

Anionic Polymerization of 1,3-Cyclohexadiene: Addition of Poly(1,3-cyclohexadienyl)lithium to Fullerene-C₆₀

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Received 25 June 2009; accepted 11 August 2009

DOI 10.1002/app.31283

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The addition of poly(1,3-cyclohexadiene) (PCHD) carbanion to fullerene-C₆₀ (C₆₀) was examined using poly(1,3-cyclohexadienyl)lithium (PCHDLi), PCHDLi/1,4-diazabicyclo[2,2,2]octane (DABCO), and PCHDLi/*N,N,N',N'*-tetramethylethylenediamine (TMEDA). The reactivity of PCHD carbanions was in the order of PCHDLi > PCHDLi/DABCO > PCHDLi/TMEDA, regardless of the polymer main chain structure. PCHDLi, PCHDLi/DABCO, and PCHDLi/TMEDA in toluene formed σ -structures, σ - and π -structures, and π -structures, respectively. The degree of localization on the terminal

carbanion was a main factor for control of this addition reaction. In addition, all 1,2-cyclohexadiene (1,2-CHD) unit sequences contributed to preventing the addition reaction. That is, large steric hindrance of the polymer main chain was another important factor to control the addition reaction. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2103–2109, 2010

Key words: anionic polymerization; 1,3-cyclohexadiene; living polymerization; poly(1,3-cyclohexadienyl)lithium; fullerenes

INTRODUCTION

The synthesis of fullerene-C₆₀ (C₆₀) end-capped polymers (C₆₀-polymers) is one of the most interesting subjects in basic polymer research and is a practical method to obtain new functional materials for a wide range of applications. For example, C₆₀-polystyrene (C₆₀-PSt),^{1–9} C₆₀-polyisoprene (C₆₀-PIp),¹ C₆₀-St-butadiene random copolymer (C₆₀-PSt/Bd),¹⁰ C₆₀-poly(ethylene oxide) (C₆₀-PEO),¹¹ C₆₀-PIp-PSt block copolymer (C₆₀-PIp-PSt),^{4,12} C₆₀-PSt-poly(1,3-cyclohexadiene) (PCHD) block copolymer (C₆₀-PSt-PCHD),¹³ C₆₀-PCHD,^{14,15} C₆₀-poly(*N*-vinylcarbazole) (C₆₀-PNVC),¹⁶ and C₆₀-poly(4-diphenylaminostyrene) (C₆₀-PDAS)¹⁷ have been synthesized by the addition of polymer carbanions to C₆₀. Among the innumerable combinations of C₆₀ and polymers, C₆₀-PCHD is an attractive precursor for the preparation of a new class of potentially high-performance polymers by the chemical modification of a residual double bond in the PCHD arm because of its thermal and chemical stability and its electrical and optoelectronic properties.

In the previous articles,^{18–37} we reported the first successful example of the (living) anionic polymerization of 1,3-cyclohexadiene (1,3-CHD), a monomer

of PCHD. Subsequently, a well-defined C₆₀-PCHD having a maximum of four arms was synthesized by the addition of poly(1,3-cyclohexadienyl)lithium (PCHDLi) to C₆₀ (Scheme 1).^{14,15} This addition reaction progressed through step-by-step reactions, and it seemed to be strongly affected by the reactivity and structure of PCHDLi.⁴ However, the main factor controlling this addition reaction was not clear until now.

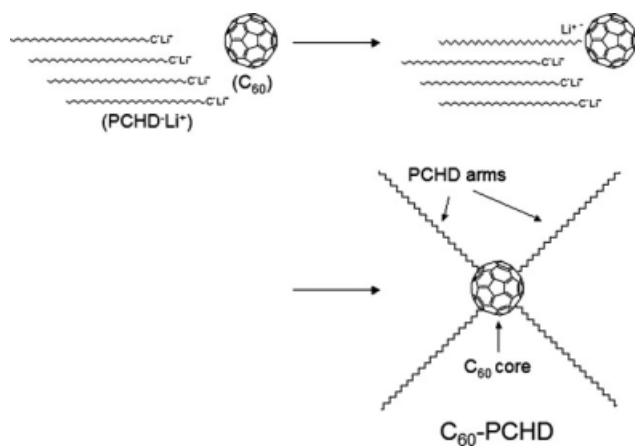
We report the mechanism of the addition reaction of PCHD carbanions and C₆₀, including a detailed description of the influence of the polymer chain-end and main chain structures on the reactivity.

EXPERIMENTAL

Materials

Cyclohexane (99.5%), toluene (99.8%), 1,3-CHD (97%), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, >99.5%) were refluxed over calcium hydride (CaH₂), and then distilled under dry argon. 1,4-diazabicyclo[2,2,2]octane (DABCO, 98%) was dried under reduced pressure. The C₆₀ (99.5%) was washed with tetrahydrofuran (THF) (C₆₀/THF = 0.10 g/200 mL) and dried under reduced pressure at room temperature (ca. 25°C) for 48 h. All other reagents were purchased from Aldrich and were used as received unless otherwise stated.

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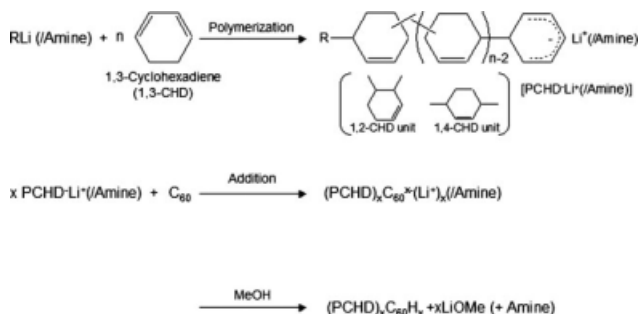
Scheme 1 Mechanism of the addition reaction of PCHDLi to C₆₀.

Preparation of PCHDLi

A well-dried 50-mL Schlenk tube was purged with dry argon, and a solvent (cyclohexane or toluene; 10 mL) and alkyllithium [*n*-butyllithium (*n*-BuLi; 1.60 mol/L in *n*-hexane), *sec*-butyllithium (*s*-BuLi; 1.40 mol/L in cyclohexane), or *tert*-butyllithium (*t*-BuLi; 1.70 mol/L in *n*-pentane)] were injected at room temperature (ca. 25°C) using syringes. If necessary, amine (DABCO or TMEDA) was then added to the solution under dry argon and the mixture was stirred for 10 min. 1,3-CHD (1.00 g; 12.5 mmol) was then supplied to this solution with a syringe ([1,3-CHD]₀/[Li]₀ = 24.0), and the reaction mixture was magnetically stirred under dry argon at room temperature for 3 hr, yielding PCHDLi (/amine) in nearly quantitative yield. The molar ratio of 1,2-addition (1,2-CHD)/1,4-addition (1,4-CHD) units was estimated by ¹H nuclear magnetic resonance (NMR) spectroscopy.²³

Addition reaction of PCHDLi (/amine)

C₆₀ (0.108 g; 0.150 mmol) was placed in a well-dried 50 mL Schlenk tube under dry argon. Toluene (35.0



Scheme 2 Addition reaction of PCHDLi (/amine) with 1,2-CHD and/or 1,4-CHD units to C₆₀.

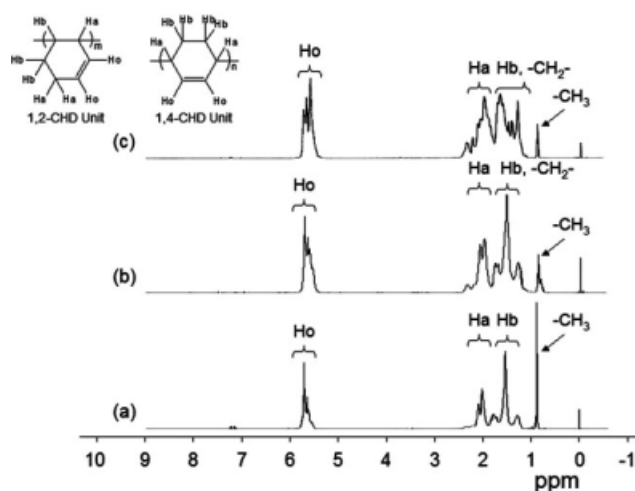


Figure 1 ¹H NMR spectra of poly(1,3-cyclohexadiene) obtained with (a) *t*-BuLi, (b) the *s*-BuLi/DABCO (1.00/1.25) system, and (c) the *n*-BuLi/TMEDA (1.00/1.25) system in a 5.0 wt % solution of CDCl₃ at 50°C. Ho : olefinic signals; Ha, Hb : aliphatic signals.

mL) was injected at room temperature (ca. 25°C) using a syringe, and the mixture was stirred for 30 min. A solution (cyclohexane or toluene) of PCHDLi (0.450 mmol) (/amine) was then added to this solution with a syringe, and the reaction mixture was magnetically stirred under dry argon at room temperature for 24 hr. After the addition reaction, dry methanol was injected to the reaction mixture in an equimolar amount to the amount of lithium atoms present in the reaction mixture to terminate the reaction. The reaction mixture was then poured into a large volume of ethanol (EtOH) to precipitate the product, which was then separated by filtration. The product was dried under reduced pressure at room temperature for 24 hr, resulting in a (light) brown powdery compound in nearly quantitative yield.

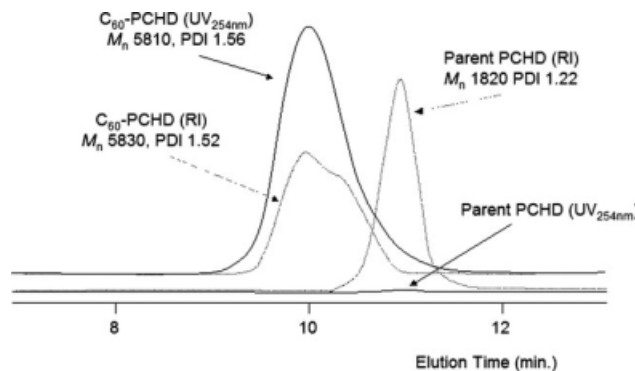


Figure 2 GPC traces of parent PCHD and C₆₀-PCHD in THF at 40°C (no. 1 in Table I). The ratio of 1,2-/1,4-CHD units = 0/100. Sample/THF = 5.00 mg/5.00 mL.

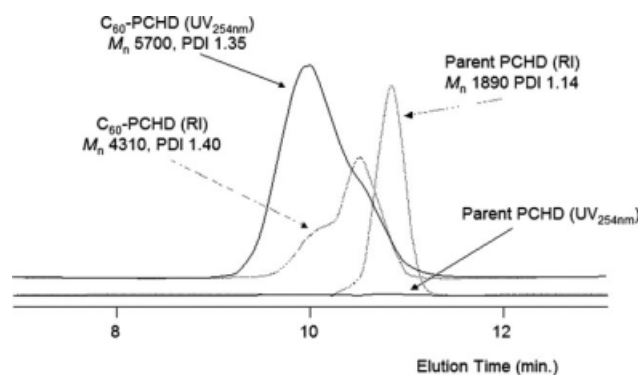


Figure 3 GPC traces of parent PCHD and C₆₀-PCHD in THF at 40°C (no. 2 in Table I). The ratio of 1,2-/1,4-CHD units = 6/94. Sample/THF = 5.00 mg/5.00 mL.

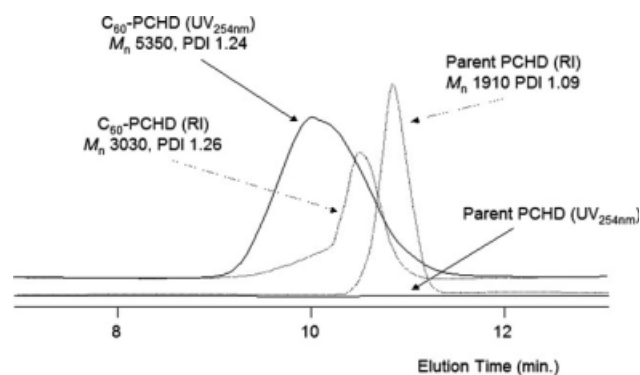


Figure 4 GPC traces of parent PCHD and C₆₀-PCHD in THF at 40°C (no. 3 in Table I). The ratio of 1,2-/1,4-CHD units = 59/41. Sample/THF = 5.00 mg/5.00 mL.

Measurements

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI, M_w/M_n) were determined using gel permeation chromatography (GPC) with a differential refractive index (RI) detector (Shimadzu RID-6A), a UV detector (Shimadzu SPD-6A), and a Shimadzu Shim-pack GPC-80M column (column length: 300 mm; column diameter: 8 mm; effective molecular weight range of 100–4,000,000) at 40°C. THF was used as the eluent with a flow rate of 1.0 mL/min. A molecular weight calibration curve was obtained using PSt standards. ¹H NMR spectra of the polymers were obtained in deuterated chloroform (CDCl₃) at 500 MHz using a Jeol ECA 500 spectrometer.

RESULTS AND DISCUSSION

Addition of PCHD carbanions to C₆₀

We previously reported the synthesis of a well-defined C₆₀-PCHD with a maximum of four arms (Scheme 1).¹⁴ On the basis of this information, three types of C₆₀-PCHD were synthesized by the addition of PCHDLi (/amine) to C₆₀ (Scheme 2).

To prepare PCHDLi (/amine), the anionic polymerization of 1,3-CHD was initiated using *t*-BuLi [or the *s*-BuLi/DABCO (1.00/1.25) or *n*-BuLi/TMEDA (1.00/1.25) systems] in cyclohexane under dry argon at room temperature for 3 hr. The molar ratios of 1,2-CHD/1,4-CHD units in PCHDLi estimated by ¹H NMR²³ were 0/100 (*t*-BuLi), 6/94 [the *s*-BuLi/DABCO (1.00/1.25) system], and 59/41 [the *n*-BuLi/TMEDA (1.00/1.25) system]. Typical ¹H NMR spectra obtained are shown in Figure 1.

Subsequently, the addition of PCHD carbanions (PCHDLi, PCHDLi/DABCO, or PCHDLi/TMEDA) to C₆₀ was performed in toluene under dry argon at room temperature for 24 hr. A (light) brown powdery compound was obtained as the addition reaction product in nearly quantitative yield.

PCHD produces almost no absorption in the region greater than 225 nm and has good solubility in THF. In contrast, C₆₀ has strong absorption peaks near 260 and 330 nm and is insoluble in THF. Therefore, C₆₀-PCHD obtained by the addition of the PCHD carbanion to C₆₀ has strong absorption in the region greater than 225 nm and is readily soluble in THF. By using this characteristic of C₆₀-PCHD, the grafting density (i.e., approximation of the number of PCHD arm molecules on C₆₀) of PCHD arms onto

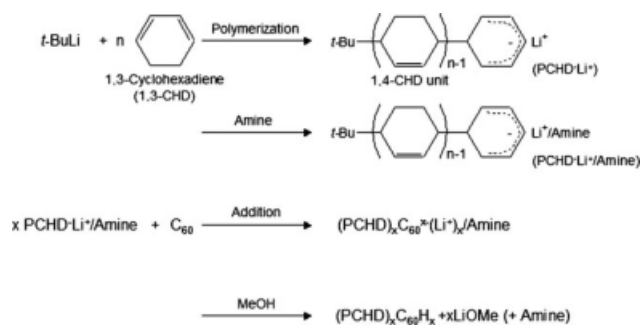
TABLE I
Addition of PCHDLi to C₆₀

No.	Initiator system (molar ratio)	C ₆₀ /PCHDLi (molar ratio)	Parent PCHD ^a (PCHD arm)			Reaction products ^b (C ₆₀ -CHD)		
			M_n (RI)	PDI	1,2-/1,4-CHD units (molar ratio) ¹³	M_n (UV ₂₅₄ nm/RI)	PDI (UV ₂₅₄ nm/RI)	Grafting density (D) ^c
1	<i>t</i> -BuLi	1/3	1820	1.22	0/100	5810/5830	1.56/1.52	3.19
2	<i>s</i> -BuLi/DABCO (1.00/1.25)	1/3	1890	1.14	6/94	5700/4310	1.35/1.40	3.02
3	<i>n</i> -BuLi/TMEDA (1.00/1.25)	1/3	1910	1.09	59/41	5350/3030	1.24/1.26	2.80

^a The preparation of PCHDLi was conducted in cyclohexane under dry argon at room temperature for 3 hr. [1,3-CHD]₀/[Li]₀ = 24.0, 1,3-CHD/solvent = 1.00/10.0 (g/mL).

^b The addition of PCHDLi to C₆₀ was conducted in toluene under dry argon at room temperature for 24 hr.

^c $D = M_n$ (UV₂₅₄ nm) of reaction products/ M_n (RI) of parent PCHD.



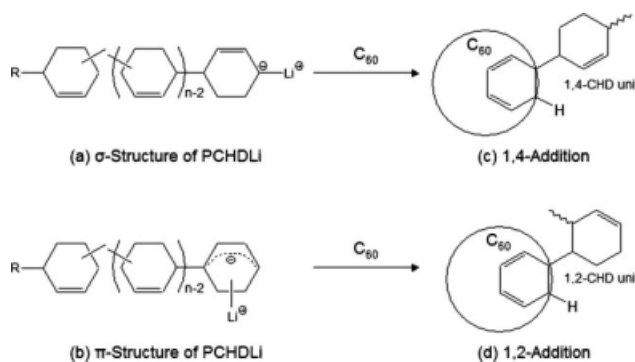
Scheme 3 Addition reaction of PCHDLi (/amine) composed of all 1,4-CHD units to C_{60} .

C_{60} can be estimated by the following procedure.¹⁴ First, the parent PCHD and addition reaction products are dissolved in THF. The M_n of each THF solution is then measured using GPC (with THF as the eluent) with RI and UV detectors set at 254 nm, a region where PCHD is no longer detected and only C_{60} -PCHD absorbs. Typical GPC chromatograms of the parent PCHD and C_{60} -PCHD are shown in Figures 2–4.

From the chromatograms obtained, the grafting density (D) of PCHD arms onto C_{60} is determined using the following formula:

$$D = M_n(\text{UV}_{254 \text{ nm}}) \text{ of addition reaction products} / M_n(\text{RI}) \text{ of parent PCHD (i.e., PCHD arms)}$$

The results obtained are summarized in Table I. D for Nos. 1, 2, and 3 was 3.19, 3.02, and 2.80, respectively, which suggests that the reactivity of PCHD carbanions is decreased by the addition of amine and/or the increase of the molar ratio of 1,2-CHD units.^{14,15} $M_n(\text{UV}_{254 \text{ nm}})$ and $M_n(\text{RI})$ were almost the same value, and the molar ratio of C_{60} /PCHDLi was 1/3, which implies that all the reaction products in no.1 are C_{60} -PCHD. However, the reaction products of nos. 2 and 3 seem to be C_{60} -PCHD containing free PCHD molecules. The results suggest that PCHD carbanions in PCHDLi, PCHDLi/DABCO, and PCHDLi/TMEDA have different reactivity because of differences in the polymer chain-end and/or main chain structure.



Scheme 4 Addition of the σ - and π -structures of PCHDLi to C_{60} .

Effects of polymer chain-end

To examine only the effects of the polymer chain-end, PCHDLi consisting entirely of 1,4-CHD units was prepared by the anionic polymerization of 1,3-CHD with $t\text{-BuLi}$ in cyclohexane, and then amine (DABCO or TMEDA) was added to prepare the PCHDLi/amine (Scheme 3). The PCHD carbanions obtained had the same polymer main chain structure and different polymer chain-end structure. Subsequently, PCHDLi/DABCO and PCHDLi/TMEDA were added to C_{60} in toluene under dry argon at room temperature for 24 hr. A (light) brown powdery compound was produced by the addition reaction in nearly quantitative yield. The results obtained are presented in Table II.

The D for nos. 1, 4, and 5 in Table II were 3.19, 3.04, and 2.84, respectively, which indicates the reactivity of PCHD carbanions is in the order of PCHDLi > PCHDLi/DABCO > PCHDLi/TMEDA. In addition, the D of nos. 2 (1,2-/1,4-CHD units = 6/94) and 4 (1,2-/1,4-CHD units = 0/100) and nos. 3 (1,2-/1,4-CHD units = 59/41) and 5 (1,2-/1,4-CHD units = 0/100) were almost the same, regardless of the polymer main chain structure. Therefore, the polymer chain-end structure of the PCHD carbanion seems to be a main factor in controlling the addition reaction of PCHD carbanions to C_{60} .

TABLE II
Effects of Polymer Chain-End

No.	Initiator	Additive (PCHDLi/additive)	Parent PCHD ^a (PCHD arm)			Reaction products ^b (C_{60} -CHD)		
			M_n (RI)	PDI	1,2-/1,4-CHD units (molar ratio) ¹³	M_n (UV _{254 nm} /RI)	PDI (UV _{254 nm} /RI)	Grafting density (D) ^c
1	$t\text{-BuLi}$		1820	1.22	0/100	5810/5830	1.56/1.52	3.19
4	$t\text{-BuLi}$	DABCO (1.00/1.25)	1850	1.20	0/100	5620/4450	1.40/1.32	3.04
5	$t\text{-BuLi}$	TMEDA (1.00/1.25)	1800	1.24	0/100	5110/3180	1.39/1.37	2.84

^a The preparation of PCHDLi was conducted in cyclohexane under dry argon at room temperature for 3 hr. $[1,3\text{-CHD}]_0/[Li]_0 = 24.0$, 1,3-CHD/solvent = 1.00/10.0 (g/mL). C_{60} /PCHDLi = 1/3.

^b The addition of PCHDLi to C_{60} was conducted in toluene under dry argon at room temperature for 24 hr.

^c $D = M_n(\text{UV}_{254 \text{ nm}})$ of reaction products/ $M_n(\text{RI})$ of parent PCHD.

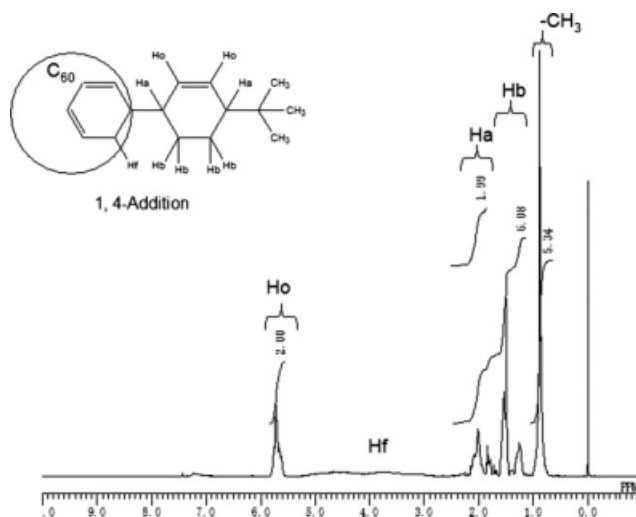


Figure 5 ¹H NMR spectrum of the grafting reaction product of the CHDLi ([1,3-CHD]₀/[*t*-BuLi]₀ = 1.00, C₆₀/CHDLi = 1/6) to C₆₀ in a 5.0 wt % solution of CDCl₃ at 50°C.

We previously reported that the structure of the PCHD carbanion can be predicted from the polymer chain structure, that is, we proposed the existence of a covalent σ -structure [Scheme 4(a)] and an ionic π -structure [Scheme 4(b)] as PCHD carbanions in PCHDLi from the analogous poly(butadienyl)-lithium.^{20,29} The σ - and π -forms of PCHDLi are considered to result in 1,4-addition (1,4-CHD unit) [Scheme 4(c)] and 1,2-addition (1,2-CHD unit) [Scheme 4(d)], respectively. Therefore, it was expected that the structure of the covalent bond between C₆₀ and a CHD unit at the polymer chain-end would depend on the structure of PCHD carbanion.

To examine the structure of the covalent bond between C₆₀ and a CHD unit, the additions of 1,3-

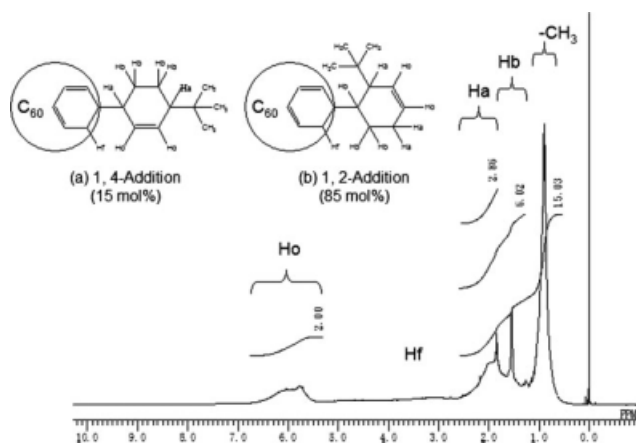


Figure 6 ¹H NMR spectrum of the grafting reaction product of the CHDLi/DABCO system (*s*-BuLi/DABCO = 1.00/1.25, [1,3-CHD]₀/[*s*-BuLi]₀ = 1.00, C₆₀/CHDLi = 1/6) to C₆₀ in a 5.0 wt % solution of CDCl₃ at 50°C.

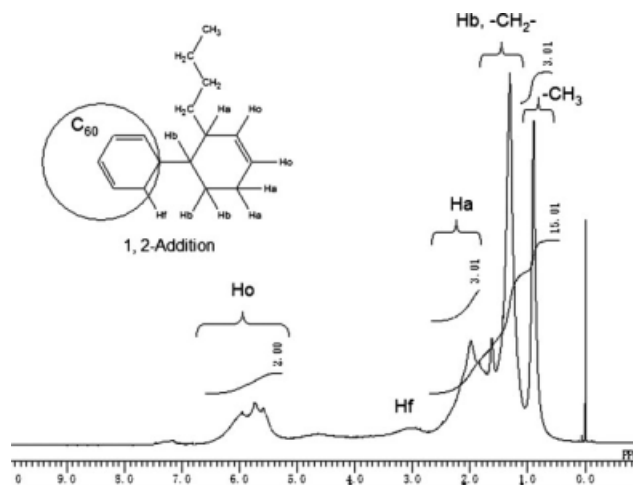
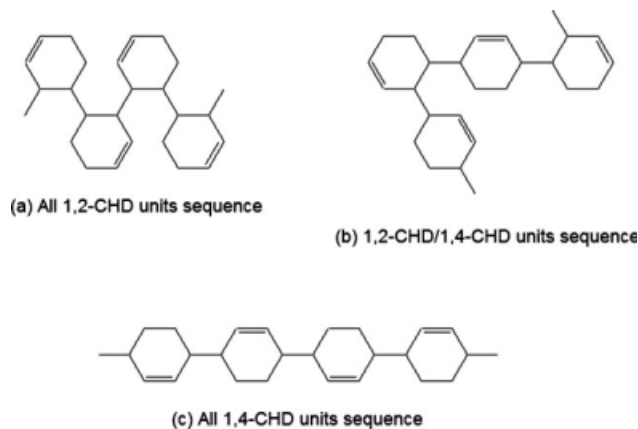


Figure 7 ¹H NMR spectrum of the grafting reaction product of the CHDLi/TMEDA system (*n*-BuLi/TMEDA = 1.00/1.25, [1,3-CHD]₀/[*n*-BuLi]₀ = 1.00, C₆₀/CHDLi = 1/6) to C₆₀ in a 5.0 wt % solution of CDCl₃ at 50°C.

cyclohexadienyllithium (CHDLi) ([1,3-CHD]₀/[*t*-BuLi]₀ = 1.00, 1,3-CHD/solvent = 0.288 g/10.0 mL, C₆₀/CHDLi = 1/6), CHDLi/DABCO (*s*-BuLi/DABCO = 1.00/1.25, [1,3-CHD]₀/[*s*-BuLi]₀ = 1.00, 1,3-CHD/solvent = 0.288 g/10.0 mL, C₆₀/CHDLi = 1/6), and CHDLi/TMEDA (*n*-BuLi/TMEDA = 1.00/1.25, [1,3-CHD]₀/[*n*-BuLi]₀ = 1.00, 1,3-CHD/solvent = 0.288 g/10.0 mL, C₆₀/CHDLi = 1/6) to C₆₀ were performed in toluene at room temperature for 24 hr as the model reactions of the terminal carbanions of PCHDLi, PCHDLi/DABCO, and PCHDLi/TMEDA, according to our previously reported method.¹⁵ ¹H NMR spectra of the reaction products obtained are given as Figures 5–7.

The covalent bond between a C₆₀ and CHD unit obtained from CHDLi onto C₆₀ formed through a 1,4-CHD unit (Ho : Ha : Hb = 2 : 2 : 4) (Fig. 5). The bond obtained from CHDLi/DABCO and C₆₀ was



Scheme 5 Polymer main chain structures of PCHD.

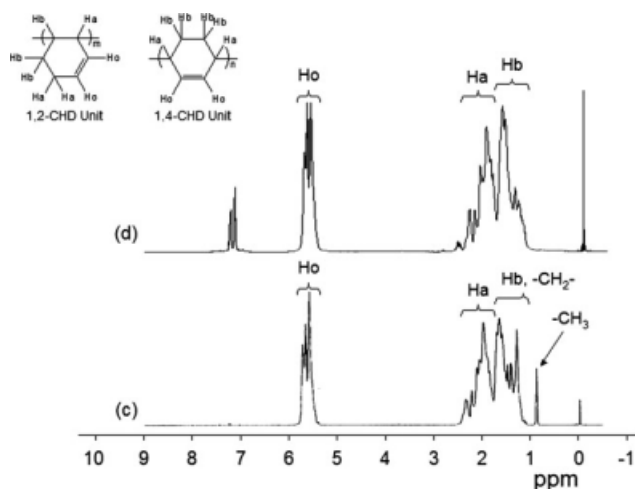


Figure 8 ^1H NMR spectra of poly(1,3-cyclohexadiene) obtained with (c) the *n*-BuLi/TMEDA (1.00/1.25)/cyclohexane system and (d) the *n*-BuLi/TMEDA (1.00/1.25)/toluene system in a 5.0 wt % solution of CDCl_3 at 50°C . Ho: olefinic signals; Ha, Hb : aliphatic signals.

formed through 1,2- and 1,4-CHD units (1,2-CHD/1,4-CHD unit = 85/15, Ho:Ha:Hb = 2.00:2.86:3.16) (Fig. 6). For CHDLi/TMEDA, the covalent bond between a C_{60} and CHD unit formed through a 1,2-CHD unit (Ho:Ha:Hb = 2:3:3; Fig. 7). Consequently, the covalent bond between a C_{60} and the CHD unit at the polymer chain-end in C_{60} -PCHD of nos. 1, 4, and 5 in Table II is thought to form through a 1,4-CHD unit, 1,2- and 1,4-CHD units, and a 1,2-CHD unit. From these results, PCHDLi in toluene is thought to form the σ -structure, such as in Scheme 4(a). PCHDLi/DABCO in toluene seems to form σ - and π -structures, such as in Schemes 4(a) and 4(b). PCHDLi/TMEDA in toluene is thought to form the π -structure, such as Schemes 4(b).

Mathis and coworkers¹ reported that the delocalized PSt carbanion has lower reactivity than the localized PSt carbanion for the addition of polystyryl-lithium (PStLi) to C_{60} . With respect to PCHDLi, PCHD carbanions in the π -structure, such as in Scheme 4(b), can be regarded as more delocalized carbanions than that in the σ -structure of Scheme 4(a).

TABLE III
Effects of Polymer Main Chain

No.	Initiator system (molar ratio)	Solvent	Parent PCHD ^a (PCHD arm)			Reaction products ^b (C_{60} -CHD)		
			M_n (RI)	PDI	1,2-/1,4-CHD units (molar ratio) ¹³	M_n ($\text{UV}_{254\text{ nm}}$ /RI)	PDI ($\text{UV}_{254\text{ nm}}$ /RI)	Grafting density (D) ^c
3	<i>n</i> -BuLi/TMEDA (1.00/1.25)	Cyclohexane	1910	1.09	59/41	5350/2880	1.24/1.26	2.80
6	<i>t</i> -BuLi/TMEDA (1.00/1.25)	Toluene	1900	1.28	90/10	1860/2330	1.50/1.38	0.98

^a The preparation of PCHDLi was conducted under dry argon at room temperature for 3 hr. $[\text{1,3-CHD}]_0/[\text{Li}]_0 = 24.0$, $1,3\text{-CHD}/\text{solvent} = 1.00/10.0$ (g/mL). $\text{C}_{60}/\text{PCHDLi} = 1/3$.

^b The addition of PCHDLi to C_{60} was conducted in toluene under dry argon at room temperature for 24 hr.

^c $D = M_n(\text{UV}_{254\text{ nm}})$ of reaction products/ $M_n(\text{RI})$ of parent PCHD.

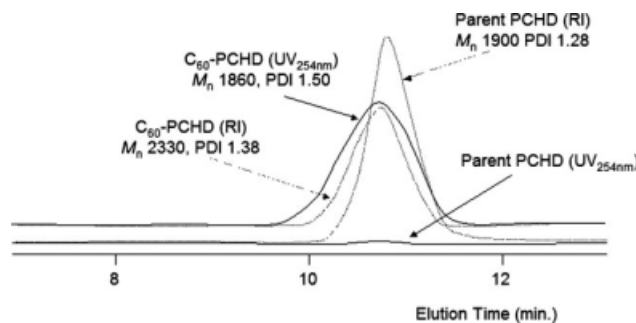


Figure 9 GPC traces of parent PCHD and C_{60} -PCHD in THF at 40°C (no. 6 in Table III). The ratio of 1,2-/1,4-CHD units = 90/10. Sample/THF = 5.00 mg/5.00 mL.

The reactivity of the PCHD carbanions in Table II is in the order of nos. 1 > 4 > 5. That is, the reactivity of the σ -structure in the addition of PCHD carbanions to C_{60} is thought to be higher than that of the π -structure. Therefore, the degree of localization on a terminal carbanion is thought to be a main factor in controlling the addition of PCHD carbanions to C_{60} .

Effects of polymer main chain

We have previously revealed that three types of polymer main chain structures, such as an all 1,2-CHD unit sequence [Scheme 5(a)], a 1,2-CHD/1,4-CHD unit sequence [Scheme 5(b)], and an all 1,4-CHD unit sequence [Scheme 5(c)] can be formed in PCHD.^{14,15,18-37}

The polymer main chain structure of PCHD (arm) in no. 3 in Table I seems to be a 1,2-CHD/1,4-CHD unit sequence, such as Scheme 5(b). Meanwhile, the polymer main chain structure of PCHD (arm) in no. 5 is an all 1,4-CHD unit sequence, such as Scheme 5(c). From the results of nos. 3 and 5, the 1,2-CHD/1,4-CHD unit sequence and all 1,4-CHD unit sequence seem to have almost the same structural effect on the addition of the PCHD carbanion to C_{60} .

To examine the structural effects of all 1,2-CHD units, PCHDLi/TMEDA consisting of almost all 1,2-CHD units [Scheme 5(a)] was prepared by anionic

polymerization of 1,3-CHD with the *t*-BuLi/TMEDA (1.00/1.25) system in toluene, and the molar ratio of 1,2-CHD/1,4-CHD units in PCHDLi was 90/10.²⁵ The ¹H NMR spectrum obtained is shown in Figure 8(d).

Subsequently, the addition of PCHDLi/TMEDA to C₆₀ was performed in toluene under dry argon at room temperature for 24 hr. Typical GPC chromatograms of the parent PCHD and C₆₀-PCHD are shown in Figure 9, and the results obtained are summarized in Table III.

In contrast to PCHD carbanions having an all 1,4-CHD unit sequence or a 1,2-CHD/1,4-CHD unit sequence, the addition reaction of the PCHD carbanion consisting of an all 1,2-CHD unit sequence was considerably difficult. *D* for no. 6 (1,2-CHD/1,4-CHD units = 90/10) was only 0.98. Although this PCHD carbanion was thought to form the π -structure, as for no. 3, *D* was remarkably decreased compared with that of no. 3 (1,2-CHD/1,4-CHD units = 59/41). That is, the steric hindrance of polymer main chain seems to affect the addition of PCHD carbanion to C₆₀ when the content of 1,2-CHD units is over 60 mol%. In other words, an all 1,2-CHD unit sequence is thought to prevent, to a considerable extent, the addition of the PCHD carbanion to C₆₀. Therefore, the large steric hindrance of the polymer main chain is thought to be another important factor in controlling the addition of the PCHD carbanion to C₆₀.

CONCLUSIONS

The addition of PCHD carbanion to C₆₀ was examined using PCHDLi, PCHDLi/DABCO, and PCHDLi/TMEDA. The reactivity of PCHD carbanions was strongly affected by the addition of amine and the increase in the molar ratio of 1,2-CHD units and was in the order of PCHDLi > PCHDLi/DABCO > PCHDLi/TMEDA, regardless of the polymer main chain structure.

With respect to polymer chain-end structure, PCHDLi in toluene formed the σ -structure, PCHDLi/DABCO in toluene formed σ - and π -structures, and PCHDLi/TMEDA in toluene formed the π -structure. The reactivity of the σ -structure in the addition of the PCHD carbanion to C₆₀ was higher than that of the π -structure. Therefore, the degree of localization on the terminal carbanion was a main factor in controlling the addition of the PCHD carbanion to C₆₀.

With regard to the polymer main chain, the 1,2-CHD/1,4-CHD unit sequence and the all 1,4-CHD unit sequence had almost the same structural effect on the addition of the PCHD carbanion to C₆₀. How-

ever, the all 1,2-CHD unit sequence prevented the addition of the PCHD carbanion to C₆₀, indicating that the large steric hindrance of the polymer main chain was another important factor in controlling the addition of the PCHD carbanion to C₆₀.

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