1,3-Cyclohexadiene Polymers. 1. Anionic Polymerization

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ABSTRACT: The anionic polymerization of 1,3-cyclohexadiene (1,3-CHD) using various initiating systems and with or without additives was studied. In contrast to the situation with linear conjugated dienes, common anionic initiators in the absence of additives fail to produce poly(1,3-cyclohexadiene) (PCHD) with controlled molecular weight (MW) and narrow molecular weight distribution (MWD) because of side reactions. However, certain additives change the nature of the polymerization dramatically. Monodentate additives do not yield controlled polymerization, while some polydentate additives, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), 1,2-dimethoxyethane (DME), and 1,4-diazabicyclo[2.2.2]-octane (DABCO), are effective in minimizing side reactions, if combined with the suitable butyllithium isomer. For example, the synthesis of PCHD samples with narrow MWD and good MW control is possible using the *n*-BuLi/DME/0 °C or *sec*-BuLi/DABCO/20 °C in benzene. The "living" character of these polymerizations is discussed.

Introduction

Synthetic polymers are an indispensable and remarkably versatile class of materials. The suitability of a polymer for a particular application is controlled by its specific structural and molecular properties such as molecular weight (MW), molecular weight distribution (MWD), local and global architecture, and functionality. To understand the relationship between polymer structure and properties, there is great interest in well-defined polymers made by living addition polymerization processes. Tremendous progress has been achieved in living polymerizations over the past two decades, thanks to the development of new polymerization methodologies.[1−4] Nevertheless, living anionic polymerization is still the most versatile technique for synthesizing polymers with well-defined structures.[5,6] Many new materials with controlled architectures, functionalities, and narrow MWD have been made using anionic polymerization.[7−9] However, most of the studies are limited to several well-behaved, mostly hydrocarbon, monomers (such as styrene, 1,3-butadiene, isoprene, etc.).

1,3-Cyclohexadiene (1,3-CHD) polymers (PCHD) are of interest from both scientific and practical standpoints.[10−18] These polymers offer the opportunity to combine microstructural control during diene polymerization with post-polymerization chemistry in order to tailor the properties of the resulting polymers. PCHD and its derivatives should have higher mechanical strength and better thermal and chemical stability compared to common, i.e., vinyl, polymers due to the alicyclic structures (six-membered rings) in the main chain. PCHD can be modified by various dehydrogenation procedures,[10−13] such as bromination followed by dehydrobromination,[10] aromatization by *p*-chloranil,[11,12] or catalytic dehydrogenation.[13] The C═C bond in PCHD can also be hydrogenated by either diimide[14] or using Pd/$BaSO_4$ under H_2 pressure.[15] It has been reported that hydrogenated PCHD has the highest T_g (231 °C) of all hydrocarbon polymers.[15] Hydrogenated PCHD polymers have good heat, weather, impact, abrasion, and chemical resistances, low water absorption, and birefringence; they also serve as good optical materials due to their excellent transparency and rigidity.[16] The copolymer of 1,3-CHD with cyclopentadiene has been used as an active element in photomicrolithographic devices, and the optical resolution is greatly enhanced by the addition of PCHD blocks.[17] It has also been proposed that PCHD may be useful as a plastic material for undersea applications because of its high hydrolytic stability.[18]

There have been many reports on the synthesis of PCHD polymers. Essentially all conventional polymerization procedures have been applied to the polymerization of 1,3-CHD. These include cationic,[10] radical,[12] Ziegler−Natta,[19] transition-metal complexes,[20,21] and anionic[22−26] polymerizations. Only low molecular weight or insoluble materials were obtained in most cases due to various side reactions. The anionic mechanism has proven to be the best way to polymerize 1,3-CHD with high conversion and molecular weight control, although side reactions, such as chain transfer and termination, have limited the maximum attainable molecular weight of PCHD. In general, the observed molecular weights are independent of conversion and do not depend on monomer or initiator concentrations under anionic polymerization conditions.[16,21,26] The formation of benzene,[21−24] cyclohexene,[21−23] and 1,4-cyclohexadiene (1,4-CHD)[24] has been observed during polymerization. Using difunctional alkali naphthalenides as initiators, molecular weights as high as 19 kg/mol (Li^+) and 38.7 kg/mol (Na^+) were obtained in 1,2-dimethoxyethane (DME), in which the polymer precipitates.[24] Very recently, Natori and co-workers reported that polymerization of 1,3-CHD anionically could be controlled using certain additives.[27−29] They used the *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) initiation system and carried out the reaction under nitrogen atmosphere (pressure up to ∼4 kg/cm^2) at 40 °C. According to their findings, the ratio of *n*-BuLi to TMEDA and the method of introducing the chemicals are crucial for obtaining "well-controlled" PCHD (polydispersity indices < 1.1). A family of PCHD homopolymers and their copolymers with styrene, butadiene, and isoprene has been made using this method.[28] However, all the samples with

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Table 1. Polymerization of 1,3-CHD Using Various Anionic Initiators (without Additives)

run	initiator	solvent/temp (°C)	[CHD] (mol/L)	[I] × 10^3 (mol/L)	yield (%)	$M_{n,Cal} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n (SEC)
1	*sec*-BuLi	benzene/20	0.53	1.40	53	29.9	7.6	2.17
2	*sec*-BuLi	benzene/20	0.59	4.69	59	9.9	7.3	1.49
3	*sec*-BuLi	ben/Hex/0[a]	1.04	5.56	68	15.0	13.1	1.22
4	*sec*-BuLi	MeCyclohex/−70[b]	0.88	3.51	83	20.0	18.8	1.43
5	*sec*-BuLi	THF/−78	1.00	7.36	47	10.9	5.1	4.92
6	benzylK	THF/−78	1.45	2.63	93	44.1	26.0	1.38
7	cumylK	THF/−78	1.29	5.75	89	17.9	15.1	1.30
8	naphthalene/K	THF/−78	1.09	6.99	98	25.0	17.4	1.40
9	*tert*-BuLi	benzene/20	1.05	3.65	75	5.8	9.5	2.07
10	*tert*-BuLi	benzene/20	1.14	9.96	49	9.1	7.1	1.77
11	PhLi	benzene/20	1.05	3.04	71	27.6	10.6	2.06

[a] Benzene/hexane: 90/10 (v/v). [b] Methylcyclohexane.

narrow MWD were less than 15 kg/mol in molecular weight. Surprisingly, other additives, even if structurally very similar to TMEDA, were found to be less effective.

This paper reports the results of polymerization of 1,3-CHD using various anionic initiators, with or without additives. The differences in the polymerization processes with regards to initiation and propagation are also discussed.

Experimental Section

Materials. Benzene (Fisher, >99%), cyclohexane (Fisher, >99%), THF (Aldrich, 99.9%), and methylcyclohexane (Aldrich, 99%) were purified according to the anionic polymerization standards, as described in the literature.[6,30] TMEDA (Aldrich, >99%), *N,N,N′,N′,N′*-pentamethyldiethylenetriamine (PMETEDA, Aldrich, 99%), DME (Acros, >99%), and 1,2-dipiperidinoethane (DPPE, Sigma, >99%) were stirred over freshly crushed CaH_2 powder for at least 24 h and distilled from potassium (K) mirror twice and finally from potassium/sodium alloy under high vacuum. Naphthalene (Aldrich, >99%) and 1,4-diazabicyclo[2.2.2]octane (DABCO, Aldrich, 98%) were sublimed under high vacuum three times and then diluted in cyclohexane and benzene, respectively. Potassium *tert*-butoxide (*t*-BuOK, Aldrich, 95%) was diluted in THF, and phenyllithium (PhLi, Aldrich, 1.8 M in ether and cyclohexane) and *tert*-butyllithium (*t*-BuLi, Aldrich, 1.5 M in pentane) were used as received. 1,3-CHD (Aldrich, 97%) was cleaned by treating over CaH_2 followed by exposure to sodium mirrors at room temperature 2−3 times for 24 h each. This "roughly" purified 1,3-CHD was finally treated with *n*-BuLi or dibutylmagnesium ($MgBu_2$ Aldrich, 1.0 M in heptane) at 0 °C for 30 min just before the polymerization. Butyllithiums (*sec*-BuLi and *n*-BuLi) were prepared by reactions of the corresponding butyl chloride with lithium powder in hexane under vacuum. Cumyl potassium (CumylK) and benzyl potassium (BenzylK) were made via published methods.[31,32]

Polymerization and Characterization. All polymerizations were performed under high vacuum using custom-made glass reactors. Break-seals allowed introduction of reagents sequentially, and constriction seal-offs permitted intermittent removal of products. The molar ratio of additive to initiator was from 1.5 to 3 unless otherwise stated. In a typical polymerization experiment, about 75 mL of pure benzene was distilled into a reactor with all the purified reagents attached via break-seals. The reactor was removed from the vacuum line after evacuation. Then about 4.3 mL of *sec*-BuLi (in hexane, 7×10^{-5} mol/mL) and 3.5 mL of DABCO (in benzene, 2.1×10^{-3} mol/mL) were introduced into the reactor. After stirring for 5 min at room temperature, 4.4 g (0.055 mol) of 1,3-CHD was added. The reaction was allowed to continue for about 6 h and terminated with degassed methanol. The polymer solutions were precipitated in a large excess of methanol with 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) added to prevented oxidative degradation. The stabilized polymer was isolated by filtration and dried under high vacuum. Number-average molecular weights (M_n) and polydispersity indices (M_w/M_n, where M_w is weight-average molecular weight) were obtained from size exclusion chromatography (SEC) relative to calibration with polystyrene (PS) standards in either THF or chloroform ($CHCl_3$). SEC in THF (flow rate: 1 mL/min; Waters Styragel 100, 500, 10^3, 10^4, and 10^5 Å columns) was obtained using a Waters 510 pump equipped with a Waters 410 differential refractometer detector; SEC in $CHCl_3$ (flow rate: 0.3 mL/min; columns: Polymer Lab. PL-Gel 5 μm MiniMIX narrow bore columns with pore size from 100 to 10^5 Å) was acquired from a Waters 2690 system with a Waters 2410 refractive index and a Waters 996 photodiode array detectors. Proton nuclear magnetic resonance (^1H NMR) experiments were carried out in $CDCl_3$ at 30 °C using a Bruker ARX-300 instrument. The 1,2 to 1,4 ratios were determined from the relative areas of protons that are adjacent to the double bond (α position) and those in β positions. 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 M_n of the product of the polymerization described above is 20.1 kg/mol with a polydispersity of 1.04, as determined by SEC in THF.

Results and Discussion

Polymerization of 1,3-CHD without Additives. 1,3-CHD was polymerized using several anionic initiators under different conditions, and the results are summarized in Table 1. This table shows that the "traditional" anionic initiators, isomers of BuLi, do not work very well in controlling the polymerization of 1,3-CHD if used without additives. *n*-BuLi only produced trace amounts of polymer (not shown in Table 1); *sec*-BuLi, *tert*-BuLi, or phenyllithium gave better results (runs 1, 2, 9, and 10 in Table 1), but the molecular weights could hardly be manipulated and the polydispersities were quite large, as a low molecular weight tail is clearly seen in the SEC trace in Figure 1a. As polymerization continued, the molecular weight increased, but there was still a tail at the low molecular weight end of the distribution (Figure 1b). This indicates that some of the anionic chains failed to grow beyond the early stage of polymerization. It is generally agreed that anionic polymerization of 1,3-CHD is difficult to control because of side reactions.[22−27] The side reactions during initiation are isomerization of the monomer to produce its 1,4-isomer and further to benzene; in some cases cyclohexene was detected.[22−25] The main side reactions during chain propagation are chain transfer through proton elimination and chain termination via hydride abstraction, as shown in Scheme 1. Under anionic polymerization conditions (strong base), chain transfer through hydride elimination (reaction a) and/or allylic proton abstraction (reaction b) always compete with chain propagation (reactions c and d). 1,4-CHD, a very reactive chain-transfer agent for alkyllithium-initiated polymerizations,[22] is almost unavoidably produced during the course of polymerization. The ability

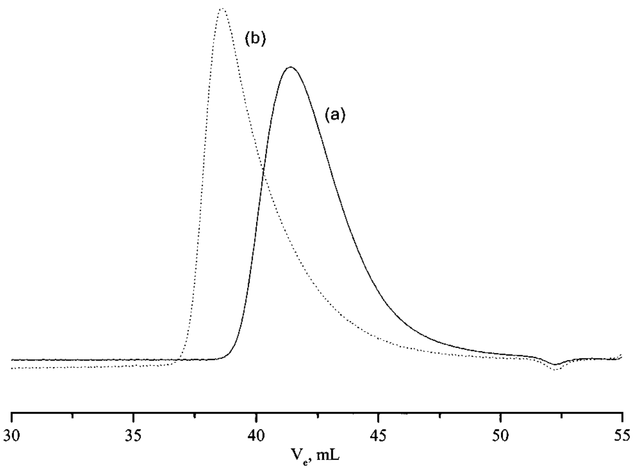
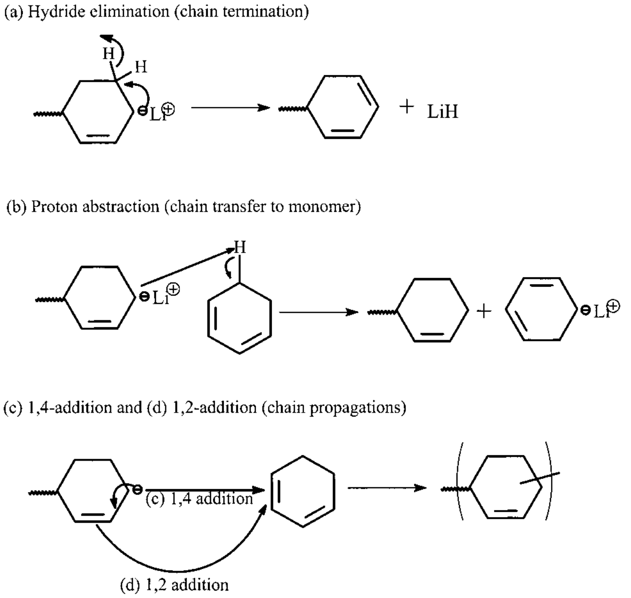


Figure 1. SEC traces of PCHD from *sec*-BuLi in benzene at 0 °C: (a) polymerization time 2 h; conversion ~43%; (b) polymerization time 6 h, conversion ~51%.

Scheme 1. Possible Reactions of PCHD Anion with 1,3-CHD



of 1,4-CHD to decrease strongly the observed molecular weight in the lithium-naphthalenide-initiated polymerization of 1,3-CHD has been demonstrated.[24] Lower polymerization temperatures also gave better results (runs 3 and 4 in Table 1), but poor solubility of the polymerization products under these conditions prevented further pursuit of this approach. Polymerization carried out in THF at low temperature also did not give the desired result (run 5 in Table 1). Since one of the possible side reactions involves hydride elimination, with the formation of stable lithium hydride (LiH) as the driving force, we anticipated that using larger counterions such as potassium could minimize this process. This was indeed the case when benzylK, cumylK, or Naphthalene/K was used (Table 1, runs 6−8): the polydispersities were narrowed, but the molecular weights of these samples were always far lower than expected. Moreover, ^{1}H NMR data revealed that the ratio of vinyl protons to nonvinyl protons is much lower than the theoretical value ($^1/_3$). Side reactions other than chain transfer or termination must be involved in these polymerization procedures.

Polymerization of 1,3-CHD with Additives. Additives play an important role in anionic polymerization.[33] They have been widely used to control the microstructures of polydienes and minimize side reactions in acrylate polymerization.[33] We have employed several monodentate additives, and the results are listed in Table 2. THF and *sec*-BuOLi, popular additives used to disrupt aggregation in anionic polymerization, failed to give positive results (runs 1 and 2 in Table 2). This suggests that chain aggregation is not the main problem in the anionic polymerization of 1,3-CHD. The *sec*-BuLi/*t*-BuOK system, regarded as “second generation” super base,[34] yielded polymers with reasonably narrow MWD (Table 2 run 3), but the molecular weights were much lower than anticipated. One possible reason is that the polymerization has to be carried out in THF at low temperature (−78 °C), and chains could not grow very long due to solubility problems (high MW PCHD has limited solubility in THF; the solubility also depends on the microstructure). Using *sec*-BuLi in THF/toluene (1/2 v/v) at −40 °C, Zhang and Rubenstein[35] selectively polymerized the styrene group in 4-(vinylphenyl)-1-butene to generate a polymer with a polystyrene backbone and functional butenyl side chains. However, their targeted molecular weight was only about 4000 g/mol. Not surprisingly, this system does not work well with 1,3-CHD (Table 2, run 4).

Polydentate additives can change anionic polymerization processes dramatically due to their chelating effect.[33] Natori and co-workers reported that the polymerization of 1,3-CHD using *n*-BuLi/TMEDA exhibits “living” character[27] and that the ratio of *n*-BuLi and TMEDA that gives living character is crucial. It is believed that chain propagation and side reactions are strongly affected by the extent of the polarization of the Li−carbon bond in PCHDLi, and chelating by TMEDA offers the proper Li−C polarization.[29] We found that the *n*-BuLi/TMEDA initiation system is difficult to handle because the resulting polymers are difficult to dissolve in common solvents (Table 2, runs 5 and 6). Good results could only be achieved for low-MW targets. *n*-BuLi/PMDETA, similar to the *n*-BuLi/TMEDA initiation system, failed to produce materials with narrow polydispersities and predictable MWs (run 7 in Table 2). This is probably because PMDETA does not chelate as effectively as TMEDA, since the former is more bulky and has an extra chelating site. Bulkiness alone may not be the sole reason for effective chelating since DABCO, also bulky, is quite effective as discussed below.

Other polydentate additives, such as DABCO, DPPE, and DME, used in combination with certain butyllithium isomers produced PCHD samples with relatively narrow MWDs and modest molecular weights as summarized in Table 2. DME, a weak-chelating agent, can be used as an effective additive under carefully chosen conditions (Table 2, runs 10−12). The ratio of 1,4 to 1,2 addition in PCHD from this system is about 69/31. A group of PCHD samples having reasonably well-controlled molecular weights were made from *n*-BuLi/DME, and the results are listed in Table 3 (runs 8−16). One typical SEC trace of PCHD made using this initiating system is shown in Figure 2a. The polydispersities are quite narrow for low molecular weight samples, but at higher MWs narrow MWD materials are elusive, at least partially due to the poor solubility of the polymer. The three isomers of butyllithium in combination with DME or TMEDA[28] yield striking

Table 2. Polymerization of 1,3-CHD Using BuLi with Additives

run	initiator	solvent/temp (°C)	additive	[Add]/[I]	[CHD] (mol/L)	$[I] \times 10^3$ (mol/L)	yield (%)	$M_{n, Cal} \times 10^{-3}$	$M_{nSEC} \times 10^{-3}$	M_w/M_n (SEC)	1,4/1,2[b]
					Monodentate Additive						
1	*sec*-BuLi	benzene/0	THF	19.2	1.02	8.16	37	10.0	2.2	4.28	
2	*sec*-BuLi	benzene/20	*s*-BuOLi	1.5	0.82	2.20	78	30.1	4.97	2.21	
3	*sec*-BuLi	THF/−78	*t*-BuOK	2.9	1.18	4.86	57	19.4	3.6	1.19	
4	*sec*-BuLi	toluene/−40[a]	THF		0.97	5.55	23	13.9	3.6	1.77	
					Polydentate Additive						
5	*n*-BuLi	cyclohexane/40	TMEDA	1.21	0.70	5.99	100	9.3	18.4	1.38	52/48
6	*n*-BuLi	cyclohexane/40	PMDETA	1.27	0.81	2.62	100	24.6	27.9	1.61	55/45
7	*n*-BuLi	benzene/20	DPPE	2.33	1.05	8.35	100	10.1	5.1	1.07	57/43
8	*sec*-BuLi	benzene/20	DPPE	3.02	1.14	7.80	92	11.7	*c*		
9	*tert*-BuLi	benzene/20	DPPE	3.09	1.04	7.65	88	10.9	*c*		
10	*n*-BuLi	benzene/0	DME	4.43	0.58	6.00	98	7.7	11.3	1.07	69/31
11	*sec*-BuLi	benzene/20	DME	4.80	1.09	3.38	16	25.9	6.3	4.73	
12	*tert*-BuLi	benzene/20	DME	4.71	1.75	6.80	9	20.6	4.9	3.18	
13	*n*-BuLi	benzene/20	DABCO	3.19	0.90	5.08	94	14.2	37.8	1.24	89/11
14	*sec*-BuLi	benzene/20	DABCO	2.47	0.79	4.29	100	14.6	20.1	1.04	93/7
15	*tert*-BuLi	benzene/20	DABCO	1.54	1.15	5.18	87	17.8	17.6	1.11	88/12

[a] THF/toluene ~ 1/2 (v/v). [b] From ^{1}H NMR. [c] Not soluble.

Table 3. Poly(1,3-cyclohexadiene) Homopolymers from BuLi and DABCO or DME

run	[additive]/[I]	[CHD] (mol/L)	$[I] \times 10^3$ (mol/L)	$M_{n,Cal} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	M_w/M_n (SEC)
		sec-BuLi/DABCO/Benzene/20 °C				
1	1.4	1.68	35.11	3.8	4.4	1.06
2	1.7	1.20	12.63	7.6	9.1	1.05
3	1.8	1.13	9.52	10.5	13.8	1.03
4	2.5	0.79	4.29	14.7	20.1	1.04
5	2.0	0.82	2.84	23.1	27.8	1.12
6	2.3	1.14	3.10	29.5	36.0	1.31
7	2.1	1.21	2.10	46.3	42.9	1.34
		n-BuLi/DME/Benzene/0 °C				
8	1.7	1.04	17.6	4.7	4.0	1.13
9	2.39	0.69	6.0	7.1	11.3	1.07
10	1.45	1.05	12.2	9.5	13.8	1.12
11	1.65	1.63	8.91	13.7	17.9	1.21
12	2.09	0.77	2.87	16.3	21.1	1.19
13	1.75	1.75	7.35	19.0	28.2	1.24
14	2.15	1.18	3.28	28.7	36.5	1.51
15	1.74	1.77	3.60	39.4	42.9	1.43
16	4.89	0.95	1.51	50.2	*a*	

[a] Not soluble.

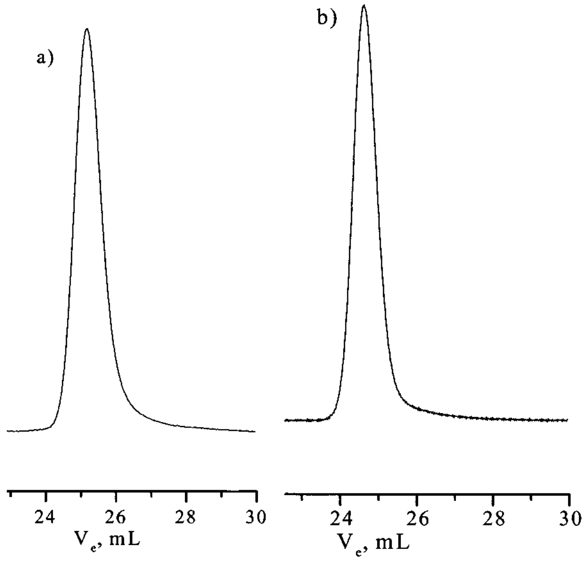


Figure 2. SEC traces of PCHD from (a) *n*-BuLi/DME at 0 °C, $M_n = 11.3$ kg/mol, $M_w/M_n = 1.07$; (b) *sec*-BuLi/DABCO at 20 °C, $M_n = 13.8$ kg/mol, $M_w/M_n = 1.03$.

differences in the polymerization processes. In contrast, the three butyllithium isomers in the presence of TMEDA give very similar results for the polymerization of styrene.[36] With *n*-BuLi, the initiation process proceeds at the same rate as propagation, but with *sec*-BuLi and *t*-BuLi the initiation is faster than propagation.[36] This alone should not cause the observed differences reported by Natori et al. in the polymerization of 1,3-CHD. Adequate data to allow elucidation of these differences were not presented. We speculate that the very reactive species generated from *tert*-BuLi/TMEDA and *sec*-BuLi/TMEDA must undergo some detrimental reactions other than initiation and propagation. For DME, these differences are not surprising since DME has limited stability toward butyllithium.[37] The protons in the β-positions are more acidic than that in TMEDA; thus, they are more readily abstracted followed by elimination. This process is fastest with *tert*-BuLi and slowest with *n*-BuLi. Lower temperatures also increase the stability of DME toward BuLi.

DPPE is also an effective additive. Some of the characteristics of PCHD obtained from BuLi isomers with DPPE are listed in Table 2 (runs 7−9). We believe that better results could be achieved if the reactions were carried out under optimal conditions with regards to solvents, temperatures, and the amount of the additive (ratios of BuLi/DPPE). The 1,4 to 1,2 ratio of the PCHD from this polymerization system is about 57/43. DABCO, a bulky chelating agent, combined with *sec*-BuLi or *tert*-BuLi gives the best control over MW and polydispersity in the polymerizations of 1,3-CHD, as indicated in Table 2 (runs 13−15) and Table 3 (runs 1−7) (also Figure 2b). The resulting PCHD has a 1,4 to 1,2 additions ratio of 93/7. By chelating with DABCO, the C−Li bond in PCHDLi becomes strongly polarized, and consequently, chain propagations were facilitated while side reactions were minimized.

The linearity of M_n with conversion is often used as an experimental criterion to document that a polymerization is living. Unfortunately, this type of plot will only detect chain transfer reactions; it is not sensitive to chain termination.[33] Natori used this plot to demonstrate that the *n*-BuLi/TMEDA/1,3-CHD system is living.[28] To test whether there is any chain termination occurring during the polymerization process, we polymerized 1,3-CHD with *n*-BuLi/TMEDA or DME by sequential addition of the monomer. Figure 3 shows the SEC traces of PCHD obtained by this approach. After

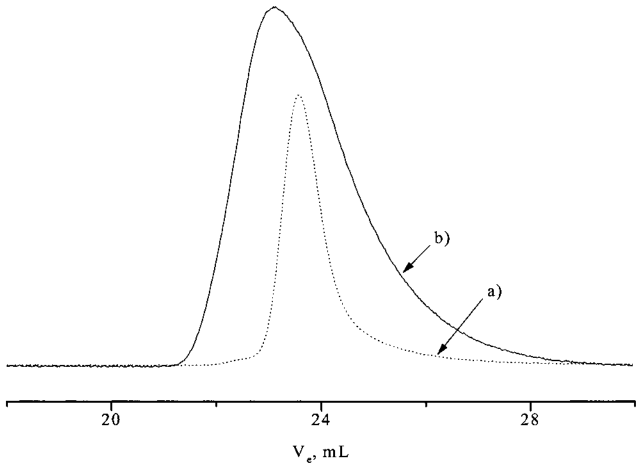


Figure 3. SEC traces of PCHD from *n*-BuLi/DME at 0 °C: (a) aliquot from first dose of monomer, $M_n = 18.4$ kg/mol, $M_w/M_n = 1.08$; (b) aliquot from second dose of monomer, $M_n = 19.7$ kg/mol, $M_w/M_n = 1.68$.

adding a second dose of monomer, the peak became significantly broader as shown in Figure 3b. This indicates that chain termination reactions do occur, with both DME and TMEDA. The large low molecular weight tail suggests that the chain transferred species could reinitiate 1,3-CHD. Detailed studies of the polymerization kinetics, microstructure, and characterization of the final products and the preparation of PCHD star and block copolymers will be published separately.

Conclusions

The synthesis of PCHD polymers using different anionic initiating systems has been studied. Compared to acyclic conjugated dienes, the anionic polymerization of 1,3-CHD is less controlled with respect to MW and polydispersity due to side reactions. This situation can be improved by using certain polydentate additives, such as DABCO and DME, combined with the suitable butyllithium isomer. Conversely, the use of monodentate additives is not very effective. Thus, the range of polymerization conditions conducive to the living polymerization of 1,3-CHD is quite limited. More specifically, we have found that *sec*-BuLi/DABCO in benzene at room temperature or *n*-BuLi/DME in benzene at 0 °C can convert 1,3-CHD to PCHD in a relatively controlled manner. The PCHD materials generated by these two initiator systems exhibit different microstructures.

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