represent the extreme case of conformational asymmetry. These materials have stimulated much research interest over the past decade, and a variety of supramolecular architectures have been observed for rod−coil block copolymer systems.[10,11] The aggregation behavior of rod−coil systems reflects two different ordering phenomena: (i) the microphase separation of the coil and rod blocks into ordered periodic structures and (ii) the tendency of the rodlike block to form anisotropic, ordered structures. Even though many fantastic structures have been observed,[11] the phase behavior, and hence the properties, of rod−coil systems are difficult to tailor because of the complexities of the interactions in the system.

However, if the stiffness of one block varies systematically while keeping the other block constant, the phase behavior could be tuned in a controlled manner. Lai et al.[12] studied the phase separation of styrene−

* To whom all correspondence should be addressed. E-mail jmays@uab.edu.

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isoprene diblock copolymers and their hydrogenated derivatives (styrene−ethylene-*alt*-propylene and vinylcyclohexanes−ethylene-*alt*-propylene copolymers). They found that the phase behavior did evolve as the conformational asymmetry parameter, ϵ, was varied, but not in a simple fashion. Gido, Mays, and their co-workers studied phase separation in polyisoprene-*block*-poly(*tert*-butyl methacrylate) (PI−PtBMA) diblock copolymers.[3] For samples with volume fraction (ϕ) > 0.30 of the "stiff" block, PtBMA, small phase boundary shifts were found, consistent with theoretical predications. However, discrepancies were observed in the volume fraction dependence of experimentally determined morphological behavior (PtBMA spherical micelles with weak lattice ordering in a PI matrix) and the theoretically calculated[13] morphology (cylinder) when $\phi_{PtBMA} < 0.30$.

Recently, we observed an unusual core−shell cylinder-in-cylinder microphase-separated morphology for the polystyrene-*block*-poly(1,3-cyclohexadiene) (PS−PCHD) system,[14] which may reflect their conformational asymmetry. This asymmetry might be expected given the fact that PCHD has para-linked cyclohexene rings incorporated into the main chain of the polymer. We are thus motivated to further explore the microphase-separated morphologies of PS−PCHD block copolymers by studying a wide spectrum of compositions. Thus, our focus in the present work is to better understand the anionic copolymerization behavior of styrene and 1,3-cyclohexadiene (1,3-CHD) under various conditions.

1,3-CHD polymers are a very interesting class of materials because of their unique structures and expected advantageous properties.[15] Zhong and Francois[16−18] synthesized PS−PCHD block copolymers using *sec*-butyllithium (*sec*-BuLi) in a nonpolar solvent by first polymerizing styrene, followed by addition of 1,3-CHD to the living PS anions. During polymerization of 1,3-CHD, they found that chain transfer to monomer was unavoidable and that some of the metalated monomer reinitiated polymerization. They eventually converted the PCHD block to poly(*p*-phenylene) (PPP). Zhou also synthesized a series of PS−PCHD block copolymers using *sec*-BuLi.[19] He used benzene/hexane mixtures as the solvent (v/v = 9/1) and ran the polymerizations at low temperatures (<5 °C) in order to minimize side reactions. Even so, chain transfer and termination reactions limited the PCHD composition in the final products. Recently, Natori and co-workers[20,21] reported that anionic polymerization of 1,3-CHD could be controlled using the *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) initiator system. Various block copolymers of 1,3-CHD with styrene, butadiene, and isoprene were made by sequential addition of the monomers. According to their findings, living PCHD (PCHDLi) and PS (PSLi) species have similar reactivity toward styrene, whereas PSLi chains hardly react with 1,3-CHD.

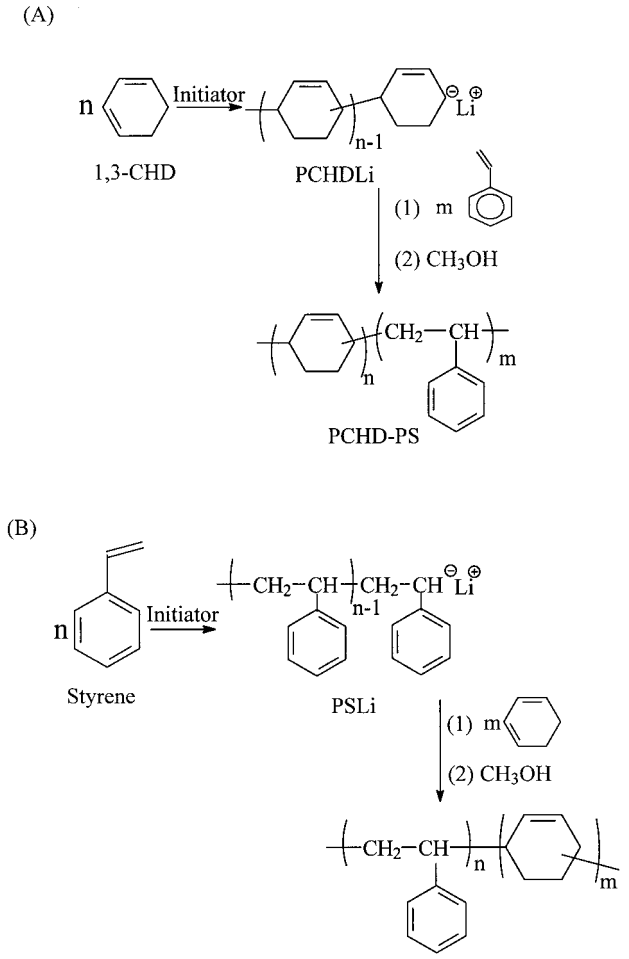
This paper reports the synthesis and characterization of a series of PS−PCHD diblock copolymers. Under appropriate conditions, high molecular weight, narrow molecular weight distributed block copolymers with high 1,3-CHD content (up to 85 wt %) can be prepared. The behavior of various initiating systems and the nature of the cross-propagation reactions are discussed. "Random" copolymerization behavior of 1,3-CHD and styrene is also described.

Experimental Section

Materials. All materials were purified to anionic polymerization standards, as reported in the literature,[22,23] and brief procedures are 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 ground calcium hydride (CaH_2) on the vacuum line overnight. After degassing several times, these solvents 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, PSLi) indicated the purity of the solvents. Tetrahydrofuran (THF, Aldrich, 99.9%) was refluxed over sodium for at least 6 h and collected into a flask containing sodium dispersion 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 that developed showed that the THF was free from impurities deleterious to anionic polymerizations. TMEDA (Aldrich, >99%) and DME (Acros, >99%) were purified using the same procedures as for THF except potassium (K, Aldrich, 98%) mirrors were used instead of sodium dispersion. Styrene (Aldrich, 99%) was dried over CaH_2 and finally distilled from dibutylmagnesium ($MgBu_2$, Aldrich, 1.0 M in heptane) and collected in ampules using a 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. Naphthalene was also purified by sublimation three times but diluted in THF. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2, sodium mirror (3 times), and finally *n*-BuLi or $MgBu_2$. Butyllithium (*sec*-BuLi or *n*-BuLi) was prepared from the reaction of 2-chlorobutane (Aldrich, ≥99%) or 1-chlorobutane (Aldrich, 99%) with lithium powder (Aldrich, high sodium, 99%) in hexane. Potassium naphthalenide was made by reacting naphthalene with a K mirror in THF at −78 °C for 2 h just before polymerization.

Polymerization. All polymerizations were carried out under high vacuum using custom-made glass reactors, and detailed procedures are outlined in the literature.[23] It is possible to synthesize PS−PCHD diblocks by either polymerizing 1,3-CHD first, followed by addition of styrene (scheme A, Chart 1), or by polymerizing styrene first, followed by addition of 1,3-CHD (scheme B, Chart 1). Both approaches were employed in this work. In a typical experiment to prepare PS−PCHD diblock copolymer, about 85 mL of purified benzene was distilled into an evacuated reactor with attached ampules containing all the necessary purified reagents. The reactor was removed from the vacuum line by heat-sealing after degassing. A 5.5 mL aliquot of *sec*-BuLi (9.7×10^{-5} mol/mL in hexanes) was added to the solution followed by 2.3 g (0.022 mol) of styrene. The polymerization started right away (deep red color) and was allowed to continue for 6 h before taking an aliquot (~1 mL) for characterization. Size exclusion chromatography (SEC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) results indicated the molecular weight of the first block was 4.52 kg/mol with a polydispersity of 1.08. About 2.5 mL of DABCO (3.2×10^{-4} mol/mL in benzene) was introduced into the reactor through a break-seal. After stirring about 5 min at room temperature, 6.4 g (0.08 mol) of 1,3-CHD was then added from another ampule. The solution turned to golden yellow quickly and was allowed to continue to polymerize for another 6 h before terminating the reaction with degassed methanol. The final product was found to have a weight-average molecular weight (M_w) of 18.6 kg/mol (from multiangle laser light scattering (MALLS)), a number-average molecular weight (M_n) of 15.4 kg/mol (from MALDI-TOF-MS), a polydispersity (M_w/M_n) of 1.03, and a composition of PCHD with 66.0 wt % (from ^{1}H NMR). For a representative PCHD−PS diblock copolymer, about 90 mL of benzene was used as solvent. After stirring of 3.1 mL of *sec*-BuLi (9.7×10^{-5} mol/mL in hexanes) with 1.6 mL of DABCO (3.2×10^{-4} mol/mL in benzene) for 5 min at room temperature, 3.0 g (0.038 mol) of 1,3-CHD was added and the polymerization was continued for 6 h. A small aliquot

Chart 1



(~1 mL) was taken to characterize the PCHD block before adding 4.4 g (0.042 mol) of styrene and allowing it to polymerize for another 6 h. The first block was found to have M_n of 11.7 kg/mol (MALDI-TOF-MS) with $M_w/M_n = 1.11$. The polymerization was stopped by adding degassed methanol. The final diblock copolymer had M_w of 41.8 kg/mol (MALLS), M_n of 44.2 kg/mol (SEC), M_w/M_n of 1.07 (SEC), and a composition of PCHD of 39.4 wt % (from ^{1}H NMR). The polymer solutions were precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added as antioxidant. The final polymer was isolated by filtering and drying under high vacuum. For some samples, solvent/nonsolvent fractionation (toluene/methanol) was used to remove homopolymer contaminants. Methanol was added slowly to the polymer solution in toluene (concentration ~ 0.5% w/v) until turbidity appeared. The solution was then heated gently while stirring to eliminate turbidity, and it was then transferred to a warm separatory funnel. This system was kept undisturbed overnight to allow phase separation. This procedure was usually repeated until SEC could detect no undesirable products.

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 10^5 Å). 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 molecular weight, 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 with a Brice-Phoenix differential refractometer, operating at 632.8 nm and calibrated with aqueous potassium chloride solutions. ^{1}H NMR experiment was carried out in $CDCl_3$ at 30 °C using a Bruker ARX 300 instrument.

MALDI-TOF-MS spectra were obtained with a PerSeptive Biosystems Voyager Elite DE instrument using linear mode. A 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.

Results and Discussion

Block Copolymerization Using BuLi without Additives. The successful control of the anionic polymerization of 1,3-CHD using certain initiating systems, as described in our previous paper,[15] suggests the possibility of making well-defined PS−PCHD diblocks of high molecular weights and having a wide range of compositions. Some of our preliminary results were presented earlier.[24] We employed several initiating systems and different polymerization sequences in this work. The conditions used and the characteristics of the resulting polymers are listed in Table 1. When styrene was polymerized by *sec*-BuLi in benzene followed by addition of 1,3-CHD without use of any additive, the PSLi initiated the polymerization of 1,3-CHD (scheme B). The cross-propagation was accompanied by a color change from orange-red to yellow within 20 s. This simple procedure works well for making PS−PCHD block copolymers with short PCHD segments and thus low PCHD content in the copolymer. As shown in Figure 1a, the SEC trace of a PS−PCHD diblock copolymer (wt % of 1,3-CHD = 5.4) is symmetrical and monomodal. However, when the targeted 1,3-CHD composition in the PS−PCHD block copolymer was high (>20%), this polymerization was not well-controlled, as indicated by the low molecular weight shoulder in the SEC chromatogram (Figure 1c). These low MW byproducts arise from side reactions such as chain transfer and/or chain termination.

Since 1,3-CHD can undergo several detrimental reactions under anionic polymerization conditions (strong base) in addition to the desired propagation,[15] the maximum attainable composition of PCHD in the copolymers with high molecular weight (>10 000 g/mol) is restricted regardless of the initial monomer ratio. The low molecular weight contaminants can be removed easily by solvent (toluene)/nonsolvent (methanol) fractionation. These results are similar to those reported by Zhong and Francois and Zhou et al.[16−19] On the basis of infrared spectra, Zhong and Francois reported that the low molecular weight shoulder was pure PCHD. Consequently, they claimed that the metalated monomer formed by chain transfer reinitiated the polymerization of 1,3-CHD. Conversely, we find that the fractionated low molecular weight material contains substantial amounts of PS, as revealed by the ^{1}H NMR spectra shown in Figure 2. The peak around 5.6 ppm is from the cyclohexene ring, and the peaks from 6.2 to 7.2 ppm are from styrene units. This is not surprising, since the initiation and chain propagation rates in the PSLi

Table 1. Characteristics of PS−PCHD Block Copolymer from BuLi with Various Additives

run	additive	[Add]/[I]	[I] × 10^3, mol/L	[ST]/[I][a]	[CHD]/[I][a]	M_n[b] × 10^{-3}	M_w/M_n[b]	comp,[c] wt % PCHD	remarks
1[d]	no additive		2.78	161.5	232.4	22.7	1.22	38.4	St first
2[d]	no additive		15.4	20.9	50.5	8.0	1.25	70.7	CHD first
3[d]	THF	16.8	4.13	71.2	64.4	15.8	1.15	43.7	St first
4[e]	TMEDA	1.25	3.52	156.5	307.7		multimodal		CHD first
5[f]	TMEDA	1.27	3.47	183.6	180.1	23.7	1.09	45.1	St first
6[f]	TMEDA	1.33	8.53	94.1	119.0		bimodal		CHD first
7	naphth/K/THF/−78 °C		11.15	58.8	55.6	19.3	1.25		St first
8	naphth/K/THF/−78 °C		8.01	81.9	119.7	23.4	1.41		CHD first
9[g]	DME	5.71	7.01	34.2	193.2	27.0	1.04	82.2	St first
10[g]	DME	5.60	5.52	58.2	163.0	33.2	1.07	81.5	CHD first
11[h]	DABCO	1.74	4.88	147.3	110.5	6.21	1.06	34.7	St first
12[h]	DABCO	1.63		103.1	91.6	44.2	1.07	39.4	CHD first

[a] Molar ratio. [b] From SEC in THF. [c] From ^{1}H NMR. [d] *sec*-BuLi in benzene at room temperature. [e] *n*-BuLi in benzene at room temperature. [f] *n*-BuLi in cyclohexane at 40 °C. [g] *n*-BuLi in benzene at 5 °C. [h] *sec*-BuLi in Benzene at room temperature.

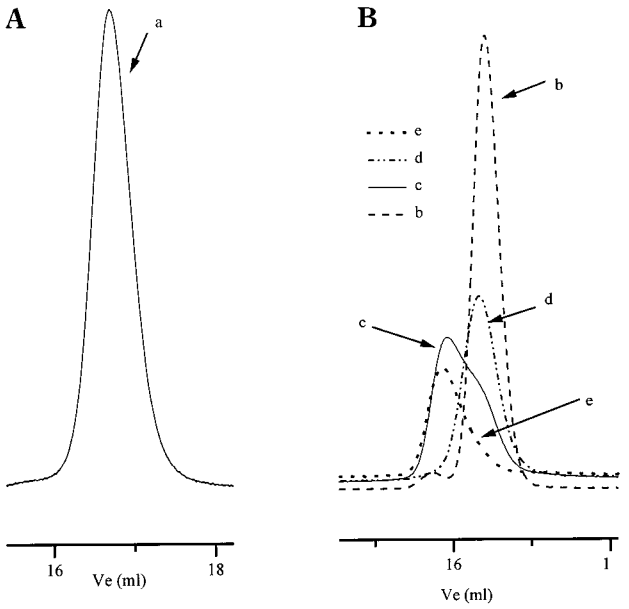


Figure 1. SEC traces (eluent THF) of PS−PCHD from *sec*-BuLi in benzene (styrene polymerized first). (A) Monomer charge: styrene/1,3-CHD = 93/7 (mole); (a) M_n = 14 100 g/mol, M_w/M_n = 1.06. (B) Monomer charge: styrene/1,3-CHD = 53/47 (mole); (b) PS block, M_n = 15 100 g/mol, M_w/M_n = 1.04; (c) PS−PCHD block before fractionation, M_n = 22 400 g/mol, M_w/M_n = 1.22; (d) fractionated solution M_n = 16 400 g/mol, M_w/M_n = 1.07; (d) fractionated solid, M_n = 28 200 g/mol, M_w/M_n = 1.05.

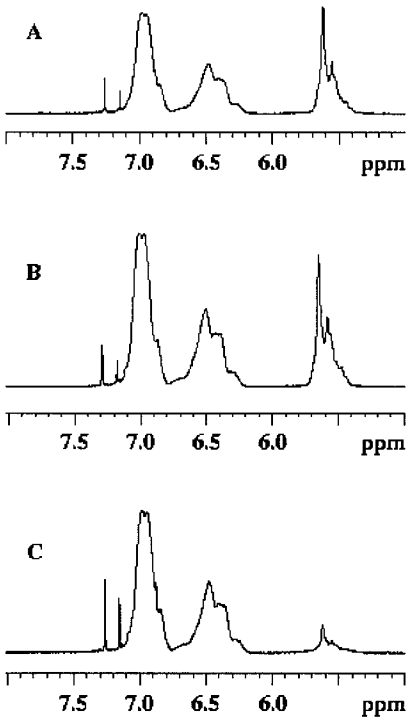


Figure 2. ^{1}H NMR spectra of PS−PCHD SEC from *sec*-BuLi in benzene (a) before fractionation, PCHD wt % = 38.4; (b) after fractionation (solid), PCHD wt % = 43.1; and (c) after fractionation (solution), PCHD wt % = 12.9.

initiated 1,3-CHD polymerizations are not fast enough to avoid the side reactions that lead to chain terminations. In addition to chain termination by hydride abstraction (one of the well-known chain-transfer reactions for this monomer), 1,4-CHD, which is always present at some level in 1,3-CHD under strong base conditions, is a very effective chain terminator.[15] Even though we cannot rule out possible reinitiation to create PCHD homopolymer quantitatively on the basis of the data at hand, the spectrum in Figure 2 strongly suggests that this process does not play a major role in our studies. In summary, the results presented above show that it is very difficult to prepare PS−PCHD samples with high 1,3-CHD content by sequential polymerization of styrene, and then 1,3-CHD, using *sec*-BuLi alone as initiator.

Table 1 also gives the characteristics of block copolymers prepared by polymerization of 1,3-CHD with *sec*-BuLi in benzene followed by the addition of styrene (scheme A). PCHDLi chains can initiate the polymerization of styrene very rapidly under these conditions, as demonstrated by the yellow color turning to red-orange instantly upon addition of styrene. SEC traces for products of this reaction are shown in Figure 3. As reported previously,[15−17] the polymerization of 1,3-CHD initiated by *sec*-BuLi in the absence of additives does not proceed in a controlled manner. The PCHD blocks are moderately polydisperse (M_w/M_n>1.2), as are the final PCHD−PS diblocks. With a short PCHD block, the resulting PCHD−PS block copolymer is monomodal (Figure 3a). However, bimodal PCHD−PS is formed when the PCHD block is longer (higher molecular weight) (Figure 3d). It is difficult to remove the low molecular weight shoulder from this material by conventional toluene/methanol fractionation. This is probably because part of the PCHDLi was deactivated before all the monomer (1,3-CHD) was consumed, and toluene is not a very good solvent for the PCHD block.[15]

More importantly, our experiments show that PCHDLi can rapidly initiate the polymerization of styrene

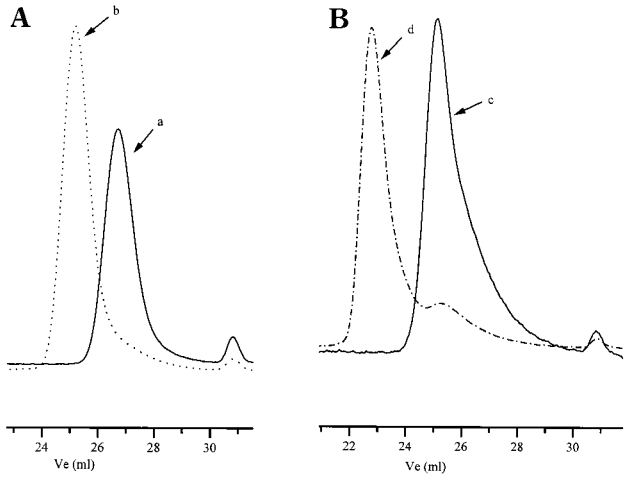


Figure 3. SEC traces (eluent THF) of PCHD-PS from *sec*-BuLi in benzene (1,3-CHD polymerized first). (A) Monomer charge: styrene/1,3-CHD = 35.2/64.8 (mole); (a) PCHD block, M_n = 5800 g/mol, M_w/M_n = 1.07; (b) PCHD−PS diblock, M_n = 10 100 g/mol, M_w/M_n = 1.09. (B) Monomer charge: styrene/1,3-CHD = 38.6/61.4 (mole); (c) PCHD block, M_n = 8100 g/mol, M_w/M_n = 1.13; (d) PCHD−PS block, M_n = 13 300 g/mol, M_w/M_n = 1.28.

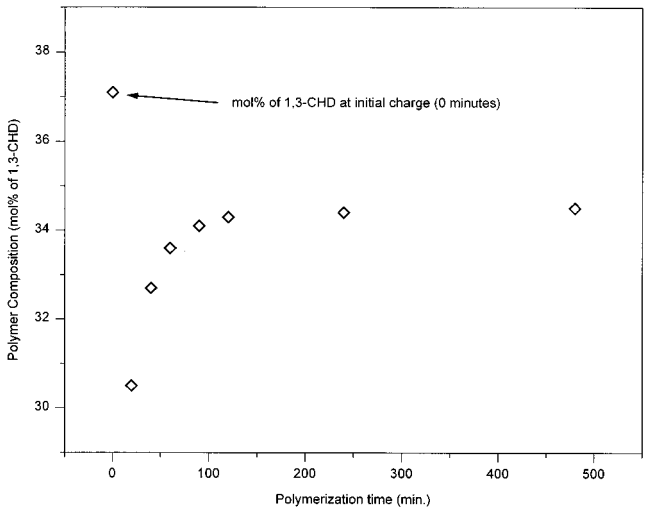


Figure 4. Compositions of PCHD in PS−PCHD copolymer (from the polymerization of 1,3-CHD and styrene simultaneously using *sec*-BuLi in benzene) vs polymerization time.

in hydrocarbon solvents even without the use of polar additives. This is in stark contrast to the copolymerization behavior of styrene and acyclic dienes.[25] When styrene and butadiene are simultaneously added to anionic initiators in hydrocarbon solvents, tapered block copolymer are formed because of the differences in reactivity ratios.[25] On the basis of our observations concerning the crossover reactions (as noted above), we anticipated "random" copolymerization behavior for styrene and 1,3-CHD. Francois et al.[18] found similar behavior in *sec*-BuLi/cyclohexane initiation system. We thus used *sec*-BuLi to polymerize styrene and 1,3-CHD simultaneously in benzene at room temperature. The composition of the polymerization products was monitored by ^{1}H NMR as a function of polymerization time, and the results are summarized in Figure 4. The monomodal character of the polymerization products as evidenced by SEC traces (Figure 5, solvent: THF) strongly suggests that they are not simple mixtures of PCHD and PS homopolymers. From Figure 4, one can

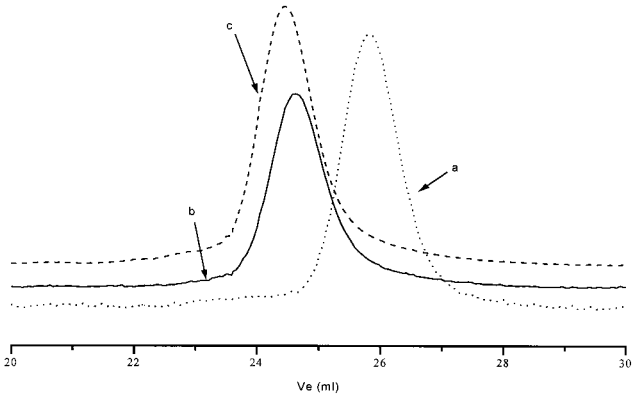


Figure 5. SEC traces (eluent THF) of PS−PCHD from the polymerization of 1,3-CHD and styrene simultaneously using *sec*-BuLi in benzene: (a) first sampling, (20 min), M_n = 5600 g/mol, M_w/M_n = 1.07; (b) third sampling, M_n = 13 200 g/mol, M_w/M_n = 1.11; (c) final product (6 h), M_n = 14 200 g/mol, M_w/M_n = 1.14.

see that the 1,3-CHD content in the polymerization products reached a rather high level quickly (30.5 mol % of 1,3-CHD in 20 min and 34.3 mol % in 120 min). Under our reaction conditions, all the monomer was consumed in about 4 h. The composition does not change much after 120 min, and it is always slightly lower in 1,3-CHD content than anticipated on the basis of the monomer charge ratio. This is likely caused by the above-mentioned side reactions, which also consume some 1,3-CHD. These findings suggest that the rate of reaction of PSLi with 1,3-CHD in benzene at room temperature is comparable to that of PCHDLi with styrene. Natori reported[21] the copolymerization behavior of 1,3-CHD with styrene in cyclohexane using the *n*-BuLi/TMEDA (4/5) initiating system at 40 °C. He found that styrene was preferentially polymerized in the initial stage, and the polymerization of 1,3-CHD started only when most of the styrene was consumed. The higher reactivity of styrene in their study may be attributed to the presence of TMEDA, which can change the polymerization behavior dramatically because of its strong chelating effects with the growing chain ends.[26] Attempts to determine the sequence distribution in the copolymers by NMR were not successful because the spectra were very complex.

The MALDI-TOF-MS spectrum of the polymerization product from the first sampling of the "random copolymerization" is shown in Figure 6a along with a spectrum of a PS−PCHD diblock with similar composition (Figure 6b). The single peak around 6000 g/mol and the monomodal SEC traces (Figure 5) suggest that the copolymerization was of a statistical nature. The drastic intensity differences in the two spectra are noteworthy. We have consistently observed that the MALDI-TOF-MS signals for PS−PCHD block copolymers are very weak.[27] A possible reason for the low response of PS−PCHD block copolymers in MALDI-TOF-MS spectra is that effective MALDI requires that individual polymer chain be dispersed in matrix crystals.[28] PCHD segments are rather rigid and tend to aggregate during the preparation of MALDI samples. Consequently, only a small portion of the PS−PCHD chains can be ionized. However, the intensity for the "random copolymerization" product is much higher than that for PS−PCHD diblock copolymers. This also implies that the styrene and 1,3-CHD units are statistically distributed in the former copolymer (i.e., not blocky), making aggregation

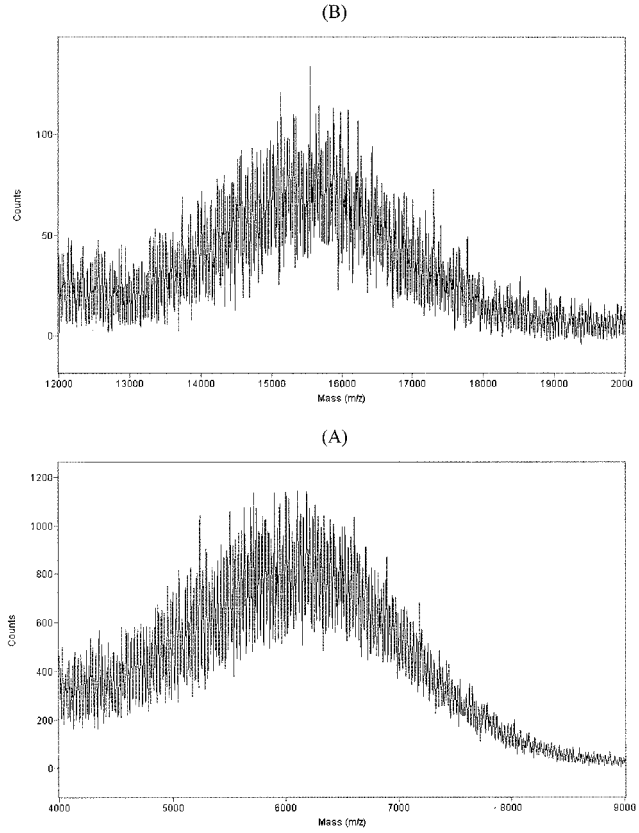


Figure 6. MALDI-TOF-MS spectra of PS−PCHD polymers: (A) "random" copolymer, M_n = 5900 g/mol, M_w/M_n = 1.03; (B) diblock copolymer, M_n = 15 400 g/mol, M_w/M_n = 1.01.

of PCHD more difficult. Furthermore, the rates of crossover reactions from PCHDLi to styrene and vice versa were comparable for the *sec*-BuLi/benzene system based on visual observations (as noted above).

Using the naphthalene/potassium initiation system in THF at −78 °C, we successfully obtained PCHD−PS−PCHD and PS−PCHD−PS triblock copolymers with monomodal molecular weight distributions; however, the MWDs are rather broad (runs 7 and 8 in Table 1).

Block Copolymerization Using BuLi with Additives. As discussed above, *sec*-BuLi alone does not polymerize 1,3-CHD in a controlled manner in hydrocarbon solvents. Therefore, it is difficult to synthesize PS−PCHD block copolymers with high molecular weights and covering a broad compositional range, as is necessary for morphological studies, using this approach. The use of certain additives can improve the situation.[15,20,21] As shown in Table 1 (run 3), a small amount of THF can have a favorable impact on block copolymer formation via polymerization of 1,3-CHD followed by the addition of styrene. However, further attempts to target higher 1,3-CHD compositions and higher molecular weights were not successful because THF does not adequately suppress the side reactions. Moreover, THF may react with *sec*-BuLi at the polymerization temperature used.[29] Natori[20,21] reported that the *n*-BuLi/TMEDA initiating system could polymerize 1,3-CHD in a "living" manner. We polymerized 1,3-CHD and styrene sequentially using this initiator system; the results are listed in Table 1 (runs 4 and 5) and Figure 7. When styrene was polymerized first, the SEC trace exhibited a tail at high molecular weight (Figure 7a). On the other hand, a low molecular weight shoulder was observed

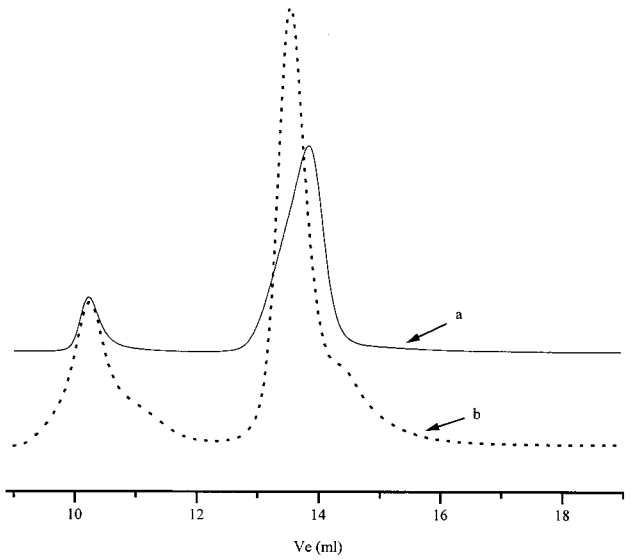


Figure 7. SEC traces (eluent THF) of PS−PCHD from *n*-BuLi/TMEDA/cyclohexane/40 °C: (a) styrene polymerized first, M_n = 23 700 g/mol, M_w/M_n = 1.09; (b) 1,3-CHD polymerized first.

in the SEC chromatogram when 1,3-CHD was polymerized first (Figure 7b). The shoulder may arise from deactivated PCHDLi. In contrast to our findings, Natori reported[21] that PCHDLi "living" chains could continue to grow by adding either styrene or 1,3-CHD. However, tailing can be seen clearly in some of their published SEC chromatograms.

A peak with extremely high molecular weight (∼1.3 million g/mol based on calibration with PS standards) was observed for many of the diblocks regardless of which monomer was polymerized first. Upon decreasing the solution concentration and repeating the SEC experiments, these peaks shifted to lower molecular weight (about 970 kg/mol calibrated with PS), and the fraction of the high molecular weight peak also decreased. When SEC experiments were run in $CHCl_3$, higher molecular weight peaks were also observed, but the positions moved to lower molecular weight (∼500 kg/mol, based on calibration with PS). Variations of the molecular weight and the fraction of high and low molecular weight components upon changing the polymer concentration or the SEC solvent suggest that micelles exist in solutions of some of these PS−PCHD block copolymers.

We reported previously[15] that the *n*-BuLi/DME or *sec*-BuLi/DABCO initiating systems could polymerize 1,3-CHD in a controlled manner with regard to molecular weight and M_w/M_n. Thus, it is natural to try to extend those approaches to the synthesis of PS−PCHD diblock copolymers. Typical results are listed in Table 1 (runs 9−12), and characterization data are given in Tables 2 and 3. Under these reaction conditions, PCHDLi efficiently initiates the polymerization of styrene and vice versa, as shown in Figure 8.

When the targeted composition for PCHD was lower than 30 wt %, the resulting PS−PCHD block copolymers were unimodal, and the polydispersities were low (M_w/M_n < 1.1). However, a shoulder corresponding to the first block was always seen in the SEC traces of the diblocks when the composition of PCHD was higher than 30 wt %. If styrene was polymerized first, this low molecular weight shoulder could be removed easily by solvent/nonsolvent fractionation (toluene/methanol), and

Table 2. Characteristics of PS−PCHD Diblock Copolymers from *sec*-BuLi/DABCO/Benzene/20 °C

run	[I] × 10^3 mol/L	[ST]/[I][a]	[CHD]/[I][a]	M_n[b] × 10^{-3}	M_w/M_n[b]	M_w[c] × 10^{-3}	M_n[d] × 10^{-3}	comp,[e] wt % PCHD
1	8.33	80.8	65.1	15.3	1.03	19.3	17.0	38.2
2	4.02	122.4	84.6	26.7	1.06	32.9	28.4	52.7
3	4.88	147.3	110.5	22.9	1.03	26.1	23.8	34.7
4	7.00	150.0	175.7	16.9	1.03	18.6	15.4	66.0
5	7.38	144.9	30.5	15.7	1.04	17.7	16.5	11.4
6	10.64	16.4	154.1	17.1	1.04	21.9	19.1	85.1

[a] Molar ratio. [b] From SEC. [c] From SEC-MALLS. [d] From MALDI-TOF-MS. [e] Via ^{1}H NMR in $CDCl_3$.

Table 3. Characteristics of PS−PCHD Diblock Copolymer from *n*-BuLi/DME/Benzene/5 °C

run	[I] × 10^3 mol/L	[ST]/[I][a]	[CHD]/[I][a]	M_n[b] × 10^{-3}	M_w/M_n[b]	M_w[c] × 10^{-3}	M_n[d] × 10^{-3}	comp,[e] wt % PCHD
1	5.00	100.4	107.6	28.9	1.05	31.3	28.2	51.0
2	4.15	144.3	53.3	20.6	1.05	25.7	24.4	21.7
3	6.92	134.7	86.1	27.8	1.04	30.5	29.5	36.8
4	7.02	34.2	192.9	27.0	1.06	28.4	26.7	82.2
5	5.06	102.6	103.8	46.1	1.08	43.8		41.7
6	7.61	92.6	111.7	30.1	1.05	32.1	31.0	52.3
7	7.89	94.4	98.7	28.7	1.04	28.9	27.8	46.0
8	7.76	81.8	119.2	30.0	1.07	33.9	30.4	62.1
9	5.15	107.4	106.0	23.5	1.05	27.1	26.6	42.3

[a] Molar ratio. [b] From SEC. [c] From SEC-MALLS. [d] From MALDI-TOF-MS. [e] Via ^{1}H NMR in $CDCl_3$.

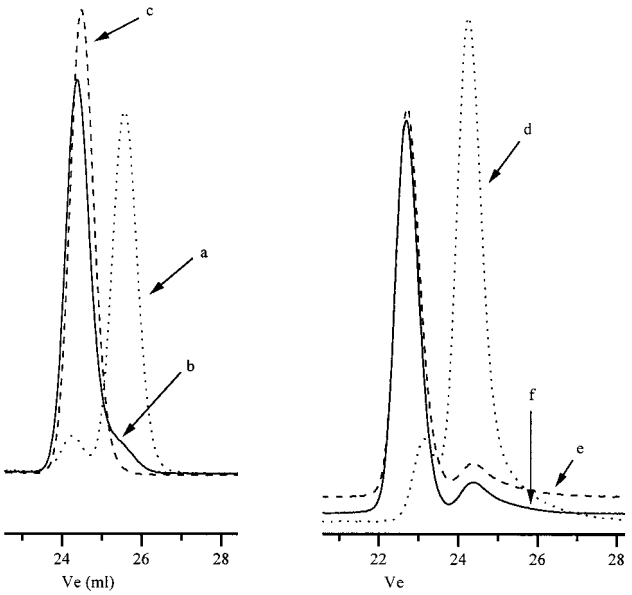


Figure 8. SEC traces (eluent THF) of PS−PCHD from *sec*-BuLi/DABCO/benzene: (A) styrene polymerized first: (a) PS block M_n = 8300 g/mol, M_w/M_n = 1.07; (b) PS−PCHD diblock before fractionation, M_n = 15 100 g/mol, M_w/M_n = 1.05; (c) PS−PCHD after fractionation, M_n = 15 300 g/mol, M_w/M_n = 1.03. (B)1,3-CHD polymerized first: (d) PCHD block, M_n = 15 700 g/mol, M_w/M_n = 1.09; (e) PS−PCHD diblock before fractionation, M_n = 43 200 g/mol, M_w/M_n = 1.10; (f) PS−PCHD diblock after fractionation, M_n = 44 300 g/mol, M_w/M_n = 1.08.

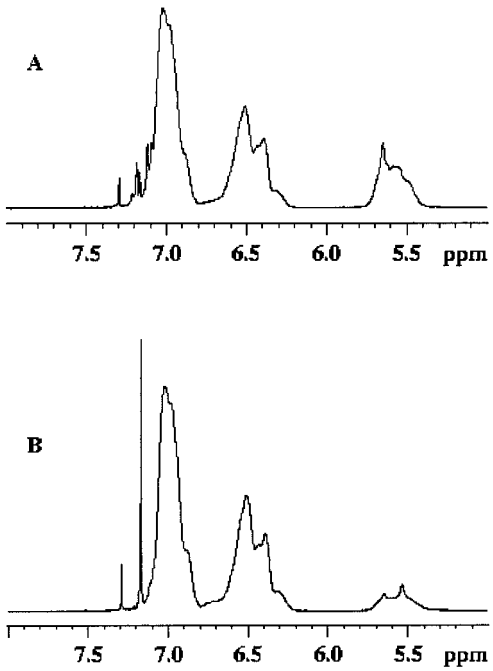


Figure 9. ^{1}H NMR spectra of PS−PCHD SEC from *sec*-BuLi/DABCO/benzene: (A) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 26.1; (B) 1,3-CHD polymerized first, fractionation solution, PCHD wt % = 11.1.

it mainly contained PS as revealed by ^{1}H NMR (Figure 9b). The compositions can be calculated from the intensities of styrene (6.2−7.2 ppm, 5H) and 1,3-CHD (5.4−5.8 ppm, 2H) repeating units. This is likely because 1,3-CHD terminated some PSLi and/or PS−PCHDLi chains. On the other hand, the low molecular weight shoulder was very difficult to remove by toluene/methanol fractionation if 1,3-CHD was polymerized first. The shoulder was probably formed by the self-termination of the PCHDLi chains, since the possibility of PCHDLi chains being terminated by styrene is low. The difficulty in removing the low molecular weight component by toluene/methanol fractionation probably arises from the poor solubility of PCHD in toluene. The fractionation solution (supernatant) of a PS−PCHD block copolymer (1,3-CHD polymerized first) contained a significant amount of PS (Figure 9a, peaks from 6.2 to 7.2 ppm), which indicates inefficient fractionation. However, we cannot exclude the possibility of PS being formed by the polymerization of styrene initiated by the metalated 1,3-CHD species (the latter formed by chain transfer).

Conclusions

We have studied the copolymerization behavior of 1,3-CHD and styrene under various reaction conditions. Well-defined PS−PCHD block copolymers having a wide range of compositions and molecular weights were synthesized and characterized. Materials with polydispersities less than 1.1, compositions as high as 85 wt % 1,3-CHD, and molecular weights as high as 44 kg/mol

could be generated, even though some fractionation is needed when the targeted molecular weight is higher than 20 kg/mol and the compositions of PCHD higher than 30 wt %. Furthermore, the polymerization and crossover rates for styrene and 1,3-CHD were found to be comparable in benzene at room temperature using *sec*-BuLi as initiator. This behavior is different from the well-known alkyllithium-initiated copolymerization behavior of styrene and acyclic conjugated dienes (e.g., isoprene, butadiene) in hydrocarbon solvents.

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