Anionic Polymerization of 1,3-Cyclohexadiene with Alkyllithium/Amine Systems. Characteristics of *n*-Butyllithium/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine System for Living Anionic Polymerization

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ABSTRACT: The *n*-butyllithium (*n*-BuLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) system (with the molar ratio of TMEDA to *n*-BuLi higher than 4/4) has been found to polymerize 1,3-cyclohexadiene to produce "living" polymer having a narrow molecular weight distribution with well-controlled polymer chain length. The rate of polymerization and polymer yield increased with increasing of the ratio of TMEDA to *n*-BuLi. The molecular weight distribution of obtained polymers became narrower with the ratio of TMEDA to *n*-BuLi. The formation of benzene generated by termination reaction was found to decrease with the ratio of TMEDA to *n*-BuLi. In contrast to 1,3-cyclohexadiene, low yield and broad molecular weight distribution were observed in the polymerization of 1,3-hexadiene and 2,4-hexadiene initiated by the *n*-BuLi/TMEDA (4/5) system. The microstructure of poly(1,3-cyclohexadiene) was determined by 2D-NMR. A high content of 1,2-units was found in the polymerization initiated by the alkyllithium/TMEDA system, while the high content of 1,4-units was observed in the cases of alkyllithium or alkyllithium/1,4-diazabicyclo[2,2,2]octane system. The ^{7}Li NMR signals of the *n*-BuLi/TMEDA systems and poly(1,3-cyclohexadienyl)lithium /TMEDA were in higher magnetic field than the signals of *n*-BuLi and poly(1,3-cyclohexadienyl)lithium, respectively, indicating the disaggregation of the lithium species.

Introduction

Living polymerization is a very important method for the synthesis of polymers and block copolymers having narrow molecular weight distributions with well-controlled polymer chain lengths. Since the first discovery of the formation of "living" polymer form styrene,[1] synthetic procedures for polymers with controlled molecular weight have been developed in several polymerization methods.[2] As for the living anionic polymerization of hydrocarbon monomers, polybutadiene, polyisoprene, styrene−butadiene block copolymer, and styrene−isoprene block copolymer have been industrially produced.

To synthesize a new type of hydrocarbon polymer having better properties than the above-mentioned polymers, the polymerization of cyclic conjugated diene has been studied, since a dramatic improvement of thermal stability, chemical stability, and mechanical strength is expected for the obtained polymers with directly connected alicyclic structures in the main chain. However, examples of the living anionic polymerization of cyclic conjugated diene have not been reported. In contrast to styrene, butadiene, and isoprene, the polymerization of cyclic conjugated diene (e.g., 1,3-cyclopentadiene, 1,3-cyclohexadiene, 1,3-cyclooctadiene) was found to be difficult, including the case of anionic polymerization with alkyllithium as initiator.[3] Obtained polymers were of low molecular weight or in low yield.

For example, low molecular weight polymers were obtained in the polymerization of 1,3-cyclohexadiene initiated by *n*-butyllithium (*n*-BuLi) using benzene, tetrahydrofuran (THF), dioxane, diethyl ether, *n*-heptane, and cyclohexane as polymerization solvent.[3a−e] In the polymerization of 1,3-cyclohexadiene initiated by Li−naphthalene, Na−naphthalene, and K−naphthalene, polymers with broad molecular weight distributions were obtained in low yield.[3c,e] A mixture of styrene-1,3-cyclohexadiene copolymer and 1,3-cyclohexadiene homopolymer was obtained in the polymerization of 1,3-cyclohexadiene using polystyryllithium as an initiator.[3g,h]

Furthermore, it has been reported that the anionic polymerization of 1,3-cyclohexadiene initiated by alkyllithiums and alkylsodiums (e.g., *n*-butyllithium, Na−naphthalene, polystyryllithium) in nonpolar solvents (e.g., *n*-hexane, cyclohexane, benzene) at room temperature, leads to low molecular weights, low yields, and broad molecular weight distributions of polymers due to the deactivation of the living ends. Several papers mention the deactivation of the living ends by chain transfer to monomer. In the polymerization of 1,3-cyclohexadiene initiated by alkyllithiums, the formation of 1,4-cyclohexadiene and benzene was observed, due to the abstraction of the allylic hydrogen of 1,3-cyclohexadiene by organolithium species competing with the propagation reaction (Scheme 1).[3a−d, g, h]

To obtain an excellent initiator for the living anionic polymerization of 1,3-cyclohexadiene, we examined the organometallic systems consisting of alkyllithiums (e.g., MeLi, *n*-BuLi, *sec*-BuLi, *t*-BuLi, PhLi) and complexing agents (e.g., amine, ether). In particular, the system

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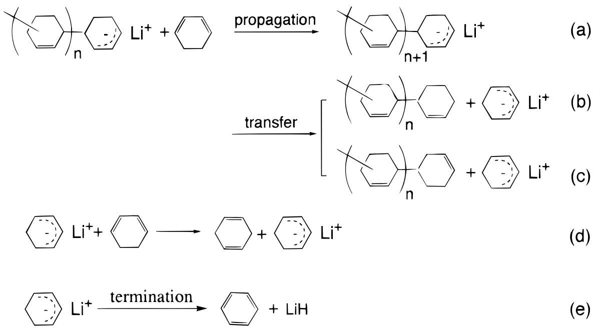
Scheme 1



obtained from *n*-BuLi and TMEDA was examined in detail.

When the cyclohexane solution of TMEDA was added into the *n*-hexane solution of *n*-BuLi at −78 °C under dry argon atmosphere, we noticed the formation of white crystals in the reaction mixture. The white crystals were isolated from the reaction mixture and dissolved into cyclohexane, and the polymerization of 1,3-cyclohexadiene was carried out using the cyclohexane solution of this white crystal as an initiator. Surprisingly, poly(1,3-cyclohexadiene) was obtained with very high yield and high molecular weight.[4] The methylcyclohexane solution of this white crystal was subjected to ^1H NMR measurement, and the isolated white crystals were confirmed to consist of *n*-BuLi and TMEDA, the ratio *n*-BuLi/TMEDA being 4/2.[5] However, the obtained poly(1,3-cyclohexadiene) did not have enough narrow molecular weight distribution.

Next, *n*-BuLi/TMEDA systems with various ratios were prepared by adding TMEDA into the cyclohexane solution of the white crystals, and the polymerization of 1,3-cyclohexadiene was carried out using the *n*-BuLi/TMEDA systems. When the ratio of TMEDA to *n*-BuLi was higher than 4/4, the polymerization of 1,3-cyclohexadiene attained the living nature. In addition, similarly excellent initiator systems for the living anionic polymerization of 1,3-cyclohexadiene were also obtained by directly mixing *n*-BuLi and TMEDA when the ratio of TMEDA to *n*-BuLi was higher than 4/4.

In the previous communication,[6a] we reported the first successful example of living anionic polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system, and we could successfully synthesize the homopolymer and the block copolymer. Furthermore, we reported the relative reactivity of 1,3-cyclohexadiene in the copolymerization with styrene and isoprene and the relative reactivity of the propagating species of living poly(1,3-cyclohexadiene) and living polystyrene.[6b] The relationship between the microstructure and properties of homopolymers, block copolymers, and their hydrogenated derivatives was also reported.[6c]

In the present paper, the characteristics of the polymerization of 1,3-cyclohexadiene initiated by various alkyllithium (RLi)/amine systems are discussed in detail. For the *n*-BuLi/TMEDA system, the ^7Li NMR analysis of alkyllithium species in the polymerization is also described.

Experimental Section

Materials. *n*-Butyllithium (*n*-BuLi, 1.44 M in *n*-hexane), *sec*-butyllithium (*sec*-BuLi, 1.0 M in cyclohexane), and *tert*-butyllithium (*t*-BuLi, 1.5 M in *n*-pentane) were used without further purification. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA), *N,N,N′,N′*-tetramethylmethylenediamine (TMMDA), *N,N,N′,N′*-tetramethyl-1,3-propanediamine (TMPDA), *N,N,N′,N′*-tetramethyl-1,6-hexanediamine (TMHDA), *N,N,N′,N′*-tetraethylethylenediamine (TEEDA), triethylamine (Et_3N), (−)-sparteine, 1,3-cyclohexadiene, 1,3-hexadiene, 2,4-hexadiene, cyclohexane, and methylcyclohexane were refluxed over calcium hydride (CaH_2) and then distilled under argon atmosphere. Styrene, stirred with neutral aluminum oxide at room temperature, was degassed to remove air in argon atmosphere and then distilled under reduced pressure. 1,4-Diazabicyclo-[2,2,2]octane (DABCO) was dried under reduced pressure in argon atmosphere.

Preparation of the *n*-BuLi/TMEDA(4/5) system: Method A. A 1.0 M cyclohexane solution of TMEDA (2 mol) was added to a 1.44 M *n*-hexane solution of *n*-BuLi (4 mol) by hypodermic syringe at room temperature (∼25 °C) under dry argon atmosphere and the mixture was stirred for 10 min. Then, this mixture was heated to 70 °C and was stirred for 10 min, corresponding to the preparation of the *n*-BuLi/TMEDA (4/2) system. Then, the mixture was cooled to 40 °C, and a 1.0 M cyclohexane solution of TMEDA (3 mol) was added resulting in the preparation of the *n*-BuLi/TMEDA (4/5) system.

Preparation of the *n*-BuLi/TMEDA(4/5) system: Method B. A 1.0 M cyclohexane solution of TMEDA (5 mol) was added to a 1.44 M *n*-hexane solution of *n*-BuLi (4 mol) by hypodermic syringe at room temperature (∼25 °C) under dry argon atmosphere and the mixture was stirred for 10 min. Then, the mixture was heated to 40 °C and was stirred for 10 min to form the *n*-BuLi/TMEDA (4/5) system.

Preparation of Polystyryllithium. A 1.0 M cyclohexane solution of *sec*-BuLi was added to the cyclohexane solution of styrene at room temperature (∼25 °C) under dry argon atmosphere ($[\text{styrene}]_0/[\text{Li}]_0 = 5$). After confirmation of the complete consumption of styrene by GC, a portion of the polymerization system was subjected to gel permeation chromatography (GPC). A cyclohexane solution of polystyryllithium (PStLi) was thus obtained ($M_n = 510$, $M_w/M_n = 1.12$, $M_{calc} = 520.75$).

General Procedure of the Polymerization of 1,3-Cyclohexadiene with Alkyllithium/Amine Systems (Vacuum Line Technique). A well-dried 100 mL Schlenk tube was purged with dry argon, and cyclohexane and alkyllithium (RLi) solution were added by hypodermic syringes at room temperature (∼25 °C). Amine was then added to this solution according to the above-mentioned method A or method B. To this solution was then supplied 1,3-cyclohexadiene, and the reaction mixture was kept stirring magnetically under argon atmosphere. After a definite period of time, dehydrated methanol was added to the polymerization mixture in an amount equimolar to the amount of lithium atoms present in the polymerization mixture, to terminate the polymerization. Then, the polymerization mixture was poured into a large amount of acetone to precipitate the polymer, which was separated by filtration. The product was dried in a vacuum for 8 h at 50 °C, to give a white powdery polymer. The conversion of monomer to polymer was estimated by GC with internal standard method from the amount of monomer and byproducts (1,4-cyclohexadiene and benzene formed by chain transfer and termination reactions) in the polymerization reaction mixture. For gel permeation chromatography (GPC) measurement, a part of the obtained polymer was dissolved in tetrahydrofuran (THF), and a Teflon filter was used to filter off the insoluble part (initiator residue) from this solution.

Polymerization of 1,3-Cyclohexadiene with the *n*-Butyllithium/TMEDA Systems (Autoclave Technique). Cyclohexane was placed in a 5 L stainless steel autoclave equipped with an electromagnetic induction stirrer in nitrogen atmosphere (about 4 kg/cm^2). To prepare the *n*-BuLi/TMEDA (4/5) system, a 1.44 M *n*-hexane solution of *n*-BuLi and a 1 M cyclohexane solution of TMEDA were added to cyclohexane in an autoclave according to method A. Next, 1,3-cyclohexadiene was supplied to this solution in the autoclave, and the polymerization was carried out under nitrogen atmosphere at 40 °C. After the polymerization, an equimolar amount of dehydrated methanol to lithium atoms was added to the reaction mixture to terminate the reaction. The separation

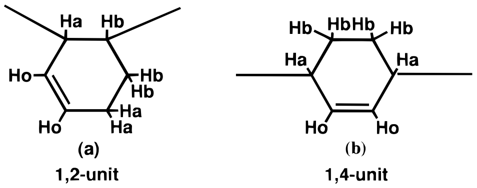


Figure 1. Structural formulas of the 1,2-unit (a) and the 1,4-unit (b).

of obtained polymer and the measurement of GC and GPC were carried out by procedures similar to those described above.

Measurements. ^{1}H NMR spectra of the polymer were measured for a 10 wt % solution in deuterated *o*-dichlorobenzene at 135 °C, using a JEOL type α-400 spectrometer operating at 400 MHz using added cyclohexane as a reference (1.4 ppm). The measurement of the two-dimensional NMR (2D-NMR) spectrum of poly(1,3-cyclohexadiene) was carried out in deuterated *o*-dichlorobenzene, and observed spectral peaks were assigned to each hydrogen atom of the polymer chain (Figure 1). With respect to monomeric units in polymer chain having a 1,2-bond (1,2-unit) and the units having a 1,4-bond (1,4-unit), there is a difference in the number of hydrogen atoms (Ha) on the carbon atoms adjacent to double bond. 1,2-Units satisfy the formula Ha/(Ha + Hb) = $^1/_2$ (Figure 1a), while 1,4-units satisfy the formula Ha/(Ha + Hb) = $^1/_3$ (Figure 1b). Therefore, the 1,2-bond/1,4-bond molar ratio can be determined by estimating the numbers of protons which are correlated to carbon atoms of the double bond. The 2D-NMR spectrum of poly(1,3-cyclohexadiene) obtained by the *n*-BuLi/TMEDA(4/5) system (method A) was measured by the H−H COSY method[7] (Figures 2 and 3). Cross-peaks were observed in the region from 5.5 to 5.8 ppm which are ascribed to hydrogen atoms bound to carbon atoms of the double bond (Figure 1 (Ho)). Cross-peaks were also observed in the region from 1.85 to 2.35 ppm which are ascribed to hydrogen atoms (Ha). In Figure 3, Hb's are not cross-peaks.

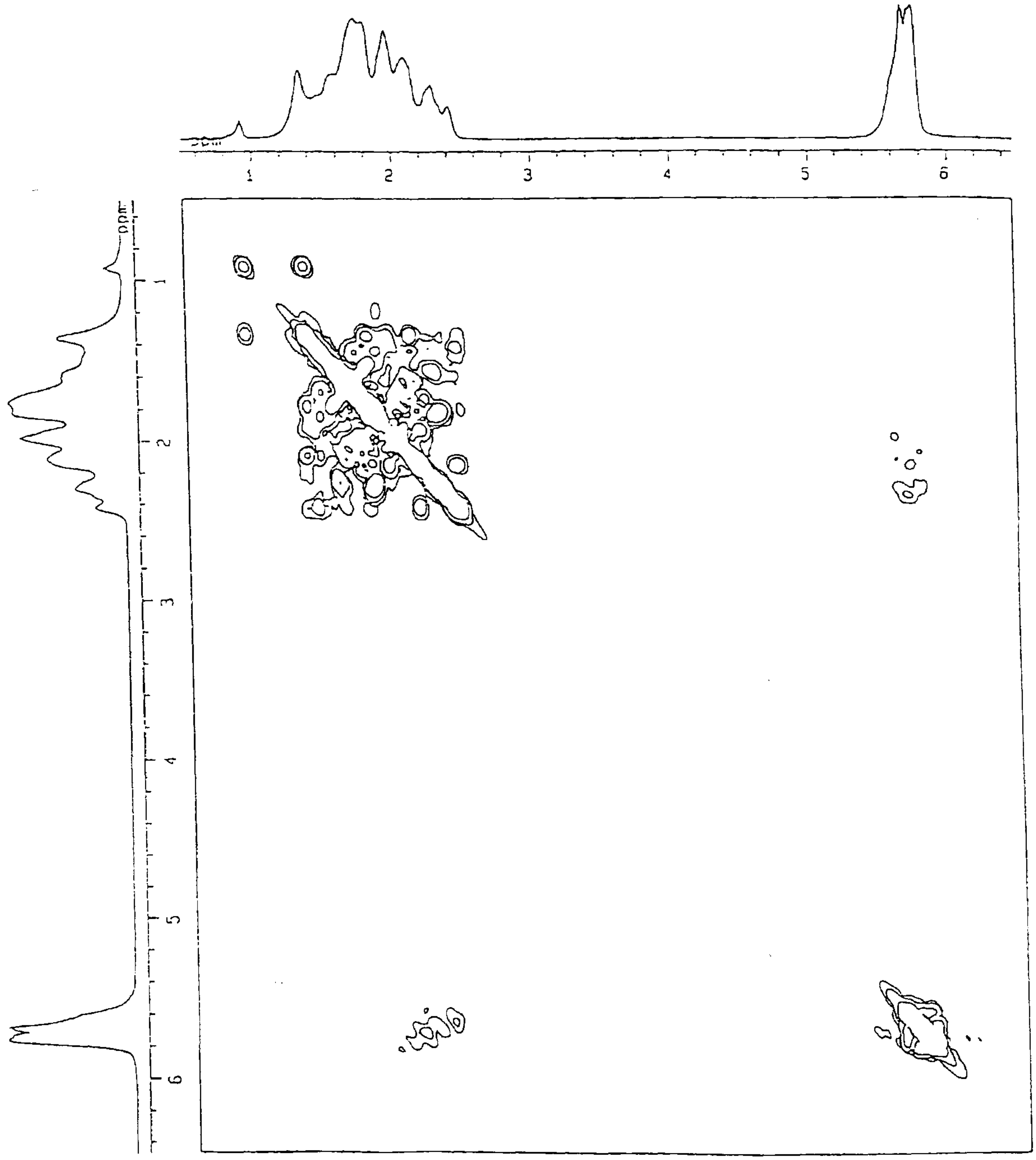


Figure 2. 2D-NMR spectrum of poly(1,3-cyclohexadiene) in 10 wt % solution of *o*-dichlorobenzene-d_4 at 135 °C.

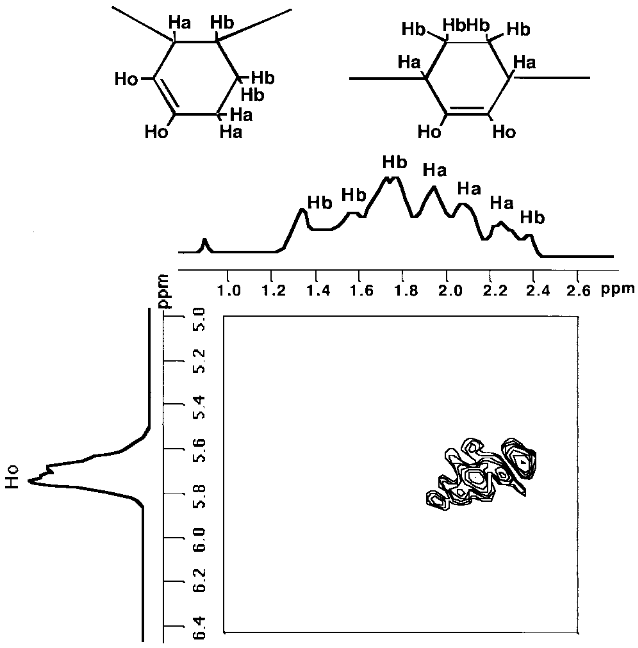


Figure 3. Assignment of proton signals for poly(1,3-cyclohexadiene).

When the molar ratio of 1,2-units to all monomeric units is represented by α, and the ratio of the area of peaks (Ha/Ha + Hb) to the area of peaks for all hydrogen atoms, exclusive of those on unsaturated carbons (Figure 1 (Ho)), is represented by *β*, α and *β* satisfy the following formula: $^3/_6\alpha + ^2/_6(1 - \alpha) = \beta$. The molar ratio of 1,2-units to 1,4-units was determined according to the above formula by α estimated on the basis of the intensity ratio of the signals of Ha and Hb.

^{7}Li NMR spectra of the initiators and living polymers were measured in methylcyclohexane using a JEOL type α-400 spectrometer operating at 155 MHz.

Since cyclohexane freezes at 6.5 °C or below, methylcyclohexane was used for measurement of ^{7}Li NMR. The 1.0 M solution of LiCl in D_2O was used as a reference (0 ppm). The methylcyclohexane solution of initiators or living polymers was placed by hypodermic syringe into a well-dried NMR tube with dry argon at room temperature (~25 °C) and methylcyclohexane was added into this solution, to obtain a 0.1 mM solution with respect to the Li atom.

Gel permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-8020 gel permeation chromatograph equipped with a differential refractometer detector. The eluent was tetrahydrofuran (THF), and the flow rate was 1.0 mL·min^{-1}. The used column was Showdex k805, k804, and k802 supplied by Showa Denko. A molecular weight calibration curve was obtained by using standard polystyrenes: M_n = 2 366 250 (M_w/M_n = 1.06), M_n = 560 750 (M_w/M_n = 1.06), M_n = 156 530 (M_w/M_n = 1.03), M_n = 66 000 (M_w/M_n = 1.03), M_n = 23 980 (M_w/M_n = 1.04), M_n = 12 200 (M_w/M_n = 1.06), M_n = 5990 (M_w/M_n = 1.04), M_n = 1680 (M_w/M_n = 1.05), and M_n = 580 (M_w/M_n = 1.18) supplied by Showa Denko. Gas chromatographic analysis (GC) was carried out using a Shimazu Type 14A gas chromatograph. Ethylbenzene was used as an internal standard substance.

Results and Discussion

***n*-Butyllithium/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine Systems for the Living Anionic Polymerization of 1,3-Cyclohexadiene.** To know the effect of molar ratio of the initiator system on the polymerization characteristics of 1,3-cyclohexadiene, polymerization was carried out using *n*-butyllithium (*n*-BuLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) systems with various molar ratios (method A and method B) in cyclohexane at 40 °C in dry argon for 120 min ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125). The results are shown in Tables 1 and 2. Initiator systems prepared by Method A and Method B exhibited a similar behavior for the polymerization of 1,3-cyclohexadiene. The molar ratio of *n*-BuLi and TMEDA composing the initiator systems strongly influenced the anionic polymerization of 1,3-cyclohexadiene. The polymerization attained the living nature as the ratio of TMEDA increased. When the ratio of TMEDA to *n*-BuLi was higher than 4/4, the polymers obtained had very narrow molecular weight distributions. On the other hand, no polymeric product was obtained in the polymerization initiated by *n*-BuLi in the absence of TMEDA ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125, 120 min, 40 °C). These results suggest that the propagating ends of living poly(1,3-cyclohexadiene) is composed of a 1/1 molar ratio of Li and TMEDA.

Table 1. Polymerization of 1,3-Cyclohexadiene by the *n*-BuLi/TMEDA Systems (Method A)[a]

no.	initiator system	yield (%)	M_n	$M_{calc}{}^b$	M_w/M_n
1	*n*-BuLi	0			
2	*n*-BuLi/TMEDA(4/2)	72	16 000	7 200	1.52
3	*n*-BuLi/TMEDA(4/3)	100	11 100	10 000	1.12
4	*n*-BuLi/TMEDA(4/4)	100	10 600	10 000	1.07
5	*n*-BuLi/TMEDA(4/5)	100	11 600	10 000	1.06
6	*n*-BuLi/TMEDA(4/6)	100	10 800	10 000	1.08
7	*n*-BuLi/TMEDA(4/7)	100	10 100	10 000	1.06
8	*n*-BuLi/TMEDA(4/8)	100	11 300	10 000	1.07

[a] [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125. [monomer(s)]/[solvent] = 10/90. Polymerization was carried out in cyclohexane; reaction temperatures 40 °C, reaction time 120 min. M_n and M_w/M_n were estimated by GPC, using polystyrene as standard. The *n*-BuLi/TMEDA system was prepare by method A. [b] $\mathrm{M_{calc}}$: FW(C_6H_8) × 125 × yield (%) × 10^{-2} = 10 000 × yield (%) × 10^{-2}.

Table 2. Polymerization of 1,3-Cyclohexadiene by the *n*-BuLi/TMEDA Systems (Method B)[a]

no.	initiator system	yield (%)	M_n	$M_{calc}{}^b$	M_w/M_n
1	*n*-BuLi	0			
2	*n*-BuLi/TMEDA(4/2)	72	16 000	7 200	1.52
3	*n*-BuLi/TMEDA(4/3)	100	11 900	10 000	1.30
4	*n*-BuLi/TMEDA(4/4)	100	10 900	10 000	1.11
5	*n*-BuLi/TMEDA(4/5)	100	11 200	10 000	1.08
6	*n*-BuLi/TMEDA(4/6)	100	10 900	10 000	1.09
7	*n*-BuLi/TMEDA(4/7)	100	11 300	10 000	1.10
8	*n*-BuLi/TMEDA(4/8)	100	11 100	10 000	1.09

[a] [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125. [monomer(s)]/[solvent] = 10/90. Polymerization was carried out in cyclohexane; reaction temperatures 40 °C, reaction time 120 min. M_n and M_w/M_n were estimated by GPC, using polystyrene as standard. The *n*-BuLi/TMEDA system was prepare by method B. [b] M_{calc}: FW(C_6H_8) × 125 × yield (%) × 10^{-2} = 10 000 × yield (%) × 10^{-2}.

To obtain polymers of high molecular weight, the polymerization of 1,3-cyclohexadiene was carried out in cyclohexane at 40 °C for 240 min, where the amount of 1,3-cyclohexadiene was 250 times that of the initiator ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 250).

As shown in Table 3, a narrower molecular weight distribution of polymers was obtained by method A than by method B. Thus, for the polymerization of 1,3-cyclohexadiene initiated by *n*-BuLi/TMEDA, method A is regarded as better than method B. As shown in Table 3, poly(1,3-cyclohexadiene) with a higher number average molecular weight than 40 000 was obtained by method A ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 500, 300 min, 40 °C).

The characteristics of living anionic polymerization of 1,3-cyclohexadiene initiated by some *n*-BuLi/TMEDA systems (4/5, method A; 4/2 and 4/0.5, method B) in

Table 3. Comparison between the *n*-BuLi/TMEDA Systems Prepared by Method A and Method B for the Polymerization of 1,3-Cyclohexadiene[a]

no.	*n*-BuLi/TMEDA	method	reaction time (min)	yield (%)	M_n	M_{calc}[b]	M_w/M_n
1[c]	4/4	A	240	100	21 000	20 000	1.16
2[c]	4/5	A	240	100	21 600	20 000	1.10
3[c]	4/4	B	240	100	20 700	20 000	1.24
4[c]	4/5	B	240	100	21 900	20 000	1.19
5[d]	4/5	A	300	100	41 300	40 000	1.30

[a] Polymerization was carried out in cyclohexane. [monomer(s)]/[solvent] = 10/90, reaction temperature 40 °C. M_n and M_w/M_n were estimated by GPC, using polystyrene as standard. [b] M_{calc}: FW(C_6H_8) × 250 × yield (%) × 10^{-2} = 20 000 × yield (%). FW(C_6H_8) × 500 × yield (%) = 40 000 × yield (%) × 10^{-2}. [c] [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 250. [d] [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 500.

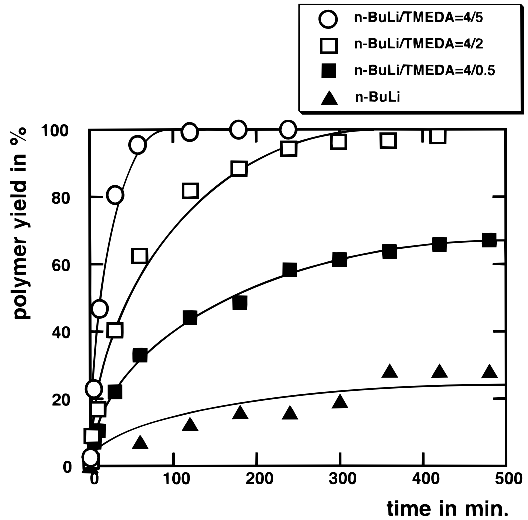


Figure 4. Conversion-time relationship of the polymerization of 1,3-cyclohexadiene with some *n*-BuLi/TMEDA systems in cyclohexane at 40 °C. [1,3-CHD]$_0$/[Li]$_0$ = 250, the ratio of *n*-BuLi/TMEDA(4/5): method A; 4/2; method B, 4.0.5.

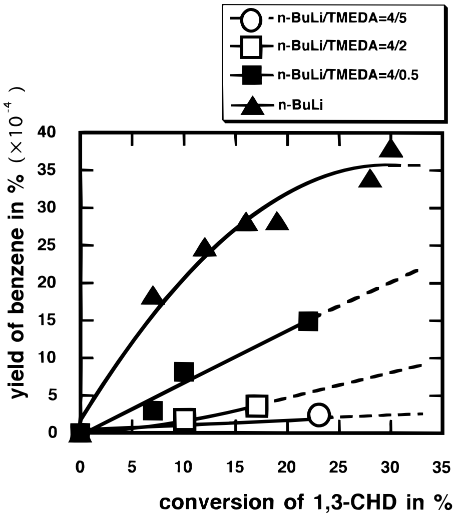


Figure 5. Relationship between the conversion of 1,3-cyclohexadiene and the amount of benzene formed inthe anionic polymerization of 1,3-cyclohexadiene initiated by some *n*-BuLi/TMEDA systems and *n*-BuLi in cyclohexane at 40 °C. [1,3-CHD]$_0$/[Li]$_0$ = 250, the ratio of *n*-BuLi/TMEDA(4/5): method A, 4/2; method B, 4/0.5.

cyclohexane was examined in further detail ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 250, 240 min, 40 °C). The results are shown in Figures 4 and 5. Figure 4 clearly shows that the rate of polymerization and polymer yield increased with the ratio of TMEDA to *n*-BuLi. On the other hand, the polymer yield was considerably low in the absence of TMEDA and the increase in polymer yield was not observed after 360 min.

The molecular weight distribution of obtained polymers became narrower with the ratio of TMEDA to *n*-BuLi (*n*-BuLi/TMEDA(4/5), method A, M_n = 18 700, M_w/M_n = 1.09, conversion 100%; 4/2, method B, M_n = 28 200, M_w/M_n = 1.41, conversion 100%; 4/0.5, method B, M_n = 16 300, M_w/M_n = 2.42, conversion 77%; *n*-BuLi, M_n = 3500, M_w/M_n = 2.27, conversion 30%). The GPC profile of poly(1,3-cyclohexadiene) was very sharp when the initiator was the *n*-BuLi/TMEDA (4/5) system (method A). The formation of benzene was found to decrease with the ratio of TMEDA to *n*-BuLi (Figure 5). On the other hand, the yield of 1,4-cyclohexadiene was found to vary from 0% to 8.4 Å × 10^{-4}% in the polymerization of 1,3-cyclohexadiene using the *n*-BuLi/TMEDA systems (4/5, 4/2, 4/0.5) and *n*-BuLi.

The formation of benzene and 1,4-cyclohexadiene is considered to be the results of the decomposition of cyclohexadienyllithium (CHDLi) with hydride elimination (Scheme 1e) and the abstraction of the allylic hydrogen of 1,3-cyclohexadiene by CHDLi (Scheme 1d), respectively.[3a−d,g,h]

Obviously, in the polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system, there is neither a transfer reaction nor a termination reaction for the abstraction of allylic hydrogen of 1,3-cyclohexadiene by organolithium species.

Polymerizations of 1,3-Hexadiene and 2,4-Hexadiene with the *n*-BuLi/TMEDA (4/5) System. To know if the suppression of abstraction of allylic hydrogen is due to the ring structure of 1,3-cyclohexadiene, the polymerization of 1,3-hexadiene and 2,4-hexadiene having an open chain structure and allylic hydrogen atoms was examined with the *n*-BuLi/TMEDA (4/5) system (method A) in cyclohexane ([monomer]$_0$/[Li]$_0$ = 125, 120 min, 40 °C).

As shown in Table 4, obtained polymers were in low yield (5−37%) and of broad molecular weight distribution (M_w/M_n = 1.75−1.93). These results were not better than the cases in the absence of TMEDA.

Thus, the decrease of the transfer reaction and termination reaction in the anionic polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system is regarded as a unique behavior of the ring structure.

Polymerization of 1,3-Cyclohexadiene with Various Alkyllithium/Amine Systems. As described above, the *n*-BuLi/TMEDA (4/5) system is an excellent initiator for the living anionic polymerization of 1,3-cyclohexadiene. Of further interest was the investigation of the polymerization by related initiator systems. 1,3-Cyclohexadiene was polymerized by various alkyllithium/amine systems (method A) in cyclohexane ([monomer]$_0$/[Li]$_0$ = 125, 120 min, 40 °C), and the results are shown in Table 5.

Poly(1,3-cyclohexadiene) having narrow molecular weight distribution and high yield was not formed with

Table 4. Polymerization of 1,3-Hexadiene and 2,4-Hexadiene with the *n*-BuLi/TMEDA(4/5) System[a]

no.	monomer	initiator system[b]	yield (%)	M_n[c]	M_{calc}[d]	M_w/M_n[c]
1	1,3-hexadiene	*n*-BuLi	42	23700	4305	1.81
2	1,3-hexadiene	*n*-BuLi/TMEDA(4/5)	37	21500	3793	1.93
3	2,4-hexadiene	*n*-BuLi	20	2500	2050	1.68
4	2,4-hexadiene	*n*-BuLiTMEDA(4/5)	5	5400	513	1.75

[a] $[\text{monomer}]_0/[\text{Li}]_0 = 1.25$. [monomer(s)]/[solvent] = 10/90. Polymerization was carried out in cyclohexane at 40 °C for 120 min. [b] The *n*-BuLi/TMEDA(4/5) sytem was prepared by method A. [c] M_n and M_w/M_n were estimated by GPC, using polystyrene as standards. [d] M_{calc}: FW(C_6H_{10}) × 125 × yield (%) × 10^{-2} = 10 250 × yield (%) 10^{-2}.

Table 5. Polymerizations of 1,3-Cyclohexadiene with Various Alkyllithium/Amine Initiator Systems (Method A)[a] **and Microstructure of Poly(1,3-cyclohexadiene)**[b]

no.	initiator system	yield (%)	M_n	M_{calc}[c]	M_w/M_n	1,2-unit (%)	1,4-unit (%)
1	*n*-BuLi	0					
2	*n*-BuLi[d]	33	3500	6600	2.27	2	98
3	*n*-BuLi/TMEDA(4/0.5)[d]	77	16300	15400	2.42	21	79
4	*n*-BuLi/TMEDA(4/2)	72	16000	7200	1.52	43	67
5	*n*-BuLi/TMEDA(4/3)	100	11100	10000	1.12	48	52
6	*n*-BuLi/TMEDA(4/4)	100	10600	10000	1.07	51	49
7	*n*-BuLi/TMEDA(4/5)	100	11600	10000	1.06	52	48
8	*n*-BuLi/TMEDA(4/6)	100	10800	10000	1.08	54	46
9	*n*-BuLi/TMEDA(4/8)	100	11300	10000	1.07	54	46
10	*n*-BuLi/TMMDA[e](4/5)	70	7600	7000	1.75	24	76
11	*n*-BuLi/TMPDA[f](4/5)	33	7900	3300	2.16		
12	*n*-BuLi/TMHDA[g](4/5)	67	8700	6700	1.95	9	91
13	*n*-BuLi/TEEDA[h](4/5)	16	1100	1600	1.14		
14	*n*-BuLi/(−)spareine(4/5)	9	700	900	1.14		
15	*n*-BuLi/DABCO[i](4/5)	100	11300	10000	1.69	21	79
16	*sec*-BuLi	8	4800	800	1.53	2	98
17	*sec*-BuLi/TMEDA(4/5)	99	10800	9900	1.53	41	59
18	*sec*-BuLi/DABCO(4/5)	99	11900	9900	1.79	2	98
19	*t*-BuLi	85	5000	8500	1.600	4	96
20	*t*-BuLi/TMEDA(4/5)	91	14700	9100	1.59	46	54
21	*t*-BuLi/DABCO(4/5)	100	12600	10000	1.40	1	99
22	PStLi	15	7400	2010	1.60	221	79
23	PStLi/TMEDA(4/5)	100	13600	10510	1.29	64	34
24	PStLi/TMMDA(4/5)	39	6600	4410	1.55	26	74
25	PStLi/TMPDA(4/5)	84	9800	8910	1.55	32	68
26	PStLi/TMHDA(4/5)	98	19700	10310	1.27	18	82
27	PStLi/DABCO(4/5)	100	13000	10510	1.14	25	75
28	PStLi/NEt$_3$(4/5)	23	5450	2810	1.45	14	86

[a] $[\text{1,3-cyclohexadiene}]_0/[\text{Li}]_0 = 125$. [monomer(s)]/[solvent] = 10/90. Polymerization was carried out in cyclohexane, reaction temperature 40 °C, reaction time 120 min. M_n and M_w/M_n were estimated by GPC, using polystyrene as standard. PStLi:Mn 510, M_w/M_n 1.12. [b] The contents of 1,2-unit (%) and 1,4-unit (%) were estimated by 2D-NMR. [c] M_{calc}: RLi/amine systems, FW(C_6H_8) × 125(250) × yield (%) × 10^{-2} = 10 000 (20 000) × yield (%) × 10^{-2}; PstLi/amine systems, FW(C_6H_8) × 125 × yield (%) × 10^{-2} + 510 = 10 000 × yield (%) × 10^{-2} + 510. [d] $[\text{1,3-cyclohexadiene}]_0/[\text{Li}]_0 = 250$. [monomer(s)]/[solvent] = 10/90. Polymerization was carried out in cyclohexane, reaction temperature 40 °C, reaction time 500 min. [e] *N*,*N*,*N*′,*N*′-Tetramethylmethylenediamine. [f] *N*,*N*,*N*′,*N*′-Tetramethyl-1,3-propanediamine. [g] *N*,*N*,*N*′,*N*′-Tetramethyl-1,6-hexanediamine. [h] *N*,*N*,*N*′,*N*′-Tetraethylethylenediamine. [i] 1,4-Diazabicyclo[2,2,2]octane.

any other initiator systems except the polystyryllithium (PStLi)/TMEDA, PStLi/TMHDA, and PStLi/DABCO systems. However, even though these initiators were used, the molecular weight distribution was not narrower than that obtained by the *n*-BuLi/TMEDA system.

Microstructure of Poly(1,3-cyclohexadiene). It has been attempted to measure ^{1}H NMR resonances to know the microstructure of poly(1,3-cyclohexadiene) of low molecular weight obtained by anionic polymerization with *n*-BuLi and coordination polymerization with $TiCl_4/AlEt_3$. However, the ^{1}H NMR spectra of these polymers were of low resolution. Thus, only insufficient information for the microstructure of the polymer chain has been obtained in the previous works.[3a,8] Although ref 8c gave a description and interpretation of the ^{13}C NMR of PCHD, it was based on 3,3′-bis(cyclohex-1-enyl) as a model compound. To know the accurate microstructure of poly(1,3-cyclohexadiene), the 10 wt % deuterated *o*-dichlorobenzene solution of polymers obtained by various alkyllithium/amine systems (method A) was subjected to 2D-MNR (135 °C). The results are shown in Table 5.

Poly(1,3-cyclohexadiene) has a structure for the main chain consisting of units formed by 1,2-addition (1,2-unit) and 1,4-addition (1,4-unit). As for the polymer initiated by the *n*-BuLi/TMEDA systems, the content of the 1,2-units in the polymer chain increased with the ratio of TMEDA to *n*-BuLi. When the ratio of TMEDA to *n*-BuLi was higher than 4/4, the content of the 1,2-units was almost the same (51−54%). The polymer initiated by the *n*-BuLi/TMMDA(4/5), *n*-BuLi/TMHDA-(4/5), *n*-BuLi/DABCO(4/5), *sec*-BuLi/TMEDA (4/5), *t*-BuLi/TMEDA (4/5), PStLi, PStLi/TMMDA (4/5), PStLi/TMPDA (4/5), PStLi/TMHDA (4/5), PStLi/DABCO (4/5), and PStLi/Et$_3$N (4/5) systems had the 1,2-units in 9−46%. 1,4-Units were predominant (98−99%) when *n*-BuLi, *sec*-BuLi, *t*-BuLi, *sec*-BuLi/DABCO (4/5), and *t*-BuLi/DABCO (4/5) systems were used as initiator. Furthermore, when the *n*-BuLi/amine systems were compared with the PStLi/amine system, 1,2-units in the latter were more abundant. The maximum content of 1,2-units was 64% with the PStLi/TMEDA(4/5) system.

The polymers having a relatively high content of 1,2-units were formed in the polymerization of 1,3-cyclo-

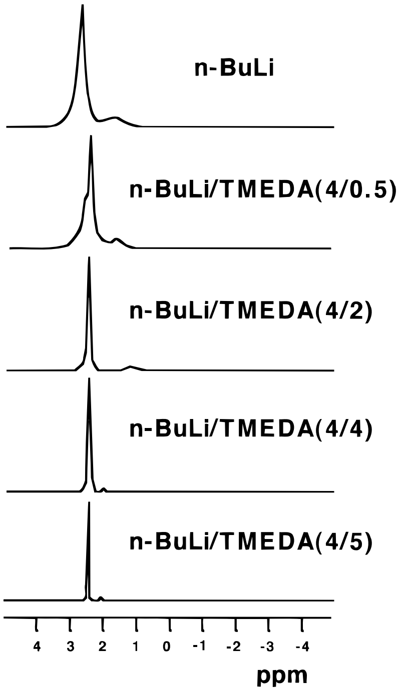


Figure 6. ^{7}Li-NMR spectra of the *n*-BuLi/TMEDA systems in methylcyclohexane at −50 °C. [Li] = 0.1 mM, the ratio of *n*-BuLi/TMEDA(4/5): method A, 4/4, 4/2; method B, 4/0.5.

hexadiene initiated by the alkyllithium/TMEDA system, while the polymers having a high content of 1,4-units were formed in the polymerization of 1,3-cyclohexadiene initiated by alkyllithium or alkyllithium/DABCO system. Thus, the microstructure of the polymer is considered to be strongly influenced by the structure of the living ends of the polymer chain consisting of carbanion, lithium cation, and amine (complexing agent).

Investigation of the ^{7}Li NMR Spectra of the *n*-BuLi/TMEDA Systems and Poly(1,3-cyclohexadienyl)lithium/TMEDA System. To know the relation between the ^{7}Li NMR spectrum of lithium species and the characteristics in the anionic polymerization of 1,3-cyclohexadiene, the ^{7}Li NMR of the *n*-BuLi/TMEDA systems and poly(1,3-cyclohexadienyl)lithium/TMEDA, which corresponds to the propagating end of the polymer, were measured in methylcyclohexane at −50 °C under dry argon atmosphere (Li: 0.1 mM).

In previous works,[9] the ^{6}Li NMR spectra of lithiopinacolonate[9a] and the anisole/*n*-BuLi system[9b] were reported, and the shift of the ^{6}Li NMR signal to a higher magnetic field was observed by adding TMEDA to these lithium compounds. In these cases, the shift was explained by the disaggregation of the lithium compounds. To our knowledge, however, ^{7}Li NMR spectra of the *n*-BuLi/TMEDA systems with various molar ratios have not been reported, though the ^{7}Li NMR spectrum has a higher sensitivity than the ^{6}Li NMR spectrum.

As shown clearly in Figure 6, the chemical shift of the ^{7}Li signal moved to a higher magnetic field when TMEDA was added to the methylcyclohexane solution of *n*-BuLi. The ^{7}Li signal of the *n*-BuLi/TMEDA systems sharpened as the ratio of TMEDA to *n*-BuLi increased. The shift of ^{7}Li signal is considered to be due to the coordination of TMEDA to *n*-BuLi and the disaggregation of *n*-BuLi. The ^{7}Li signals of the *n*-BuLi/TMEDA systems did not change too much with the change in the ratio of *n*-BuLi/TMEDA from 4/0.5 to 4/5.[10]

Similar to the case of *n*-BuLi, the ^{7}Li signal of the poly(1,3-cyclohexadienyl)lithium (PCHDLi)/TMEDA system obtained by the living anionic polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA(4/5) system in cyclohexane at 40 °C (method A) was in higher magnetic field than the signal of poly(1,3-cyclohexadienyl)lithium (PCHDLi) obtained by the polymerization with *t*-BuLi in the absence of TMEDA in cyclohexane at 40 °C.[11] This result indicates the coordination of TMEDA to Li of PCHDLi.

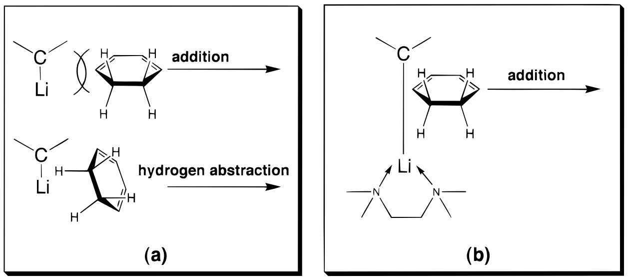
Characteristics of the Alkyllithium/Amine System for Anionic Polymerization of 1,3-Cyclohexadiene. It is well-known that tertiary amines form complexes with alkyllithium. Among these, one of the most reactive is that formed with *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA). The *n*-BuLi/TMEDA complex is monomeric in solution,[12] and the metal−carbon bond is thought to be strongly polarized. This complex easily causes the metalation reaction of organic compounds having acidic hydrogens (e.g., benzene, toluene, and *p*-xylene)[13] and the polymerization reaction of olefins such as ethylene, styrene, butadiene, and isoprene.[12,14] The effect of alkyllithium/amine complexes to the microstructure of polydienes such as polybutadiene and polyisoprene was also reported in the anionic polymerization. It is well-known that an increase in the content of 1,2-unit was observed in the polymerization of butadiene initiated by alkyllithiums (*n*-BuLi, *sec*-BuLi, and *t*-BuLi) by adding amine, ether, and other electron donors to hydrocarbon polymerization solvents.[15]

Similarly, the increase in the content of 1,2-unit was observed in the polymerization of 1,3-cyclohexadiene initiated by alkyllithium/amine systems (Table 5). Thus, the existence of a covalent σ-allyl structure and an ionic π-allyl structure of poly(1,3-cyclohexadienyl)lithium (PCHDLi) is expected from the analogy with poly(butadienyl)lithium, and the σ-form and the π-form of PCHDLi are considered to lead to 1,4-units and 1,2-units, respectively. The increase in the content of 1,2-unit is regarded as the result of the increase in the π-form of PCHDLi. In particular, TMEDA is considered to lead to a higher content of the π-form of PCHDLi by strongly polarizing the Li−carbon bond.

The addition and hydrogen abstraction reactions in the anionic polymerization of 1,3-cyclohexadiene are also thought to be strongly affected by the extent of the polarization of the Li−carbon bond in PCHDLi. The polymerization of 1,3-cyclohexadiene initiated by the *n*-BuLi/TMEDA system (Tables 1-3, Figures 4-6) was accelerated when compared with the polymerization initiated by *n*-BuLi in the absence of TMEDA. This is considered to be due to the high reactivity of the *n*-BuLi/TMEDA and PCHDLi/TMEDA complexes having a polarized metal−carbon bond, coordinative unsaturation of the metal and the monomeric structure of *n*-BuLi and PCHDLi. Rather surprisingly, however, the metalation (Scheme 1b,c) was found not to be accelerated.

As shown in Scheme 2, the length of the C−Li bond of PCHDLi is considered a very important factor for the suppression of the metalation. In the absence of TMEDA, the length of the C−Li bond of PCHDLi is considered too short for the insertion of 1,3-cyclohexadiene, and the reaction with PCHDLi is considered to be very difficult. On the other hand, steric hindrance between

Scheme 2



allylic hydrogens of 1,3-cyclohexadiene and the C−Li of PCHDLi is not considered to be so large. Thus, the abstraction of the allylic hydrogen of 1,3-cyclohexadiene is possible with PCHDLi. Consequently, the addition and hydrogen abstraction become competitive (Scheme 2a).

By the coordination of TMEDA to lithium, the C−Li bond of PCHDLi becomes strongly polarized, and the C−Li bond is considered to be enough long for the insertion of 1,3-cyclohexadiene (Scheme 2b), where the addition becomes much faster than hydrogen abstraction. As a result, the polymerization of 1,3-cyclohexadiene initiated by the *n*-BuLi/TMEDA system attains to the living nature.

Conclusion

The polymerization of 1,3-cyclohexadiene initiated by the *n*-BuLi/TMEDA system exhibits a unique behavior. The polymerization is accelerated by the presence of TMEDA when compared with the polymerization initiated by *n*-BuLi in the absence of TMEDA. On the other hand, metalation of 1,3-cyclohexadiene, leading to chain transfer and termination reactions, is not accelerated in the *n*-BuLi/TMEDA system. This is in clear contrast to the polymerization of acyclic dienes with allylic hydrogens such as 1,3-hexadiene and 2,4-hexadiene initiated by the *n*-BuLi/TMEDA system. The ring structure of 1,3-cyclohexadiene and the length of the C−Li bond of the growing species are considered the most important factors for the living nature of polymerization.

From these results, the development of a new method of suppressing metalation in the anionic polymerization of cyclic dienes can be expected by using alkyllithium/amine complexes.

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(10) Another small peak was always observed in the ^{7}Li NMR spectra. This is not due to *t*-BuOLi which is one of the possible impurities as confirmed by comparison with *t*-BuOLi separately prepared.

(11) Since 1,3-cyclohexadiene did not polymerize when *n*-BuLi was the initiator, *t*-BuLi was used. See Table 5, nos. 1 and 19.

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