

Synthesis of Functionalized Fullerene-C₆₀ by the Living Anionic Polymerization Technique

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ABSTRACT: The synthesis of functionalized fullerene-C₆₀ (C₆₀) was performed using living anionic polymerization. The metalation of the benzylic hydrogen atom on toluene or *p*-substituted toluene was conducted with the alkyllithium/amine system, and examined by living anionic polymerization of 1,3-cyclohexadiene. The number of carbanions bonded onto C₆₀ was estimated by the grafting reaction of living polymer onto C₆₀. The *tert*-butyllithium/*N,N,N',N'*-tetramethylethylenediamine system was an

effective metalation reagent, and toluene-, *p*-xylene-, 4-methyltriphenylamine-functionalized C₆₀s having good solubility were successfully synthesized. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1372–1378, 2011

Key words: addition of carbanion; alkyllithium/amine system; functionalized fullerene; living anionic polymerization; metalation

INTRODUCTION

Since the first discovery of the formation of a “living” polymer from styrene (St),¹ living anionic polymerization has been one of the most attractive polymerization techniques in polymer chemistry. A variety of well-controlled polymer chain structures (e.g., homopolymer, copolymer, block copolymer, graft copolymer, comb-like polymer, star-shaped polymer, and end-functionalized polymer) can be synthesized using this polymerization technique.

It is well-known to polymer chemists that living anionic polymerization has excellent initiator efficiency and stable active polymer-ends. Consequently, some researchers noticed that this polymerization technique potentially had the ability to act as an excellent indicator for organic reactions. For example, Goto et al. examined the reactivity of the *sec*-butyllithium/amine system to the metalation (i.e., metal-hydrogen exchange reaction) of the benzylic hydrogen atom on toluene (or its derivatives) by the living anionic polymerization of St.² Mathis et al. estimated the number of living polystyrene (PSt) (i.e., benzyl carbanion) molecules bonded onto fullerene-C₆₀ (C₆₀) through the living anionic polymerization technique.³ We also showed some examples using the living anionic polymerization technique as an indicator for organic reactions.^{4–7} For

example, the reactivity of the alkyllithium (RLi)/amine system to the metalation of the benzylic hydrogen atom on toluene was examined by the living anionic polymerization of 1,3-cyclohexadiene (1,3-CHD).⁴ The numbers of living poly(1,3-cyclohexadiene) (PCHD) (i.e., cyclohexadienyl carbanion) molecules and the living poly(4-diphenylaminostyrene) (PDAS) (i.e., 4-diphenylaminobenzyl carbanion) molecules bonded onto C₆₀ were estimated by the living anionic polymerization technique.^{5–7}

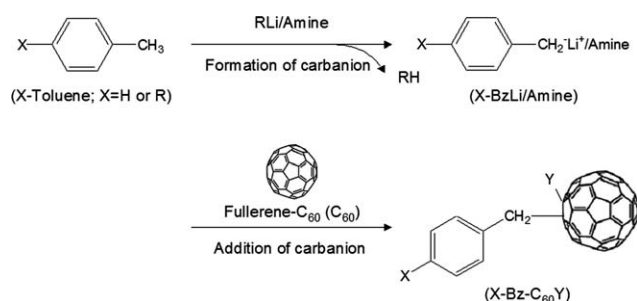
We considered that the living anionic polymerization technique with the RLi/amine system would be an effective indicator for the preparation of a variety of carbanions from toluene or *p*-substituted toluene (X-Toluene; X = H or R), and expected that these carbanions would facilitate the synthesis of functionalized C₆₀. The preparation of several carbanions from X-toluene in the form of the X-benzylolithium (X-BzLi)/amine system and the addition of those carbanions onto C₆₀ were then attempted (Scheme 1). In this article, we reported an effective method for the synthesis of functionalized C₆₀ by the living anionic polymerization technique.

EXPERIMENTAL

Materials

1,3-CHD (97%), *N,N,N',N'*-tetramethylethylenediamine (TMEDA; ≥99.5%), cyclohexane (99.5%), *p*-xylene (≥99.0%), and toluene (99.8%) were refluxed over calcium hydride (CaH₂) and then distilled under dry argon. 1,2,3,4-Tetrahydronaphthalene

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Scheme 1 Synthesis of functionalized C₆₀.

(Tetralin: 99%) and St ($\geq 99.0\%$), stirred with neutral aluminum oxide at room temperature, were degassed by argon bubbling to remove air and then distilled under reduced pressure over CaH₂. C₆₀ (99.5%) was washed with tetrahydrofuran (THF) and dried under reduced pressure. 1,4-Diazabicyclo2,2,2 octane (DABCO; 98.0%) and 4-methyltriphenylamine (MTPA; $>98\%$) were dried under reduced pressure. MTPA was purchased from Tokyo Chemical. All other reagents were purchased from Aldrich and were used as received unless otherwise stated.

Metalation reaction

X-Toluene (X = H or R) (1.20 mmol) was placed in a well-dried 50-mL Schlenk tube under dry argon, and a solvent (10 mL) and *tert*-butyllithium (*t*-BuLi; 1.70 mol/L in *n*-pentane) (1.00 mmol) were added at room temperature ($\sim 25^\circ\text{C}$) using a syringe. Amine (TMEDA or DABCO) (1.25 mmol) was then added to this solution under dry argon, and the mixture was stirred for 30 min as the metalation of the benzylic hydrogen atom on X-toluene (i.e., the preparation of carbanion in the form of the X-BzLi/amine system) occurred.

To examine the yield of carbanion, 1,3-CHD (1.00 g; 12.5 mmol) was added to the metalation reaction product using a syringe ($[\text{1,3-CHD}]_0/[\text{Li}]_0 = 75.0$ or 17.5), and the reaction mixture was magnetically stirred under dry argon at room temperature for 2 h. After polymerization, dry methanol (MeOH) was added to the reaction mixture in an equimolar amount to the lithium (Li) atoms present to terminate the reaction. The polymerization mixture was then poured into a large volume of ethanol (EtOH) to precipitate the polymer, which was separated by filtration. The product was dried under reduced pressure at room temperature for 24 h, resulting in a white powdery polymer in nearly quantitative yield.

Addition reaction

C₆₀ (0.108 g; 0.150 mmol) was placed in a well-dried 50-mL Schlenk tube under dry argon. Toluene (35.0 mL) was injected at room temperature ($\sim 25^\circ\text{C}$)

using a syringe and the mixture was stirred for 30 min. A solution of the X-BzLi/amine system (0.900 mmol; C₆₀/Li = 1/6) was then added to this solution with a syringe, and the reaction mixture was magnetically stirred under dry argon at room temperature for 24 h. After the addition reaction, dry MeOH was injected into the reaction mixture in an equimolar amount to the amount of Li atoms present in the reaction mixture to terminate the reaction. The reaction mixture was then poured into a large volume of MeOH to precipitate the product, which was then separated by filtration. The product was dried under reduced pressure at room temperature for 24 h, resulting in a brown powdery compound in nearly quantitative yield.

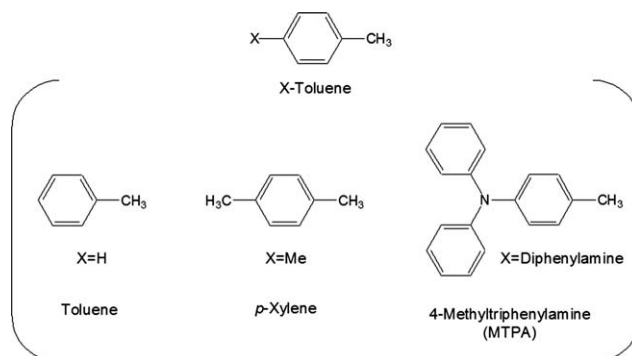
Measurements

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) 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 and ¹³C NMR spectra of the functionalized C₆₀ and polymers were obtained in deuterated THF (THF-*d*₈) or chloroform (CDCl₃) at 500 MHz using a Jeol ECA 500 spectrometer.

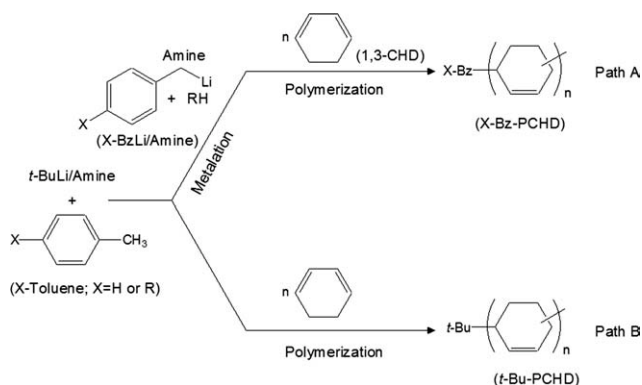
RESULTS AND DISCUSSION

Preparation of the X-BzLi/amine system as carbanion

In this study, toluene, *p*-xylene, and MTPA were used as X-toluene (Scheme 2). To obtain the X-BzLi/amine system as the carbanion, the metalation of X-toluene with the *t*-BuLi/TMEDA (or DABCO) system was performed under dry argon for 30 min. Next, 1,3-CHD was added to this reaction



Scheme 2 X-Toluene for the functionalization of C₆₀.



Scheme 3 Examination of the metalation of X-toluene with the *t*-BuLi/amine system using living anionic polymerization of 1,3-CHD.

mixture and the polymerization was carried out under dry argon for 2 h. The ^1H NMR measurements for each polymer obtained were then performed to examine the yield of carbanion.

As we reported in a previous article,⁴ PCHD initiated by the X-BzLi/amine system (Path A) has the X-benzyl residue at the polymer chain-end. PCHD initiated by *t*-BuLi/amine system (Path B) has the *t*-butyl residue at the polymer chain-end (Scheme 3). Therefore, the yield of carbanion in the form of the X-BzLi/amine system can be determined by the molar ratio of the X-benzyl residues/*t*-butyl residues obtained from the ^1H NMR spectra of PCHD (i.e., the molar ratio of X-benzyl residues/*t*-butyl residues and the yield of carbanion seem to be equivalent). The molar ratio of the X-benzyl residues/*t*-butyl residues is calculated by the following formula:⁴

$$\text{X-Benzyl residues}/t\text{-butyl residues (mol/mol)}$$

$$= (\alpha/\text{number of aromatic protons})/(\beta/\text{number of methyl protons})$$

where α : Peak area of aromatic protons (Hp), β : Peak area of methyl protons ($\text{H}_{t\text{-Bu}}$).

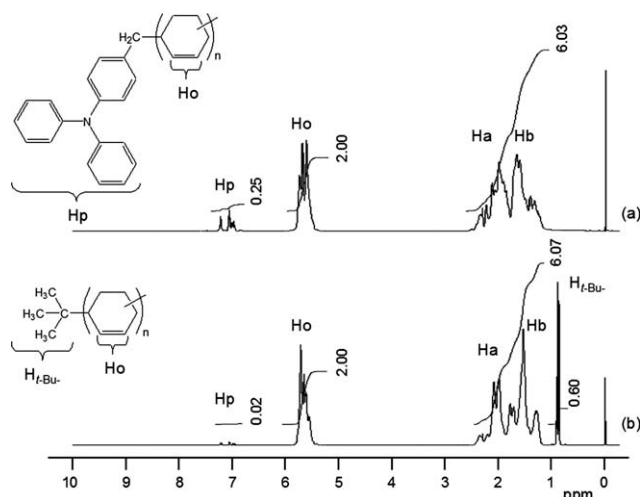


Figure 1 ^1H -NMR spectra of PCHD initiated by the metalation products of MTPA with the *t*-BuLi/TMEDA system (a) and the *t*-BuLi/DABCO system (b) in a 3.0 wt % solution of CDCl_3 at 50°C .

Figure 1 shows typical ^1H NMR spectra of PCHD initiated by the metalation products of MTPA with the *t*-BuLi/TMEDA system [Fig. 1(a)] and the *t*-BuLi/DABCO system [Fig. 1(b)] in cyclohexane. The peaks from 5.49 to 5.85 ppm (Ho), from 1.85 to 2.50 ppm (Ha), and from 1.10 to 1.85 ppm (Hb) were assigned to olefinic, methine, and methylene protons, respectively, on the cyclohexadiene (CHD) units in the polymer chain.⁸ The peaks near 0.9 ppm ($\text{H}_{t\text{-Bu}}$) were assigned to methyl protons in the *t*-butyl residues of *t*-BuLi. The small peaks near 7.2 ppm (Hp) were assigned to aromatic protons in the triphenylamino group at the polymer chain-end (i.e., X-benzyl residues of X-BzLi; X = diphenylamine).

In the case of the *t*-BuLi/TMEDA system as a metalation reagent for MTPA, there was no peak near 0.9 ppm [Fig. 1(a)]. Therefore, the yield of carbanion in this metalation reaction was thought to be 100%.

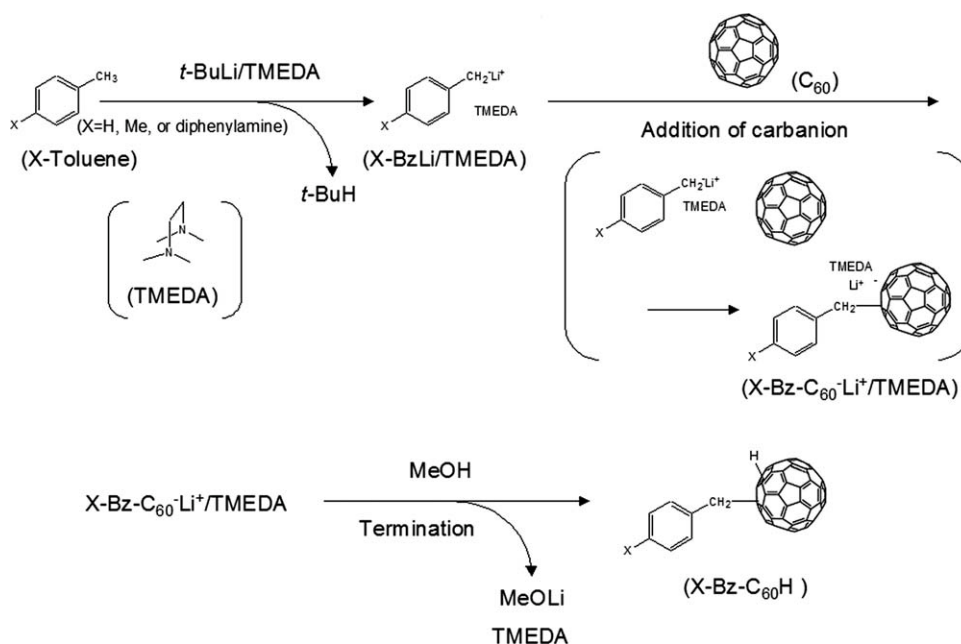
TABLE I
Preparation of the X-BzLi/Amine System as Carbanion

No.	Metalation ^a			Polymerization ^b		Yield of carbnion (%) ^c
	X-Toluene	Amine	Solvent	M_n (RI)	PDI	
1	Toluene	TMEDA	Toluene	3720	1.15	100
2	Toluene	DABCO	Toluene	7100	1.24	99
3	<i>p</i> -Xylene	TMEDA	<i>p</i> -Xylene	1450	1.20	100
4	<i>p</i> -Xylene	DABCO	<i>p</i> -Xylene	15,200	1.34	98
5	MTPA	TMEDA	Cyclohexane	4810	1.32	100
6	MTPA	DABCO	Cyclohexane	1540	1.17	2.1
7	MTPA	TMEDA	Tetralin	5490	1.64	100
8	MTPA	DABCO	Tetralin	4280	1.21	43

^a The metalation of X-toluene with the *t*-BuLi/amine system was conducted under dry argon at room temperature for 30 min. X-Toluene/*t*-BuLi = 1.20/1.00 (mol/mol).

^b The polymerization of 1,3-CHD was carried out in dry argon at room temperature for 2 h [$1,3\text{-CHD}]_0/[\text{Li}]_0 = 38.0/1.00$ (Nos. 1 and 2), 17.5/1.00 (Nos. 3–8) (mol/mol).

^c X = Benzyl residues/*t*-butyl residus (mol/mol)⁴.



Scheme 4 Synthesis of functionalized C₆₀ using the metalation product of X-toluene with the *t*-BuLi/TMEDA system.

When the *t*-BuLi/DABCO system was used as a metalation reagent for MTPA, the molar ratio of the X-benzyl residues/*t*-butyl residues was (0.02/14)/(0.60/9) = 2.10/97.9 [Fig. 1(b)], indicating that the yield of carbanion is only 2.1% in this metalation reaction.

Table I summarizes the results of the metalation of X-toluene with the *t*-BuLi/TMEDA (or DABCO) system. For toluene and *p*-xylene, almost quantita-

tive yields of benzyl carbanion were obtained by the *t*-BuLi/TMEDA and *t*-BuLi/DABCO systems (Nos. 1–4 in Table I). With regard to MTPA, which has a nitrogen atom (a typical electron donor) in the X group, only the *t*-BuLi/TMEDA system gave 100% yield of 4-diphenylaminobenzyl carbanion (Nos. 5 and 7 in Table I) due to its strong nucleophilicity.⁴ The yield of 4-diphenylaminobenzyl carbanion from MTPA was below 50% in the case of the *t*-BuLi/

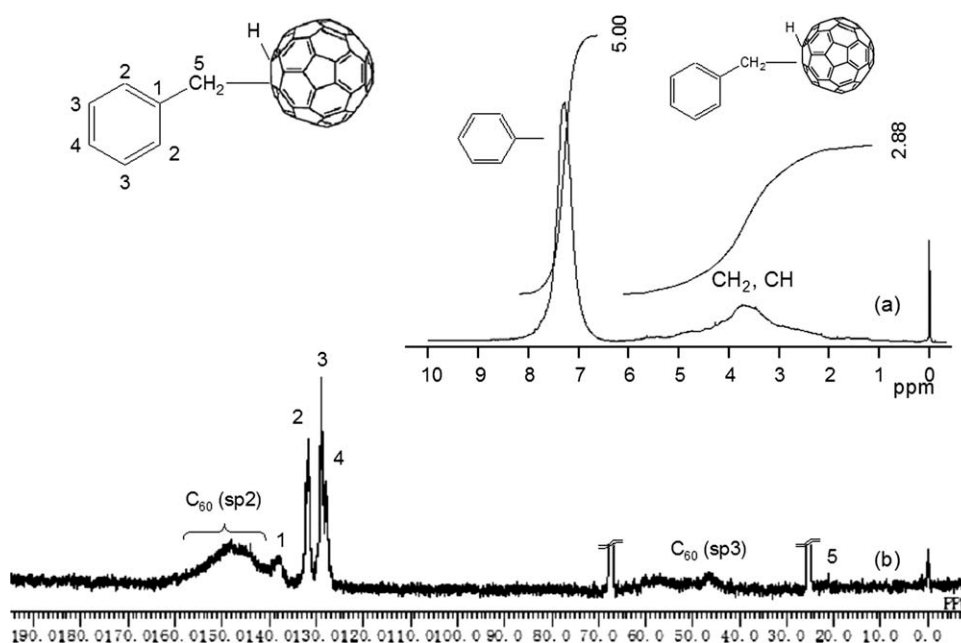


Figure 2 ¹H (a) and ¹³C (b) NMR spectra of toluene-functionalized C₆₀ in a 7.0 wt % solution of THF-*d*₈ at 50°C.

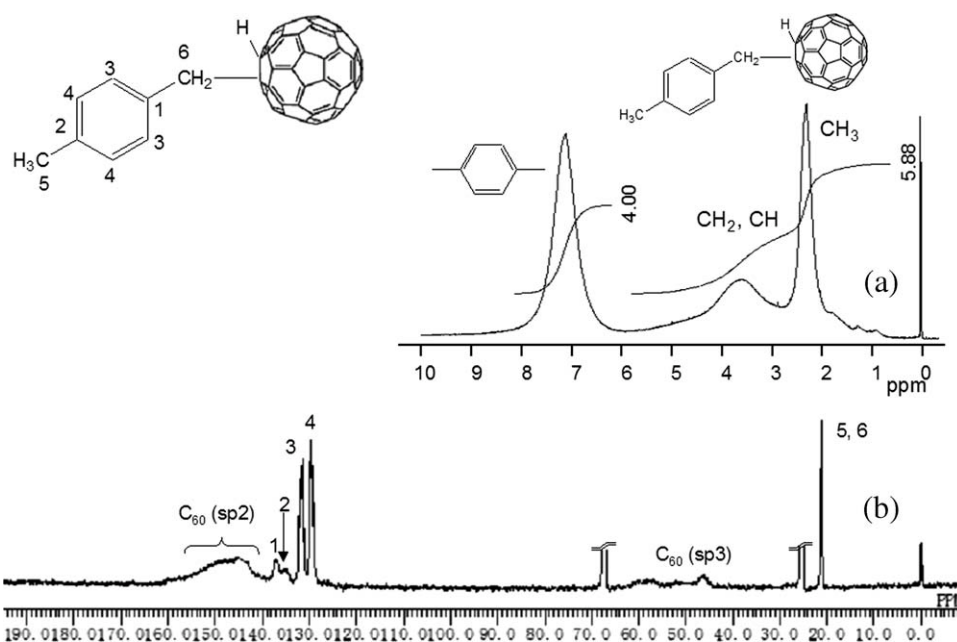


Figure 3 ^1H (a) and ^{13}C (b) NMR spectra of *p*-xylene-functionalized C_{60} in a 7.0 wt % solution of $\text{THF-}d_8$ at 50°C .

DABCO system (Nos. 6 and 8 in Table I). Therefore, it was concluded that the *t*-BuLi/TMEDA system was an appropriate metalation reagent for X-toluene.

Addition of carbanion onto C_{60} using the X-BzLi/TMEDA system

To obtain the functionalized C_{60} , the addition of carbanion onto C_{60} using the X-BzLi/TMEDA system ($\text{X} = \text{H}$, Me, and diphenylamine) was performed under dry argon for 24 h [$\text{C}_{60}/\text{Li} = 1/6$ (mol/mol)] (Scheme 4). After the addition reaction, all products obtained were easily soluble in THF, although the original C_{60} was insoluble in THF.

In the case of toluene as X-toluene ($\text{X} = \text{H}$), the metalation product No. 1 in Table I was used as the corresponding X-BzLi/TMEDA system. Typical ^1H and ^{13}C NMR spectra of the toluene-functionalized C_{60} are shown in Figure 2. In the ^1H NMR spectrum [Fig. 2(a)], the aromatic proton signal was observed in the region from 6.5 to 7.3 ppm, and the methylene (CH_2) and methine (CH on C_{60}) signals were observed in the region from 1.2 to 5.8 ppm. The ratio of aromatic protons/methylene+methine protons was 5/3, which suggested the successful addition of benzyl carbanion onto C_{60} . In the ^{13}C NMR spectrum [Fig. 2(b)], the peaks at 138, 132, 129, and 128 ppm of the toluene-functionalized C_{60} were assigned to the 1, 2, 3, and 4 carbons, respectively. The peaks around 21 ppm were assigned to the 5 carbon. The broad peaks around 147 and 46 ppm are likely to be due to the sp^2 and sp^3 carbons on C_{60} .⁷ Therefore,

the formation of toluene-functionalized C_{60} was confirmed.

With respect to *p*-xylene as X-toluene ($\text{X} = \text{Me}$), metalation product No. 3 in Table I was used as the corresponding X-BzLi/TMEDA system. Typical ^1H and ^{13}C NMR spectra of the *p*-xylene-functionalized C_{60} are shown in Figure 3. In the ^1H NMR spectrum [Fig. 3(a)], the aromatic proton signal was observed in the region from 6.2 to 7.8 ppm, and the methylene (CH_2) and methine (CH on C_{60}) signals were observed in the region from 1.5 to 5.5 ppm. The methyl (CH_3) proton signal was observed in the region from 1.8 to 2.6 ppm. The ratio of aromatic protons/methylene+methine+methyl protons was 4/6, which suggested the successful addition of benzyl carbanion onto C_{60} . In the ^{13}C NMR spectrum [Fig. 3(b)], the peaks at 137, 135, 132, and 129 ppm of the *p*-xylene-functionalized C_{60} were assigned to the 1, 2, 3, and 4 carbons, respectively. The peaks around 21 ppm were assigned to the 5 and 6 carbons. The broad peaks around 147 and 46 ppm are likely to be due to the sp^2 and sp^3 carbons on C_{60} .⁷ Therefore, formation of the *p*-xylene-functionalized C_{60} was confirmed.

As we previously reported, the number of carbanions bonded to C_{60} can be estimated by the addition of the corresponding living polymers onto C_{60} .⁵⁻⁷ To determine the number of benzyl carbanions bonded to C_{60} , a grafting reaction of the polystyryllithium (PStLi)/TMEDA system onto C_{60} [$\text{C}_{60}/\text{Li} = 1/3$, $1/4$, and $1/6$] was performed as the model reaction for the addition of benzyl carbanion onto C_{60} using the X-BzLi/TMEDA system ($\text{X} = \text{H}$ or Me). The PSt-

TABLE II
Grafting Reaction of the PStLi/TMEDA System onto C₆₀

No.	C ₆₀ /Li	PSt arm molecule ^a			Grafting reaction product ^b				
			<i>M_n</i> (RI)	PDI		<i>M_n</i> (UV _{330nm})	PDI	<i>M_n</i> (RI)	Grafting density (<i>D</i>) ^c
9	1/3	PSt-1	3640	1.17	C ₆₀ -PSt-1	5310	1.85	4710	1.49
10	1/4	PSt-2	3620	1.19	C ₆₀ -PSt-2	5760	1.43	4870	1.59
11	1/6	PSt-3	3860	1.15	C ₆₀ -PSt-3	6200	1.37	4940	1.61

^a The PStLi/TMEDA system was prepared by living anionic polymerization of St with the *t*-BuLi/TMEDA system in cyclohexane (10 mL) at room temperature for 3 h [*St*]₀/*t*-BuLi]₀ = 36.0/1.00 (mol/mol). *t*-BuLi/TMEDA = 1.00/1.25 (mol/mol). St/cyclohexane = 10/90 (vol./vol.).

^b The grafting reaction of PStLi/TMEDA system onto C₆₀ was conducted in toluene under dry argon at room temperature for 24 h.

^c *D* = *M_n* (UV_{330nm}) of reaction products/*M_n* (RI) of PSt arms.^{5–7}

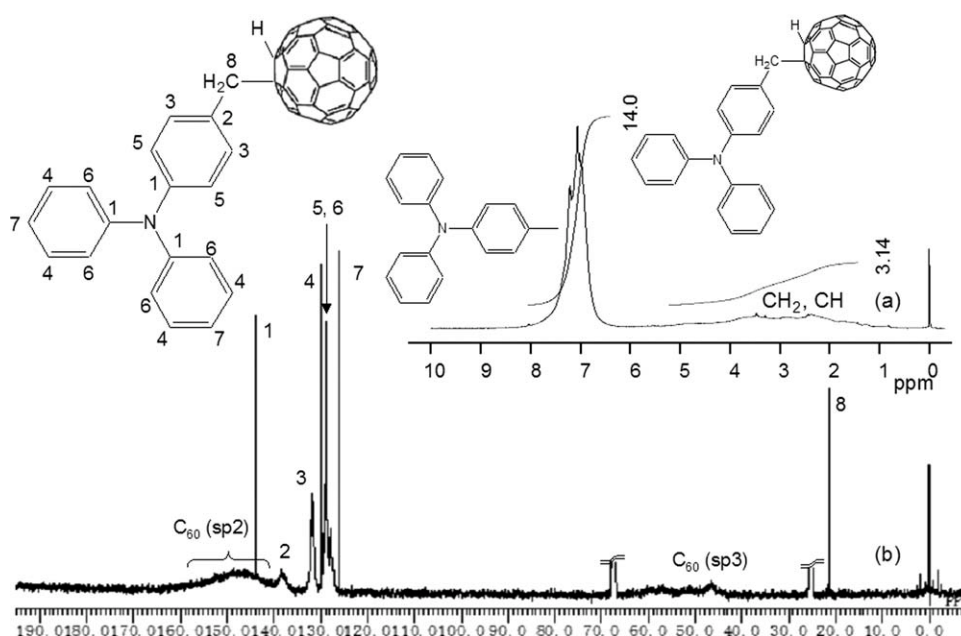


Figure 4 ¹H (a) and ¹³C (b) NMR spectra of MTPA-functionalized C₆₀ in a 7.0 wt % solution of THF-*d*₈ at 50°C.

functionalized C₆₀ was obtained in almost quantitative yield.* The grafting density (*D*; i.e., approximation of the number of PSt arm molecules on C₆₀) of PSt arms onto C₆₀ was then estimated according to the previously reported procedure,^{5–7} except a UV detector set at 330 nm was used.[†] The results

*The PStLi/TMEDA system was prepared by living anionic polymerization of St with the *t*-BuLi/TMEDA system in cyclohexane (10 mL) at room temperature for 3h. [*St*]₀/*t*-BuLi]₀ = 36.0/1.00 (mol/mol). *t*-BuLi/TMEDA=1.00/1.25 (mol/mol). St/cyclohexane = 10/90 (vol./vol.). The grafting reaction of PStLi/TMEDA system onto C₆₀ was conducted in toluene under dry argon at room temperature for 24 h.

[†]PSt produces almost no absorption in the region greater than 320 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, PSt-functionalized C₆₀ has strong absorption in the region greater than 320 nm, and is readily soluble in THF.

obtained are summarized in Table II. The *D* of PSt arms onto C₆₀ was ~ 1.50, regardless of the molar ratio of C₆₀/Li. Therefore, toluene- and *p*-xylene-functionalized C₆₀ obtained in this study (C₆₀/Li = 1/6) seem to have on average 1.50 functional groups on C₆₀.

In the case of MTPA as X-toluene (X = diphenylamine), the metalation product No. 5 in Table I was used as the corresponding X-BzLi/TMEDA system. Typical ¹H and ¹³C NMR spectra of the MTPA-functionalized C₆₀ are shown in Figure 4. In the ¹H NMR spectrum [Fig. 4(a)], the aromatic proton signal was observed in the region from 6.6 to 7.8 ppm, and the methylene (CH₂) and methine (CH on C₆₀) signals were observed in the region from 1.2 to 4.8 ppm. The ratio of aromatic protons/methylene+methine protons was 14/3, which suggested the successful addition of 4-diphenylaminobenzyl carbanion onto C₆₀. In the ¹³C NMR spectrum [Fig. 4(b)], the peaks

at 144, 138, 132, 130, and 126 ppm of the MTPA-functionalized C₆₀ were assigned to the 1, 2, 3, 4, and 7 carbons, respectively. The peaks around 129 ppm were assigned to the 5 and 6 carbons. The broad peaks around 147 and 46 ppm are likely to be due to the sp² and sp³ carbons on C₆₀.⁷ Therefore, formation of the MTPA-functionalized C₆₀ was confirmed.

As we previously revealed, the number of 4-diphenylaminobenzyl carbanions bonded onto C₆₀ is one, regardless of the molar ratio of C₆₀/Li.⁷ Therefore, MTPA-functionalized C₆₀ obtained in this study (C₆₀/Li = 1/6) has one functional group on C₆₀.

CONCLUSIONS

The synthesis of functionalized C₆₀ was attempted using the living anionic polymerization technique. The preparation of several carbanions in the form of the X-BzLi/amine system was performed by the metalation of the benzylic hydrogen atom on X-toluene with the RLi/amine system. The yield of carbanion was examined by living anionic polymerization of 1,3-CHD, and it was found that the *t*-BuLi/TMEDA system was an appropriate metalation reagent for X-toluene. The metalation of X-toluene (X = H, Me, and diphenylamine) with the *t*-BuLi/TMEDA system gave the corresponding X-BzLi/TMEDA system (i.e., carbanion) in quantitative

yield. On average, 1.50 benzyl carbanions and one 4-diphenylaminobenzyl carbanion could bond onto one C₆₀ molecule, and all products obtained were easily soluble in THF, although the original C₆₀ was insoluble in THF. From the results of the ¹H and ¹³C NMR spectra, the successful synthesis of the toluene-, *p*-xylene-, and MTPA-functionalized C₆₀ was confirmed. The living anionic polymerization technique with the *t*-BuLi/TMEDA system was an effective indicator for the preparation of a variety of carbanions from toluene or *p*-substituted toluene (X-Toluene; X = H or R), and these carbanions facilitated the synthesis of functionalized C₆₀.

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