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Model Linear Block Co-, Ter-, and Quaterpolymers of 1,3-Cyclohexadiene with Styrene, Isoprene, and Butadiene

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ABSTRACT: The following linear block co-, ter-, and quaterpolymers of 1,3-cyclohexadiene (CHD) with styrene (S), isoprene (I), and butadiene (B) were synthesized by sequential anionic polymerization: PS-*b*-PCHD, PI-*b*-PCHD, PB-*b*-PCHD, PS-*b*-PB-*b*-PCHD, PB-*b*-PS-*b*-PCHD, PB-*b*-PI-*b*-PCHD, and PS-*b*-PB-*b*-PI-*b*-PCHD. *sec*-Butyllithium with either *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or 1,4-diazobicyclo[2.2.2]octane (DABCO) was used as the initiating system. In all cases CHD was the last monomer added. The polar additive (TMEDA or DABCO) was always introduced to the polymerization solution prior to the addition of CHD and isoprene. The microstructures of the polydienes obtained in the different environments were determined by NMR spectroscopy. Thorough characterization by size exclusion chromatography coupled with multiangle laser light scattering, laser differential refractometry, osmometry, and NMR spectroscopy revealed that the synthesized polymeric materials exhibit high molecular and compositional homogeneity.

Introduction

Anionic polymerization has been extensively used for the synthesis of novel linear[1] and nonlinear[2] polymeric systems with two chemically different blocks. In contrast, only limited information[3] is available for linear three-component polymers and even less for the corresponding nonlinear structures. Most of the triblock terpolymers synthesized so far have consisted of poly(styrene) (PS), poly(isoprene) (PI), or poly(butadiene) (PB) and a more polar third block like poly(methyl methacrylate), poly(2-vinylpyridine), poly(4-vinylpyridine), or poly(ethylene oxide).[2] Phase separation studies have been carried out on these materials.[3] The combination of two dienes in the same terpolymer has received minor attention due to the belief that the two polydienes would be miscible.

Polycyclohexadiene (PCHD) is a very interesting polydiene due to its improved thermal, chemical, and mechanical properties.[4,5] It can be dehydrogenated to polyphenylene (PPP), a highly conductive polymer,[6] either by tetrachloro-1,4-benzoquinone (*p*-chloranil)[7] or by halogenation followed by pyrolysis.[8] It can also be converted to polycyclohexylene (PCHE) by homogeneous[9] or heterogeneous hydrogenation.[4] PCHE has the highest glass transition temperature ($T_g \sim 200$ °C for 1,4-PCHE and $T_g \sim 250$ °C for 1,2-PCHE) among all hydrocarbon polymers, low specific gravity, high heat resistance, high flexural modulus, etc.[10]

Almost all initiating systems have been applied to the polymerization of 1,3-CHD, including radical,[11] cationic,[12,13] Ziegler−Natta,[8,12−14] anionic,[7,8,12] and transition metal complexes.[15,16] Stereocontrolled polymerization was also performed within tris(*o*-phenylenedioxy)cyclotriphosphazene clathrate[17] or thiourea complexes channels.[18] The best results were obtained by anionic polymerization, but side reactions (chain transfer and termination) hamper control over molecular weight and molecular weight distribution.[19,20] By using polar additives, both initiation and propagation rates are increased, and thus the probability of side reactions is diminished. Natori was the first to report the controlled anionic polymerization of 1,3-CHD with the *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA) initiating system in a 4/5 molar ratio.[21] The microstructure of the obtained PCHD was ~50% 1,2.[22,23] By using the above initiating system, random copolymers of CHD with butadiene, styrene, and isoprene as well as di- and triblock copolymers of CHD with butadiene or styrene were synthesized.[24] Using the *n*-BuLi/TMEDA initiating system and divinylbenzene, Long et al. were able to synthesize PCHD stars,[25] which after hydrogenation produced polycyclohexylene stars.[26] 1,4-Diazabicyclo[2.2.2]octane (DABCO) with *sec*-BuLi was used as another initiating system by Hong and Mays,[27] leading to PCHD with ~90% 1,4 microstructure. With the DABCO initiating system, block copolymers of styrene and CHD,[28] three-arm star homopolymers, and star-block copolymers of styrene and CHD were prepared.[29] Miktoarm stars with one polycyclohexadiene arm and two or three polybutadiene arms were also prepared using the same system and transformed to the corresponding miktoarm stars of PCHE and polyethylene (PE) by complete hydrogenation.[30]

In this paper we report the synthesis and molecular characterization of linear block co-, ter-, and quaterpolymers of 1,3-CHD with styrene, isoprene, and butadiene (Scheme 1) by sequential anionic polymerization using the lithium counterion and the additives TMEDA and DABCO. The microphase separation of these materials will appear in a forthcoming paper.[31]

Experimental Section

Materials. The purification procedures for styrene (S), isoprene (I), butadiene (B), and benzene to the standards

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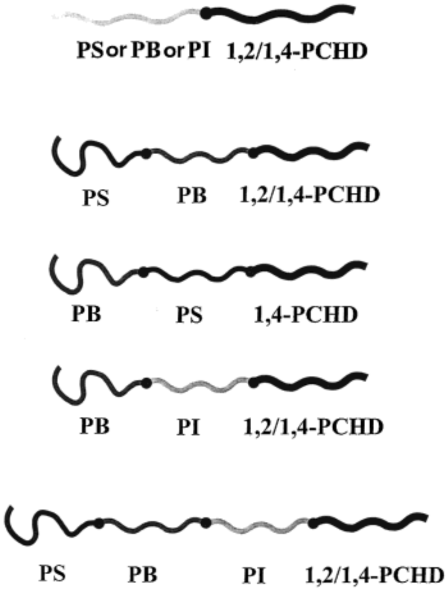
Scheme 1



required for anionic polymerization have been described in detail elsewhere.[32] *sec*-Butyllithium (*sec*-BuLi) was prepared under vacuum from *sec*-butyl chloride (Merck, 99%) and a lithium dispersion in 15% *n*-hexane (Aldrich with 2% sodium, 98%). 1,3-Cyclohexadiene (1,3-CHD, Aldrich, 97%) was stirred overnight over CaH_2 and distilled three times in a vacuum line over sodium mirrors; then it was distilled in a flask containing *n*-BuLi and allowed to react for 30 min at 0 °C. The purified 1,3-CHD was distilled into calibrated ampules and was used immediately. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA, Aldrich, 99.5+%) was stirred overnight over CaH_2 and then stirred over three sodium mirrors, distilled into calibrated ampules, and diluted with benzene. 1,4-Diazabicyclo-[2.2.2]octane (DABCO, Aldrich, 98%) was purified by sublimation three times under vacuum and diluted with benzene.

Polymerization. All polymerizations were carried out under high vacuum, in *n*-BuLi washed and benzene rinsed glass reactors, provided with break-seals and constrictions.[32] *sec*-BuLi was the initiator, benzene was the solvent, and TMEDA or DABCO was used as polar modifier in appropriate ratios ([*sec*-BuLi]/[TMEDA] = 4/5 and [*sec*-BuLi]/[DABCO] = 1/2). All polymers were made by sequential addition of monomers, where 1,3-CHD was always added last.

Synthesis Example of PS-b-PB-b-PI-b-(1,4-PCHD) (19/20/22/39). PS^-Li^+ with $M_n = 13K$ was synthesized by reacting 4.3 g (41.2 mmol) of styrene with 0.33 mmol of *sec*-BuLi in 200 mL of C_6H_6. 0.5 g of the living polymer was terminated with 0.38 g (11.9 mmol) of MeOH, was precipitated in a 10-fold excess of methanol containing ~0.05% w/v 2,6-di-*tert*-butyl-4-methylphenol (BHT, stabilizer), was left for complete dryness under vacuum, and was used for molecular characterization. The remaining 3.8 g of the macroanion was reacted with 3.8 g (70.4 mmol) of butadiene for the synthesis of PS-*b*-PB^-Li^+ ($M_{nPS}/M_{nPB} = 13K/13K$) inside the polymerization apparatus, and the reaction was left to complete for 24 h. 0.5 g of the diblock copolymer was terminated with 0.40 g (12.5 mmol) of MeOH, was precipitated in a 10-fold excess of methanol, was left for complete dryness under vacuum, and was used for molecular characterization. In the one half of the remaining PS-b-PB^-Li^+ (3.6 g), 1.9 g (27.9 mmol) of isoprene and 0.27 mmol of DABCO (DABCO is inserted in a molar ratio with *sec*-BuLi equal to [*sec*-BuLi]/[DABCO] = 1/2) were added and left to react for 24 h to ensure complete reaction of the added monomer. With the addition of the polar additive DABCO the 3,4-microstructure of the PI component in the triblock terpolymer ($M_{nPS}/M_{nPB}/M_{nPI} = 13K/13K/14K$) is increased as exhibited from the ^{1}H NMR. 0.5 g of the triblock terpolymer was terminated with 0.5 g (15.6 mmol) of MeOH and was as well precipitated in a 10-fold excess of methanol, was left for complete dryness under vacuum, and was used for molecular characterization. The remaining 5 g of the macroanion was finally reacted with 2.47 g (30.9 mmol) of 1,3-CHD and was left to react for 24 h at low temperature, ~5 °C. Aliquots from the polymerization apparatus were taken in order to monitor the procedure. It was found that after 12−14 h the polymerization was complete, but for precaution reasons it was left for 24 h before termination. The final quaterpolymer was terminated with a small quantity of 1 g (31.2 mmol) of MeOH and precipitated in a 10-fold excess of methanol, was left for complete dryness under vacuum, and was used for molecular characterization. The microstructures of the polydienic blocks were analyzed with ^{1}H NMR in $CDCl_3$ at 30 °C (Table 1). The other half of the PS-b-PB^-Li^+ (3.6 g) was used for the synthesis of PS-b-PB-b-PI-b-(1,2-PCHD) (15/16/18/51). The procedure was exactly the same but TMEDA was used instead of DABCO.

The final polymer was dried under vacuum to constant weight. In most cases fractionation of the final product to remove some accidentally deactivated precursors was performed. When PS was the deactivated precursor, toluene/methanol was the solvent/nonsolvent pair, but when PB, PI, PB-*b*-PI, and PS-*b*-PB-*b*-PI were the accidentally killed precursors, a toluene/hexane (2/1) mixture was the solvent and methanol the nonsolvent.

Characterization. SEC experiments in THF were carried out at 30 °C using a Waters 510 pump, a Waters 410 differential refractometer detector, and a Waters 996 photodiode detector (flow rate: 1 mL/min; columns: Waters 100, 500, 10^3, 10^4, and 10^5 Å pore sizes). The concentration of the injected solution sample was approximately 0.1% w/v in all cases. Calibration curves were constructed using seven polystyrene standards with molecular weights ranging from 4×10^3 to 1.5×10^6. Toluene was used as an internal standard. SEC experiments in chloroform (flow rate: 1 mL/min) were performed at 30 °C on a Waters 2690 system with a Waters 2410 refractive index detector. Two Polymer Laboratories 5 μm PL-gel MiniMIX narrow bore columns with pore size from 100 to 10^5 Å were used. The system was connected to a Wyatt DAWN DSP multiangle laser light scattering (MALLS) detector equipped with 5 mW linearly polarized He−Ne laser operating at 632.8 nm. The MALLS unit had 18 detectors with fixed angles ranging from 22° to 147°. The refractive index increments (d*n*/d*c*) in $CHCl_3$ at 30 °C were measured with a Brice-Phoenix differential refractometer, operating at 632.8 nm and calibrated with aqueous potassium chloride solutions. The d*n*/d*c* values for 1,4-PCHD, PB, PI, and PS in $CHCl_3$ are given in Table 1, whereas for the final fractionated co-, ter-, and quaterpolymers containing 1,4-PCHD the d*n*/d*c* values are given in Tables 2, 3, and 4, respectively. The measured d*n*/d*c* values agree well with those calculated by using the d*n*/d*c* values of the corresponding homopolymers through the well-known equation[33]

$$\left(\frac{dn}{dc}\right)_{\text{final}} = X_{1,4-\text{PCHD}}\left(\frac{dn}{dc}\right)_{1,4-\text{PCHD}} + X_{\text{PS}}\left(\frac{dn}{dc}\right)_{\text{PS}} + X_{\text{PI}}\left(\frac{dn}{dc}\right)_{\text{PI}} + X_{\text{PB}}\left(\frac{dn}{dc}\right)_{\text{PB}}$$

where $X_{1,4-\text{PCHD}}$, X_{PS}, X_{PI}, and X_{PB} are the 1,4-PCHD, PS, PI, and PB weight fractions determined by ^{1}H NMR. Because of the poor solubility of 1,2-PCHD in $CHCl_3$ and THF, its copolymers form micelles (see Results and Discussion); consequently, the $\bar{M}_w$ values obtained were much higher than the real ones and therefore are not included in the tables.

Number-average molecular weights $\bar{M}_n$ were obtained by membrane osmometry[34] (MO) at 40 °C in toluene with a Jupiter Instrument Co. (Jupiter, FL) model 231 with RC-51 membranes. Toluene was dried over calcium hydride and distilled just prior to use. The $\bar{M}_n$ values from MO were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots where π is the osmotic pressure and c is the concentration in g/mL. In

Table 1. Microstructure of the Polydienes Synthesized under Different Environments and the Corresponding (d*n*/d*c*) Values

	microstructure[a]			
polydiene (initiating system, solvent)	1,4 (wt %)	1,2 (wt %)	3,4 (wt %)	(d*n*/d*c*) (mL/g)[b] ($CHCl_3$)
PB (*sec*-BuLi, benzene)	90	10		0.083
PI (*sec*-BuLi/DABCO, benzene)	47	4	49	0.073
PI (*sec*-BuLi/TMEDA, benzene)	21	15	64	0.068
1,4-PCHD (*sec*-BuLi/DABCO, benzene)	90	10		0.125
1,2-PCHD (*n*-BuLi/TMEDA, benzene)	45	55		
PS				0.131

[a] ^1H NMR in $CDCl_3$ at 30 °C. [b] Experimental value determined by differential refractometry in $CHCl_3$ at 30 °C.

Table 2. Molecular Characteristics of Diblock Copolymers of 1,3-Cyclohexadiene (CHD) with Styrene (S), Butadiene (B), or Isoprene (I)

	first block		diblock copolymer				
sample	M_w [a] × 10^{-3} (g/mol)	M_w/M_n [b]	M_n [c] × 10^{-3} (g/mol)	d*n*/d*c* (mL/g)	M_w [a] × 10^{-3} (g/mol)	M_w/M_n [b]	PCHD[d] (wt %)
PS-*b*-(1,4-PCHD)	21.4[b]	1.03	40.2	0.136[e]/0.128[f]	48.1	1.12	55
PS-*b*-(1,2-PCHD)	21.4[b]	1.03	39.3			1.21	50
PB-*b*-(1,4-PCHD)	21.4	1.03	42.5	0.120[e]/0.109[f]	49.2	1.16	62
PB-*b*-(1,2-PCHD)	21.4	1.03	41.9			1.20	53
PI-*b*-(1,4-PCHD)	32.1	1.06	51.2	0.115[e]/0.105[f]	69.9	1.19	60
PI-*b*-(1,2-PCHD)	27.7	1.09	47.4			1.27	54

[a] MALLS in $CHCl_3$ at 25 °C. [b] SEC in THF at 30 °C calibrated with polystyrene standards. [c] M_n by membrane osmometry in toluene at 40 °C. [d] ^1H NMR in $CDCl_3$ at 30 °C. [e] Experimental value determined by differential refractometry in $CHCl_3$ at 30 °C. [f] Calculated value.

Table 3. Molecular Characteristics of Linear Terpolymers of 1,3-Cyclohexadiene (CHD) with Styrene (S), Butadiene (B), and Isoprene (I)

	first block		diblock		terpolymer			
sample	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]	M_n [c] × 10^{-3} (g/mol)	d*n*/d*c* (mL/g)	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]
PS-*b*-PB-*b*-(1,4-PCHD) (17/43/40)[d]	6.4	1.03	20.7	1.04	29.0	0.116[e]/0.108[f]	32.8	1.05
PS-*b*-PB-*b*-(1,2-PCHD) (17/43/40)	6.4	1.03	20.7	1.04	28.0			1.06
PS-*b*-PB-*b*-(1,4-PCHD) (34/32/34)	11.0	1.05	22.5	1.03	33.5	0.114[e]/0.114[f]	36.0	1.09
PS-*b*-PB-*b*-(1,2-PCHD) (32/28/40)	11.0	1.05	22.5	1.03	33.7			1.07
PB-*b*-PS-*b*-(1,4-PCHD) (17/34/49)	9.1	1.03	25.0	1.07	39.0	0.124[e]/0.120[f]	48.3	1.12
PB-*b*-PI-*b*-(1,4-PCHD) (25/29/46)	11.7	1.03	25.6	1.04	38.0	0.106[e]/0.100[f]	44.6	1.10
PB-*b*-PI-*b*-(1,2-PCHD) (32/39/29)	11.7	1.03	24.9	1.05	35.7			1.09

[a] MALLS in $CHCl_3$ at 25 °C. [b] SEC in THF at 30 °C. [c] M_n by membrane osmometry in toluene at 40 °C. [d] Wt % composition by ^1H NMR in $CDCl_3$. [e] Experimental value determined by differential refractometry in $CHCl_3$ at 30 °C. [f] Calculated value.

Table 4. Molecular Characteristics of Linear Quaterpolymers of 1,3-Cyclohexadiene (CHD) with Styrene (S), Butadiene (B), and Isoprene (I)

	first block		diblock		terpolymer		quaterpolymer			
sample	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]	M_n [c] × 10^{-3} (g/mol)	d*n*/d*c* (mL/g)	M_w [a] × 10^{-3} (g/mol)	$M_w/$ M_n [b]
PS-*b*-PB-*b*-PI-*b*-(1,4-PCHD) (19/20/22/39)[d]	13.8	1.03	25.4	1.05	38.6	1.10	52.6	0.111[e]/0.106[f]	62.5	1.14
PS-*b*-PB-*b*-PI-*b*-(1,2-PCHD) (15/16/18/51)	13.8	1.03	25.4	1.05	39.0	1.07	51.1			1.15
PS-*b*-PB-*b*-(1,4-PCHD)-*b*-PI	27.5[c]	1.03	56.0[c]	1.03	60.0[c]	1.07	197			1.08

[a] MALLS in $CHCl_3$ at 25 °C. [b] SEC in THF at 30 °C. [c] M_n by membrane osmometry in toluene at 40 °C. [d] Wt % composition by ^1H NMR in $CDCl_3$. [e] Experimental value determined by differential refractometry in $CHCl_3$ at 30 °C. [f] Calculated value.

all cases of polymers containing 1,4-PCHD the correlation coefficient was better than 0.99, but for copolymers containing 1,2-PCHD the correlation coefficient varied from 0.84 to 0.98. Toluene is a better solvent than $CHCl_3$ and THF for the other blocks accompanying PCHD ($\delta_{Tol} = 18.2$; $\delta_{THF} = 18.6$; $\delta_{CHCl_3} = 19.0$; $\delta_{PI} = 16.7$; $\delta_{PB} = 17.6$; $\delta_{PS} = 18.6$), which helped solubilize the copolymers, yielding the $\bar{M}_n$ values reported in the tables. These values appear to be reasonable, and clearly $\bar{M}_n$ values will be much less affected than $\bar{M}_w$ values by micellization. Light scattering measurements were not performed in toluene since, except for PS, the d*n*/d*c* values of the polymers in this solvent are relatively low.

The microstructures of the polydienic blocks obtained under the different experimental conditions were analyzed using ^1H NMR spectroscopy (Bruker-ARX 300) in $CDCl_3$ at 30 °C. The results are given in Table 1.

For PCHD the 1,2 to 1,4 ratios of the homopolymer were determined from the relative areas of protons that are adjacent to the double bond [α position (1.85−2.35 ppm)] and those in β positions (1.25−1.85 ppm).[22,27,35] Each 1,2 unit has three α protons and three β protons, while a 1,4 unit has two α protons and four β protons. The compositions of the terpolymers and quaterpolymers containing PB, PI, and PCHD were calculated by taking into account the microstructure of the polydienes

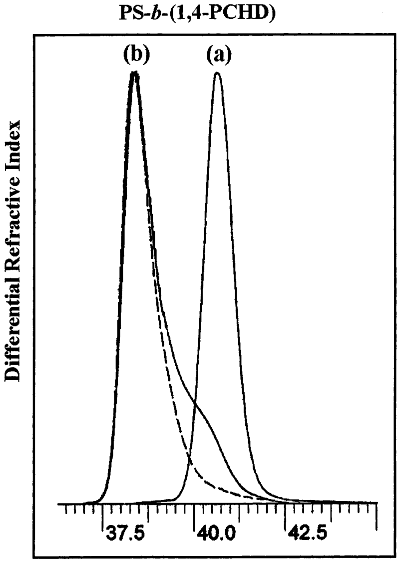
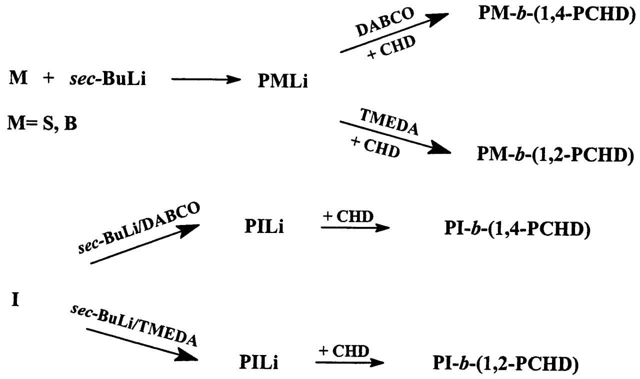


Figure 1. SEC chromatograms in THF for the synthesis of PS-*b*-(1,4-PCHD) (M_w = 48.1K, Table 2) diblock copolymer: (a) PS block; (b) unfractionated (continuous line) and fractionated (broken line) PS-*b*-(1,4-PCHD) diblock copolymer.

Scheme 2



under different environments (Table 1). (PBd: $n_{1,4-\mathrm{PB}} = 9n_{1,2-\mathrm{PB}}$; PI (DABCO): $n_{1,4-\mathrm{PI}} = 12n_{1,2-\mathrm{PI}}$; PI (TMEDA): $n_{1,4-\mathrm{PI}} = 1.4n_{1,2-\mathrm{PI}}$).

Results and Discussion

Diblock Copolymers. The reactions used to prepare diblock copolymers of 1,3-cyclohexadiene (PCHD) with styrene (S), butadiene (B), and isoprene (I) are given in Scheme 2.

The polymerization of styrene and butadiene was initiated with *sec*-BuLi in benzene at room temperature. After completion of the polymerization, the solution was divided into two approximately equal parts in two reactors. In one part DABCO was inserted in a molar ratio 2/1 to the $\mathrm{PS^-Li^+}$ or $\mathrm{PB^-Li^+}$ and stirred for 10 min, and then 1,3-cyclohexadiene was added. In the other part TMEDA was introduced in a molar ratio 5/4 to the $\mathrm{PS^-Li^+}$ or $\mathrm{PB^-Li^+}$ and stirred for 10 min, and 1,3-cyclohexadiene was then added. Polymerizations of CHD were allowed to proceed for 24 h at 5 °C. The polymerization of isoprene was initiated with both *sec*-BuLi/DABCO and *sec*-BuLi/TMEDA initiating systems. After the completion of the polymerization, 1,3-cyclohexadiene was added.

The molecular characteristics of the diblock copolymers are shown in Table 2. Characteristic chromatograms from the synthesis of the PS-*b*-(1,4-PCHD) diblock copolymer are shown in Figure 1. Although in some cases minor deactivation of the first block occurred from impurities of the polar additive or the second monomer (Figure 1), well-defined diblock copolymers were obtained after fractionation.

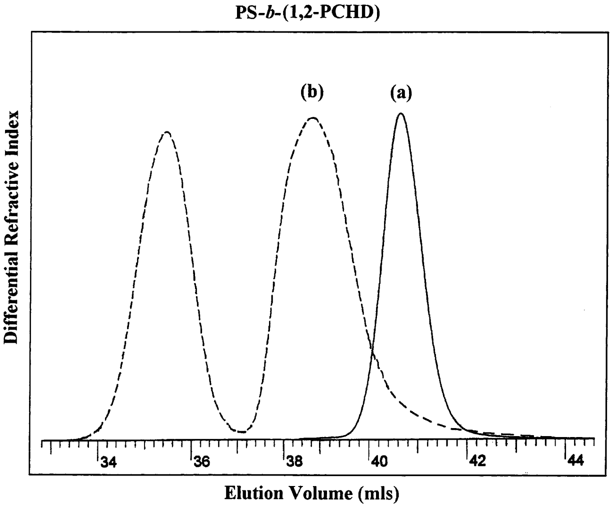


Figure 2. SEC chromatograms in THF for the synthesis of PS-*b*-(1,2-PCHD) (M_n = 39.3K, Table 2) diblock copolymer: (a) PS block; (b) fractionated PS-*b*-(1,2-PCHD) diblock copolymer (broken line).

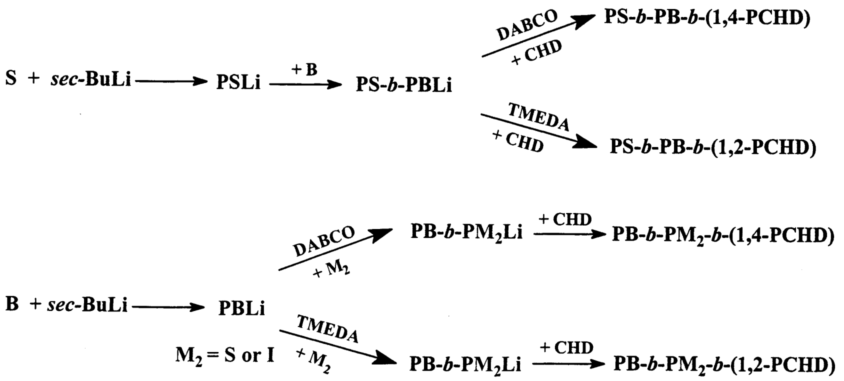
In all diblock copolymers containing 1,2-PCHD a second peak corresponding to extremely high molecular weight (~10^6 g/mol) material was observed in SEC chromatograms in both THF and $\mathrm{CHCl_3}$. An example is given in Figure 2. By decreasing the solution concentration the percentage of this peak was decreased, and its position was shifted to lower molecular weight. A similar observation was reported by Mays et al.[28] This peak can be possibly attributed to micelle formation in THF or $\mathrm{CHCl_3}$, due to the poor solubility of 1,2-PCHD in these solvents.

Linear Terpolymers. The synthetic procedure for the preparation of linear terpolymers is shown in Scheme 3.

In the case of PS-*b*-PB-*b*-[(1,4-PCHD) or (1,2-PCHD)] linear terpolymers, the monomers were added sequentially, where TMEDA or DABCO was inserted before 1,3-cyclohexadiene (last monomer). In the case of PB-*b*-PS-*b*-(1,4-PCHD), DABCO was added before the addition of styrene,[36] to accelerate the slow initiation of styrene from polybutadienyllithium. 1,3-Cyclohexadiene was finally added to the solution. For PB-*b*-PI-*b*-[(1,4-PCHD) or (1,2-PCHD)] terpolymers, DABCO or TMEDA was introduced before the addition of isoprene. The molecular characteristics of the final fractionated materials are reported in Table 3.

SEC chromatograms monitoring the synthesis of the PS-*b*-PB-*b*-(1,4-PCHD) terpolymer are shown in Figure 3. Fractionation was not necessary for this material. Its ^{1}H NMR spectrum is given in Figure 4. Figure 5 shows SEC chromatograms (RI and UV detector) of the precursors and the final PS-*b*-PB-*b*-(1,2-PCHD) terpolymer. A relatively small second peak is observed only at the RI detector. This peak can be attributed to PCHD homopolymer, since both the PS and PS-*b*-PB precursors are visible with the UV detector. Despite the presence of a polar additive and the low temperature (~5 °C),

Scheme 3



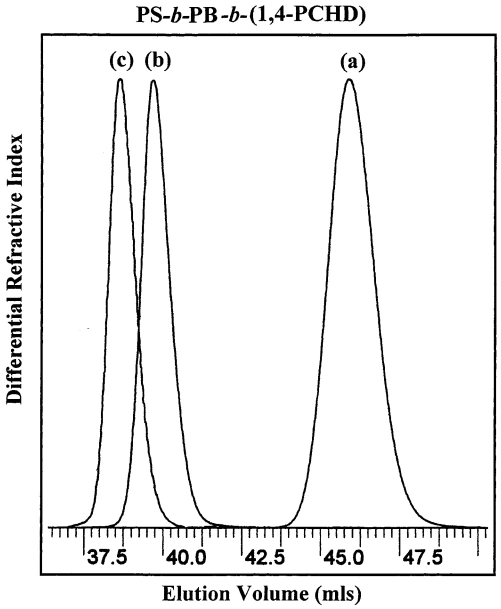


Figure 3. Monitoring the synthesis of PS-*b*-PB-*b*-(1,4-PCHD) (17/43/40, Table 3) terpolymer by SEC: (a) PS block; (b) PS-*b*-PB precursor; (c) PS-*b*-PB-*b*-(1,4-PCHD) terpolymer.

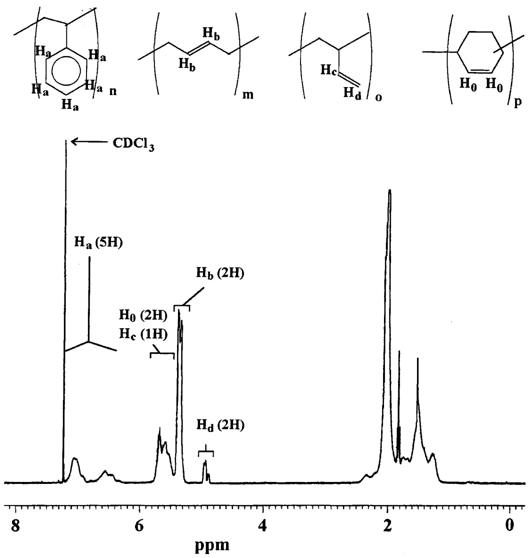


Figure 4. ^{1}H NMR of the PS-*b*-PB-*b*-(1,4-PCHD) (17/43/40, Table 3) terpolymer in $CDCl_3$ at 30 °C.

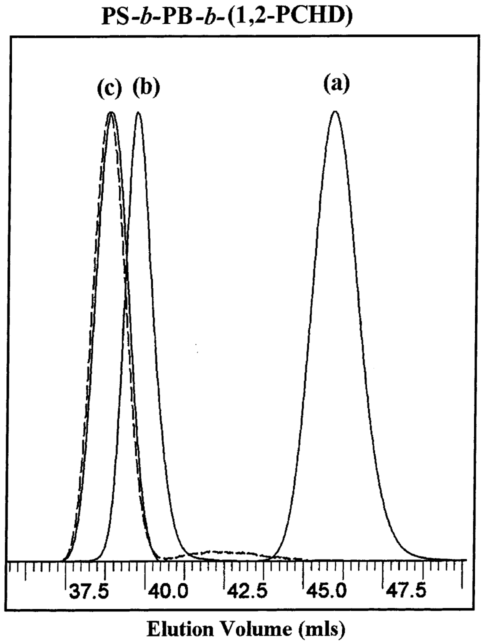
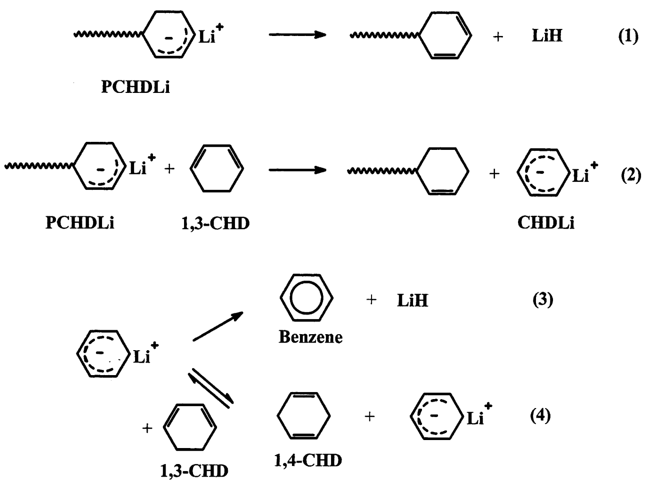


Figure 5. Monitoring the synthesis of PS-*b*-PB-*b*-(1,2-PCHD) (17/43/40, Table 3) terpolymer by SEC: (a) PS block; (b) PS-*b*-PB precursor; (c) UV (continuous line) and RI response (broken line) of PS-*b*-PB-*b*-(1,2-PCHD) terpolymer.

Scheme 4



some chain transfer and termination occur,[20,22,27] leading to PCHD homopolymer according to the reactions shown in Scheme 4. Reaction 1 is a chain termination reaction via hydride abstraction, and reaction 2 corresponds to chain transfer toward the monomer through proton elimination. The second reaction produces $CHD^{-}Li^{+}$, which is capable of reinitiating the polymerization of 1,3-cyclohexadiene, producing PCHD homopolymer (reaction 4).

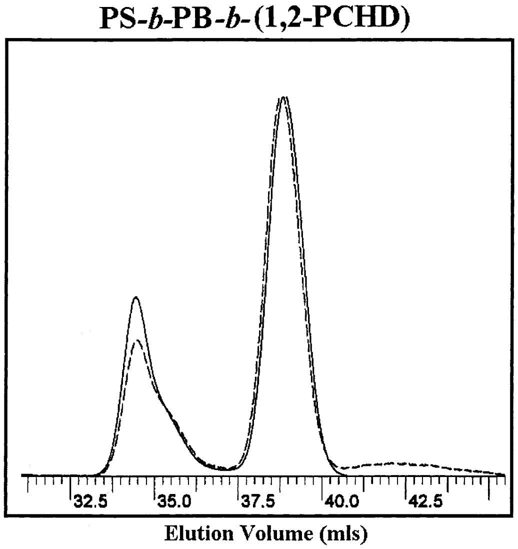


Figure 6. UV (continuous line) and RI response (broken line) of PS-*b*-PB-*b*-(1,2-PCHD) (17/43/40, Table 3) terpolymer by SEC in THF.

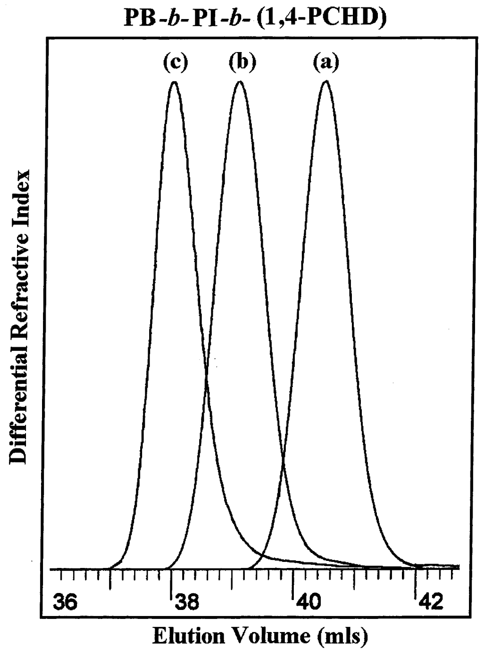


Figure 7. Monitoring the synthesis of PB-*b*-PI-*b*-(1,4-PCHD) (25/29/46, Table 3) terpolymer by SEC: (a) PB block; (b) PB-*b*-PI precursor; (c) fractionated PB-*b*-PI-*b*-(1,4-PCHD) terpolymer.

All SEC chromatograms of polymers containing 1,2-PCHD showed a second peak at high molecular weight (~500 000 g/mol), as is shown for the PS-*b*-PB-*b*-(1,2-PCHD) terpolymer in Figure 6. This peak is also attributed to micelles but is smaller than that seen for the diblock copolymers containing 1,2-PCHD. This observation can be explained by the lower weight fraction of 1,2-PCHD in the terpolymers (~40%, diblocks ~50%).

In Figure 7, SEC chromatograms from each stage of the synthesis of the PB-*b*-PI-*b*-(1,4-PCHD) terpolymer are exhibited, and in Figure 8 the ^{1}H NMR spectrum of the final fractionated PB-*b*-PI-*b*-(1,4-PCHD) terpolymer is shown. This terpolymer is unique and noteworthy since it contains, for the first time, three different dienes in a series of decreasing flexibility.

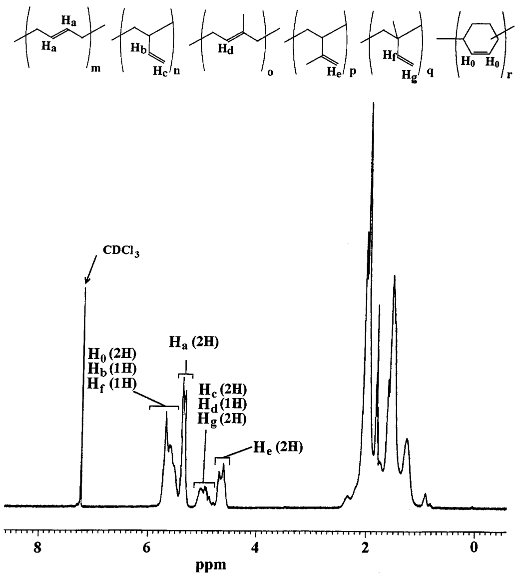
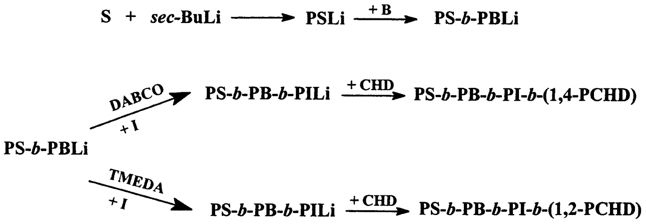


Figure 8. ^{1}H NMR of the fractionated PB-*b*-PI-*b*-(1,4-PCHD) (25/29/46, Table 3) terpolymer in CDCl$_3$ at 30 °C.

Scheme 5



Linear Quaterpolymers. A schematic representation of the sequence of reactions used to prepare PS-*b*-PB-*b*-PI-*b*-[(1,4-PCHD) or (1,2-PCHD)] linear quaterpolymers is exhibited in Scheme 5.

sec-BuLi was the initiator for the polymerization of styrene, and butadiene was the second monomer added. After the completion of the polymerization of butadiene, the living diblock copolymer PS-*b*-PB$^-$Li$^+$ was divided in to two equal volumes in two reactors. In one part of PS-*b*-PB$^-$Li$^+$, DABCO, then isoprene, and finally 1,3-cyclohexadiene were sequentially added to produce the quaterpolymer of PS-*b*-PB-*b*-PI-*b*-(1,4-PCHD). This procedure was monitored by SEC, and the chromatograms are reported in Figure 9. The ^{1}H NMR spectrum of the final fractionated quaterpolymer is exhibited in Figure 10. For the synthesis of the PS-*b*-PB-*b*-PI-*b*-(1,2-PCHD), TMEDA was used instead of DABCO during the sequential addition of the monomers. Molecular characteristics of the quaterpolymers are given in Table 4.

The synthesis of a PS-*b*-PB-*b*-(1,4-PCHD)-*b*-PI quaterpolymer was achieved by sequential addition of monomers and the addition of DABCO before 1,3-cyclohexadiene. By using this procedure, some active anionic centers were deactivated due to side reactions during the polymerization of 1,3-cyclohexadiene, as is shown in Scheme 4, leading to less control over the polymerization of the last monomer. The need for absolute control of the polymerization of all blocks was the main reason for the addition of 1,3-cyclohexadiene as the last monomer in all cases. An additional reason for not introducing PCHD as the first block is that any deactivated PCHD formed is very difficult to remove by fractionation.[29,30]

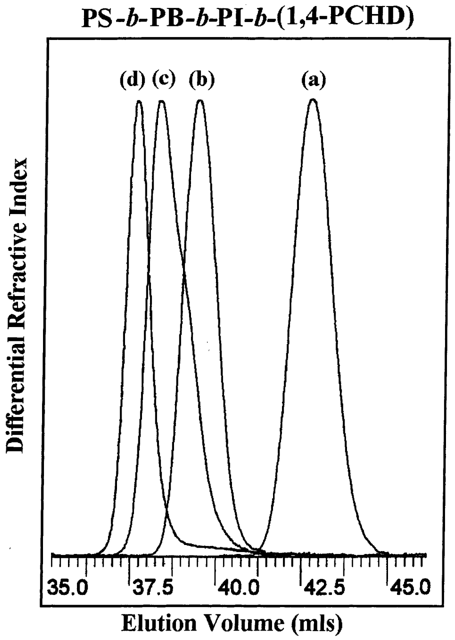


Figure 9. SEC chromatograms monitoring the synthesis of PS-*b*-PB-*b*-PI-*b*-(1,4-PCHD) (19/20/22/39, Table 4) quaterpolymer: (a) PS block; (b) PS-*b*-PB precursor; (c) PS-*b*-PB-*b*-PI precursor; (d) fractionated PS-*b*-PB-*b*-PI-*b*-(1,4-PCHD) quaterpolymer.

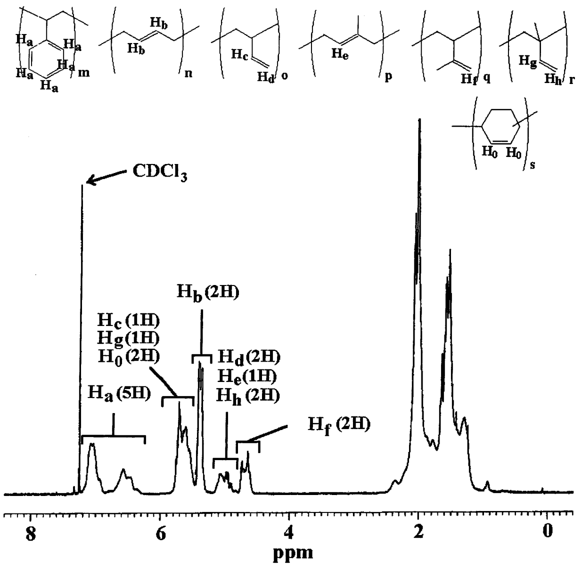


Figure 10. ^{1}H NMR of the fractionated PS-*b*-PB-*b*-PI-*b*-(1,4-PCHD) (19/20/22/39, Table 4) quaterpolymer in $CDCl_3$ at 30 °C.

Conclusions

Linear block co-, ter-, and quaterpolymers of 1,3-cyclohexadiene with styrene, butadiene, and isoprene can be successfully synthesized by sequential anionic polymerization using *sec*-butyllithium as initiator and TMEDA or DABCO as additive. The combined characterization results obtained using size exclusion chromatography coupled with multiangle laser light scattering, osmometry, and NMR spectroscopy, as well as the good agreement between the d*n*/d*c* values determined experimentally and calculated, indicate a high degree of molecular and compositional homogeneity. The microstructure of polycyclohexadiene obtained in the presence of DABCO was mainly 1,4 (90 wt %) while with TMEDA the 1,2 microstructure was predominate (~55 wt %). The microstructure of PI was also altered in the presence of the above additives. Because of the limited solubility of 1,2-PCHD in THF and $CHCl_3$, its copolymers formed micelles and thus revealed extra peaks in the SEC chromatograms obtained in these solvents.

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