Degradation of the Covalent Carbon–Carbon Bond Between Fullerene-C_{60} and Poly(1,3-cyclohexadiene)

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ABSTRACT: The degradation of fullerene-C_{60} (C_{60}) end-capped poly(1,3-cyclohexadiene) (C_{60}-PCHD) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was examined to reveal the nature of the covalent carbon–carbon bond between C_{60} and PCHD (C_{60}-PCHD bond). The number average molecular weight (M_n) of C_{60}-PCHD decreased with an increase in the degree of dehydrogenation, and the elimination of a PCHD arm from a C_{60} occurred. The degradation of the C_{60}-PCHD bond *via* a 1,4-CHD unit was faster than that *via* a 1,2-CHD unit, whereas the C_{60}-poly(cyclohexane) bond was stable. The degradation of the C_{60}-PCHD bond with DDQ was caused by the dehydrogenation of a CHD unit adjoining a C_{60} core. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2923–2931, 2010

Key words: anionic polymerization; degradation; fullerene; living polymerization

INTRODUCTION

The synthesis of fullerene-C_{60} (C_{60}) end-capped polymers (C_{60}-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, C_{60}-polystyrene (C_{60}-PSt),[1] C_{60}-polyisoprene (C_{60}-PIp),[1] C_{60}-PIp-PSt block copolymer (C_{60}-PIp-PSt),[2] C_{60}-PSt-poly(1,3-cyclohexadiene) (PCHD) block copolymer (C_{60}-PSt-PCHD),[3] C_{60}-PCHD,[4] C_{60}-poly(*N*-vinylcarbazole) (C_{60}-PNVC),[5] and C_{60}-poly(4-diphenylaminostyrene) (C_{60}-PDAS)[6] were synthesized by the grafting reaction of polymer carbanions onto C_{60}. Among the innumerable combinations of C_{60} and polymers, C_{60}-poly(*para*-phenylene) (C_{60}-PPP) has been recognized as one of the most attractive structures, because excellent optical, electrical, and opto-electrical properties are expected from this polymer. The only synthetic route to realize such a polymeric structure has been the dehydrogenation of C_{60}-PCHD. Therefore, characterizing the nature of the covalent carbon–carbon bond between a C_{60} and PCHD polymer chain-end (C_{60}-PCHD bond) is very much essential.

Some researchers have reported that the covalent carbon–carbon bond between a C_{60} moiety and polymer chain-end (C_{60}-polymer bond) showed different properties compared with an ordinary carbon–carbon bond in the polymer chain. For example, Ginzburg et al. and Mathis et al. reported that the covalent carbon–carbon bond between a C_{60} and PSt polymer chain-end (C_{60}-PSt bond) was weaker than an ordinary carbon–carbon bond in PSt.[7–10] The elimination of the PSt arm from a C_{60} was observed during heat treatment of C_{60}-PSt because of the thermal cleavage of the C_{60}-PSt bond.[8–10] In the case of the covalent carbon-carbon bond between a C_{60} and PIp polymer chain-end (C_{60}-PIp bond), Hadjichristidis et al. reported the low stability of C_{60}-PIp-PSt in which a PIp chain is directly attached to a C_{60}. They hypothesized that the elimination of the PIp-PSt arm from a C_{60} was because of the cleavage of the C_{60}-PIp bond via a 1,5-sigmatropic H-shift.[2] With respect to the C_{60}-PCHD bond, François et al. and we noticed that the elimination of both PCHD-PSt[3] and PCHD[4] arms from C_{60}-PCHD-PSt and C_{60}-PCHD was observed in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, a typical strong dehydrogenation reagent). However, the mechanism of this degradation reaction has been unclear until now.

Recently, we reported that a well-defined C_{60}-PCHD, having a maximum of four arms, was obtained by the grafting reaction of poly(1,3-cyclohexadienyl)lithium (PCHDLi) onto C_{60} (Scheme 1).[4,11] The thermal stability of the C_{60}-PCHD bond was also revealed (the C_{60}-PCHD bond was very stable at room temperature. When C_{60}-PCHD was stored at room temperature for 2 months, the M_n of C_{60}-PCHD remained unaltered).[12] These C_{60}-PCHD polymers provide an interesting opportunity to study the
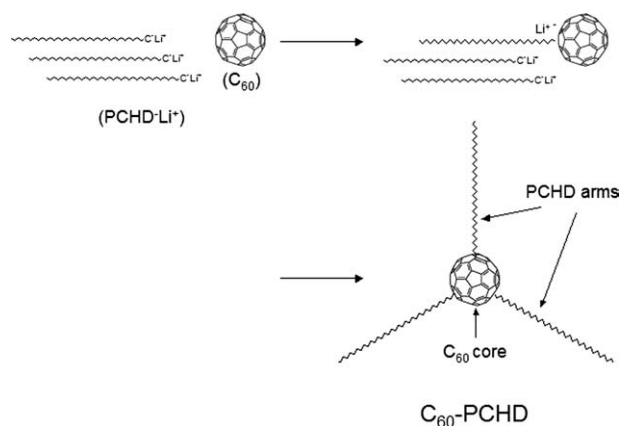
Scheme 1   Grafting reaction of PCHDLi onto C_{60}.[4]

properties and degradation mechanism of the C_{60}-PCHD bond.

In this article, we report the degradation reaction of the C_{60}-PCHD bond with DDQ. The influence of polymer chain structure and the mechanisms of elimination of a PCHD arm from a C_{60} are also described in detail.

EXPERIMENTAL

Materials

1,3-Cyclohexadiene (1,3-CHD) (97%), N,N,N',N'-tetramethylethylenediamine (TMEDA; ≥99.5%), cyclohexane (99.5%), toluene (99.8%), and o-xylene (97%) were refluxed over calcium hydride (CaH_2) and then distilled under dry argon. The C_{60} (99.5%) was washed with tetrahydrofuran (THF) and dried under reduced pressure. 1,4-Diazabicyclo[2,2,2]octane (DABCO; 98%), p-toluenesulfonyl hydrazide (TSH, 97%), and DDQ (98%) were dried under reduced pressure. All other reagents were purchased from Aldrich and were used as received unless otherwise stated.

Preparation of PCHDLi for PCHD arm

A well-dried, 50-mL Schlenk tube was purged with dry argon, and cyclohexane (10.0 mL) and $tert$-butyllithium (t-BuLi; 1.70 mol/L in n-pentane) were injected at room temperature (ca. 25°C) using syringes. 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 h, resulting in the preparation of PCHDLi in almost quantitative yield. If necessary, amine (DABCO or TMEDA) was then added to this PCHDLi solution under dry argon (PCHDLi/Amine = 1.00/1.25) and the mixture was stirred for 10 min. The molar ratio of 1,2-CHD/1,4-CHD units (=1,2-

addition/1,4-addition) was estimated by ^{1}H NMR spectroscopy.[13]

Preparation of C_{60}-PCHD[4]

C_{60} (0.108 g; 0.150 mmol) was placed in a well-dried 50-mL Schlenk tube under dry argon. Toluene (35.0 mL) was added at room temperature (ca. 25°C) using a syringe, and the mixture was stirred until C_{60} dissolved completely. A cyclohexane solution of PCHDLi (or PCHDLi/amine complex) was then added to this solution with a syringe (PCHDLi; 0.450 mmol), and the reaction mixture was magnetically stirred under dry argon at room temperature. After grafting of PCHDLi onto C_{60}, dry methanol (MeOH) was injected to the reaction mixture in an equimolar amount to the amount of lithium atoms present in the reaction mixture, in order to terminate the reaction. Then, the reaction mixture was poured into a large volume of ethanol (EtOH) to precipitate the polymer, which was then separated by filtration. The product was dried under reduced pressure at room temperature for 24 h, resulting in a (light) brown powdery polymer in almost quantitative yield.

Dehydrogenation of C_{60}-PCHD with DDQ[4]

C_{60}-PCHD (0.20 g, containing ca. 2.50 mmol of CHD units) was placed into a 50-mL Schlenk tube and dried under reduced pressure. The Schlenk tube was alternately evacuated and filled with dry argon several times. 1,2-Dichlorobenzene (DCBz, 20 mL) was then added with a syringe, and the mixture was stirred until the polymer was fully dissolved. DDQ (2.27 g, 10 mmol, 400% with respect to CHD units) was added under dry argon and the reaction mixture was magnetically stirred under dry argon. After the dehydrogenation, the reaction mixture was poured into a large volume of isopropanol (IPA) to precipitate the reaction product, which was then separated by filtration. The product was washed with an excess amount of EtOH and dried under reduced pressure at room temperature for 24 h, resulting in a brown powdery product in almost quantitative yield. The degree of dehydrogenation was estimated by ^{1}H-NMR spectroscopy.[13]

Hydrogenation of C_{60}-PCHD

C_{60}-PCHD (0.20 g, containing ca. 2.50 mmol of CHD units) and TSH (1.86 g, 10.0 mmol) were placed into a 100-mL three-necked round-bottom flask equipped with a reflux condenser and dried under reduced pressure. The round-bottom flask was alternately evacuated and filled with dry argon several times. Dry o-xylene (50 mL) was added with a syringe, and

TABLE I
Synthesis of C$_{60}$-PCHD

			Parent PCHD[a] (PCHD arm)			Grafting reaction products[b] (C$_{60}$-CHD)		
No.	Initiator	Amine (PCHDLi/Amine)	M_n (RI)	PDI	1,2-/1,4-CHD Units (Molar Ratio)[13]	M_n (UV$_{254nm}$/RI)	PDI (UV$_{254nm}$/RI)	Grafting Density (D)[c]
1	*t*-BuLi		1860	1.23	0/100	5800/5820	1.55/1.50	3.12
2	*t*-BuLi	DABCO (1.00/1.25)	1880	1.22	0/100	5640/4280	1.40/1.42	3.00
3	*t*-BuLi	TMEDA (1.00/1.25)	1900	1.20	0/100	5380/3550	1.36/1.38	2.83

[a] The preparation of PCHDLi was conducted in cyclohexane under dry argon at room temperature for 3 h. [1,3-CHD]$_0$/[Li]$_0$ = 24.0, 1,3-CHD/solvent = 1.00/10.0 (g/mL). C$_{60}$/PCHDLi=1/3.
[b] The grafting reaction of PCHDLi onto C$_{60}$ was conducted in toluene under dry argon at room temperature for 24 h.
[c] $D = M_n$ (UV$_{254\,nm}$) of grafting reaction products / M_n (RI) of parent PCHD.

the mixture was stirred until the polymer was completely dissolved. The reaction mixture was then magnetically stirred under dry argon at 145°C for 5 h. After the hydrogenation, a white granular by-product precipitate was formed and removed by filtration. The filtrate was poured into a large volume of MeOH to precipitate the polymer, which was then separated by filtration. The product was washed with excess amount of MeOH and dried under reduced pressure at room temperature for 24 h, resulting in a light brown powdery polymer at almost quantitative yield.

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) equipment 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, and the flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained using polystyrene standards. ^{1}H-NMR spectra of the polymers were measured in deuterated chloroform (CDCl$_3$) at 500 MHz, using a Jeol ECA 500 spectrometer. Elemental analysis of Cl was performed using a combustion ion chromatography (a Shimazu HIC-10A ion chromatograph coupled with a Mitsubishi AQF-100 automation combustion system).

RESULTS AND DISCUSSION

Conformation of the formation of C$_{60}$-PCHD

In a previous paper,[4] we reported the synthesis of C$_{60}$-PCHD with a well-defined polymer chain structure through the grafting reaction of PCHDLi onto C$_{60}$ (Scheme 1). Based on this information, three

types of C$_{60}$-PCHDs were synthesized by the grafting reaction of PCHDLi onto C$_{60}$ as the evaluation samples.

To prepare PCHDLi, anionic polymerization of 1,3-CHD initiated by *t*-BuLi was conducted under dry argon at room temperature for 3 h, resulting in the preparation of PCHDLi in almost quantitative yield (1,2-CHD/1,4-CHD units = 0/100). If necessary, amine (DABCO or TMEDA) was then added to this PCHDLi solution to prepare the PCHDLi/amine complex. The living polymers obtained were thought to have the same polymer main chain structure and different polymer chain-end structure. Subsequently, the grafting reactions of PCHDLi (or the PCHDLi/DABCO complex or the PCHDLi/TMEDA complex) onto C$_{60}$ were performed under dry argon at room temperature for 24 h (C$_{60}$/PCHDLi = 1/3). The C$_{60}$-PCHDs were obtained in nearly quantitative yield.

As explained in a previous paper,[4] PCHD produces almost no UV absorption in the region greater than 225 nm, and has good solubility in THF. In contrast, C$_{60}$ has strong absorption peaks near 260 and 330 nm, and is insoluble in THF. Therefore, C$_{60}$-PCHD obtained by the grafting of PCHDLi onto C$_{60}$ shows strong absorption in the region greater than 225 nm, and is readily soluble in THF.[4] Using this characteristic of C$_{60}$-PCHD, the grafting density (i.e., approximation of the number of PCHD arm molecules on C$_{60}$) of PCHD arms onto C$_{60}$ can be estimated by the following procedure. First, the parent PCHD and grafting reaction products are dissolved in THF. The M_n of each THF solution is then measured using GPC (using THF as the eluent) with a RI detector and a UV detector set at 254 nm, a region where the PCHD is no longer detected and only C$_{60}$-PCHD absorbs. From the chromatograms obtained, the grafting density (D) of PCHD arms onto C$_{60}$ is determined using the following formula:

$D = M_n$ (UV$_{254\,nm}$) of grafting reaction products/ M_n (RI) of parent PCHD (i.e., PCHD arms). The results obtained are summarized in Table I.
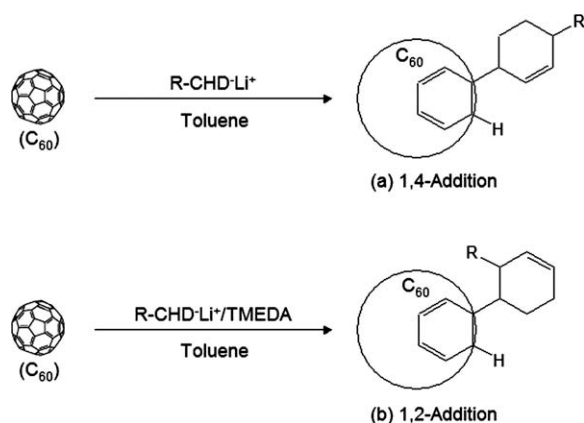
The grafting reaction of PCHDLi onto C$_{60}$ was strongly affected by coordination of amine. In the

case of the grafting reaction product of No. 1, $M_n(UV_{254\ nm})$ and $M_n(RI)$ 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.[11] The D for Nos. 1–3 in Table I were 3.12, 3.00, and 2.83, respectively, which indicates the reactivity of PCHDLis is in the order of PCHDLi > PCHDLi/DABCO complex > PCHDLi/TMEDA complex.

As we reported in a previous paper,[12] the C_{60}-CHD bond obtained from (1,3-cyclohexadienyl)-lithium (CHDLi) onto C_{60} (e.g., the grafting reaction product of experiment No. 1 in Table I) is formed through a 1,4-CHD unit [Scheme 2(a)], and the bond obtained from the CHDLi/TMEDA complex onto C_{60} (e.g., the grafting reaction product of experiment No. 3 in Table I) forms through a 1,2-CHD unit [Scheme 2(b)].

To examine the C_{60}-PCHD bond in the grafting reaction product of experiment No. 2 in Table I, the grafting reaction of the CHDLi/DABCO complex (t-BuLi/DABCO = 1.00/1.25, [1,3-CHD]$_0$/[t-BuLi]$_0$ = 1.00, 1,3-CHD/solvent = 0.288 g/10.0 mL, C_{60}/CHDLi = 1/6) was performed as the model reaction of a terminal carbanion to form the PCHDLi/DABCO complex. The ^{1}H-NMR spectrum of the reaction products obtained is shown in Figure 1. The molar ratio of Ha/Hb in Figure 1 was 2.83/3.26. Therefore, the C_{60}-CHD bond obtained from the CHDLi/DABCO complex onto C_{60} is thought to form in a ratio of 1,2-CHD/1,4-CHD units of 79/21 [i.e., Scheme 2(a)/Scheme 2(b) = 21/79].

From the results obtained, the covalent bond between a C_{60} and PCHD arm in the grafting reaction product of experiment No. 1 in Table I is thought to form through a 1,4-CHD unit, such as in Scheme 2(a). The bond in the grafting reaction product of experiment No. 2 in Table I seems to form

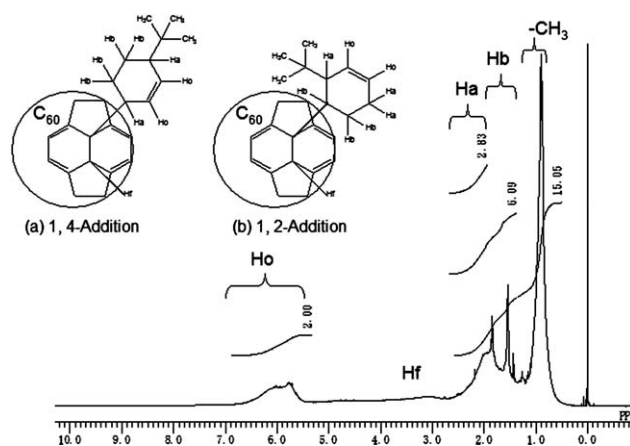**Figure 1** ^{1}H-NMR spectrum of the grafting reaction product of the CHDLi/DABCO (4/5) complex (t-BuLi/DABCO = 1.00/1.25, [1,3-CHD]$_0$/[t-BuLi]$_0$ = 1.00, C_{60}/CHDLi = 1/6) to C_{60} in 5.0 wt % solution of CDCl$_3$ at 50°C.

through 1,4-CHD and 1,2-CHD units [Schemes 2(a) and 2(b)]. The C_{60}-PCHD bond in the grafting reaction product of experiment No. 3 in Table I is thought to form through a 1,2-CHD unit, such as in Scheme 2(b).

Degradation of the C_{60}-PCHD bond with the dehydrogenation reaction

As described above, with respect to C_{60}-PCHD-PSt and C_{60}-PCHD, the elimination of PCHD-PSt[3] and PCHD[4] arms from a C_{60} was observed in the presence of DDQ, although the breaking of ordinary carbon–carbon bonds in the polymer chain was not observed in the dehydrogenation reaction of PCHD with DDQ.[13–16] Thus, the C_{60}-PCHD bond seems to be considerably affected by the dehydrogenation reaction with DDQ.

To reveal the mechanism of the degradation of the C_{60}-PCHD bond, the dehydrogenation of C_{60}-PCHD (the grafting reaction product of experiment No. 1 in Table I) with DDQ was performed in DCBz under dry argon at room temperature for 1 week. The DCBz solution of C_{60}-PCHD alone (the grafting reaction product of experiment No. 1 in Table I) was also stirred under dry argon at room temperature for 1 week as a comparison.[12] The results obtained are shown in Figures 2 and 3.

As displayed in Figure 2, the M_n remained unaltered for the DCBz solution of C_{60}-PCHD alone stirred under dry argon at room temperature for 1 week. Thus, the C_{60}-PCHD bond is considered stable at room temperature in the absence of DDQ. Meanwhile, when the DCBz solution of C_{60}-PCHD with DDQ was stirred for 1 week, a remarkable decrease of M_n was observed for C_{60}-PCHD.
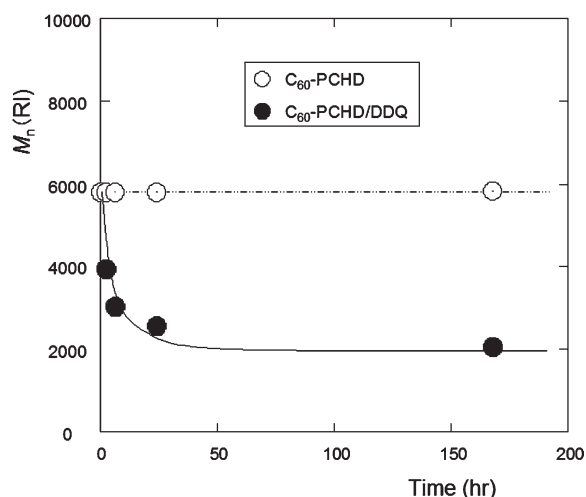

Scheme 2 Addition of CHDLi and CHDLi/TMEDA complex to C_{60}.[12]

Figure 2 Time-M_n relationship of C_{60}-PCHD in DCBz under dry argon at room temperature for 1 week.

Scheme 3 Elimination of PCHD arm molecules from a C_{60}.

Figuer 3 shows the relationship between the M_n of C_{60}-PCHD and the degree of dehydrogenation[13–16] of the PCHD arm using DDQ. The M_n of C_{60}-PCHD readily decreased with an increase in the degree of dehydrogenation. When the degree of dehydrogenation was saturated the decrease of M_n in C_{60}-PCHD was also saturated, approaching the M_n of parent PCHD (experiment No. 1 in Table I). Therefore, the elimination of PCHD arms from C_{60} is thought to be caused by the dehydrogenation of C_{60}-PCHD with DDQ (Scheme 3). Furthermore, the elimination seems to result from the degradation of a C_{60}-PCHD bond caused by the dehydrogenation of cyclohexadiene (CHD) units adjoining a C_{60} core.

Figure 4 shows the ^{1}H-NMR spectra of C_{60}-PCHD (a) (the grafting reaction product of experiment No. 1 in Table I) and its dehydrogenated product (b). The olefinic proton signals (Ho) were found to decrease with the passage of reaction time, and new aromatic signals (Hp at ca. 7.50 ppm) appeared. After 24 h, only a small olefinic proton signal remained at 5.70 ppm.

Influence of polymer chain-end structure on the degradation of C_{60}-PCHD

From the results of Figure 3, the degradation of the C_{60}-PCHD bond seems to be caused by the dehydrogenation of CHD units adjoining a C_{60} core. If so, the structure of the CHD unit adjoining a C_{60} core is expected to strongly affect the degradation of C_{60}-PCHD, because the rate of dehydrogenation of a 1,4-CHD unit with DDQ is considerably faster than that of a 1,2-CHD unit.[13–16]

As explained above, the C_{60}-PCHD bond in the grafting reaction product of experiment No. 1 in Table I is thought to form through a 1,4-CHD unit, such as in Scheme 2(a). The grafting reaction
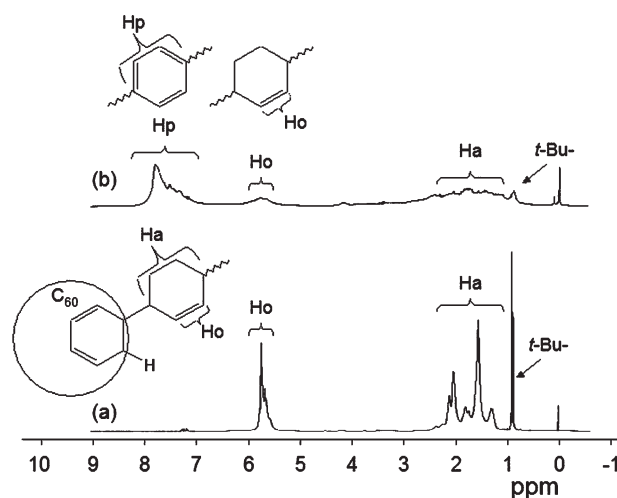

Figure 3 Relationship between M_n and the degree of dehydrogenation of C_{60}-PCHD with DDQ.

Figure 4 ^{1}H-NMR spectra of C_{60}-PCHD (No. 1 in Table I) in 5.0 wt % solution of CDCl$_3$ at 50°C (a) and its dehydrogenated product in 5.0 wt % solution of THF-d_8 at 50°C (b).

TABLE II
Influence of Polymer Chain-End Structure on the Degradation of C_{60}-PCHD

No.	Sample	1,2-/1,4-CHD Units (Molar Ratio)[13]	Before dehydrogenation		After dehydrogenation[a]	
			M_n (UV$_{254nm}$/RI)	PDI (UV$_{254nm}$/RI)	M_n (UV$_{254nm}$/RI)	PDI (UV$_{254nm}$/RI)
4	C_{60}-PCHD[b]	0/100	5800/5820	1.55/1.50	2010/2060	1.48/1.44
5	C_{60}-PCHD[c]	0/100	5640/4280	1.38/1.42	2420/2330	1.41/1.38
6	C_{60}-PCHD[d]	0/100	5380/3550	1.36/1.38	2660/2440	1.39/1.35

[a] The dehydrogenation of C_{60}-PCHD with DDQ was carried out in 1,2-dichlorobenzene at room temperature for 1 week. CHD units/DDQ = 1/4 (mol/mol).
[b] C_{60}-PCHD was synthesized as the grafting reaction product of No. 1 in Table I.
[c] C_{60}-PCHD was synthesized as the grafting reaction product of No. 2 in Table I.
[d] C_{60}-PCHD was synthesized as the grafting reaction product of No. 3 in Table I.

product of experiment No. 2 in Table I seems to form through 1,4-CHD and 1,2-CHD units [Schemes 2(a,b)]. The grafting reaction product of experiment No. 3 in Table I is thought to form through a 1,2-CHD unit such as in Scheme 2(b).

To confirm the above hypothesis, dehydrogenation using these three types of C_{60}-PCHDs (i.e., the grafting reaction products of experiment Nos. 1–3 in Table I) with DDQ was performed in DCBz under dry argon at room temperature for 1 week. The results obtained are summarized in Table II.

The degradation of the C_{60}-PCHD bond was strongly affected by the structure of the CHD unit adjoining a C_{60} core. After dehydrogenation, the M_n of dehydrogenated product decreased with an increase of the molar ratio of 1,4-CHD units in the CHD unit adjoining a C_{60} core. With respect to the dehydrogenation products, the order of M_n was No. 4 < No. 5 < No. 6. Thus, the degradation of the C_{60}-PCHD bond seems to be caused by the dehydrogenation of the CHD unit adjoining a C_{60} core. To confirm this expectation, the dehydrogenation of C_{60}-CHD, which was obtained by the grafting reaction of the CHDLi/TMEDA complex onto C_{60} [n-Butyllithium (n-BuLi; 1.60 mol/L in n-hexane)/ TMEDA=1.00/1.25, [1,3-CHD]$_0$/[n-BuLi]$_0$ = 1.00, 1,3-CHD/solvent = 0.288 g/10.0 mL, C_{60}/CHDLi = 1/6],[12] with DDQ was performed in DCBz at 90°C for 96 h (CHD units/DDQ=1/4). A brown powdery product was obtained in almost quantitative yield.
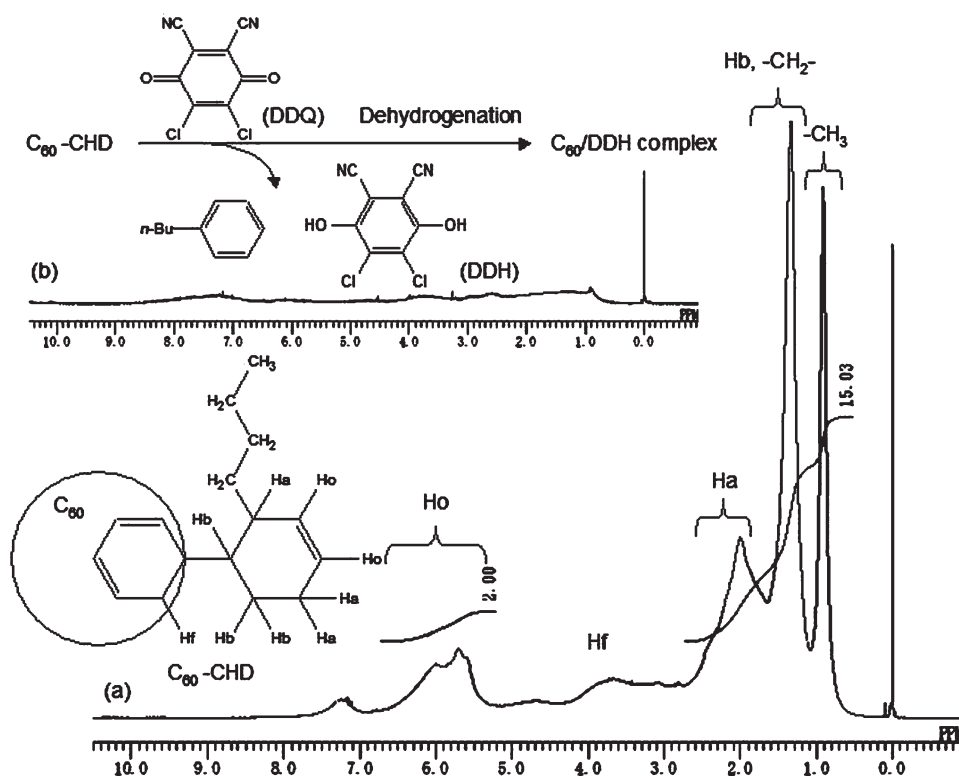

Figure 5 ^{1}H-NMR spectra of C_{60}-CHD (a) and C_{60}/DDH (=1/1) complex (b) in a 7.0 wt % solution of THF-d_8 at 50°C.
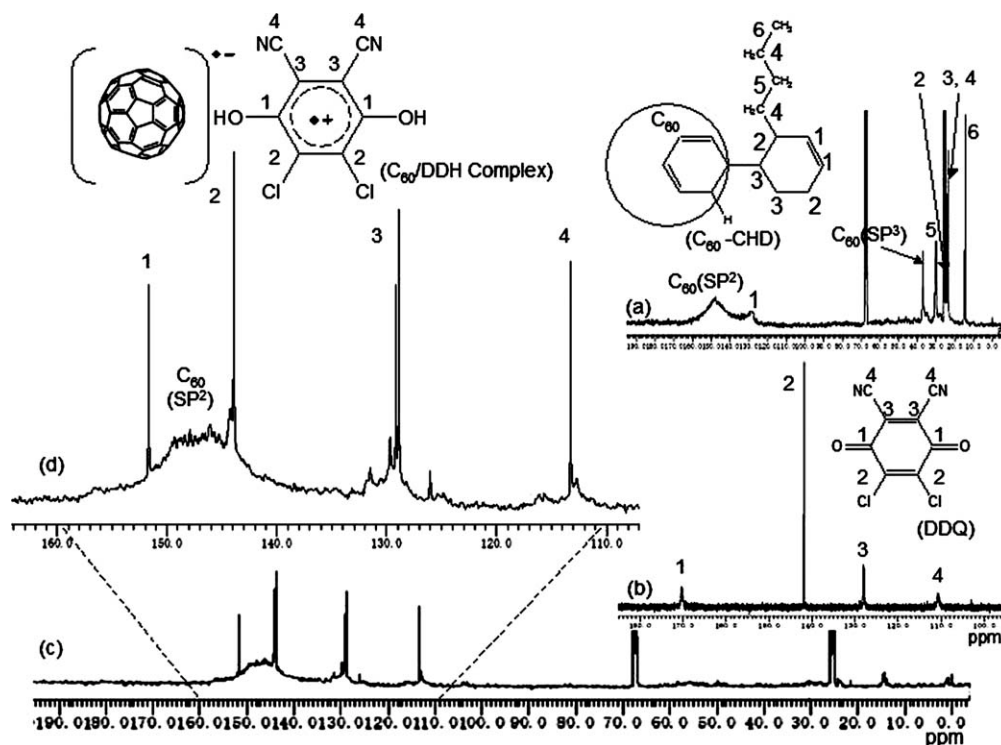
Figure 6 ^{13}C NMR spectra of C$_{60}$-CHD (a), DDQ (b), and C$_{60}$/DDH (=1/1) complex (c, d) in a 7.0 wt % solution of THF-d_8 at 50°C.
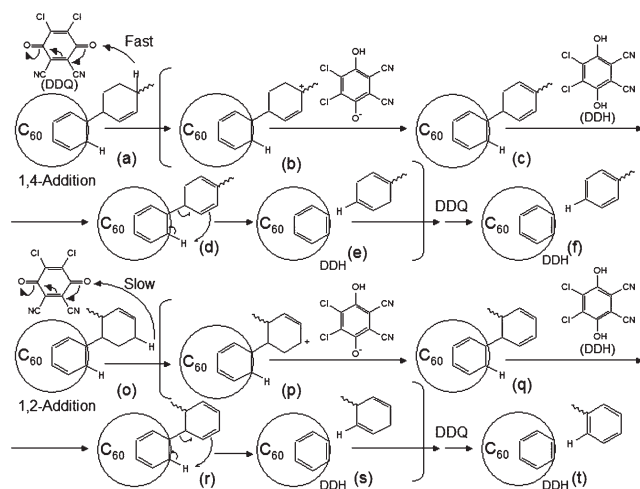
This product was air-stable and readily soluble in organic solvents, such as acetone, N,N-dimethylformamide, and THF, although the original C$_{60}$ was insoluble in these solvents.

Figure 5 shows the ^{1}H-NMR spectra of C$_{60}$-CHD [Fig. 5(a)] and the dehydrogenation reaction product [Fig. 5(b)]. The olefinic (Ho) and aliphatic (Ha, Hb, —CH$_2$–, —CH$_3$) proton signals [Ho/(Ha+Hb+-CH$_2$-+-CH$_3$) = 2/15] are observed in Figure 5(a), which also shows an n-butyl (n-Bu) group (a residue from n-BuLi)/CHD group = 1/1. The broad proton signal around 3.8 ppm is assigned to the hydrogen on C$_{60}$ (Hf). Meanwhile, almost no proton signals are observed in Figure 5(b), suggesting all CHD groups on C$_{60}$-CHD are completely eliminated through the dehydrogenation reaction and n-butylbenzene is obtained. In this reaction, DDQ is converted to 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDH) as the result of dehydrogenation reaction. Therefore, it is expected that the C$_{60}$/DDH complex forms, similar to the C$_{60}$/hydroquinone complex.[17]

Figure 6 shows typical ^{13}C-NMR spectra of C$_{60}$-CHD [Fig. 2(a)], DDQ [Fig. 6(b)], and the dehydrogenation reaction product [Fig. 6(c,d)]. As shown in Figure 2(a), the peaks around 146 and 37 ppm are assigned to the sp2 and sp3 carbons on C$_{60}$.[5,6] The peaks at 130, 25, and 23 ppm correspond to the 1, 2, and 3 carbons on the cyclohexene ring of CHD, and the peaks at 30, 23, and 14 ppm are assigned to the 5, 4, and 6 carbons in the n-Bu group. The ^{13}C-NMR

signals of the free DDQ were observed around 170(C1), 142(C2), 128(C3), and 111(C4) ppm [Fig. 6(b)]. For the ^{13}C-NMR spectra of the dehydrogenation reaction product [Fig. 6(c,d)], the peaks at 152, 144, 129, and 113 ppm are assigned to the C1, C2, C3, and C4 carbons, respectively, on DDH, showing a remarkable diamagnetic shift of the ^{13}C-NMR signal of the hydroxyl carbon (C1). The peaks around 146 ppm are assigned to the sp2 carbons on C$_{60}$.[5,6] Furthermore, ^{13}C-NMR signals from the n-Bu and CHD groups are not observed in Figure 6(c). Consequently, the C$_{60}$/DDH complex is thought to be formed. Furthermore, elemental analysis showed that the chlorine (Cl) content in the C$_{60}$/DDH complex was 7.80 wt %, which was very close to the value calculated from the C$_{60}$/DDH = 1/1 [(35.5 × 2)/(723+227) = 0.0747; chlorine: 7.47 wt%]. Therefore, the reaction product from C$_{60}$-CHD and DDH was confirmed to be the C$_{60}$/DDH (= 1/1) complex by examination of ^{1}H, ^{13}C-NMR spectra and elemental analysis.

Scheme 4 shows the possible degradation mechanism of the C$_{60}$-PCHD bond. The abstraction of an allylic hydrogen atom of a 1,4-CHD unit adjoining a C$_{60}$ core [Schemes 4(a) and 4(b)] seems to be relatively fast. The diene unit structure [Scheme 4(c)] is assumed to be unstable and is immediately eliminated from the C$_{60}$ core via a 1,5-sigmatropic H-shift [Schemes 4(d) and 4(e)].[2,12] The complexation between C$_{60}$ and DDH occurs. As a result, the C$_{60}$-

Scheme 4 Mechanism of the degradation reaction of the C_{60}-PCHD bond.

Figure 7 ^{1}H-NMR spectra of C_{60}-PCHD (a) (No. 1 in Table I) and its completely hydrogenated product (C_{60}-PCHE) (b) (No. 7 in Table III) in 5.0 wt % solution of $CDCl_3$ at 50°C.

PCHD bond formed through the 1,4-CHD unit seems to be easily degraded (Table II). On the other hand, the abstraction of an allylic hydrogen atom in the 1,2-CHD units adjoining a C_{60} core [Schemes 4(o) and 4(p)] seems to be slow compared with that of 1,4-CHD units [Schemes 4(a,b)]. Therefore, the degradation of the C_{60}-PCHD bond formed through the 1,2-CHD unit [Scheme 4(o)] is relatively slow, although the diene unit structure [Scheme 4(q)] is assumed to be unstable and is immediately eliminated from a C_{60} core via a 1,5-sigmatropic H-shift [Schemes 4(r) and 4(s)].[2,12]

Effect of hydrogenation of CHD units adjoining a C_{60} core

From the results obtained, the degradation of the C_{60}-PCHD bond with DDQ seems to be caused by dehydrogenation of the CHD unit adjoining a C_{60} core. If this CHD unit cannot be dehydrogenated, the degradation of the C_{60}-PCHD bond with DDQ is expected to be suppressed. For instance, the hydrogenation of a residual double bond in a CHD unit adjoining a C_{60} core can be expected to strongly affect the elimination of a PCHD arm molecule from a C_{60} core in C_{60}-PCHD. To confirm this supposition,
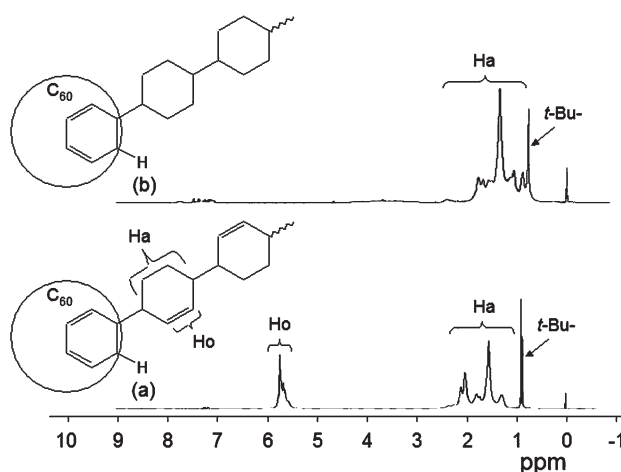
the hydrogenation of C_{60}-PCHD (the grafting reaction product of No. 1 in Table I) with TSH (a typical hydrogenation reagent, which can hydrogenate an aliphatic unsaturated bond but not an aromatic unsaturated bond[17]) was conducted in o-xylene at 145°C for 5 h [the ratio of CHD units/TSH = 1/4 (mol/mol)]. Subsequently, the ^{1}H-NMR spectra for C_{60}-PCHD and its hydrogenation reaction products were obtained in $CDCl_3$.

Figure 7 shows typical ^{1}H-NMR spectra of C_{60}-PCHD measured before and after hydrogenation. The olefinic signals of PCHD arm molecules in C_{60}-PCHD [Ho at 5.7 ppm, Fig. 7(a)] completely disappeared, indicating complete hydrogenation of the double bond in the PCHD arm molecule containing the CHD unit adjoining the C_{60} core [Fig. 7(b)]. Methyl (CH_3) signals on t-butyl end-groups in the PCHD arm molecule from the t-BuLi initiator used in the preparation of PCHDLi were observed near 0.9 ppm before and after hydrogenation. Therefore, C_{60}-PCHD [Fig. 7(a)] is thought to be converted to C_{60} end-capped polycyclohexane (PCHE) (C_{60}-PCHE), which has no double bond in the polymer chains, nor in the cyclic units adjoining the C_{60} core

TABLE III
Influence of the Residual Double Bond in the CHD Unit on the Degradation of C_{60}-PCHD

No.	Sample	Before dehydrogenation		After dehydrogenation[a]	
		M_n (UV$_{254nm}$/RI)	PDI (UV$_{254nm}$/RI)	M_n (UV$_{254nm}$/RI)	PDI (UV$_{254nm}$/RI)
4	C_{60}-PCHD[b]	5800/5820	1.55/1.50	2010/2060	1.48/1.44
7	C_{60}-PCHE[c]	5650/5690	1.41/1.38	5600/5780	1.43/1.39

[a] The dehydrogenation of C_{60}-polymer with DDQ was carried out in 1,2-dichlorobenzene at room temperature for 1 week. Monomer units/DDQ = 1/4 (mol/mol).
[b] C_{60}-PCHD was synthesized as the reaction product of No. 1 in Table I.
[c] C_{60}-PCHE was prepared by the complete hydrogenation of C_{60}-PCHD (reaction product of No. 1 in Table I).

[Fig. 7(b)]. PCHE showed almost no absorption in the region greater than 225 nm. In contrast, C_{60}-PCHE showed strong absorption in the region greater than 225 nm, and was readily soluble in THF. From the results of GPC analyses, the M_n (UV_{254nm}/RI) and PDI (UV_{254nm}/RI) of the C_{60}-PCHE obtained were 5650/5690 and 1.41/1.38, respectively. Subsequently, the dehydrogenation of C_{60}-PCHE with DDQ was carried out in DCBz at room temperature for 1 week.

Table III summarizes the results before and after the dehydrogenation reaction of C_{60}-PCHD and C_{60}-PCHE. In contrast to the case of C_{60}-PCHD (No. 4 in Table III), the M_n (UV_{254nm}/RI) of C_{60}-PCHE was nearly the same before and after dehydrogenation with DDQ (No. 7 in Table III). Furthermore, the GPC peak corresponding to the parent PCHE was not observed after dehydrogenation. Thus, the elimination of PCHE arm molecules from a C_{60} core was suppressed during the dehydrogenation reaction of C_{60}-PCHE with DDQ.

The difference in molecular structure of the cyclic unit adjoining a C_{60} core in C_{60}-PCHD [Fig. 7(a)] and C_{60}-PCHE [Fig. 7(b)] is only the existence of a double bond. Nevertheless, the stability of C_{60}-PCHE is considerably greater than that of C_{60}-PCHD. Thus, the double bond in the CHD unit adjoining a C_{60} core is a key structure for the degradation of the C_{60}-PCHD bond with DDQ. Therefore, it was concluded that the dehydrogenation of the CHD unit adjoining a C_{60} core was the key reaction for the degradation of the C_{60}-PCHD bond with DDQ.

CONCLUSIONS

The degradation of C_{60}-PCHD with DDQ was examined to reveal the nature of the C_{60}-PCHD bond. C_{60}-PCHD with a well-defined polymer chain structure was synthesized by the grafting reaction of PCHDLi onto C_{60}. The C_{60}-PCHD bond was considerably affected by the dehydrogenation with DDQ. The M_n of C_{60}-PCHD decreased with an increase in the degree of dehydrogenation, and the elimination of a PCHD arm from a C_{60} occurred. The C_{60}-PCHD bond formed through a 1,4-CHD unit was easily degraded, whereas the degradation of the C_{60}-PCHD bond formed through a 1,2-CHD unit was relatively slow. C_{60}-PCHE was stable during the dehydrogenation reaction with DDQ. Therefore, the degradation of the C_{60}-PCHD bond with DDQ was caused by the dehydrogenation of the CHD unit adjoining a C_{60} core.

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