1234 *Macromolecules* **2004,** *37,* 1234−1242

Anionic Synthesis and Characterization of ω-Hydroxyl-Functionalized Poly(1,3-cyclohexadiene)

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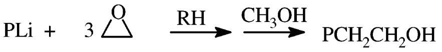
Received March 21, 2003

ABSTRACT: The amount of chain transfer to monomer during the alkyllithium-initiated polymerization of 1,3-cyclohexadiene has been evaluated by characterization of the products from ethylene oxide termination. The products were separated by column chromatography and characterized by SEC, TLC, ^{1}H NMR, and MALDI−TOF MS. The highest yields (90%) of ω-hydroxyl-functionalized poly(1,3-cyclohexadiene) [M_n(calcd) = 3000] were obtained in benzene or in the presence of *N,N,N′N′*-tetramethylethylenediamine (TMEDA) or lithium 2,3-dimethyl-3-pentoxide (LDP); in the presence of 1,4-diazobicyclo[2.2.2]octane (DABCO), the yield was 81%. All unfunctionalized polymer fractions exhibited lower M_n values and broader molecular weight distributions compared to functionalized polymers; the exact masses determined by MALDI−TOF MS were consistent with termination by chain transfer to monomer and not decomposition by loss of lithium hydride. The occurrence of reinitiation after chain transfer was investigated by MALDI−TOF MS; reinitiation occurs in the presence of DABCO but not in the presence of either TMEDA or LDP.

Introduction

The alkyllithium-initiated, anionic polymerization of 1,3-cyclohexadiene (CHD) has been of continuing interest since the first reports showing that the resulting polymer could be dehydrogenated to form poly(phenylene).[1,2] Later investigations delineated the mechanism of alkyllithium-initiated polymerization involving chain transfer to monomer as an integral step ($k_{tr}/k_p = 0.029$ at 20 °C and 0.0095 at 5 °C in cyclohexane).[3,4] Recent reports have described controlled polymerizations of CHD using *sec*-butyllithium with 1,4-diazabicyclo[2.2.2]-octane (DABCO)[5] or even living polymerizations with *n*-butyllithium in the presence of *N,N,N′N′*-tetramethylethylenediamine (TMEDA).[6−8] However, the claims of living polymerization in the presence of TMEDA were not reproducible under high vacuum conditions.[5] Long and workers[9,10] have reported that both controlled number-average molecular weight and narrow molecular weight distribution polymers were obtained using the *n*-butyllithium /TMEDA system under an inert atmosphere of nitrogen.

A number of experimental criteria can be used to determine whether a given polymerization system is living or not.[11,12] The criteria that have been used for 1,3-cyclohexadiene polymerization include the ability to (a) obtain an observed number-average molecular weight that is in agreement with the stoichiometric molecular weight, (b) obtain a narrow molecular weight distribution polymer (M_w/M_n <1.1),[13] and (c) prepare block copolymers. Another useful criterion is that, if all of the anionic chains are living when all of the monomer has been consumed, the chain ends can be quantitatively functionalized by electrophilic termination. Of course, for this criterion to be useful, the functionalization reaction must be quantitative. One such functionalization reaction is the reaction of polymeric organolithium compounds with ethylene oxide (eq 1). A variety of experimental probes have established that this reaction is quantitative and proceeds without oligomerization of ethylene oxide at the chain end using 3−4 equiv of ethylene oxide, hydrocarbon solution and reaction times of 12 h or less.[14−16] Using larger excesses of ethylene oxide and longer reaction times still provides quantitative functionalization, but oligomerization of ethylene oxide at the chain end has been detected by ^{1}H NMR spectroscopy and MALDI−TOF mass spectrometry.[15,16]



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Francois and co-workers[17] have described the synthesis of functionalized poly(1,3-cyclohexadienes) by effecting terminations with succinic anhydride, ethylene sulfide and chlorotriethyoxysilane; however, the resulting functionalized polymers were not well characterized. Long and co-workers[18] effected the termination of poly(1,3-cyclohexadienyl)lithium with chlorotrimethysilane and reported that the trimethylsily functionalized polymer was obtained in quantitative yield as determined by ^{1}H NMR spectroscopy. However, these results are inconclusive with respect to the role of chain transfer in the alkyllithium-initiated polymerization of 1,3-cyclohexadiene.

The role of chain transfer in these polymerizations can be quantitatively evaluated using functionalizations with ethylene oxide; the functionalized polymers can be separated quantitatively from the nonfunctional polymer by column chromatography. The molecular weight distribution for the nonfunctional polymer will be different from the functional polymer (broader distribution and lower number-average molecular weight for nonfunctional polymer) if chain transfer reactions are occurring.

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10.1021/ma034360t CCC: $27.50

Herein are reported the results of a systematic investigation of the use of ethylene oxide functionalization to prepare ω-hydroxyethylpoly(1,3-cyclohexadiene) using *sec*-butyllithium as initiator in hydrocarbon solution to probe the role of chain transfer to monomer under a variety of experimental procedures reported to yield controlled or living polymerizations. The resulting ω-hydroxyethylpoly(1,3-cyclohexadiene)s were of interest for preparation of the corresponding macromonomers and copolymerization of the macromonomers to form polyphenylene comb-type branches after dehydrogenation.

Experimental Section

Materials. Cyclohexane (Fisher, >99%) and benzene (Fisher, >99%) were purified as described previously.[19] 1,4-Diazobicyclo-[2.2.2]octane (DABCO) (Aldrich, 98%) was mixed with freshly ground CaH_2, sublimed under vacuum three times and then diluted in benzene. *N,N,N′N′*-Tetramethylethylenediamine (TMEDA) was dried over CaH_2 and distilled into an ampule followed by flame sealing. 1,3-Cyclohexadiene (Aldrich, 97%) was dried over CaH_2, degassed on a vacuum line, distilled onto sodium dispersion, distilled onto neat dibutylmagnesium (Lithium Division, FMC Corp.) and finally distilled into ampules followed by flame sealing. Methanol (99+ %, Aldrich) was degassed on the vacuum line and distilled into an ampule containing a break-seal. *sec*-Butyllithium (Lithium Division, FMC Corp., 1.43 M in hexane), *n*-butyllithium (Lithium Division, FMC Corp., 1.68 M in hexane), 3-(*tert*-butyldimethylsiloxy)-1-propyllithium (Lithium Division, FMC Corp., 0.49 M in toluene), and 3-(*tert*-butyldimethylsiloxy)-2,2-dimethyl-1-propyllithium (Lithium Division, FMC Corp., 0.79 M in toluene) were used as received after double titration analysis.[20] Ethylene oxide (99.5+ %, Aldrich) was condensed onto CaH_2, degassed on a vacuum line several times and stirred for 3 h. It was then vacuum distilled onto neat dibutylmagnesium (Lithium Division, FMC Corp.), the mixture stirred for 1 h, the product distilled into an ampule equipped with a break-seal, the product diluted with benzene, and the ampule flame-sealed.

2,3-Dimethyl-3-pentanol (Aldrich, 99%) was dried over CaH_2, degassed, and distilled into ampules followed by flame sealing of the ampules. This ampoulized 2,3-dimethyl-3-pentanol was taken into a recirculating, argon atmosphere drybox and diluted with benzene in a flask with a Rotaflo stopcock. A slightly less than 1 M amount of *sec*-BuLi was added slowly to the alcohol solution and the solution was stirred for 1 h. The flask was taken out of the drybox, the solvent was removed under vacuum, and the corresponding lithium alkoxide was dried on a vacuum line at 45 °C for 2 h to remove the excess amount of alcohol. The flask was then taken into the drybox and the lithium alkoxide was diluted with benzene. The desired amount of lithium alkoxide was transferred into an ampule equipped with a break-seal and a Rotaflo stopcock. The ampule was taken out of the drybox and sealed off from the vacuum line.

Polymerizations. Functionalization by Terminating with Ethylene Oxide. The polymerizations were performed in all-glass, sealed reactors using standard high-vacuum techniques.[21] In the absence of additive, a typical functionalization procedure was as follows: 1.2 mL of *sec*-BuLi (1.43 M) was introduced into a reactor by syringe under a flow of dry nitrogen. After heat-sealing the initiator inlet, benzene (100 mL) was distilled into the reactor. Then the reactor was heat-sealed off from the vacuum line using a hand torch. 1,3-Cyclohexadiene (6.3 mL) was introduced by ampule, and the reaction proceeded for the desired amount of time at the desired temperature. The resulting poly(1,3-cyclohexadienyl)-lithium was functionalized by the addition of ethylene oxide (0.50 mL, in 7 mL of benzene; 6 equiv relative to *sec*-BuLi) from an ampule. After 12 h, the reaction was quenched with a small amount (0.5 mL) of ampulized, degassed methanol. The polymer was precipitated into acetone, filtered, and dried overnight in a vacuum oven. When DABCO was used as additive, the benzene solution of DABCO was introduced into the reactor by syringe under a flow of dry nitrogen after the introduction of *sec*-BuLi. Benzene (100 mL) was distilled into the reactor and the reactor was heat-sealed off from the vacuum line. After the mixture was stirred for a few minutes, 1,3-cyclohexadiene (6.3 mL) was introduced by ampule. The reaction proceeded for 6 h at room temperature followed by functionalization with ethylene oxide, followed by the standard workup described previously. When using TMEDA as additive, a TMEDA ampule was attached to the reactor, and the TMEDA was added to the reactor and stirred with *n*-BuLi for 10 min at room temperature and then 10 min at 40 °C before addition of monomer. The polymerization proceeded for 2 h followed by functionalization with ethylene oxide and the standard workup. When using lithium alkoxide as additive, the lithium alkoxide solution was attached to the reactor in an ampule, added to the reactor, and stirred with *sec*-BuLi for 10 min before addition of monomer. The polymerization proceeded for 24 h followed by functionalization with ethylene oxide and standard workup. The functionalized and unfunctionalized PCHDs were separated by silica gel (230−400 mesh, EM Science) column chromatography using toluene/cyclohexane (1/3, v/v) as eluent to remove the unfunctionalized PCHD and then THF to recover the functionalized PCHD. The functionality was determined by weighing the functionalized and unfunctionalized fractions after column chromatography.

Functionalization by Using Protected Functionalized Initiator. The protected functionalized alkyllithium initiator was added to the reactor by syringe under a flow of dry nitrogen. Then the above procedures were followed. A typical procedure was as follows: 5.4 mL of 3-(*tert*-butyldimethylsiloxy)-1-propyllithium (0.49 M) was introduced into a reactor by syringe under a flow of dry nitrogen. After the initiator inlet was heat sealed, cyclohexane (100 mL) was distilled into the reactor. Then the reactor was heat-sealed off from the vacuum line using a hand torch. 1,3-Cyclohexadiene (9.4 mL) was introduced by ampule, and the reaction proceeded for 24 h at room temperature. The reaction was quenched with a small amount (0.5 mL) of ampulized, degassed methanol. The polymer was precipitated into acetone, filtered, and dried overnight in a vacuum oven.

Characterization. Size exclusion chromatographic analysis (SEC) was performed using a Waters 150-C+ instrument equipped with RI and viscosity detectors (Viscotek model 150R) and four Phenomenex Phenogel columns (500, 10^3, 10^4 and 10^5 Å) and a mixed bed column (Phenogel 5μ M2). The molecular weight was determined by universal calibration based on polystyrene standards (Polymer Laboratories). The SEC measurements were performed at 30 °C in THF at a flow rate of 0.6 mL/min. ^{1}H NMR spectra were obtained using a Varian Unity Plus 750 MHz spectrometer with $CDCl_3$ as solvent. The mass spectra were acquired using a Bruker REFLEX-III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with a LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed extraction ion source and a two-stage, gridless reflector. Mass spectra were obtained in the reflector mode. Solutions of dithranol (20 mg/mL), end-functionalized polymer (10 mg/mL), and silver trifluoroacetate (10 mg/mL) were made in tetrahydorfuran (THF). These solutions were mixed in the ratio matrix: cationizing salt: polymer (10:1:2) and 0.5 μL was deposited on the sample holder. The attenuation of the nitrogen laser was set at 70%.

Results and Discussion

Functionalization by Terminating Poly(1,3-cyclohexadienyl)lithium (PCHDLi) with Ethylene Oxide. Two experimental procedures were investigated initially to detect chain transfer using ethylene oxide functionalization: (A) *sec*-BuLi in benzene at room temperature in the presence of DABCO which was reported to be controlled by Hong and Mays (eq 2);[5] (B)

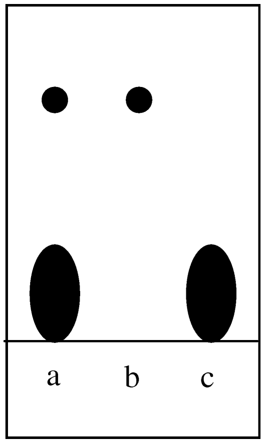
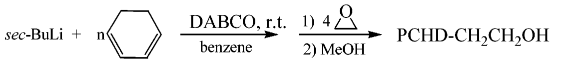


Figure 1. Representative TLC chromatograms of PCHDs from both procedure A and procedure B: (a) crude functionalized PCHD; (b) unfunctionalized PCHD; (c) pure functionalized PCHD. (Eluent: toluene/cyclohexane = 1:3.)

n-BuLi/ TMEDA in cyclohexane at 40 °C which was reported to be living by Natori and Inoue (eq 3).[6−8] The ethylene oxide functionalization was effected using 4 equiv of ethylene oxide for 12 h, i.e., conditions that provide quantitative functionalization without oligomerization. [14−16] The calculated number-average molecular weights were approximately 3000. For both experimental procedures, the TLC chromatograms of the crude polymers showed both functionalized and unfunctionalized PCHDs as shown in Figure 1a. Because of the presence of the polar hydroxyl group in the functionalized PCHD, the functionalized PCHD remains at the initial spotting position while the unfunctionalized PCHD moves with the solvent front to the top of the TLC plate.



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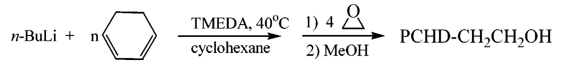


(3)

The SEC chromatograms for the crude PCHD, the pure functionalized, and unfunctionalized PCHDs are shown in Figure 2, and the results are listed in Table 1. Both systems produced unfunctionalized PCHDs, 19% for the *sec*-BuLi/DABCO system, and 10% for *n*-BuLi/ TMEDA system, respectively. The presence of DABCO gave good control for the crude PCHD sample with respect to predicted number-average molecular weight and narrow polydispersity. The *n*-BuLi/TMEDA system gave a slightly higher observed number-average molecular weight than the calculated value and also narrow polydispersity for the crude sample. It is also important to note that the M_n(obsd) values for the functionalized samples are higher than those for the unfunctionalized polymers and the molecular weight distributions are also much narrower for the functionalized polymers. The microstructures of PCHDs were determined by high resolution 750 MHz ^{1}H NMR.[22] The *sec*-BuLi/DABCO system gave 89% 1,4-microstructure and the *n*-BuLi/ TMEDA system gave 36% 1,4-microstructure, in agreement with previous studies.[5−9]

The structures of the functionalized and unfunctionalized PCHDs were also confirmed by MALDI−TOF mass spectrometric analysis as shown in Figure 3. MALDI−TOF mass spectrometry[23] is a powerful method to determine the chemical structure of polymers, especially the determination of their terminal groups. End groups are difficult to characterize using other routine methods, such as NMR and FTIR, due to the low concentration of the terminal groups. The mass spectra of crude PCHDs before column chromatography are shown in the top spectrum and both of them exhibit two distributions corresponding to functionalized PCHD and unfunctionalized PCHD. The mass spectra of the purified functionalized PCHD (middle spectra) and unfunctionalized PCHD (lower spectra) are also shown in Figure 3. The small spectra in the center correspond to the whole mass spectra and the larger spectra below correspond to the expanded mass spectral regions for the two center peaks of the major distribution. In the expanded spectrum, the peak at mass-to-charge ratio (*m*/*z*) 2611 for the functionalized PCHD (A) has the exact mass for the silver adduct of a PCHD 30-mer with one butyl end group, one hydrogen and one ethylene oxide unit {m/z 30 × 80.06 [$(C_6H_8)_{30}$] + 57.06 (C_4H_7) + 1.01 (H) + 44.05 (CH_2CH_2O) + 106.90 ($^{107}Ag^+$) = 2610.86}. The peak at *m*/*z* 2691 corresponds to the 31-mer in the same series. The peak at *m*/*z* 2931 for the functionalized PCHD (B) has the exact mass for the silver adduct of a PCHD 34-mer with one butyl end group and one ethylene oxide unit {m/z 34 × 80.06 [$(C_6H_8)_{34}$] + 57.06 (C_4H_7) + 1.01 (H) + 44.05 (CH_2CH_2O) + 106.90 ($^{107}Ag^+$) = 2931.06}. The peak at *m*/*z* 3011 corresponds to the 35-mer in the same series. The peak at *m*/*z* 1466 for the unfunctionalized PCHD (A) has the exact mass for the silver adduct of a PCHD 16-mer with one butyl end group and one hydrogen {m/z 16 × 80.06 [$(C_6H_8)_{16}$] + 57.06 (C_4H_7) + 1.01 (H) + 106.90 ($^{107}Ag^+$) = 1445.93}. The peak at *m*/*z* 1526 corresponds to the 17-mer in the same series. The peak at *m*/*z* 1446 for the unfunctionalized PCHD (B) has the exact mass for the silver adduct of a PCHD 16-mer with one butyl end group and one hydrogen {m/z 16 × 80.06 [$(C_6H_8)_{16}$] + 57.06 (C_4H_7) + 1.01 (H) + 106.90 ($^{107}Ag^+$) = 1445.93}. The peak at *m*/*z* 1526 corresponds to the 17-mer in the same series. The weak, unresolved metastable peaks in Figure 3 are marked by an asterisk (∗). These broad unresolved signals are mainly due to fragments of $[M + Ag]^+$, generated either in the ion source or in the flight tube of the mass spectrometer. Such signals can readily be distinguished from actual product signals by several tests. First, they are broad and their abundance is strongly dependent on laser power; second, they disappear or weaken upon detection in the linear TOF mode.[24]

The unfunctionalized PCHD fractions exhibited lower molecular weights than the calculated molecular weights as expected for the occurrence of chain transfer to monomer which forms dead polymer chains with $M_n(\text{obsd}) < M_n(\text{calcd})$. The molar mass distributions for the unfunctionalized polymers (see Figure 3) are also broader for the unfunctionalized PCHDs compared to the corresponding functionalized PCHDs.

Besides chain transfer, another reason for the low functionality in the presence of DABCO and TMEDA may be that these Lewis bases accelerate the decomposition of the propagating lithium chain ends.[25] The mechanism for chain transfer and chain decomposition are shown in eqs 4 and 5, respectively.[26] If chain transfer occurs, the chain end would correspond to the cyclohexenyl group, while if chain decomposition and hydride elimination occur, the chain end would be the

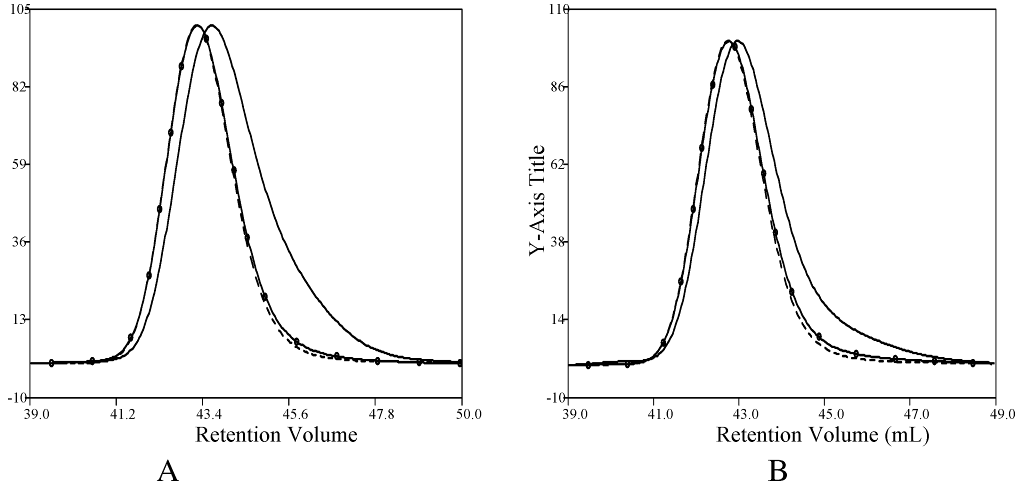


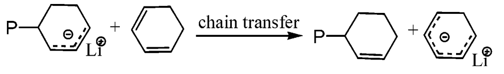
Figure 2. SEC chromatograms for PCHDs (solid line, unfunctionalized PCHD; dashed line, functionalized PCHD; line with circle, crude PCHD): (A) *sec*-BuLi/DABCO in benzene at room temperature; (B) *n*-BuLi/ TMEDA at 40 °C.

Table 1. Results for Functionalization of PCHD Using Ethylene Oxide as Terminating Reagent

entry	A	B	C	D
initiator	*sec*-BuLi/DABCO = 1:2.5	*n*-BuLi/TMEDA = 4:5	*sec*-BuLi	*sec*-BuLi/ROLi = 1:5
yield, %	100	100	99	93
M_n(calcd)	3000	2900	3000	2800
M_n(obsd) [a]	2900	3400	2300	2000
M_w/M_n[a]	1.03	1.03	1.14	1.11
funct. M_n[b]	2900	3400	2600	2100
funct. M_w/M_n[b]	1.02	1.03	1.18	1.07
unfunct. M_n[b]	2500	2000	1500	1400
unfunct. M_w/M_n[b]	1.07	1.1	1.46	1.15
functionality,[c] %	81	90	90	90
1,4-content,[d] %	89	36	97	90

[a] For crude product. [b] From SEC with universal calibration. [c] Isolated by column chromatography. [d] From ^{1}H NMR.

cyclohexadienyl group which is 2 mass units less than the cyclohexenyl group. However, this peak is not observed in the mass spectra of the unfunctionalized PCHDs. The mass spectral results are consistent with the proposal that the unfunctionalized PCHDs are produced by the chain transfer to monomer reaction (eq 4).



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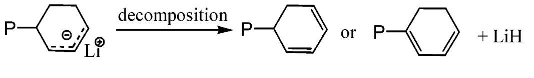
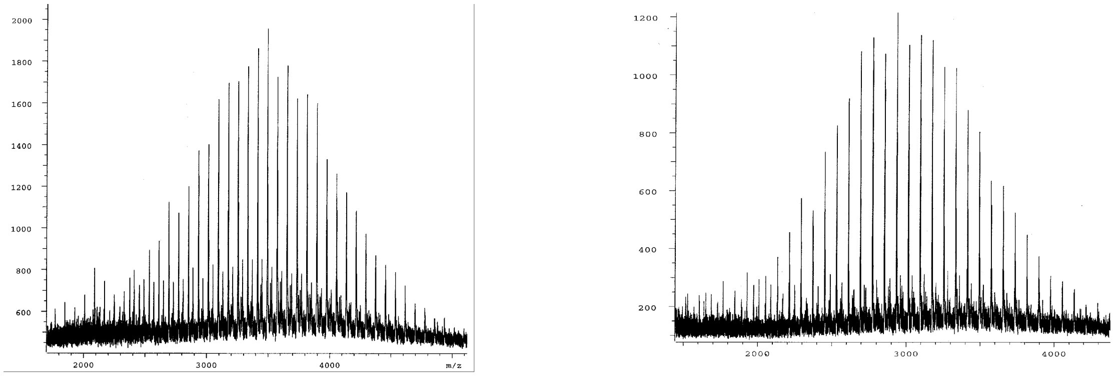


(5)

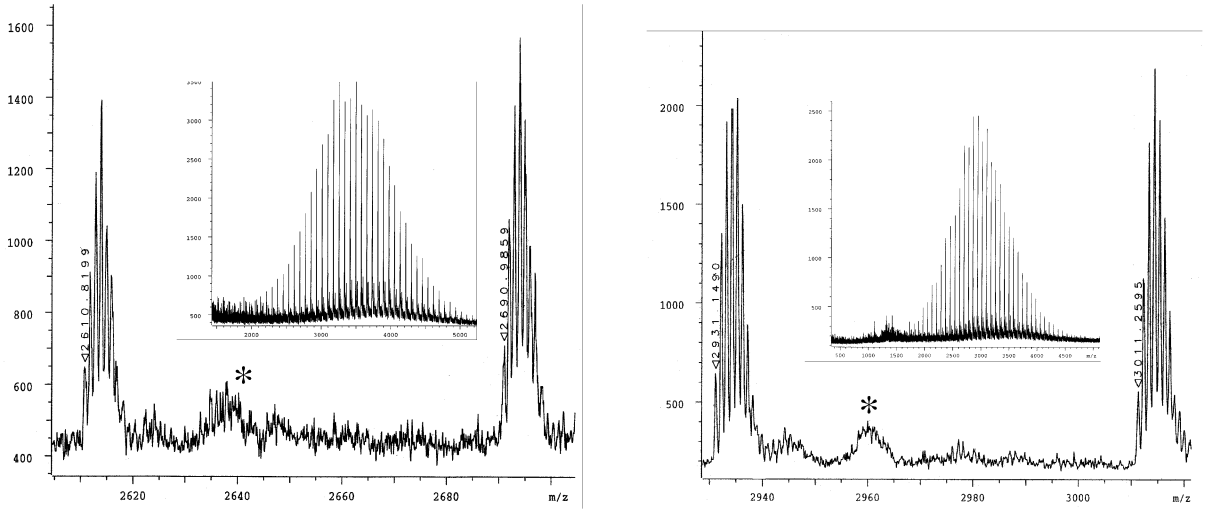
Although it was claimed that the *sec*-BuLi/DABCO[5] and the *n*-BuLi/TMEDA systems[6−8] gave controlled and living character, respectively, for alkyllithium-initiated polymerization of 1,3-cyclohexadiene, it is obvious from the chromatographic analyses and mass spectrometry results that significant amounts of unfunctionalized PCHDs were obtained even at low molecular weight ($M_n \approx 3000$). These chain transfer processes reduce the yield of chain-end functionalized polymers.

To attempt to obtain higher chain end functionalization yields, other experimental variables such as solvent and temperature were investigated for the *sec*-butyllithium initiated polymerization of 1,3-cyclohexadiene and the results are listed in Table 2. The agreement between the observed number-average molecular weight and the calculated number-average molecular weight as well as the polydispersity (M_w/M_n) were used as screening criteria for controlled polymerization. To get high 1,4-microstructure, the nonpolar solvents, benzene and cyclohexane, were used. When cyclohexane was used as solvent (Table 2, entries 1−4), lower temperature gave narrower polydispersity and somewhat better agreement between the M_n(obsd) and M_n(calcd), although the observed molecular weights were always lower than the calculated molecular weights. Narrow MWD polymers ($M_w/M_n < 1.1$)[13] were not obtained even at 0 °C. The polymerization in cyclohexane was very slow and insoluble crystalline PCHD was formed in these systems making the reaction heterogeneous.[27] When benzene was used as solvent (entries 5 and 6), the initiation rate was faster than in cyclohexane as indicated by the color change from colorless to yellowish which is the characteristic color for poly(1,3-cyclohexadinyl)lithium. This is in good agreement with the results by Lefebvre and Dawans,[1] who reported that polymerization in benzene solution was faster and had a much higher conversion than in cyclohexane. Polymerization in benzene also provided somewhat better control ($M_w/M_n = 1.11$) compared with that in cyclohexane.

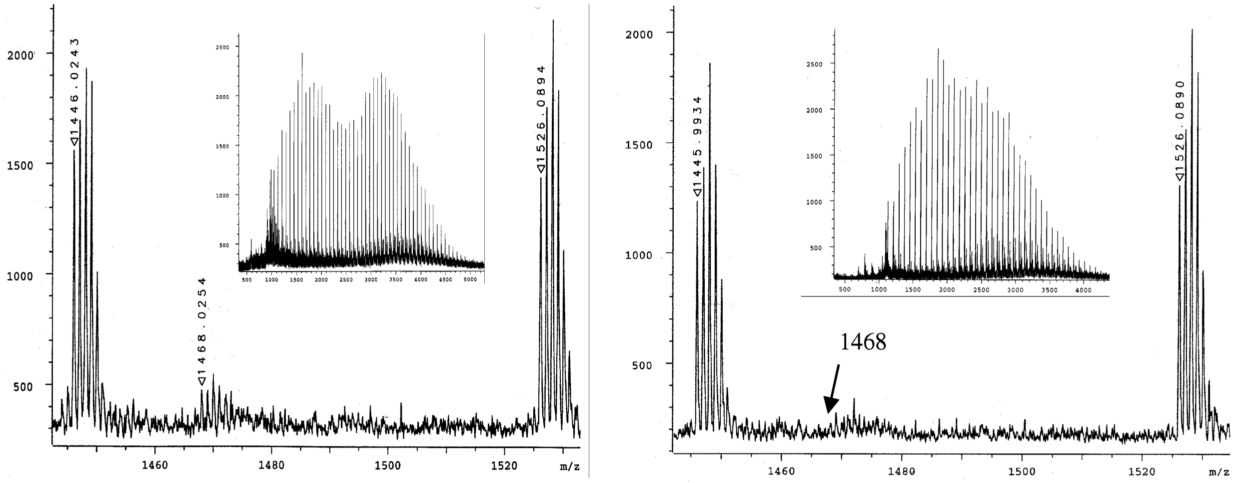
Lithium salts such as lithium bromide, lithium chloride, and lithium alkoxide are known to change the reactivity of organolithium compounds.[28−30] Lithium salts cross-associate with the anionic chain ends to form mixed aggregates.[31−34] Lithium chloride is used to control the anionic polymerization of methacrylates.[35] It was envisioned that the use of these lithium salts might change the relative rate constant for propagation (k_p) vs chain transfer (k_{tr}), and perhaps decrease the chain transfer constant ($C_{tr} = k_{tr}/k_p$). Hong and Mays[5] studied the anionic polymerization of 1,3-cyclohexadiene using *sec*-BuLi as initiator in the presence of lithium *sec*-butoxide. This polymerization failed to produce



Crude PCHD (**A**) Crude PCHD (**B**)



functionalized PCHD (**A**) functionalized PCHD (**B**)



unfunctionalized PCHD (**A**) unfunctionalized PCHD (**B**)

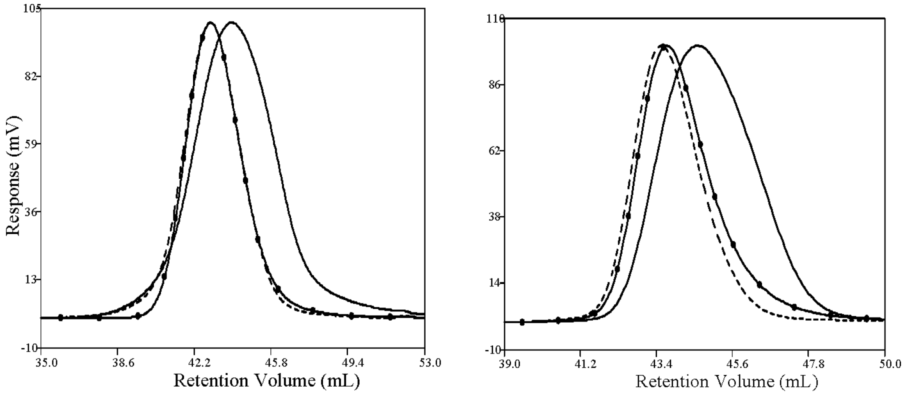
Figure 3. MALDI–TOF mass spectra of PCHDs: (A) *sec*-BuLi/DABCO in benzene at room temperature; (B) *n*-BuLi/ TMEDA at 40 °C.

PCHDs with controlled molecular weight and narrow molecular weight distribution. Lithium 2,3-dimethyl-3-pentoxide was chosen for this study because of its good solubility in hydrocarbon solvents.[36–38] Table 2 (entries 7–11) shows the effects of addition of lithium chloride, lithium bromide, and lithium 2,3-dimethyl-3-pentoxide on the polymerization of 1,3-cyclohexadiene. Lithium bromide and lithium 2,3-dimethyl-3-pentoxide decreased the propagation rate; the yield of polymer was 87% in 24 h for lithium bromide and 95% after 2 days for the lithium alkoxide, respectively. Lithium chloride did not affect the propagation rate; i.e., the yield was 97% after 24 h. Polydispersities for lithium bromide and lithium chloride were broad which suggests that the rate of the chain transfer reaction is not reduced relative to propagation. On the other hand, for M_n(calcd) = 3,000, the polydispersity using the lithium alkoxide was narrow ($M_w/M_n = 1.09$), and M_n(obsd) was close to M_n(calcd) in

Table 2. Effects of Additives and Reaction Conditions on Anionic Polymerization 1,3-Cyclohexadiene

entry	initiator	temp, °C	time	solvent[a]	yield, %	M_n(calc)	M_n(obs)	M_n/M_w
1	*sec*-BuLi	40	5 h	c	100	3000	2000	1.42
2	*sec*-BuLi	room temp	24 h	c	100	3100	2500	1.27
3	*sec*-BuLi	5	4 days	c	92	3000	2400	1.22
4	*sec*-BuLi	0	6 days	c/h = 7:1	97	2900	2400	1.16
5	*sec*-BuLi	room temp	24 h	b	100	3000	2100	1.11
6	*sec*-BuLi	5 °C	2 days	b	98	2500	2000	1.11
7	*sec*-BuLi/LiCl = 1:6	room temp	24 h	c	97	3100	2300	1.50
8	*sec*-BuLi/LiBr = 1:6	room temp	24 h	c	87	3000	2400	1.24
9	*sec*-BuLi/ROLi = 1:5	room temp	2 days	c	95	3000	2800	1.09
10	*sec*-BuLi/ROLi = 1:5	room temp	2 days	c	60	10 000	4600	1.46
11	*sec*-BuLi/ROLi = 1:5	room temp	5 days	b	65	10 000	8000	1.96

[a] Key: (c) cyclohexane; (h) hexane. (b) benzene.



C **D**

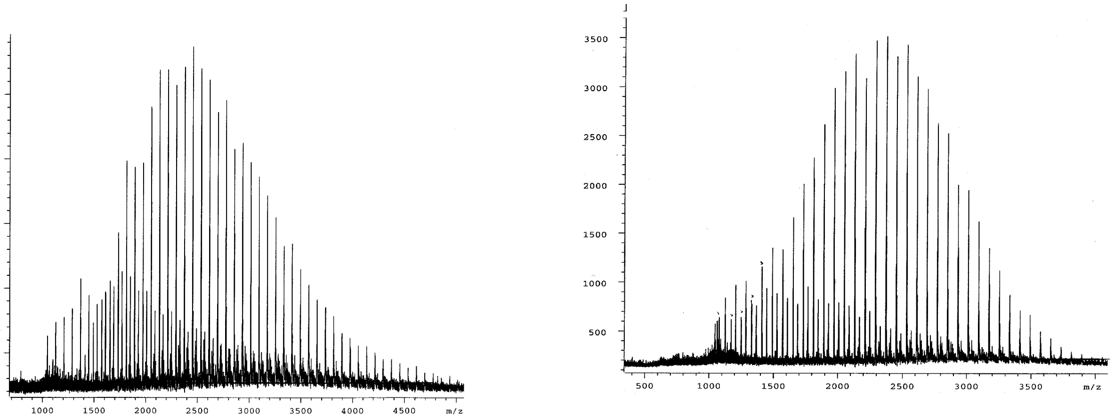
Figure 4. SEC chromatograms for PCHDs (solid line, unfunctionalized PCHD; dashed line, functionalized PCHD; line with circle, crude PCHD): (C) *sec*-BuLi in benzene at 5 °C; (D) *sec*-BuLi/ROLi in benzene at room temperature.

cyclohexane, which suggests that the contribution from the chain transfer reaction has been reduced. However, when the calculated molecular weights were increased [entries 10 and 11; M_n(calcd) = 10 000], the yields were low and the molecular weight distributions were broader in both benzene and cyclohexane. The reason may be that decomposition[39] of the propagating chain end may be promoted in the presence of lithium alkoxide; it was observed that the characteristic yellowish color for poly(1,3-cyclohexadienyl)lithium was gone after 2 days (entries 10 and 11). It was reported by Finnegan and Kutta[40] that lithium alkoxides accelerated the rate of decomposition of *n*-butyllithium to form butene and lithium hydride.

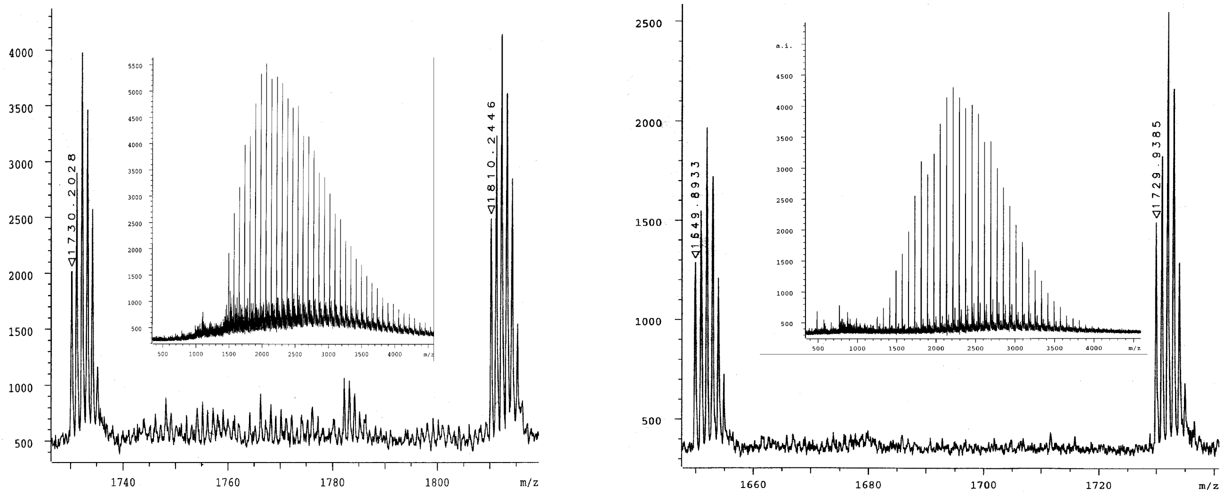
Two entries in Table 2 which gave controlled polymerizations were chosen to investigate for functionalization efficiency with ethylene oxide: (C) *sec*-BuLi in benzene at 5 °C (entry 6); (D) *sec*-BuLi in benzene at room temperature in the presence of lithium alkoxide (entry 9). After functionalization of the corresponding poly(1,3-cyclohexadienyl)lithiums with ethylene oxide, the functionalized and unfunctionalized PCHDs were separated and characterized by the same methods discussed before. SEC chromatograms for the crude PCHD and functionalized and unfunctionalized PCHDs are shown in Figure 4, and the results are listed in Table 1.

It was again confirmed by SEC that the unfunctionalized PCHDs exhibited much lower molecular weights than M_n(calcd) and M_n(obsd) for the functionalized polymers. The functionality was 90% for the PCHDs prepared both at 5 °C and in the presence of the lithium alkoxide, but the M_n(obsd) were slightly lower than the M_n(calcd)s. With respect to the polydispersity, the lithium alkoxide gave narrower distribution than the use of low temperature as listed in Table 2. These two polymerizations give predominantly 1,4-microstructure but the use of lower temperature in the absence of additive gave the highest 1,4 content (97%).

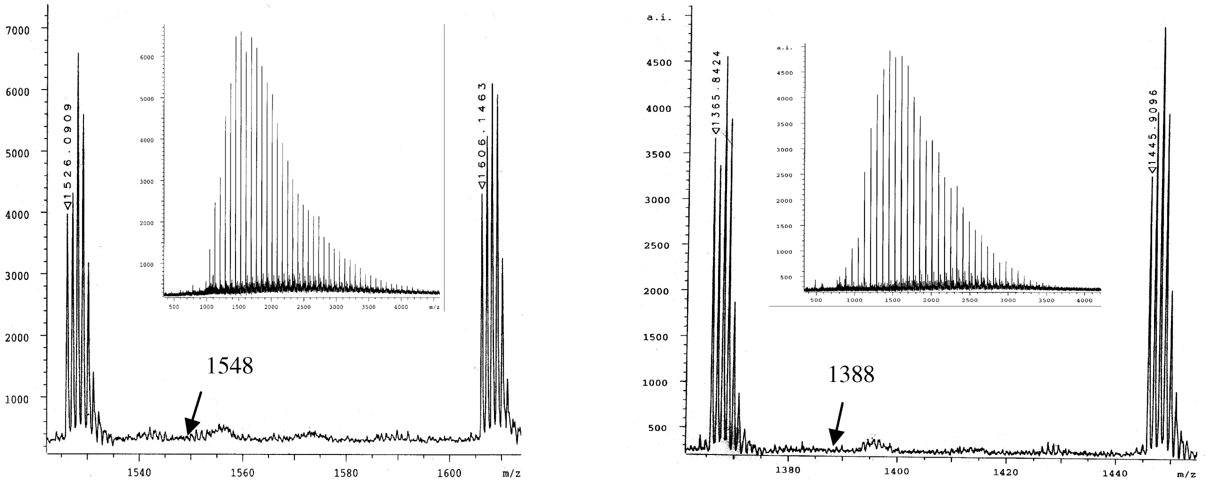
The structures of the functionalized and unfunctionalized PCHDs were again confirmed by MALDI−TOF mass spectral analysis as shown in Figure 5. The crude PCHDs before column chromatography are shown at the top, and both of them have two distributions corresponding to the functionalized PCHD and unfunctionalized PCHD. The mass spectra of the functionalized PCHD and unfunctionalized PCHD are shown in the middle and bottom of Figure 5, respectively. The small spectra in the center correspond to the whole mass spectra and the spectra below are the expanded mass spectra for two center peaks of the major distribution. In the expanded spectrum, the peak at *m*/*z* 1730 for functionalized PCHD (C) has the exact mass for the silver adduct of PCHD 19-mer with one butyl end group, one hydrogen and one ethylene oxide unit {*m*/*z* 19 × 80.06 [$(C_6H_8)_{19}$] + 57.06 (C_4H_7) + 1.01 (H) + 44.05 (CH_2CH_2O) + 106.90 ($^{107}Ag^+$) = 1730.16}. The peak at *m*/*z* 1810 corresponds to the 20-mer in the same series. The peak at *m*/*z* 1650 for functionalized PCHD (D) has the exact mass for the silver adduct of PCHD 18-mer with one butyl end group and one ethylene oxide unit {*m*/*z* 18 × 80.06 [$(C_6H_8)_{18}$] + 57.06 (C_4H_7) + 1.01 (H) + 44.05 (CH_2CH_2O) + 106.90 ($^{107}Ag^+$) = 1650.10}. The peak at *m*/*z* 1730 corresponds to the 19-mer in the same series. The peak at *m*/*z* 1526 for unfunctionalized PCHD (**C**) has the exact mass for the silver adduct of PCHD 17-mer with one butyl end group and one hydrogen {*m*/*z* 17 × 80.06 [$(C_6H_8)_{17}$] + 57.06 (C_4H_7) + 1.01 (H) + 106.90 ($^{107}Ag^+$) = 1525.99}. The peak at *m*/*z* 1606 corresponds to the 18-mer in the same series. The peak at *m*/*z* 1366



crude product (**C**) crude product (**D**)



functionalized PCHD (**C**) functionalized PCHD (**D**)



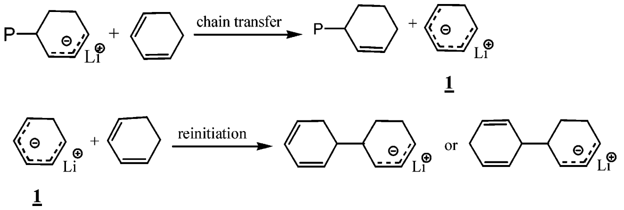
unfunctionalized PCHD (**C**) unfunctionalized PCHD (**D**)

Figure 5. MALDI−TOF mass spectra of PCHDs: (C) *sec*-BuLi in benzene at 5 °C; (D) *sec*-BuLi/ROLi in benzene at room temperature.

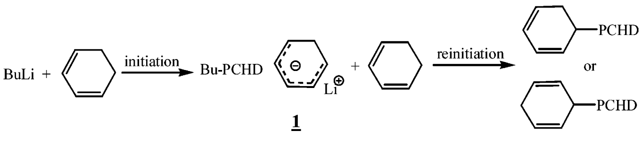
for unfunctionalized PCHD (D) has the exact mass for the silver adduct of PCHD 15-mer with one butyl end group and one hydrogen {m/z 15 × 80.06 [$(C_6H_8)_{15}$] + 57.06 (C_4H_7) + 1.01 (H) + 106.90 ($^{107}Ag^+$) = 1365.87}. The peak at m/z 1446 corresponds to the 16-mer in the same series. No peak corresponding to the decomposition of the chain end (loss of lithium hydride from PCHDLi) was observed which supports the proposal that the unfunctionalized PCHDs are formed by the chain transfer to monomer reaction during the polymerization.

Although *n*BuLi/ TMEDA at 40 °C system gave high functionality (90%) and very good control of molecular weight and polydispersity, the corresponding PCHD has 64% of 1,2-microstructure which is not desirable for preparation of highly conjugated poly(*p*-phenylene)

Scheme 1. Mechanism of Chain Transfer and Reinitiation



Scheme 2. Initiator Residues Formed by Initiation and Reinitiation

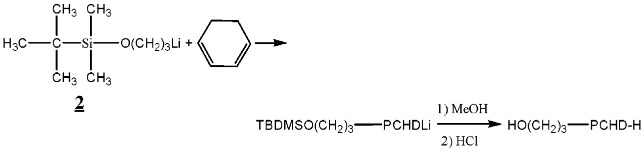


(PPP). It is concluded that the use of *sec*-BuLi/ ROLi gives good functionalization results (90% functionality) and high 1,4-microstructure (90%).

Functionalization Using Functionalized Initiators The use of alkyllithium initiators that contain functional groups provides a versatile method for the quantitative preparation of end-functionalized polymers and macromonomers.[12] For a living anionic polymerization, each functionalized initiator molecule will produce one macromolecule with the functional group from the initiator residue at the initiating chain end. In the case of polymerization of 1,3-cyclohexadiene where chain transfer to monomer occurs, if the metalated monomer resulting from chain transfer does not reinitiate the polymerization of another chain, every chain should have the functional group although some of the chains will be dead as a result of the chain transfer reaction. Therefore, before investigating the use of functionalized initiators, it was necessary to determine the extent of the reinitiation by the metalated monomer (**1**) resulting from chain transfer (Scheme 1).

There are conflicting reports concerning the reinitiation reaction after chain transfer to monomer in the alkyllithium-initiated polymerization of 1,3-cyclohexadiene. Francois and Zhong[4] first provided experimental evidence for reinitiation. They prepared polystyrene-*block*-poly(1,3-cyclohexadiene) in cyclohexane using *sec*-butyllithium as initiator by sequential addition with the styrene block prepared first. After fractionation, they obtained PCHD homopolymer as determined by infrared spectroscopy. On the basis of this observation, they concluded that there was reinitiation in this system. When Hong and Mays[41] prepared polystyrene-*block*-poly(1,3-cyclohexadiene) in benzene using *sec*-butyllithium as initiator by sequential addition with styrene block prepared first, after fractionation, only polystyrene homopolymer was obtained as determined by ^{1}H NMR, and they claimed that the reinitiation did not play a major role. However, when they used DABCO as additive, they could not exclude the possibility of reinitiation.

Scheme 3. Reaction Scheme for Protected Functionalized Initiator



In this study, MALDI−TOF mass spectrometry was used to determine whether there was reinitiation in the polymerization of 1,3-cyclohexadiene. *sec*-Butyllithium and *n*-butyllithium were used as initiators. Four polymerizations and functionalizations were performed analogous to the ones mentioned in the previous section in order to access the importance of reinitiation: (A) *sec*-BuLi/DABCO (1/2.5) in benzene at room temperature; (B) *n*-BuLi/TMEDA (4/5) in cyclohexane at 40 °C; (C) *sec*-BuLi in benzene at 5 °C; (D) *sec*-BuLi/ROLi (1/5) in benzene at room temperature. On the basis of the mechanism of reinitiation (Scheme 1), if there is reinitiation in the polymerization of 1,3-cyclohexadiene, the initiator residues (1,3-cyclohexadienyl or 1,4-cyclohexadienyl with $m/z = 79$) should be 22 mass units heavier than those initiated by butyllithium (butyl with $m/z = 57$) (Scheme 2).

Only the unfunctionalized PCHD spectra were selected in order to simplify the analysis since either the functionalized or unfunctionalized PCHDs has the same behavior with respect to the reinitiation and can provide the desired information. For example, for polymerization A (DABCO as additive), the 16-mer of this distribution is expected to produce a signal at m/z 16×80.06 $(C_6H_8)_{16} + 57.06$ $(C_4H_7) + 1.01$ (H) $+ 106.90$ $(^{107}Ag^+) = 1445.93$, as indeed is observed at 1446 in Figure 3 [unfunctionalized PCHD (A)]. However, a small peak at m/z 1468 which is 22 mass units above m/z 1466 is also observed. This indicates that there is some reinitiation in this system. When unfunctionalized PCHD with M_n(calcd) = 10 000 was separated, the reinitiation peaks became larger. For polymerization B (*n*-BuLi/TMEDA), the 16-mer of this distribution is expected to produce a signal at m/z 16×80.06 $(C_6H_8)_{16} + 57.06$ $(C_4H_7) + 1.01$ (H) $+ 106.90$ $(^{107}Ag^+) = 1445.93$, as indeed is observed at m/z 1446 in Figure 3 [unfunctionalized PCHD (B)]. There is no peak shown at m/z 1468 which would correspond to the reinitiation peak. This indicates that there is no reinitiation in this system. For polymerization C (no additive, in benzene at 5 °C), the 17-mer of this distribution is expected to produce a signal at m/z 17×80.06 $(C_6H_8)_{17} + 57.06$ $(C_4H_7) + 1.01$ (H) $+$ 106.90 $(^{107}Ag^+) = 1525.99$, as indeed is observed at m/z 1526 in Figure 5 [unfunctionalized PCHD (C)]. There is no peak shown at m/z 1548 which would correspond to the reinitiation peak. For polymerization D (lithium alkoxide as additive), the 15-mer of this distribution is expected to produce a signal at m/z 15×80.06 $(C_6H_8)_{15}$ $+ 57.06$ $(C_4H_7) + 1.01$ (H) $+ 106.90$ $(^{107}Ag^+) = 1365.87$, as indeed is observed at m/z 1366 in Figure 5 [unfunctionalized PCHD (D)]. There is no peak shown at m/z 1388 which would correspond to the reinitiation peak. These MALDI−TOF mass spectrometry results confirm

Table 3. Results of Polymerization of 1,3-Cyclohexadiene in Benzene Using Functionalized Initiators

initiator	time, h	yield, %	solvent[c]	M_n(calcd)	M_n(obsd)	M_n/M_w
TBDMS−O$(CH_2)_3$Li[a]	24	100	c	2900	5400	1.68
TBDMS−$OCH_2C(CH_3)_2$−CH_2Li	24	92	b	2500	6400	1.86
TBDMS−O$(CH_2)_3$Li/DABCO	24	100	b	3100	11 700	1.74
TBDMS−$OCH_2C(CH_3)_2$−CH_2Li/ROLi[b]	48	trace	b	3000	<2000	

[a] TBDMS = *tert*-butyldimethylsiloxy. [b] ROLi = 2,3-Dimethyl-3-pentoxylithium. [c] Key: (c) cyclohexane; (b) benzene.

Hong and Mays' observations[41] that there was no reinitiation in the absence of additive (C) but that there was reinitiation in the presence of DABCO (A). It can also be concluded that there is no reinitiation in either the *sec*-BuLi/ROLi (D) or *n*-BuLi/TMEDA (B) systems.

From the above studies, it is clear that there is no reinitiation in the absence of DABCO. Therefore, functionalized initiators can be used to prepare α-hydroxyl functionalized poly(1,3-cyclohexadiene)s. The functionalized initiators, 3-(*tert*-butyldimethylsiloxy)-1-propyllithium, **2**, and 3-(*tert*-butyldimethylsiloxy)-2,2-dimethyl-1-propyllithium, **3**, were used for the preparation of α-hydroxyl functionalized poly(1,3-cyclohexadiene)s. The reactions are shown in Scheme 3 for **2**. These two initiators have been used successfully to polymerize dienes such as isoprene and butadiene;[42−44] however, they did not work well for the polymerization of styrene.[45] The results for polymerization of 1,3-cyclohexadiene using these functionalized initiators are shown in Table 3. Much higher observed molecular weights (almost double the calculated molecular weight) and broader molecular weight distributions were observed which indicates that these initiators are not efficient initiators for CHD polymerization. When this type of phenomenon was observed for the 3-(*tert*-butoxy)-1-propyllithium- initiated polymerization of styrene,[45] it was proposed that cross-association of initiator with the propagating polymeric organolithium was the reason for the lack of molecular weight control; controlled molecular weight and narrow polydispersity were obtained by adding a Lewis base such as THF to breakup the cross-association. Because the presence of THF in the polymerization of 1,3-cyclohexadiene will give high 1,2 microstructure which is not desired in our research, DABCO was used as Lewis base to breakup the cross-association. The results were not good with respect to control of the molecular weight and the polydispersity. Adding lithium alkoxide did not help either, since only trace amounts of PCHD were obtained. It is concluded that the use of these functionalized initiators is not an efficient method to prepare hydroxyl-functionalized poly(1,3-cyclohexadiene).

Conclusions

Hydroxyl-end-capped poly(1,3-cyclohexadiene) has been obtained using different initiator systems to polymerize 1,3-cyclohexadiene followed by termination with ethylene oxide. The highest functionality obtained was 90%. The functionalized PCHDs were obtained by quantitative removal of unfunctionalized PCHDs by column chromatography. The unfunctionalized PCHDs exhibited much lower number-average molecular weights than the calculated molecular weight as expected for the occurrence of chain transfer to monomer which forms dead polymer chains. A mechanistic study for chain transfer using MALDI TOF MS confirmed that no reinitiation occurs in the absence of additive or in the presence of lithium 2,3-dimethyl-3-pentoxide or TMEDA. In contrast, reinitiation was observed in the presence of DABCO.

Acknowledgment. The authors are grateful to the Lithium Division, FMC, for providing samples of *sec*-butyllithium and Dynasol Elastomeros and Sartomer for financial support.

References and Notes

(1) Lefebvre, G.; Dawans, F. *J. Polym. Sci., Part A* **1964**, *2*, 3277.
(2) Cassidy, P. E.; Marvel, C. S.; Ray, S. *J. Polym. Sci., Part A* **1965**, *3*, 1553.
(3) Zhong, X. F.; Francois, B. *Makromol. Chem.* **1990**, *191*, 2735.
(4) Francois, B.; Zhong, X. F. *Makromol. Chem.* **1990**, *191*, 2743.
(5) Hong, K.; Mays, J. W. *Macromolecules* **2001**, **34**, 782.
(6) Natori, I. *Macromolecules*, **1997**, *30*, 3696.
(7) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 982.
(8) Natori, I.; Inoue, S. *Macromolecules* **1998**, *31*, 4687.
(9) Williamson, D. T.; Elman, J. F.; Madison, P. H.; Pasquale, A. J.; Long, T. E. *Macromolecules* **2001**, *34*, 2108.
(10) Williamson, D. T.; Glass, T. E.; Long, T. E. *Macromolecules* **2001**, *34*, 6144.
(11) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.
(12) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(13) Fetters, L. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Kroschwitz, J. I.; Ed.; Wiley: New York, 1987; Vol 10, p 19.
(14) Quirk, R. P.; Mathers, R. T.; Ma, J.-J. Wesdemiotis, C.; Arnould, M. A. *Macromol. Symp.* **2002**, *183*, 17.
(15) Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2002**, *35*, 2912.
(16) Ji, H.; Sato, N.; Nonidez, W. K.; Mays, J. W. *Polymer* **2002**, *43*, 7119.
(17) Si-Ahmed, L.; Nuesch, F.; Zuppiroli, L.; Francois, B. *Macromol. Chem. Phys.* **1998**, *199*, 625.
(18) Williamson, D. T.; Glass, T. E.; Long, T. E. *Macromolecules* **2001**, *34*, 6144.
(19) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(20) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(21) Morton, M.; Fetters, L. *Rubber Chem. Technol.* **1975**, *48*, 359.
(22) Sharaby, Z.; Martan, M.; Jagur-Grodzinski, J. *Macromolecules* **1982**, *15*, 1167.
(23) Mondaudo, G.; Lattimer, R. P. *Mass Spectrometry of Polymers*, Montaudo, G., Lattimer, R. P., Eds.; CRC Press: Boca Raton, FL, 2002; Chapter 10.
(24) DeHoffmann, E.; Charette, J.; Stroobant, V. *Mass Spectrometry. Principles and Applications*, John Wiley & Sons: Chichester, England, 1996.
(25) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133.
(26) Mango, L. A.; Lenz, R. W. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1971**, *12*, 402.
(27) Quirk, R. P.; You, F. Zhu, Z.; Cheng, S. Z. D. *Macromol. Chem. Phys.* **2003**, *204*, 755.
(28) Glaze, W.; West, R. *J. Am. Chem. Soc.* **1960**, *82*, 4437.
(29) Hsiel, H. L. *J. Polym. Sci.: Part A-1* **1970**, *8*, 533.
(30) Waack, R.; Doran, M. A. *Chem. Ind.* **1964**, 496.
(31) Novak, D. P.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 3793.
(32) Wang, J. S.; Warin, R.; Jerome, R.; Teyssie, P. *Macromolecules* **1993**, *26*, 6776.
(33) Waack, R.; Doran, M. A.; Baker, E. B. *Chem. Commun.* **1967**, 1291.
(34) Boutillier, J.-M.; Favier, J.-C.; Hemery, P.; Sigwalt, P. *Polymer* **1996**, *37*, 5197.
(35) Fayt, R.; Forte, R.; Jacobs, C.; Jerome, R.; Ouhadi, T.; Teyssie, P. *Macromolecules* **1987**, *20*, 1442.
(36) Ashraf, A.; Smith, S. D.; Satkowski, M. M.; Spontak, R. J.; Clarson, S. J.; Lipscomb, G. G. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1994**, *35* (1), 581.
(37) Smith, S. D.; Ashraf, A.; Clarson, Stephen, J. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1993**, *34* (2), 672.
(38) Smith, S. D.; Ashraf, A. *Polym. Prepr. (Am. Chem. Soc., Polym. Chem. Div.)* **1994**, *35* (2), 466.
(39) Glaze, W. H.; Adams, G. M. *J. Am. Chem. Soc.* **1966**, *88*, 4653.
(40) Finnegan, R. A.; Kutta, H. W. *J. Org. Chem.* **1965**, *30*, 4138.
(41) Hong, K.; Mays, J. W. *Macromolecules* **2001**, **34**, 3540.
(42) Shepherd, N.; Stewart, M. J. (to The Secretary of State for Defense in the U.K.), US Patent 5 362 699, 1994.
(43) Handlin, D. L. J.; Bening, R. C.; Willis, C. L. (to Shell Oil Company), US Patent 5 376 745, 1994.
(44) Quirk, R. P.; Jang, S. H.; Yang, H.; Lee, Y. *Macromol. Sym.* **1998**, *132*, 281.
(45) Quirk, R. P.; Jang, S. H.; Han, K.; Yang, H.; Rix, B.; Lee, Y. Anionic Synthesis of Hydroxyl-Functionalized Polymers Using Protected, Functionalized Alkyllithium and Isoprenyllithium Initiators. In *Functional Polymers: Modern Synthetic Methods and Novel Structures*; Patil, A. O., Schulz, D. N., Novak, B. M., Eds.; ACS Symposium Series 704; American Chemical Society: Washington, DC, 1998; p 71a.

MA034360T