Living Anionic Polymerization of 1,3-Cyclohexadiene with the *n*-Butyllithium/*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine System. Copolymerization and Block Copolymerization with Styrene, Butadiene, and Isoprene

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ABSTRACT: The *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine system has been found to polymerize 1,3-cyclohexadiene to produce a "living" polymer having a narrow molecular weight distribution. Ternary block copolymers with narrow molecular weight distribution could be synthesized from 1,3-cyclohexadiene, styrene, and butadiene with very high efficiency. The relative reactivity of 1,3-cyclohexadiene, styrene, and isoprene in the copolymerization was found to be in the order styrene, isoprene, and 1,3-cyclohexadiene. In contrast, the relative reactivity of the propagating species of living poly(1,3-cyclohexadiene) was higher than that of the propagating species of living polystyrene.

Introduction

Synthesis of copolymers and block copolymers with narrow molecular weight distribution and well-defined structure is a subject of fundamental as well as practical importance. In this respect, living polymerizations have been developed for a variety of monomers.[1] In particular, hydrocarbon copolymers having directly connected alicyclic structure derived from cyclic conjugated diene in the main chain is of much interest, since a dramatic improvement of thermal stability, chemical stability, and mechanical strength is expected for such copolymers.

However, examples of living polymerization of cyclic conjugated diene for the synthesis of copolymer and block copolymer with a controlled polymer chain structure have not been reported.[2] For example, low molecular weight random copolymers were obtained in the cationic copolymerizations of 1,3-cyclopentadiene with isobutene and α-methylstyrene.[2a,b] In the copolymerizations of 1,3-cyclohexadiene with butadiene and isoprene using a π-allyl complex of nickel as a catalyst, random copolymers were obtained in low yields.[2c] For copolymerization of 1,3-cyclohexadiene and acrylonitrile in the presence of zinc chloride, alternating copolymers (indicated by ^{1}H NMR) were obtained in low yields.[2d−f] A mixture of homopolymers was obtained in the anionic copolymerization of 1,3-cyclohexadiene and styrene initiated by alkyllithium compounds.[2g,h]

In the previous communication,[3] we reported the first successful example of living anionic polymerization of 1,3-cyclohexadiene with the *n*-butyllithium (*n*-BuLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) system, and we could successfully synthesize a 1,3-cyclohexadiene-styrene binary copolymer with narrow molecular weight distribution and a well-controlled polymer chain length.

In the present paper, we report the syntheses of 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene and 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymers with narrow molecular weight distribution and well-controlled molecular weight. We also describe the investigations of the relative reactivity of 1,3-cyclohexadiene in the copolymerization with styrene and isoprene and relative reactivity of the propagating species of living poly(1,3-cyclohexadiene) and living polystyrene.

Experimental Section

Materials. *n*-Butyllithium (*n*-BuLi, 1.44 M in *n*-hexane) was used without further purification. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA), 1,3-cyclohexadiene, isoprene, and cyclohexane were refluxed over calcium hydride and then distilled under argon atmosphere. Styrene, stirred with neutral aluminum oxide at room temperature, was degassed to remove air under argon atomosphere and then distilled under reduced pressure. Butadiene was used as 30% solution in cyclohexane.

Polymerization. Cyclohexane, *n*-butyllithium (*n*-BuLi), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (the molar ratio of *n*-BuLi/TMEDA, 4/2) were placed in a 5 L stainless steel autoclave equipped with an electromagnetic induction stirrer. The solution was stirred for 10 min at room temperature (~25 °C) under nitrogen atmosphere (about 4 kg/cm^2), then was warmed to 70 °C, and was stirred for another 10 min and cooled to 40 °C. TMEDA was then added to this solution in order to bring the molar ratio of *n*-BuLi/TMEDA to 4/5. Monomer was supplied to this solution in the autoclave, and polymerization was carried out under dry nitrogen atmosphere at 40 °C. After this period of time, dehydrated methanol was added to the polymerization mixture in an equimolar amount 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 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

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termination reactions in the anionic polymerization of 1,3-cyclohexadiene) in the polymerization reaction mixture.

For block copolymerization, homopolymerization of the first monomer was carried out with the *n*-BuLi/TMEDA (4/5) system in cyclohexane. After confirmation of the complete consumption of the first monomer by GC, a portion of the polymerization system was subjected to gel permeation chromatography (GPC), and the second monomer was introduced to the remainder under dry nitrogen atmosphere. Ternary block copolymerization was carried out by a procedure similar to that described above.

For 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.

Measurements. ^{1}H NMR spectra of the polymer were measured for 10 wt % solution in deuterated *o*-dichlorobenzene at 135 °C using a JEOL Type-400 spectrophotometer operating at 400 MHz using added cyclohexane as a reference (1.4 ppm). Gel permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-8082 gel permeation chromatograph equipped with a differential refractometer detector. The eluent was tetrahydrofuran (THF), and flow rate was 1.0 mL·min^{-1}. The columns used were 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 Shimadzu Type 14A gas chromatograph. Ethylbenzene was used as an internal standard substance.

Results and Discussion

Block Copolymerizations of 1,3-Cyclohexadiene with Styrene and Butadiene Initiated by the *n*-BuLi/TMEDA (4/5) System. The successful binary block copolymerization described in the previous paper[3] suggests the possibility of the synthesis of multiblock copolymers with controlled molecular weight. We attempted the synthesis of 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene and 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymers having poly(1,3-cyclohexadiene) sequences by the block copolymerization of 1,3-cyclohexadiene with styrene and butadiene with the *n*-butyllithium (*n*-BuLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (4/5) system.

Synthesis of the 1,3-Cyclohexadiene−Styrene−1,3-Cyclohexadiene Ternary Block Copolymer. As the first stage, the living prepolymer of 1,3-cyclohexadiene was prepared by polymerization with the *n*-BuLi/TMEDA (4/5) system at 100% conversion, where the molar amount of 1,3-cyclohexadiene was 125 times that of the initiator ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125) and the polymerization was carried out under dry nitrogen for 120 min at 40 °C. The number average molecular weight (M_n) and molecular weight distribution (MWD) were 12 400 and M_w/M_n = 1.09, respectively. For the polymerization of the second stage, styrene was added into the above reaction mixture and the polymerization was continued under similar polymerization conditions to that describe above, where the molar amount of styrene was 384 times that of the initiator ([styrene]$_0$/[Li]$_0$ = 384). The conversion of styrene after 120 min was 100% and the number average molecular weight (M_n) of polymer increased from 12 400 to 51 800, retaining a narrow molecular weight distribution (M_w/M_n = 1.09). For the polymerization of the third stage, 1,3-cyclohexadiene was added into the above binary block copolymer solution and the polymerization was continued ([1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125). The conversion of 1,3-cyclohexadiene after 300 min was 96%. The number average molecular weight (M_n) and molecular weight distribution (MWD) of this ternary block copolymer were 64 000 and M_w/M_n = 1.14, respectively.

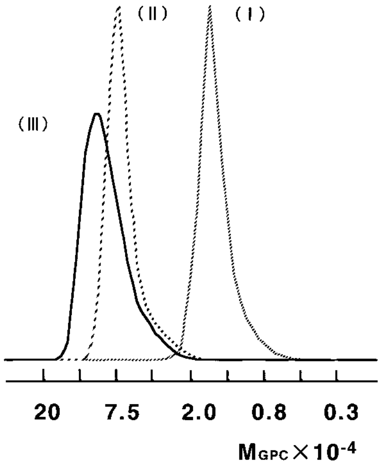

Figure 1. GPC profiles of 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer and of the corresponding prepolymers initiated by the *n*-BuLi/TMEDA (4/5) system. [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125, [styrene]$_0$/[Li]$_0$ = 384, and [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 125, in cyclohexane at 40 °C. Key: (I) Prepolymer of 1,3-cyclohexadiene, M_n = 12 400, M_w/M_n = 1.09, conversion = 100%; (II) 1,3-cyclohexadiene−styrene binary block copolymer, M_n = 51 800, M_w/M_n = 1.09, conversion of styrene = 100%; (III) 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer, M_n = 64 000, M_w/M_n = 1.14, conversion of 1,3-cyclohexadiene = 96%. M_n and M_w/M_n were estimated by GPC calibrated with standard polystyrene.

The obtained 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer was soluble in cyclohexane, tetrahydrofuran (THF), and chloroform. A transparent colorless strong plastic film could be obtained by casting from the cyclohexane solution of this polymer.

Figure 1 shows typical GPC profiles of the ternary block copolymer obtained after the third stage of polymerization and those of the corresponding prepolymers (binary block copolymer and homopolymer). The GPC profile of the binary block copolymer (II) obtained after the second stage of polymerization clearly shifted toward the higher molecular weight region than that of the prepolymer of 1,3-cyclohexadiene (I), retaining the narrow molecular weight distribution. After the third stage of polymerization, the GPC profile of the ternary block copolymer (III) also shifted toward the higher molecular weight region than that of the binary block copolymer (II). Furthermore, neither the peak corresponding to the prepolymer of 1,3-cyclohexadiene nor that corresponding to the 1,3-cyclohexadiene−styrene binary block copolymer was observed after the third stage polymerization. Thus, the polymerization of styrene was initiated from the living end of poly(1,3-cyclohexadiene) with very high efficiency (almost 100%) to produce the 1,3-cyclohexadiene−styrene binary block copolymer, and 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer was obtained in an almost quantitative yield by the polymerization of 1,3-cyclohexadiene initiated from the living end of the 1,3-cyclohexadiene−styrene binary block copolymer. These results confirm the “living polymerization” behavior of

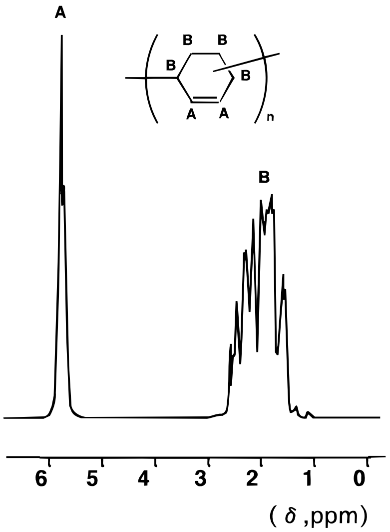

Figure 2. ^{1}H NMR spectrum of poly(1,3-cyclohexadiene) in 10 wt % solution of *o*-dichlorobenzene-d_4 at 135 °C.

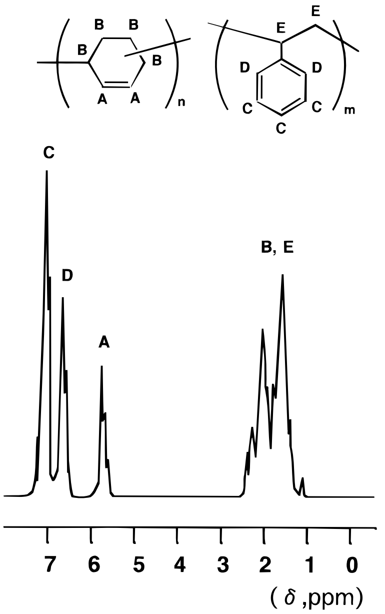

Figure 3. ^{1}H NMR spectrum of 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer in 10 wt % solution of *o*-dichlorobenzene-d_4 at 135 °C.

the polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system.

Figure 2 shows the ^{1}H NMR spectrum of poly(1,3-cyclohexadiene) obtained in the first stage polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system. Peaks A are assigned to the hydrogen atoms bound to carbon atoms of the double bond of the 1,3-cyclohexadiene (CHD) units. Peaks B are assigned to all hydrogen atoms bound to carbon atoms of the single bonds of the CHD units. The poly(1,3-cyclohexadiene) had a structure of the main chain consisting of units formed by 1,2-addition (1,2-CHD units)and 1,4-addition (1,4-CHD units). The ratio of 1,2- and 1,4-units was 53/47 as estimated by 2D-NMR.[4]

Figure 3 shows ^{1}H NMR spectrum of 1,3-cyclohexadiene−styrene-1,3−cyclohexadiene ternary block copolymer obtained in the third stage polymerization. The hydrogen atoms bound to *meta* position and *para* position of the styrene (St) units and those of the *ortho* positions are assigned to peaks C and D, respectively. Peaks E are due to the hydrogen atoms connected with the single bonds of St units. Therefore, the composition of the 1,3-cyclohexadiene−styrene−1,3-cyclohexadiene ternary block copolymer can be estimated by the ratio of the area of peaks A and the area of peaks D, and the observed ratio (CHD block/St block = 38.6/61.4) was in good agreement with the expected value (CHD block/St block = 39.4/60.6).

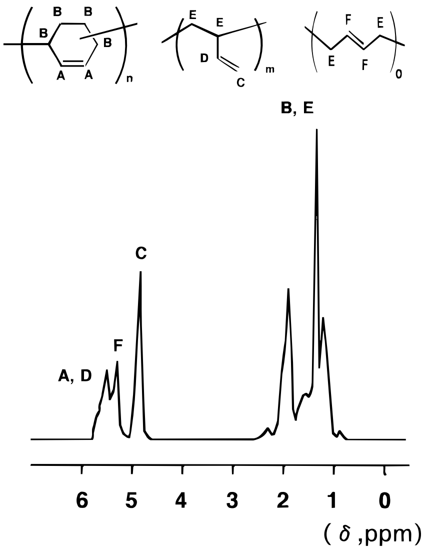

Figure 4. ^{1}H NMR spectrum of 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymer in 10 wt % solution of *o*-dichlorobenzene-d_4 at 135 °C.

Synthesis of the 1,3-Cyclohexadiene−Butadiene−1,3-Cyclohexadiene Ternary Block Copolymer. The living prepolymer of 1,3-cyclohexadiene was prepared by the polymerization with the *n*-BuLi/TMEDA (4/5) system ($[\text{1,3-cyclohexadiene}]_0/[\text{Li}]_0 = 125$, 120 min, 40, 96% conversion, the ratio of 1,2- and 1,4-units being 51/49). Butadiene (Bd) was then added into the above reaction mixture ($[\text{butadiene}]_0/[\text{Li}]_0 = 370$). After 60 min, the conversion of butadiene was 99%. 1,3-Cyclohexadiene was added into the above binary block copolymer solution ($[\text{1,3-cyclohexadiene}]_0/[\text{Li}]_0 = 125$) to continue the reaction. The conversion of 1,3-cyclohexadiene after 300 min was 95%. The number average molecular weight (M_n) and molecular weight distribution (MWD) of this ternary block copolymer were 41 000 and $M_w/M_n = 1.15$, respectively.

The obtained 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymer was soluble in cyclohexane, tetrahydrofuran (THF), and chloroform. A transparent colorless tough elastic film could be obtained by casting from the cyclohexane solution of this polymer.

Figure 4 shows the ^{1}H NMR spectrum of the 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymer. Peaks A and B are due to the hydrogen atoms connected with the double bond and single bonds of the CHD units, respectively. The hydrogen atoms bound to the methylene carbon ($-\text{C}{=}\text{CH}_2$) and methyne carbon ($-\text{CH}{=}\text{C}$) of the double bond of the 1,2-Bd units are assigned to peaks C and D, respectively. The peaks *E* and *F* are due to the hydrogen atoms connected with the carbon atoms of the single bonds of the 1,2-Bd and 1,4-Bd units and the double bond of the 1,4-Bd units ($-\text{CH}{=}\text{CH}-$), respectively.

Therefore, the composition of the 1,3-cyclohexadiene−butadiene−1,3-cyclohexadiene ternary block copolymer

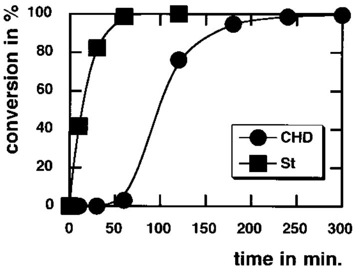

Figure 5. Time–conversion curve for the copolymerization of 1,3-cyclohexadiene and styrene with the *n*-BuLi/TMEDA (4/5) system in cyclohexane at 40 °C. $[1,3\text{-cyclohexadiene}]_0/[\text{styrene}]_0/[\text{Li}]_0 = 249/192/1$; concentration of each monomer was 20 wt %.

can be estimated by the ratio of the sum of areas of peaks A + D + F, the area of peaks C, and the sum of areas of peaks B + E. The molar contents of CHD units (α), 1,2-Bd units (β) and 1,4-Bd units (γ) satisfy the following formulas: $2\alpha + \beta + 2\gamma =$ the sum of areas of peaks A + D + F, $2\beta =$ the area of peaks C, and $6\alpha + 3\beta + 4\gamma =$ the sum of areas of peaks B + E. The molar ratio of CHD units to Bd units was determined according to the above formulas by the estimated based on the area ratio of peaks A + D + F, C, and B + E.

In fact, a good agreement was obtained between the observed ratio (CHD block/Bd block = 39.6/60.4) and the expected value (CHD block/Bd block = 40.3/59.7).

Relative Reactivity of 1,3-Cyclohexadiene in the Copolymerization with Styrene and Isoprene. The successful ternary block copolymerizations described above suggested the possibility of synthesis of random copolymer having a narrow molecular weight distribution (MWD) with a well-controlled chain length. We attempted the synthesis of 1,3-cyclohexadiene/styrene, 1,3-cyclohexadiene/isoprene, and 1,3-cyclohexadiene/styrene/isoprene random copolymers with the *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (4/5) system.

Copolymerization of 1,3-Cyclohexadiene and Styrene. Polymerization of a mixture of 1,3-cyclohexadiene and styrene with the *n*-BuLi/TMEDA (4/5) system as initiator was carried out under dry nitrogen atmosphere for 300 min at 40 °C $[1,3\text{-cyclohexadiene}]_0/[\text{styrene}]_0/[\text{Li}]_0 = 249/192/1$; $[\text{Li}]_0 = 4.85$ mmol/L).

Figure 5 shows typical time–conversion curves for the copolymerization of 1,3-cyclohexadiene and styrene. In the initial stage of polymerization, styrene was polymerized predominantly. When most of styrene was consumed, the polymerization of 1,3-cyclohexadiene started. This polymerization behavior suggests that the polymerization of 1,3-cyclohexadiene was initiated by the living ends of polystyrene. The conversions of styrene and 1,3-cyclohexadiene were 100% after 60 min and 100% after 300 min, respectively. As a result, the copolymer obtained from 1,3-cyclohexadiene and styrene ($M_n = 34\,100$, $M_w/M_n = 1.15$) is considered to have a structure close to a binary block copolymer, and the random copolymer was not obtained in this copolymerization. It should be noted that the GPC peak is unimodal and the molecular weight distribution is very narrow, indicating that the product is not a mixture of homopolymers.

Thus, the relative reactivity of styrene was found much higher than that of 1,3-cyclohexadiene in the copolymerization initiated with the *n*-BuLi/TMEDA (4/5) system.

Copolymerization of 1,3-Cyclohexadiene and Isoprene. In the polymerization of a mixture of 1,3-cyclohexadiene and isoprene by the *n*-BuLi/TMEDA (4/5) system ($[1,3\text{-cyclohexadiene}]_0/[\text{isoprene}]_0/[\text{Li}]_0 = 249/293/1$, 360 min, 40 °C), selective polymerization of isoprene was observed in the initial stage of polymerization. The polymerization of 1,3-cyclohexadiene started when most of isoprene was consumed. The conversions of isoprene and 1,3-cyclohexadiene were 100% after 120 min and 93% after 360 min, respectively. As a result, the copolymer obtained from 1,3-cyclohexadiene and isoprene (unimodal GPC peak, $M_n = 42\,200$, $M_w/M_n = 1.39$) is considered to have a structure close to a binary block copolymer. Thus, isoprene was found to be more reactive than 1,3-cyclohexadiene in the copolymerization with the *n*-BuLi/TMEDA (4/5) system.

Copolymerization of 1,3-Cyclohexadiene, Styrene, and Isoprene. In the polymerization of a mixture of 1,3-cyclohexadiene, styrene, and isoprene with the *n*-BuLi/TMEDA (4/5) system ($[1,3\text{-cyclohexadiene}]_0/[\text{styrene}]_0/[\text{isoprene}]_0/[\text{Li}]_0 = 167/127/193/1$, 480 min, 40 °C), styrene was polymerized selectively in the initial stage of polymerization. When most of the styrene was consumed, polymerization of isoprene followed. The polymerization of 1,3-cyclohexadiene started in the final stage of polymerization. The conversions of styrene, isoprene, and 1,3-cyclohexadiene were 100% after 60 min, 100% after 240 min, and 88% after 480 min, respectively. Thus, the copolymer obtained from 1,3-cyclohexadiene, styrene, and isoprene (unimodal GPC peak, $M_n = 35\,300$, $M_w/M_n = 1.73$) is considered to have a structure close to a tenary block copolymer.

Thus, the relative reactivity of 1,3-cyclohexadiene, styrene, and isoprene in the copolymerization with the *n*-BuLi/TMEDA (4/5) system was found to be in the order styrene, isoprene, and 1,3-cyclohexadiene.

Copolymerization of 1,3-Cyclohexadiene and Isoprene Initiated with the Living Prepolymer of 1,3-Cyclohexadiene. To confirm the selective reaction between monomer with a higher reactivity and the living polymer ends, the copolymerization of 1,3-cyclohexadiene and isoprene initiated with the living prepolymer of 1,3-cyclohexadiene was examined.

First, the living prepolymer of 1,3-cyclohexadiene was prepared by the polymerization of 1,3-cyclohexadiene with the *n*-BuLi/TMEDA (4/5) system ($[1,3\text{-cyclohexadiene}]_0/[\text{Li}]_0 = 249$, 40 °C. After 20 min, the conversion of 1,3-cyclohexadiene was 46%. Subsequently, isoprene was added into the above reaction mixture (living prepolymer of 1,3-cyclohexadiene and 1,3-cyclohexadiene monomer) and the polymerization was further continued for 360 min. When isoprene was added, the polymerization of 1,3-cyclohexadiene was interrupted and isoprene was polymerized predominantly. Upon consumption of nearly all of the isoprene, the polymerization of 1,3-cyclohexadiene started again. The conversions of isoprene and 1,3-cyclohexadiene were 100% after 120 min and 97% after 380 min, respectively. As a result, the copolymer obtained here from 1,3-cyclohexadiene and isoprene (unimodal GPC peak, $M_n = 45\,300$, $M_w/M_n = 1.52$) is considered to have a structure close to a tenary block copolymer.

Thus, isoprene has much higher relative reactivity than 1,3-cyclohexadiene in the copolymerization initiated with the living ends of poly(1,3-cyclohexadiene)/TMEDA (4/5) system.

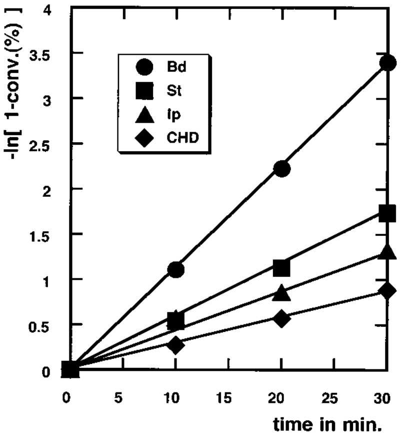

Figure 6. First-order plots for the homopolymerization of 1,3-cyclohexadiene, styrene, butadiene, and isoprene with the *n*-BuLi/TMEDA (4/5) system in cyclohexane at 40 °C. [1,3-cyclohexadiene]$_0$/[Li]$_0$ = 249, [styrene]$_0$/[Li]$_0$ = 192, [butadiene]$_0$/[Li]$_0$ = 370, and [isoprene]$_0$/[Li]$_0$ = 293; concentration of each monomer was 10 wt %.

Rate of Homopolymerization. Since the relative reactivities of styrene and isoprene are much higher than that of 1,3-cyclohexadiene in the copolymerization initiated with the alkyllithium/TMEDA (4/5) system, we expected that the rate of homopolymerization of 1,3-cyclohexadiene is much lower than that of styrene and isoprene. Then, we studied the kinetics of the homopolymerizations of 1,3-cyclohexadiene (1,3-CHD), styrene (St), butadiene (Bd), and isoprene (Ip), respectively.

The polymerization was carried out in 10 wt % solution in cyclohexane under dry nitrogen atmosphere at 40 with the *n*-BuLi/TMEDA (4/5) system, where the amounts of 1,3-cyclohexadiene, styrene, butadiene, and isoprene were 249, 192, 370, and 293 times that of the initiator ([Li]$_0$ = 6.06 mmol/L), respectively.

The results are shown in Figure 6. First-order kinetics with respect to monomer concentration were observed in the homopolymerization of 1,3-cyclohexadiene, styrene, butadiene, and isoprene initiated with the *n*-BuLi/TMEDA (4/5) system. As seen in Figure 6, the rates of homopolymerization of 1,3-cyclohexadiene, styrene, butadiene, and isoprene were found to be in the order butadiene, styrene, isoprene, and 1,3-cyclohexadiene. This order was the same as the relative reactivity of monomers as found in the studies of copolymerization. However, the difference in the rates of homopolymerization of 1,3-cyclohexadiene, styrene, and isoprene was far smaller than the difference expected from the relative reactivities of these monomers in the copolymerization described above.

Relative Reactivity of the Propagating Species. Since the above observations are considered due to different orders of relative reactivity of monomers and that of the propagating species, the reactivities of the propagating species of poly(1,3-cyclohexadiene) and of polystyrene were compared, by taking advantage of living nature of the polymerization of 1,3-cyclohexadiene.

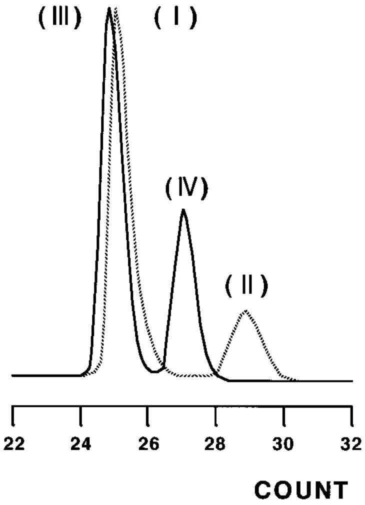

Figure 7. GPC profiles of the polymerization of styrene initiated by the mixture of living poly(1,3-cyclohexadiene) and living polystyrene in cyclohexane at 40 °C. [styrene]$_0$/[living poly(1,3-cyclohexadiene)]$_0$/[living polystyrene]$_0$ = 24/1/1. Broken line: prepolymer mixture of the living poly(1,3-cyclohexadiene) [(I), M_n = 11 950, M_w/M_n = 1.06] and living polystyrene [(II), M_n = 990, M_w/M_n = 1.06]. Solid line: the reaction products of the living polymer mixture and styrene [(III) M_n = 14,490, M_w/M_n = 1.04; (IV) M_n = 3,460, M_w/M_n = 1.05].

First, the living poly(1,3-cyclohexadiene) [(I), M_n = 11 950, M_w/M_n = 1.06] and the living polystyrene [(II), M_n = 990, M_w/M_n = 1.06] were synthesized by the polymerization of 1,3-cyclohexadiene and styrene with the *n*-BuLi/TMEDA (4/5) system, respectively. Then, an equimolar cyclohexane solution of the living poly(1,3-cyclohexadiene) (0.15 mmol) and the living polystyrene (0.15 mmol) was prepared by mixing these living polymer solutions, and styrene (7.26 mmol) was added into this solution, where the molar amount of styrene was 24 times that of the propagating species. The polymerization was carried out under dry nitrogen atmosphere for 60 min at 40 °C.

The result is shown in Figure 7. The broken line represents the GPC profile of prepolymer mixture of the living poly(1,3-cyclohexadiene) (I) and living polystyrene (II). The solid line represents the GPC profile of the reaction products of the living polymer mixture and styrene. In this GPC chromatogram, two peaks are observed [(III) M_n = 14 490, M_w/M_n = 1.04, and (IV) M_n = 3460, M_w/M_n = 1.05]. Peak III is regarded as the reaction product of the living poly(1,3-cyclohexadiene) (I) and styrene, and peak IV, as the reaction product of the living polystyrene (II) and styrene. Neither the peak corresponding to the living poly(1,3-cyclohexadiene) (I) nor that corresponding to the living polystyrene (II) is observed in the GPC profile of the reaction products after adding styrene. Thus, the living ends of poly(1,3-cyclohexadiene) and polystyrene are considered to have similarly reacted with styrene monomer, respectively. The results suggest that reactivities of the propagating species of living poly(1,3-cyclohexadiene) and living polystyrene are almost equal to styrene because the extents of the increase in number average molecular weight I → III and II → IV are almost the same (about 2500).

Next, the polymerization of 1,3-cyclohexadiene (9.90 mmol) initiated with a mixture of the living poly(1,3-cyclohexadiene) [(V), M_n = 7790, M_w/M_n = 1.05, 0.30 mmol] and the living polystyrene [(VI), M_n = 980, M_w/M_n = 1.06, 0.30 mmol] was examined (60 min, 40 °C). The result is shown in Figure 8. The GPC profile of mixture of the living poly(1,3-cyclohexadiene) (V) and living polystyrene (VI) is represented by the broken line. In the GPC profile of the reaction products of the living polymer mixture and 1,3-cyclohexadiene (solid line), two

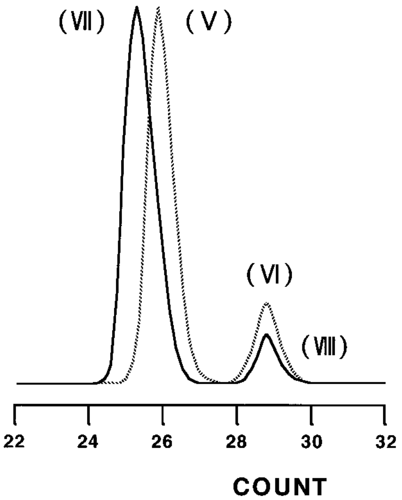

Figure 8. GPC profiles of the polymerization of 1,3-cyclohexadiene initiated by the mixture of living poly(1,3-cyclohexadiene) and living polystyrene in cyclohexane at 40 °C. [1,3-cyclohexadiene]$_0$/[living poly(1,3-cyclohexadiene)]$_0$/[living polystyrene]$_0$ = 16.5/1/1. Broken line: prepolymer mixture of the living poly(1,3-cyclohexadiene) [(I), $M_n = 7790$, $M_w/M_n = 1.05$] and living polystyrene [(II), $M_n = 980$, $M_w/M_n = 1.06$]. Solid line: the reaction products of the living polymer mixture and 1,3-cyclohexadiene [(III) $M_n = 10\ 600$, $M_w/M_n = 1.06$; (IV) $M_n = 1{,}000$, $M_w/M_n = 1.04$].

peaks are observed [(VII) $M_n = 10\ 600$, $M_w/M_n = 1.06$; (VIII) $M_n = 1000$, $M_w/M_n = 1.04$].

The reaction product of the living poly(1,3-cyclohexadiene) and 1,3-cyclohexadiene is regarded as peak VII, since there is no peak corresponding to the living poly(1,3-cyclohexadiene) (V). In contrast, peak VI hardly moved, since peak VI and peak VIII correspond to the almost same number average molecular weight (about 1000). These results suggest that the living polystyrene hardly reacted with 1,3-cyclohexadiene monomer.

Surprisingly, the propagating species of living poly(1,3-cyclohexadiene) has a much higher reactivity than the propagating species of living polystyrene. Since the propagating species of living poly (1,3-cyclohexadiene) has a very high reactivity to 1,3-cyclohexadiene monomer, the difference in the rates of homopolymerizations of 1,3-cyclohexadiene, styrene, and isoprene is far smaller than the difference expected from the relative reactivities of those monomers in the copolymerization. To our knowledge, this is the first example of studies on the relative reactivity of different propagating species using the mixture of living polymers in the living anionic polymerization, not only for 1,3-cyclohexadiene but also for styrene, butadiene, and isoprene.

Conclusion

The system of alkyllithium (RLi)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) is an excellent initiator for the living anionic polymerization of 1,3-cyclohexadiene. This initiator system makes it possible to obtain binary, ternary, or multiple block copolymers from 1,3-cyclohexadiene, styrene, butadiene, and isoprene. The relative monomer reactivity of 1,3-cyclohexadiene was lower than that of styrene and isoprene in the living anionic copolymerization with the *n*-BuLi/TMEDA (4/5) system. In contrast, the relative reactivity of the propagating species of living poly(1,3-cyclohexadiene)/TMEDA (4/5) system to 1,3-cyclohexadiene monomer was much higher than that of the propagating species of living polystyrene.

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