Synthesis of 1,4-Dipolystyryldihydro[60]fullerenes by Using 2,2,6,6-Tetramethyl-1-polystyroxypiperidine as a Radical Source

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ABSTRACT: This is the first report of the synthesis of well-defined disubstituted polymer derivatives of C_{60} by a radical mechanism. Narrow-polydispersity polystyryl adducts with TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), prepared by the nitroxyl-mediated "living" radical polymerization technique, were heated with a 4-fold excess (in molar ratio) of C_{60} in *o*-dichlorobenzene at 145 °C to give 1,4-dipolystyryldihydro[60]fullerenes (yields 60−80%). A low-mass model compound 2-benzoyloxy-1-phenylethyl adduct with TEMPO gave essentially the same result. These disubstituted derivatives retained the redox properties of C_{60} and gave UV−vis spectra characteristic of 1,4-bisadducts. A possible mechanism by which disubstituted derivatives are selectively produced was discussed.

Introduction

C_{60}, a representative of the fullerene family, has attracted much attention due to its unique physical and chemical properties.[1] Various methods for the chemical modification of C_{60} have been reported not only for fundamental studies[2] but also for application purposes.[3] In order to overcome the low solubility and poor processability of C_{60}, incorporation of C_{60} molecules into polymer chains is gaining particular interest.

Fullerene-containing polymers[4−8] reported so far can be classified into four types. The first type is polymers with fullerene units incorporated into main chain (in-chain type).[4] The second is those bearing pendant fullerene (on-chain type).[5] The third is fullerene-incorporating polymer networks (cross-link type), where fullerene acts as a cross-linking site.[6] The fourth is fullerene-terminated telechelic polymers, i.e., polymers having one or two fullerene end groups (end-chain type).[7,8] In particular, many attempts have been made for the preparation of C_{60}-endcapped polymers: Samulski *et al.*[7] reported the preparation of polystyrene-(PS-) multisubstituted fullerenes, which they designated "flagellenes", by the use of nucleophilic addition of C_{60} to living anionic polymer species. To regulate the addition number, an excess equivalent of C_{60} was effective. By this principle, PS-monosubstituted C_{60} with a well-defined structure was prepared.[9] Frey *et al.*[10] also prepared PS-monosubstituted C_{60} by the reaction of C_{60} with the amino-functionalized polystyrene prepared by living anionic polymerization. We reported the preparation of poly(vinyl ether)-monosubstituted C_{60} by the addition of living cationic polymerization species to 2-(1-octynyl)-1,2-dihydro[60]fulleren-1-ide ion.[11]

On the other hand, the preparation of PS−C_{60} adducts by the radical mechanism[12−14] has been attempted by carrying out the copolymerization of C_{60} with styrene in bulk or in solution initiated spontaneously or with azobis(isobutytonitrile) or benzoyl peroxide. But the reaction products were, in many cases, a mixture of poorly defined multiadducts of PS, and it seems very difficult to prepare PS−C_{60} adducts with a well-defined structure by the usual radical polymerization methods.

This paper deals with the first synthesis of well-defined polymer derivatives of [60]fullerene by the addition reaction between C_{60} and the polystyryl radical derived from a PS−TEMPO adduct, where TEMPO is 2,2,6,6-tetramethylpiperidinyl-1-oxy. For this purpose, we prepared several PS−TEMPO adducts with narrow-polydispersity PS[15] of varying lengths and also a low-mass model compound BS−TEMPO,[16,17] where BS is a 2-benzoyloxy-1-phenylethyl group. These adducts are expected to produce polystyryl (or benzoyloxystyryl) radicals at high temperatures by the cleavage of the C−ON bond. An independent experiment has confirmed that TEMPO does not add to C_{60}. So the system we employ is much simpler than the conventional ones. A similar reaction was reported recently,[18] but the reaction products therein reported are quite different from those obtained here and, in our opinion, poorly defined. Some discussion will be given about the reaction mechanism and the electric properties of the products.

Experimental Section

Measurements. NMR spectra were observed at 270 MHz for ^{1}H and 100 MHz for ^{13}C NMR. Mass spectra were measured with a Finnigan TSQ 7000 spectrometer. Cyclic voltammetry was conducted on a BAS electro-analyzer CV-50W using a three-electrode cell with a glassy-carbon working electrode, a platinum counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potential was corrected against ferrocene added immediately after each measurement.

Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merck, particle size 0.040−0.063 mm, 230−400 mesh ASTM) as a stationary phase.

Gel permeation chromatography (GPC) was carried out in tetrahydrofuran (THF) on a Tosoh HLC-802UR chromatograph (Tokyo, Japan) equipped with polystyrene gel columns (G2500H6 + G3000H6 + G4000H6; exclusion limit = 1.0×10^6; 8.0 mm i.d. × 60 cm) and refractive index/ultraviolet dual-mode detectors. The system was calibrated with Tosoh standard PSs.

Materials. C_{60} was separated from a commercial C_{60}/C_{70} mixture (ca. 80:20 by weight; Term Co.) by the use of a Norit carbon−silica gel column. THF was freshly distilled from sodium benzophenone ketyl before use. *o*-Dichlorobenzene (ODCB) was distilled over CaH_2. Benzonitrile was distilled over P_2O_5. Commercially obtained styrene and benzoyl peroxide (BPO; Nacalai Tesque, Japan) were purified by the standard methods described elsewhere.[19] TEMPO (Aldrich) was used as received.

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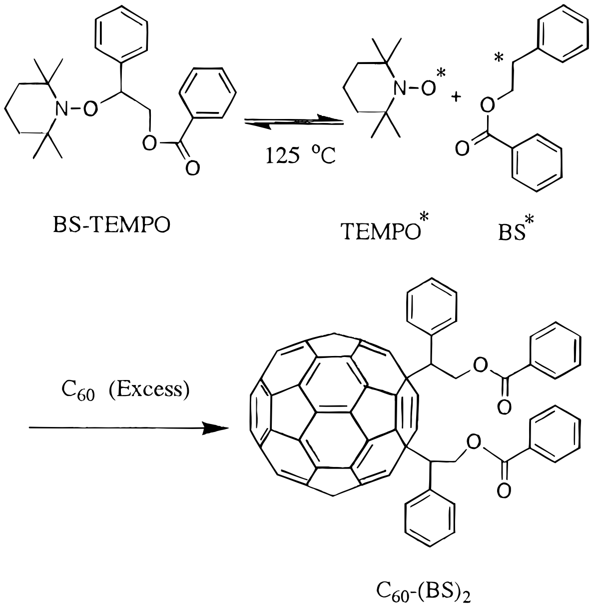
Preparation of PS−TEMPO and BS−TEMPO. PS−TEMPO adducts were prepared as described previously.[20] In a typical run, a mixture of styrene, BPO (6.80×10^{-2} mol L^{-1}), and TEMPO (7.14×10^{-2} mol L^{-1}) was charged in a glass tube, degassed with several freeze−thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 95 °C for 3.5 h and at 125 °C for 4 h to yield a polymer. The polymer was recovered as a precipitate from a large excess of methanol, purified by reprecipitation with a chloroform (solvent)/methanol (nonsolvent) system, and thoroughly dried (conversion: 14.5%), which, according to the PS-calibrated GPC, had a number-average molecular weight M_n of 2400 and a M_w/M_n ratio of 1.14. A chain-extension test[20] indicated that this sample contained a fraction of inactive species (without a TEMPO moiety at the chain end) in about 5%.

The BS−TEMPO adduct was prepared as reported previously.[16] BPO (0.80 mol L^{-1}) and TEMPO (0.96 mol L^{-1}) were dissolved in styrene and heated at 95 °C for 3.5 h after degassing. The crude product was purified by column chromatography, and BS−TEMPO was obtained in 42% yield.

Preparation of C_{60}−BS Adduct. The C_{60}−BS adduct was prepared as follows. BS−TEMPO (6.90×10^{-4} mol L^{-1}) and C_{60} (2.78×10^{-3} mol L^{-1}) were dissolved in ODCB, charged in a glass tube, degassed with several freeze−thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 125 °C for 24 h. The product was subjected to column chromatography to afford a C_{60}−BS adduct in 69% yield;[21] ^{1}H NMR (270 MHz, $(CD_3)_2CO/CS_2 = 1:4$) δ 8.52−7.35 (m, 6H, aromatic), 7.35−6.98 (m, 14H, aromatic), 5.44 (m, 4H, O−CH_2), 4.47 (m, 2H, CH−Ph); ^{13}C NMR (100 MHz, $(CD_3)_2CO/CS_2 = 1:4$) δ 168.34, 168.25, 168.14, 168.06 (CO in previous 4 peaks), 157.39, 157.30, 156.64, 156.50, 154.30, 153.92, 153.19, 152.82, 151.63, 151.60, 151.52, 151.25, 151.16, 151.18, 150.76, 150.60, 150.21, 150.18, 149.93, 149.88, 148.99, 148.65, 148.52, 148.27, 148.21, 148.16, 148.09, 148.04, 147.73, 147.67, 147.62, 147.53, 147.42, 147.38, 147.33, 147.31, 147.25, 147.18, 147.17, 147.11, 147.04, 146.91, 146.54, 146.44, 146.12, 146.37, 146.30, 146.28, 146.22, 146.16, 146.14, 146.08, 145.91, 145.87, 145.74, 148.67, 145.65, 146.62, 145.57, 145.56, 145.39, 145.31, 145.30, 145.18, 145.03, 144.68, 144.61, 144.28, 144.19, 143.76, 143.01, 142.36, 141.94, 141.85, 141.71, 141.61, 144.58, 141.56, 140.21, 140.07, 139.39, 139.29, 139.06, 137.11, 136.59, 136.47, 139.01, 135.98, 135.94, 135.72, 133.55, 133.46, 133.21, 133.17, 133.09, 133.01, 132.98, 132.64, 132.89, 132.80, 132.76, 132.72, 132.64, 132.61, 132.29, 131.96, 131.87, 131.92, 131.76, 131.71, 131.68, 131.59, 131.51, 131.48, 131.41, 131.39, 131.30, 131.24, 131.13, 130.99, 130.85, 130.44, 130.31, 129.30, 128.99, 128.96 (126 signals, sp^2-carbons in the C_{60} core and the phenyl group), 68.85, 68.63, 68.10, 67.76 (CH_2−O in the previous four peaks), 64.87, 64.86, 64.78, 64.75 (quaternary sp^3-C in the C_{60} core in previous four peaks), 58.93, 58.83, 58.66, 57.99 (CH−Ph in the previous four peaks); UV−vis (cyclohexane) λ_{max} 210 nm (log ϵ 5.40), 257 (5.02), 328 (4.53), 440 (3.70), 540 (sh, 3.06), 620 (sh, 2.77), 684 (2.42); Anal. Calcd for $C_{90}H_{26}O_4$: C, 92.31; H, 2.24; N, 0.00. Found: C, 91.99; H, 2.10; N, 0.00; MS (+FAB) *m/z* 1194 (M + Na^+), 1172 (M + H^+), 720 (C_{60}^+).

Preparation and Purification of C_{60}−PS Adducts. In a typical run, PS−TEMPO (6.90×10^{-4} mol L^{-1}) and C_{60} (2.78×10^{-3} mol L^{-1}) were dissolved in ODCB (5.00 mL), charged in a glass tube, degassed with several freeze−thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 145 °C for 24 h. The product was a mixture of C_{60}−PS adducts, unreacted PS, and unreacted C_{60}. The following methods were used for purification of the samples: Since the solubility of C_{60} in THF is very low, virtually all (unreacted) C_{60} was removed as a precipitate by pouring the reaction mixture into THF (50 mL). The supernatant was dried by evaporation, to which 5.0 mL of benzene was added to dissolve the polymer. To this solution, 5.0 mL of methanol was slowly added and the precipitate was recovered by decantation. Since C_{60}−PS adducts and PS (or PS−TEMPO) have largely different solubilities in organic solvents, this process was effective enough to separate C_{60}−PS (precipitate) from PS (in solution). In fact, it was confirmed that the supernatant contained no C_{60} derivatives and that the PS−TEMPO adduct was perfectly soluble in the benzene/methanol mixture. All of the precipitate was carefully collected by centrifugation. The decanted solution was confirmed to contain only unreacted PS by ^{1}H NMR, UV, and GPC.

Scheme 1



Results and Discussion

C_{60}−BS Adduct. As a model reaction of PS−TEMPO with C_{60}, we investigated the reaction of BS−TEMPO with C_{60} at 125 °C in ODCB. The ^{1}H NMR spectrum of the purified product was very different from that of BS−TEMPO, and indicated the structure of the product to be a bisadduct, C_{60}−$(BS)_2$ (Scheme 1). Each signal derived from the BS unit was broadened, and the signals relevant to TEMPO were absent. The result of elemental analysis was consistent with the bisadduct structure, i.e., C, 92.0 (92.3); H, 2.1 (2.2); and N, 0 (0), where the values in parentheses are theoretical. Mass spectrum also supported this structure, i.e., the molecular ion peak (M^+) appeared at 1171 in agreement with the theoretical value of 1171.2. Thus, we can conclude that this C_{60} derivative has two BS units with no TEMPO moiety.

It is known that disubstituted C_{60} derivatives show characteristic UV−vis absorption depending on the relative positions of substitution. Figure 1 shows the UV−vis spectrum of C_{60}−$(BS)_2$ in comparison to those of 1,4-difluorenyldihydro[60]fullerene (C_{60}−$(Flu)_2$)[22] and 1-(1-octynyl)-2-isobutoxyethyl-1,2-dihydro[60]fullerene (Octynyl−C_{60}−IBVE)[23] which were previously reported. Clearly, the spectrum of C_{60}−$(BS)_2$ is very different from that of Octynyl−C_{60}−IBVE, and quite similar to that of C_{60}−$(Flu)_2$. Both C_{60}−$(BS)_2$ and C_{60}−$(Flu)_2$ exhibit a broad absorption at around 440 nm. This shows that C_{60}−$(BS)_2$ is a 1,4-disubstituted derivative, not a 1,2 type.

The ^{13}C NMR spectrum is shown in Figure 2. In addition to the four characteristic peaks (a−d), aromatic carbons derived from the C_{60} and phenyl moieties were observed between 110 ppm and 160 ppm. Interestingly, each of the peaks a through d splits into four peaks. Multiple peak-splitting is also seen for the aromatic carbons.

Most of the reported C_{60} derivatives carrying two identical substituents at the 1,4-positions have a C_{2v} symmetry. In contrast, the 1,4-C_{60}−$(BS)_2$ does not have this symmetry due to the two asymmetric carbons (c) of the 2-benzoyloxy-1-phenylethyl group directly attached to the C_{60} core, and therefore it should exhibit

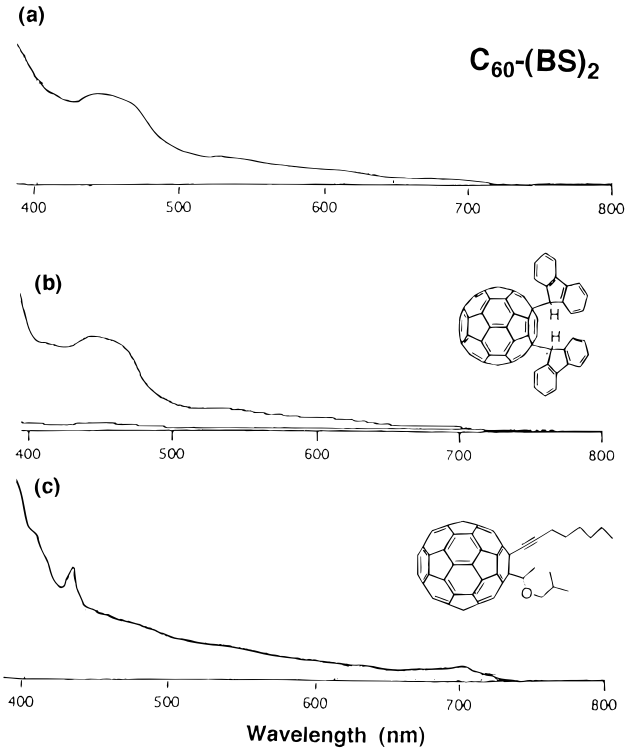


Figure 1. UV−vis spectra of (a) C_{60}−$(BS)_2$, (b) C_{60}−$(Flu)_2$ and (c) octynyl−C_{60}−IBVE in cyclohexane.

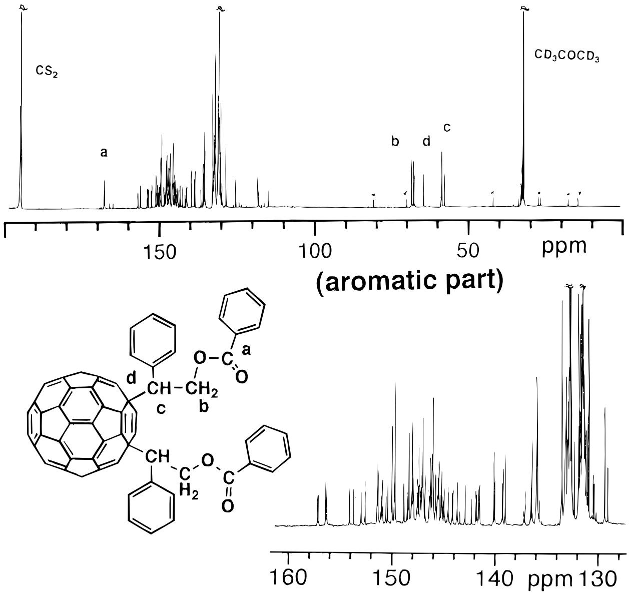


Figure 2. ^{13}C NMR spectrum of C_{60}−BS in $CS_2/(CD_3)_2CO$ = 4:1.

116 signals for the sp^2 carbons of the C_{60} core. (Actually, 126 peaks including those derived from the phenyl group were discernible in the spectrum.) A similar phenomenon was observed for a C_{60} derivative having a chiral phosphine−borane moiety.[24] With all these data, we conclude that the product that we obtained is 1,4-bis(2-benzoyloxy-1-phenylethyl)dihydro[60]fullerene. As has been described, the preparation procedure is very simple, and should be practically useful as a method to functionalize C_{60}.

C_{60}−PS Adducts. We investigated the reaction of four PS−TEMPO samples with C_{60} according to Scheme 2. Table 1 shows the reaction conditions. The yield of the purified product, which we designate C_{60}−PS, ranged form 60% to 80%, showing no appreciable dependence on the molecular weight of the PS moiety.

Scheme 2

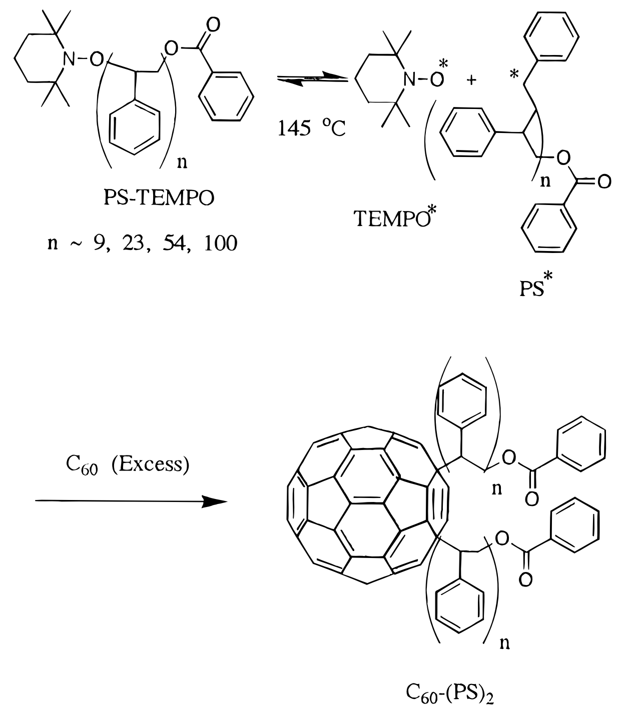


Table 1. Reaction of PS−TEMPO with C_{60}[a]

code	M_n (M_w/M_n)[b]	% yield[c]
PS−TEMPO-1000	1040 (1.11)	56
PS−TEMPO-2400	2400 (1.14)	75
PS−TEMPO-5500	5500 (1.18)	67
PS−TEMPO-10000	10000 (1.14)	78

[a] In *o*-dichlorobenzene (145 °C, 24 h); [PS−TEMPO] = 3.5×10^{-5} mol L^{-1} and $[C_{60}] = 1.4 \times 10^{-4}$ mol L^{-1} in all cases. [b] By PS-calibrated GPC. [c] 100 × (wt of PS in C_{60}−PS)/(wt of PS−TEMPO).

We characterized the samples of C_{60}−PS by ^1H and ^{13}C NMR, UV−vis, and GPC. Figure 3 shows the ^{13}C NMR spectra of C_{60}−PS-1000, where the attached number shows an approximate value of M_n of the PS moiety. In addition to the peaks derived from PS, aromatic carbons derived from C_{60} and the ipso carbon in PS are observed between 140 and 160 ppm.

Figure 4 shows the GPC curves of C_{60}−PS-5500 recorded by different detectors. The PS moiety is detectable by both UV-270 nm and RI, but not by UV-430 nm, while the C_{60} moiety is detectable by all UV-430 nm, UV-270 nm, and RI. The three GPC curves of C_{60}−PS-5500 are nearly identical with each other, which indicates chemical uniformity of the polymer. Very interestingly, the three curves retain the narrow polydispersity and commonly show an M_n value of 11600, which is about twice that of the PS−TEMPO adduct. Similar results were obtained for all other samples (Table 2). This indicates that the reaction of PS−TEMPO with C_{60} also leads to a bisadduct.

Figure 5 compares the UV−vis spectra from C_{60}−$(BS)_2$ and C_{60}−PS-1000 solutions of the same concentration. Clearly, the two spectra are very similar to each other. This means that the polymer derivative is also a 1,4-bisadduct, like C_{60}−$(BS)_2$. On the basis of the molar absorption coefficient of C_{60}−$(BS)_2$ at 440 nm, the M_n of the polymer derivatives was estimated (Table 2). Table 2 shows that the values of M_n by GPC and those by UV well agree with each other, and both are close, in most cases, to those calculated for the bisadduct structure. However, the GPC value for the lowest-M_n sample is significantly smaller than the UV and theo-

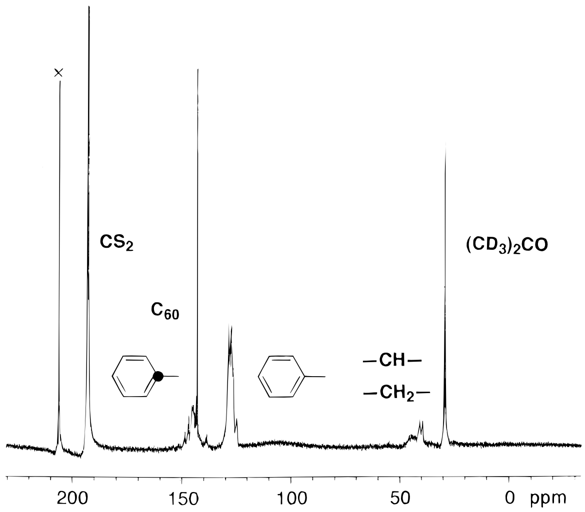


Figure 3. ^{13}C NMR spectrum of C_{60}−PS-1000 in $CS_2/(CD_3)_2CO$ = 4:1.

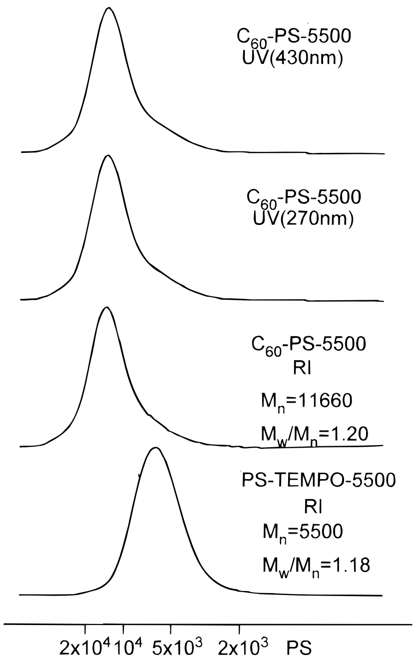


Figure 4. GPC curves of C_{60}−PS-5500 by UV (430 and 270 nm) and RI compared with the curve for PS−TEMPO-5500 by RI.

Table 2. Molecular Weights of PS−TEMPO and C_{60}−PS Estimated by GPC and UV Spectroscopy

M_n (M_w/M_n) by GPC		M_n by UV (440 nm)[a]	M_n calcd
PS−TEMPO	C_{60}−PS	C_{60}−PS	$C_{60}-(PS)_2$
1040 (1.11)	1410 (1.23)	2750	2800
2400 (1.14)	4600 (1.24)	7000	5500
5500 (1.18)	11600 (1.20)	10000	11700
10000 (1.14)	20100 (1.26)	20000	20700

[a] Calculated based on the molar absorption coefficient of $C_{60}-(BS)_2$ of 5.01×10^3 mol^{-1} mL cm^{-1}.

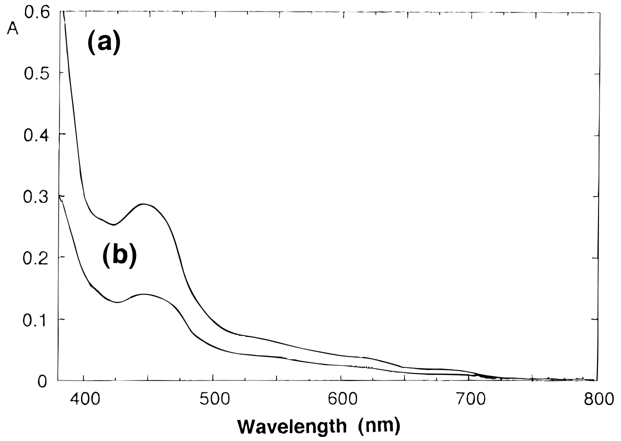


Figure 5. UV−vis spectra from (a) C_{60}−BS (5.8×10^{-5} mol L^{-1}) and (b) C_{60}−PS-1000 solutions of the same weight concentration in cyclohexane.

retical values. This implies that the C_{60} moiety contributes little to the hydrodynamic volume of the molecule because of its compact size and/or poor solubility, leading to an underestimation of M_n by the PS-caliblated GPC. As the size of the PS moiety increases, the relative importance of the C_{60} moiety should decrease and the GPC values will become more reliable, as is in fact observed (Table 2). We thus conclude that the reaction of PS−TEMPOs with C_{60} produces well-defined PS-disubstituted 1,4-dihydro[60]fullerenes, selectively.

Reaction Mechanism. Possible reactions in a C_{60}/PS−TEMPO system at a high temperature may include

$$\text{PS}-\text{TEMPO} \rightleftarrows \text{PS}^* + \text{TEMPO}^* \tag{1}$$

$$\text{PS}^* + C_{60} \rightarrow \text{PS}-C_{60}^* \tag{2}$$

$$\text{PS}-C_{60}^* + \text{PS}^* \rightarrow C_{60}-(\text{PS})_2 \tag{3}$$

$$2\text{PS}^* \rightarrow (\text{PS})_2 \text{ (mainly)} \tag{4}$$

$$2\text{PS}-C_{60}^* \rightleftarrows \text{PS}-C_{60}-C_{60}-\text{PS} \tag{5}$$

$$\text{PS}-C_{60}^* + \text{TEMPO}^* \rightleftarrows \text{PS}-C_{60}-\text{TEMPO} \tag{6}$$

An independent experiment has confirmed that TEMPO* does not add to C_{60}.

Reaction 1 is the reversible dissociation of the polystyroxyamine, whose dissociation and combination (association) rate constants are known.[20,25] The dissociation rate constant at 145 °C is fairly large (9.4×10^{-3} s^{-1}),[25] so that the concentrations of PS* and TEMPO* would reach their quasi-stationary values at an early stage of the heat treatment (≤1 min) after the initial rapid increase from virtually zero values at time zero. Reaction 2 is the addition to C_{60}, and the C_{60} radical thus produced can be capped by another PS radical to produce a 1,4-bisadduct, reaction 3, as we have seen above. Competitively to this can occur reactions 5 and 6. Reaction 5 is the dimerization reported by Morton *et al*,[26] which actually is a reversible reaction (due to the steric instability) with the equilibrium more inclined toward the radical side at higher temperatures. Since reactions 5 and 6 are reversible ones and reaction 3 is an irreversible one, the C_{60} dimer and the C_{60}−TEMPO adduct would eventually become minor in population, even if they may be populated at some stage of the heat treatment. In fact, no TEMPO moiety was detected in the main product, and the molar ratio of the PS and C_{60} moieties in the main product was 2 to 1 in all cases (see above). Reaction 4, which can also occur competitively to section 3, would be unimportant when [PS*] is small enough and reaction 2 is much faster than reaction 4, or $[\text{PS}^*] \ll [\text{PS}-C_{60}^*]$. This seems to be the case, since only a small amount of PS dimer (<10%) was detected in the (benzene/methanol)-soluble fraction which consisted predominantly of homo-PS chains.

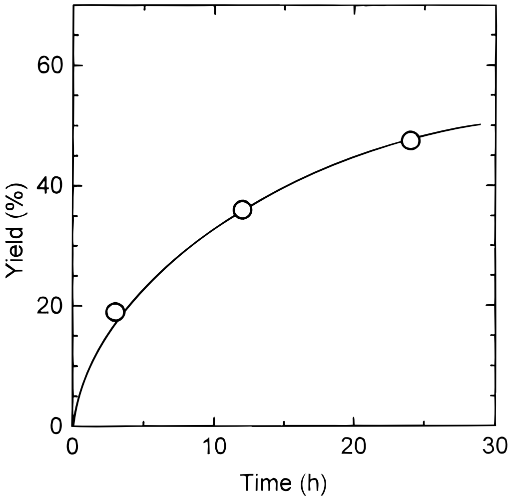


Figure 6. Time−conversion curve for the reaction of C_{60} with PS−TEMPO-3700 at 125 °C.

An independent experiment suggests that, at 145 °C, the reaction seems to be completed within 1 h, and little increase in conversion is expectable with a longer heat treatment. We recently observed that a TEMPO radical deactivates a PS radical by abstracting the β-proton, producing a hydroxyamine and a terminally unsaturated PS.[27,28] The first-order decomposition rate constant of PS−TEMPO due to this mechanism is 4.2×10^{-5} s^{-1} at 145 °C.[28] This value means that after 5 h of the heat treatment at 145 °C, for example, about 50% of the PS−TEMPO adduct decomposes spontaneously. Thus a long heat treatment at a high temperature is not recommended.

To examine the reactions more closely, we have made a test run at a lower temperature, 125 °C, with other conditions unchanged. At this temperature, the decomposition rate is roughly $^1/_{10}$ of that at 145 °C,[28] and all other reactions should also be slower. Figure 6 shows that the conversion gradually increases with time, suggesting that a maximum conversion is reached after several tens of hours. A GPC analysis showed that a main product is again a PS-bisadduct, independent of time. Namely, an increase in reaction time increases the amount of the product but does not change its characteristics.

There are two possible reasons why bisadducts are selectively produced. One is the rather small molar ratio of PS−TEMPO to C_{60} in the feed (1:4, in the present experiments). However, if the addition of PS radicals to C_{60} occurs randomly in proportion to the number of the (unreacted) double bonds of the C_{60} moiety, one would expect to obtain, e.g., a tetrasubstituted compound, according to

$$C_{60}-(PS)_2 + 2PS^* \rightarrow C_{60}-(PS)_4 \qquad (7)$$

with a molar ratio of about $^1/_4$ (weight ratio of about $^1/_2$) relative to the bisadduct. In the actual products, however, tetramers are hardly detectable or, if there are any, much less than expected for the random process (cf. Figure 4). It follows that the bisadducts have a rather high barrier against a further addition of PS*. This barrier may be an entropic (excluded-volume) or a chemical effect (or both) caused by the two PS substituents already attached to the C_{60} core. In any case, it is understandable that the addition of PS* to $C_{60}-(PS)_2$, which is a polymer−polymer reaction, is much slower than the addition of PS* to C_{60}, a reaction between a polymer and a low-mass compound. In this regard, we expect that the decrease of the PS chain length would decrease the selectivity for disubstitution, increasing the chance of multiple additions.

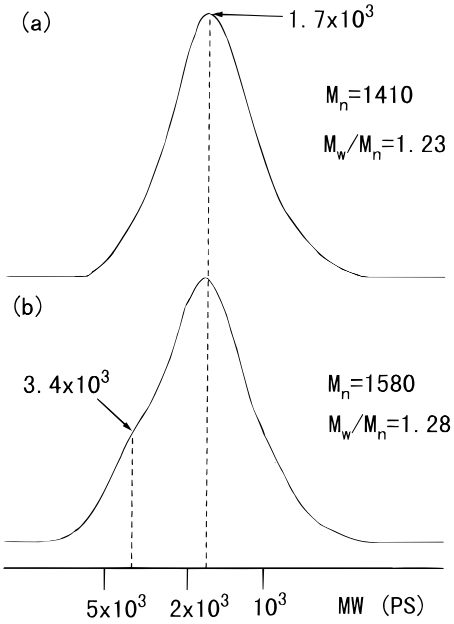


Figure 7. GPC curves for the main products obtained by the heat treatment (145 °C) of PS−TEMPO-1000/C_{60} mixtures with [PS−TEMPO]/[C_{60}] = $^1/_4$ (a) and $^1/_2$ (b).

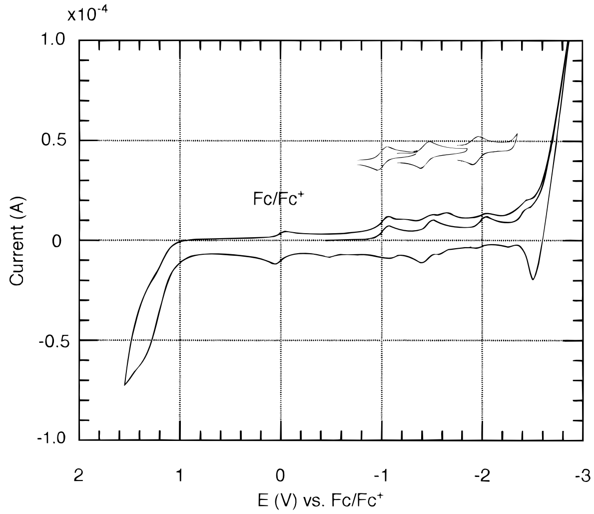


Figure 8. Cyclic voltammogram of $C_{60}-(BS)_2$. Insets show the individual reduction waves measured separately. Potential was measured in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 mol L^{-1}) as a supporting electrolyte; scan rate, 0.1V s^{-1}.

In Figure 7, we compare the GPC charts for the two runs carried out with the shortest PS−TEMPO available (M_n = 1040) with a feed molar ratio of PS−TEMPO to C_{60} of (a) 1:4 and (b) 1:2. Chart b exhibits an obvious shoulder in the molecular weight region corresponding to that of the tetramer, as expected. Thus, in order to obtain bisadducts with a high selectivity, the use is recommended of an excess amount of C_{60} and/or a high-molecular weight, and preferably, narrow-polydispersity PS−TEMPO or equivalent radical source.

Redox Properties. The redox properties of the new compounds $C_{60}-(PS)_2$ and $C_{60}-(BS)_2$ were examined by cyclic voltammetry. Figure 8 demonstrates an example of the voltammogram of $C_{60}-(BS)_2$. Although some weak bumps are observed with a wide sweeping range, the only reproducible waves were a single irreversible oxidation peak and three reversible waves as in the case

Table 3. Results of Cyclic Voltammetry[a]

sample	reversible, $E_{1/2}$ (V)		
	E_{red}^1 (V)	E_{red}^2 (V)	E_{red}^3 (V)
C_{60}	−0.93	−1.36	−1.85
C_{60}−(BS)$_2$	−1.00	−1.41	−1.94
C_{60}−(PS-1000)$_2$	−0.98	−1.40	−1.92
C_{60}−(PS-2400)$_2$	−1.00	−1.39	−1.95
C_{60}−(PS-5500)$_2$	−1.00	−1.44	−2.01
C_{60}−(PS-10000)$_2$	−0.99	−1.40	−2.03

[a] Potential in volts vs ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0.05 mol L^{-1}) as a supporting electrolyte; scan rate, 0.1 V s^{-1}.

of C_{60}. The numerical values obtained are summarized in Table 3. The reduction potentials of C_{60}−(BS)$_2$ and C_{60}−(PS)$_2$ were generally close to those of C_{60}, only about 0.1 V negatively larger than the latter, in agreement with the general tendency of disubstituted C_{60} derivatives.[29]

Conclusions

Narrow-polydispersity polystyryl adducts with TEMPO (PS−TEMPOs), prepared by the nitroxyl-mediated "living" radical polymerization technique, were heated with C_{60} in *o*-dichlorobenzene at 145 °C. The products consisted of three components: (1) unreacted C_{60}, which could readily be recovered as the only insoluble component in THF, (2) polystyryl adducts with C_{60}, and (3) unreacted PS or PS−TEMPO. Owing to the large difference in solubility between C_{60} derivatives and PS or PS−TEMPO, components 2 and 3 were easily separable in a benzene/methanol mixture. The C_{60} derivatives thus obtained with a 60−80% yield were found to be 1,4-dipolystyryldihydro[60]fullerenes, predominantly. A low-mass model compound 2-benzoyloxy-1-phenylethyl adduct with TEMPO gave essentially the same result.

Main reasons for the selective production of the bisadducts in these systems were suggested to be an excess (4-fold excess) of C_{60} relative to PS−TEMPO (or BS−TEMPO) in the feed and/or the potential barrier of the PS moieties of the bisadducts that restricts a further addition of PS radicals to the C_{60} moiety. The instabilities of the C_{60}−TEMPO and C_{60} dimers at high temperatures might be another reason for the bisadduct selectivity.

The disubstituted derivatives thus synthesized retained the redox properties of C_{60} and gave UV−vis spectra characteristic of 1,4-bisadducts of C_{60}.

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