Addition of Polystyryl Radicals from TEMPO-Terminated Polystyrene to C_{60}

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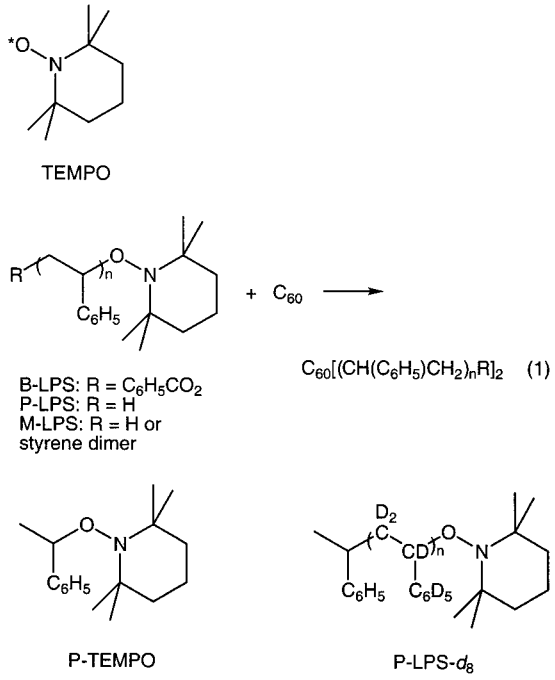
ABSTRACT: Living polystyrene with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) end groups and C_{60} in molar ratios of 1:1 to 4:1 were heated in 1,2-dichlorobenzene solutions to 80−130 °C to produce polymers containing C_{60} units. Multidetector size exclusion chromatographic (SEC) analyses of the recovered polymers showed molar masses corresponding with one, two, and sometimes three of the polystyrene chains. The one-chain components were mixtures of fullerene-containing and fullerene-free macromolecules. The two-chain components contained an average of one fullerene unit per macromolecule, and the three-chain components contained an average of more than one fullerene per macromolecule. Analogy to low molar mass diadducts of alkyl radicals to C_{60} indicates that the polymeric diadducts are isomeric mixtures.

Introduction

The best characterized polymers of C_{60} ([60]fullerene) have been prepared by additions of living polymer chains to C_{60} and by additions of nitrene and amine groups of polymers to C_{60}.[1−4] Additions of several polymer chains to one C_{60} unit are likely because each C_{60} molecule has 30 strained and potentially reactive double bonds. To obtain fullerene polymers with narrow molar mass distributions, the polymer that adds to the C_{60} must be prepared by a living polymerization method, and the number of chains that add must be controlled. Products from living anionic polystyrene and C_{60} contain as few as one to as many as six chains per fullerene unit, depending on relative amounts of reactants, counterions, and solvent,[5−9] and in some cases C_{60} with a specific number of polystyrene chains has been isolated.[8,9]

Radical polymerization of styrene and C_{60} in solution produces branched copolymers with heterogeneous compositions in which some macromolecules contain many fullerene units and others contain none.[10−19] In attempts to control radical polymerization with C_{60} using TEMPO as a mediator, reaction of TEMPO-terminated polystyrene (living polystyrene, LPS) with C_{60} in a 1:4 molar ratio at 125−145 °C in benzene solution gave a polymer whose structure was assigned as 1,4-dipolystyryl-1,4-dihydro[60]fullerene, as shown in eq 1, on the basis of SEC (size exclusion chromatography) analyses, UV−vis spectra, and ^{13}C NMR spectra.[20,21] Living polystyrene also has been added to C_{60} via atom transfer radical polymerization.[22] We report here that molar ratios of living polystyrene/C_{60} in the range 1:1 to 4:1 in 1,2-dichlorobenzene (oDCB) solutions produce mixtures of polystyrene/C_{60} containing one, two, and three polymer chains.



Experimental Section

Materials. C_{60} (≥99.5% pure) was obtained from the MER Corp. (Tucson, AZ). *o*-Dichlorobenzene (oDCB, Aldrich), tetrahydrofuran (THF, Aldrich), hexanes (A.C.S. reagent), and methanol (A.C.S. reagent) were used as received. Styrene was distilled under vacuum and passed through alumina before use. Benzoyl peroxide (Aldrich) and TEMPO (Aldrich) were used as received. Styrene-d_8 (Aldrich, 98+% D) was passed through alumina. The methylene signals at 5.21 and 5.78 ppm in its ^1H NMR spectrum had about twice as much area per hydrogen as the aromatic (7.2−7.6 ppm) and methine (6.65 ppm) signals. 1-Phenylethyl-TEMPO (P-TEMPO, 1-phenyl-1-(2,2,6,6-tetramethyl-1-piperidinyloxy)ethane)[23] from Binrad Industries, Inc., was used as received.

Measurements. Size exclusion chromatography was performed with a Hewlett-Packard series 1100 chromatograph equipped with a diode array UV−vis detector and with one or three 30 cm PLgel 10 μm mixed-B columns (Polymer Laboratories, Amherst, MA) thermostated at 25 or 40 °C. The eluent

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Table 1. Preparations of Living Polystyrenes

sample	initiator, mg (mmol)	styrene, g (mmol)	TEMPO, mg (mmol)	yield, g
B′-LPS/S	BPO, 112.8 (0.470)	4.16 (40.0)	74.8 (0.400)	1.64[b]
B-LPS/S	BPO, 96.8 (0.400)	4.16 (40.0)	74.8 (0.400)	1.97
B-LPS	BPO, 968 (4.00)	41.6 (400)	749 (4.00)	15
M-LPS	none	2.73 (26.2)	51.2 (0.274)	1.04[b]
P-LPS	P-TEMPO, 103.6 (0.400)	0.832 (8.00)	none	0.481[c]
P-LPS-d_8	P-TEMPO, 103.6 (0.400)	0.896 (8.00)	none	0.616

[a] BPO = dibenzoyl peroxide. [b] From ^{1}H NMR analysis of the reaction mixture. [c] Material insoluble in methanol. Another 32 mg was recovered from the methanol solution.

Table 2. Conditions and Yields of Reactions of Living Polystyrene with C_{60}

expt[a]	living polystyrene[b]	molar ratio[c]	time, h	temp, °C	LPS, mg	C_{60}, mg	oDCB, mL	yield, mg	% yield polymer[d]	% yield PS/C_{60}[e]
4	B′-LPS/S	2.13	24	80	860	30.9	6	292.9	34	19
6	B-LPS/S	2.27	24	100	1040	37.4	6	152	15	12
8	B-LPS	2.14	24	100	502	24.8	6	237.1	47	14
11	B-LPS	2.14	15	130	502	24.8	7	301.5	60	30
16	B-LPS	1.07	168	130	502	49.6	6	211.0	42	26
17	B-LPS	2.14	168	130	502	24.8	6	251.3	50	25
18	B-LPS	4.29	168	130	502	12.4	6	222.3	44	21
24	M-LPS	2.01	24	130	258.9	26.5	6	180.2	69	30

[a] A list of 25 experiments is in the Supporting Information. [b] B = benzoyloxy end group; M = mixed end groups from self-initiation of styrene polymerization. [c] Living polystyrene/C_{60}. [d] 100(weight of product)/(weight of living polystyrene). [e] (% yield polymer)(fraction of chains bound to fullerene).

Table 3. Relative Molecular Weights from Simulated SEC Chromatograms

		260 nm		330 nm			
expt	sample	$P_{t(2)}$[b]	$P_{t(1)}$[b]	$P_{t(2)}$[b]	$P_{t(1)}$[b]	%F(1)[c]	%PS/F[d]
	B′-LPS/S		8 700				
4	B′-PS/C_{60}	19 500	8 000	17 700	7 600	46	56
	B-LPS/S		6 300				
6	B-PS/C_{60}	15 000	6 300	15 300	6 100	66	83
	B-LPS		11 850				
8	B-PS/C_{60}	29 300	12 300	28 500	11 700	20	30
11	B-PS/C_{60}	27 000	11 700	27 000	12 000	38	51
16	B-PS/C_{60}	28 500	12 000	27 800	11 700	46	62
17	B-PS/C_{60}	31 700	12 000	30 900	11 900	27	51
18	B-PS/C_{60}	30 600	11 400	30 500	12 800	24	47
	M-LPS		9 200				
24	M-PS/C_{60}	14 800	6 900	14 800	6 900	14	44

[a] A list of 25 experiments is in the Supporting Information. [b] P_t = molecular weight at the peak top relative to polystyrene standards. [c] %F(1) = % of one-chain peak at 260 nm that contains fullerene. [d] % PS/F = % of chains bound to fullerene.

was THF at a flow rate of 1 mL min^{-1}. Solutions containing 5 mg mL^{-1} of polymer were filtered through a 0.2 μm micropore membrane and injected in 20 μL aliquots. The chromatograms were analyzed using the first-order polynomial method of the GPC macro of the HP Chemstation calibrated with polystyrene standards of 800, 2000, 9000, 17 500, and 100 000 molecular weight. Molecular weights equivalent to linear polystyrene standards (P_w and P_n) were calculated from data at 260 and 330 nm. NMR spectra at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C were referenced to TMS using $CDCl_3$ as solvent.

Multidetector SEC Analyses. The multidetector size exclusion chromatographic system was described earlier.[17] SEC analysis in THF used three 7.5 mm × 300 mm PLgel mixed-C columns (Polymer Laboratories). Fullerenes were detected by UV absorbance at 330 nm, mass of polymer by differential refractive index (DRI), and specific solution viscosity by differential viscometry (DV). Detectors were connected in series in the order UV, DV, DRI. Intrinsic viscosities ([η], dL g^{-1}) were calculated at each retention volume from measured viscosities and mass concentrations, and absolute molecular weights (M_w and M_n) were calculated from a universal calibration curve. Whole polymer intrinsic viscosities and molecular weight averages were calculated in the normal manner by summation of values across the molecular size distribution.

Polymer Syntheses. All preparations of living polystyrene and polystyrene/C_{60} were carried out by mixing the reactants in a glass tube, degassing, sealing the tube under vacuum, and heating. Amounts of materials are in Table 1. Reaction conditions and yields are in Table 2. Relative molecular weights are in Table 3.

Benzoyloxy Living Polystyrene (B-LPS). A homogeneous mixture of 968 mg of benzoyl peroxide (4.0 mmol), 41.6 g of styrene (400 mmol), and 748.8 mg of TEMPO (4.8 mmol) was divided into two equal parts and heated at 130 °C for 13.5 h. One tube was chilled and opened. The contents were pipetted dropwise into methanol, and the precipitate was centrifuged. The solid was purified by three precipitations from dichloromethane into methanol, one precipitation into hexane, and one more into methanol and was dried under vacuum to yield 15 g (69%) of light tan powder; P_w 11 800, P_n 7700. Samples B-LPS/S (P_t 6300, Table 3) and B′-LPS/S (P_w 8000, P_n 6500), which contained both living polystyrene and styrene monomer, were prepared by the same method. The solution was used directly for reactions with C_{60} without isolation of the living polystyrene.

Mixed Living Polystyrene (M-LPS). A homogeneous mixture of 3.0 mL of styrene (26 mmol) and 51 mg of TEMPO (0.32 mmol) was heated at 130 °C for 24 h. The product was precipitated twice into hexane and twice from dichloromethane into methanol and dried under vacuum to yield 1.04 g (38%) of tan powder: P_w 9000, P_n 7400.

1-Phenylethyl Living Polystyrene (P-LPS). A mixture of 103.6 mg of P-TEMPO (0.40 mmol) and 832 mg of styrene (8.0 mmol) was heated at 130 °C for 30 h. The product was precipitated once into methanol and dried under vacuum to

give 481 mg of a white powder. Another 32 mg of solid was recovered by evaporation of the filtrate. A ^{1}H NMR spectrum taken before product isolation showed a 50:50 mixture of styrene/polystyrene from integrated areas of the vinyl proton peaks of styrene and the benzylic proton peaks of polystyrene. The polymer had $DP_n = 10$ and $M_n = 1300$ (including the 1-phenylethyl and TEMPO end groups) from integrated areas of the benzyl protons and the two methyl proton peaks of TEMPO at 0.2−0.5 ppm. 1-Phenylethyl living polystyrene-d_8 (P-LPS-d_8) was prepared from P-TEMPO and styrene-d_8 by the same method to give 616 mg of methanol-insoluble solid (P_n 1200) and 92 mg of methanol-soluble solid.

Polystyrene/C_{60} from Benzoyloxy Living Polystyrene and C_{60} and from Mixed Living Polystyrene and C_{60}. The living polystyrene and C_{60} were dissolved in oDCB with mechanical stirring. The amounts of materials, times, and temperatures are listed in Table 2. After heating, the polymers were isolated by two precipitations into hexane and two precipitations into methanol. The hexane filtrate from the first precipitation had a pale purple color, indicating some unreacted C_{60}.

Polystyrene/C_{60} from 1-Phenylethyl Living Polystyrene and C_{60} and from 1-Phenylethyl Living Polystyrene-d_8 and C_{60}. The P-LPS or P-LPS-d_8 (100 mg, ca. 0.08 mmol) and 100 mg (0.138 mmol) of C_{60} in 20 mL of oDCB were heated to 130 °C for 3 days. The mixture was evaporated to a black powder by rotary evaporation at 100 °C. The solid was mixed thoroughly with THF, and a fine black powder (mostly unreacted C_{60}) was separated by filtration to leave a clear brown solution, which was evaporated to leave a dark brown film. The film was dissolved in a minimal amount of dichloromethane, and the solution was added dropwise to stirring methanol to precipitate a second fraction of solid. Both solid samples were dried under vacuum at 45 °C.

Results

Living Polystyrenes. The living polystyrene samples listed in Table 1 were prepared by five different methods. (1) Benzoyl peroxide, excess styrene, and TEMPO were heated to 130 °C in oDCB. Benzoyloxy living polystyrene (B-LPS) was isolated by precipitations into hexane and methanol to remove low molar mass components, including methanol-soluble oligomers. (2**)** Benzoyloxy living polystyrenes that contained styrene monomer (B-LPS/S and B′-LPS/S) were made by the same method but without isolation of the polymer. (3) Mixed living polystyrene (M-LPS) was formed by self-initiated polymerization of styrene in the presence of TEMPO at 130 °C and isolated by precipitations into hexanes and into methanol. (4) 1-Phenylethyl TEMPO[23] gave 1-phenylethyl living polystyrene (P-LPS), which was isolated by precipitation into methanol. (5) 1-Phenylethyl-TEMPO and styrene-d_8 gave 1-phenylethyl living polystyrene-d_8 (P-LPS-d_8).

Addition of LPS to C_{60}. Table 2 reports conditions for many reactions of living polystyrene with C_{60}. The source of the living polystyrene, the molar ratio of living polystyrene/C_{60}, time, temperature, and presence or absence of styrene monomer were varied. All products were analyzed by SEC with simultaneous UV detection of mass of polymer at 260 nm and of fullerene components at 330 nm.

A typical SEC analysis of the product mixture from reaction of living polystyrene sample B-LPS/S (which contained styrene monomer) to C_{60} in a 2:1 molar ratio is shown in Figure 1. The experimental data from detection at 260 nm were simulated as the sum of two Gaussian peaks to determine the relative amounts of the two components in the bimodal chromatogram. In this example the areas of the two simulated peaks are

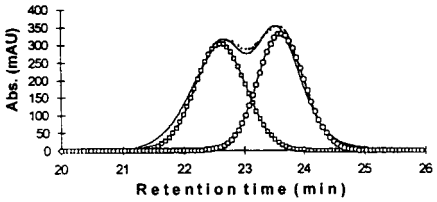

Figure 1. Size exclusion chromatograms of an adduct of living polystyrene and C_{60} (Tables 2 and 3, experiment 6). The solid line is experimental at 260 nm. The dotted line, which differs from the solid line only in the valley between peaks, is the simulation.

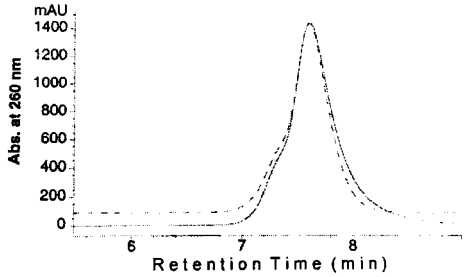

Figure 2. Experimental chromatograms at 260 nm of an adduct of living polystyrene and C_{60} (Tables 2 and 3, experiment 17) before (solid line) and after (dotted line) precipitation into methanol.

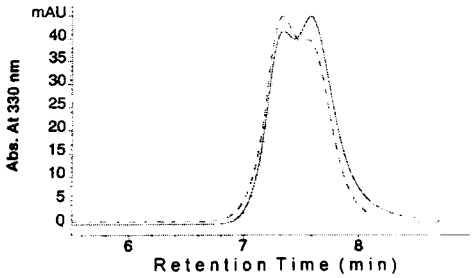

Figure 3. Experimental chromatograms at 330 nm from the same experiments as in Figure 2.

equal, and the molar masses relative to standard polystyrenes from the simulations are $P_n = 14\,000$ ($P_w/P_n = 1.14$) and $P_n = 6000$ ($P_w/P_n = 1.10$). The actual P_w/P_n values are slightly larger because of small deviations of the simulations from the experimental data at shortest and longest retention times. Because the complete analysis of P_w and P_n from the simulated chromatograms was laborious, all other measurements from simulated chromatograms refer to the relative molar masses at the peak tops, which are designated P_t. In the case of Figure 1 these are $P_t(2) = 15\,000$ and $P_t(1) = 6300$. P_t data are reported in Table 3 for all of the samples in Table 2.

All products from living polystyrene and C_{60} were isolated by precipitation into methanol. Figures 2 and 3 show an example of how the product distribution changed slightly during isolation. The 260 nm chromatogram (Figure 2) shows a smaller relative amount of the two-chain component than that of Figure 1. After precipitation of the polymer, there was a small decrease in the relative amount of low molar mass material, a small increase in the relative amount of high molar mass material, and no significant change of the retention time at the peak top. The 330 nm chromatogram (Figure 3), which detects only fullerenes, shows approximately equal amounts of fullerene in the one-chain and two-chain components. There was a small increase in the relative amount of fullerene in the two-chain

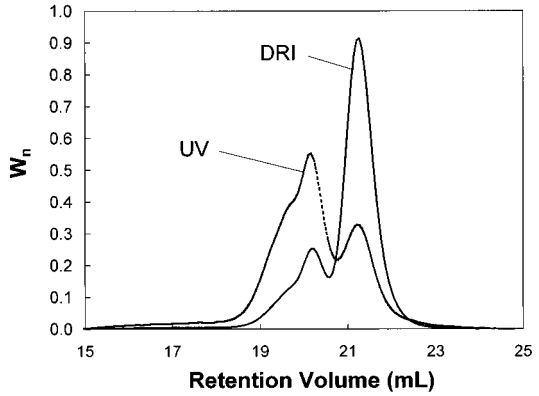

Figure 4. Experimental chromatograms at higher resolution with UV and DRI detection of an adduct of living polystyrene and C_{60} after precipitation (as in Figures 2 and 3).

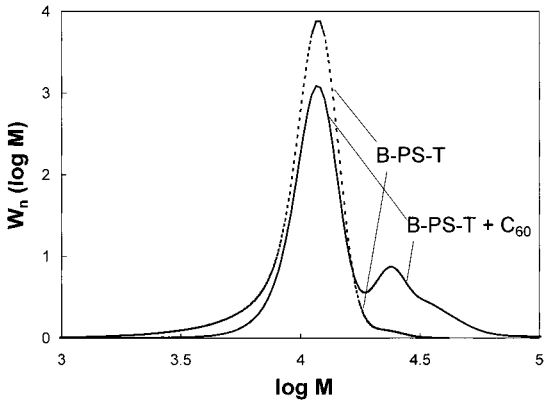

Figure 5. Absolute molar mass distributions from the DRI and DV chromatograms of an adduct of living polystyrene and C_{60} (from Tables 2 and 3, experiment 17) and of its living polystyrene precursor (dashed line).

component after precipitation, which is due to the removal of a small amount of fullerene-containing material from the lower molar mass component. Because the changes in composition after precipitation are small, they have no significant effect on the interpretation of the rest of the observations.

Fullerene Content of the Polymers. Simultaneous detection at 330 and 260 nm enabled SEC analysis of both the mass distribution and the fullerene distribution of every polystyrene/C_{60} sample. Selected samples were analyzed also by a multidetector SEC system to determine absolute molecular weight via intrinsic viscosity and universal calibration.[17,24] The original chromatograms shown in Figure 4 of the polystyrene/C_{60} from experiment 17 (Tables 2 and 3) have two peaks and a shoulder at short retention time. RI detection shows mainly one-chain polymer, while UV shows mainly two-chain and three-chain polymers. The absolute molar mass results are shown in Figure 5, along with the chromatogram of the parent living polystyrene sample. The largest mass fraction has the same molar mass (11 850) as the starting living polystyrene. The second peak has molar mass 23 900, twice that of the starting living polystyrene, and a reasonable estimate of the molar mass of an unresolved peak in the shoulder is 37 000, which is about 3 times that of the starting living polystyrene. Thus, the sample has components that contain one, two, three, and more of the original living polystyrene chains, in order of decreasing mass fraction. The one- and two-chain polymers have viscosity−molecular weight−hydrodynamic volume relationships

Table 4. Molar Extinction Coefficients of [60]Fullerene Derivatives

sample	$\epsilon_{330} \times 10^{-4}$	ref
PMMA/C_{60}[a]	3.64	17
1,4-$C_{60}[C(CH_3)_2CO_2CH_3]_2$	2.52	19
1,16-$C_{60}[C(CH_3)_2CO_2CH_3]_2$	1.89	19
$C_{60}[CH(C_6H_5)CH_2O_2CC_6H_5]_2$[b]	3.4	21
P-PS-d_8/C_{60}[c]	4.7	this work

[a] High conversion polymer from MMA and 1 wt % of C_{60} made by radical initiation and containing an average of 6 alkyl groups per fullerene unit. [b] A mixture of isomers. [c] Fullerene content was 9.8% by quantitative ^{13}C NMR analysis.

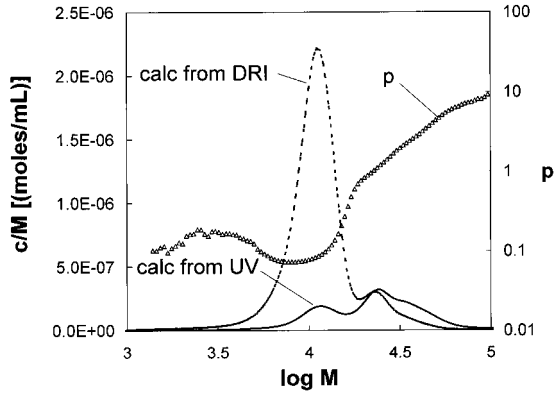

Figure 6. Molar chromatograms of an adduct of living polystyrene and C_{60} (from Tables 2 and 3, experiment 17) from DRI detection of polymer, UV detection of fullerene components, and DV for universal calibration. *P* is the molar ratio of macromolecules to fullerene subunits.

that are similar to that of linear polystyrene. Thus, there are probably few if any branched molecules present in the two main modes of the distribution.

From the mass detected by RI, the fullerene absorbance at 330 nm, and the molar extinction coefficient of fullerenes at 330 nm, the mass percent of fullerene in the polymer can be calculated at any retention time (or molar mass) in the chromatogram. This calculation depends critically on the extinction coefficient (ϵ) of the fullerenes, which is difficult to measure because (a) the fullerene content of polymeric samples cannot be measured accurately, (b) the polymers contain varied numbers of alkyl groups on the fullerene, and (c) for each different number of alkyl groups there are regio- and diastereoisomers. Table 4 reports the extinction coefficients of three low molar mass and two polymeric samples. The ϵ value for a polystyrene/C_{60} was calculated from a quantitative ^{13}C NMR analysis of the sample H-PS-d_8/C_{60} prepared from styrene-d_8 using gated decoupling to null the NOE and a long relaxation delay.[19] Its C_{60} content was 9.8 ± 1.0% from comparison of the signal areas of the phenyl ring carbons at 125−130 ppm and the backbone carbons at 40−50 ppm, with the signal area of quaternary aromatic carbons of fullerenes and ipso carbons of phenyl rings at 135−155 ppm.

The ϵ value for PMMA/C_{60} in Table 4 is an average of measurements of five different samples, each of which contained 1.0 mass % fullerene and an average of six alkyl groups per fullerene unit.[17,19] We used the ϵ value of PMMA/C_{60} for all fullerene components and the absolute molar masses from Figure 5 to calculate molar chromatograms of the mass distribution and the fullerene distribution (Figure 6). The one-chain peak at 10 500 in the mass chromatogram is much larger than the peak at 11 500 in the fullerene chromatogram, which means

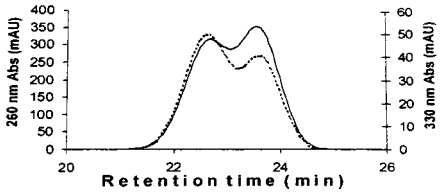

Figure 7. Experimental chromatograms at 260 nm (solid line) and 330 nm (dashed line) of an adduct of living polystyrene and C_{60} (from Tables 2 and 3, experiment 6) made in the presence of excess monomer.

that most of the one-chain peak is due to molecules that contain no fullerene. The maxima of the two-chain peaks at 20 900 in the mass chromatogram and 21 900 in the fullerene chromatogram are due to nearly equal numbers of molecules. Therefore, the two-chain component contains an average of one fullerene unit per macromolecule. The components at molar mass >21 900 contain more than one fullerene per macromolecule. For example, at mass 33 000 there is an average of two fullerenes per molecule. Four different samples were analyzed by the molar chromatogram method, and the numbers of fullerenes per macromolecule calculated at the top of the two-chain peak were 1.0, 1.0, 1.0, and 0.7, or an average of 0.9. We recognize that the calculation of the fullerene molar chromatograms has a large probable error due to the assumed ϵ value of the mixed fullerenes. The data in Table 4 suggest that a reasonable error limit for ϵ is ±25%, which means that the average number of fullerene units per macromolecule is 0.7−1.2 at the top of the two-chain peak. Similarly, all samples at molar mass >21 900 have an average of more than one fullerene per macromolecule.

The Fraction of Living Polystyrene Chains That Add to C_{60}. Figure 7 shows the simulated SEC results from the polystyrene/C_{60} sample of experiment 6 (Tables 2 and 3). The molar masses at the peak tops are $P_t(2) = 15\,000$ and $P_t(1) = 6300$ in the 260 nm chromatogram and $P_t(2) = 15\,300$ and $P_t(1) = 6100$ in the 330 nm chromatogram. In all simulated chromatograms the value of $P_t(2)$ was 2.0−2.5 times the value of $P_t(1)$, and there was no significant difference between the $P_t(2)$ and $P_t(1)$ values from 260 nm chromatograms and those from 330 nm chromatograms. In Figure 7 the amount of polymer is greater for the one-chain peak, while the fullerene content is greater for the two-chain peak (shown also in Figure 6). Since the two-chain peak contains an average of one fullerene unit per macromolecule, the one-chain peak must contain less than one fullerene per macromolecule, which probably is due to both unreacted living polystyrene and to dead polystyrene that lacks a TEMPO end group.

From simulated chromatograms such as those of Figure 7, we calculated approximate percents of fullerene-containing molecules in the one-chain components [%F(1)] and percents of polymer chains bound to fullerene (%PS/F) as follows: Since the two-chain peak in both chromatograms is due to molecules containing one fullerene, and the relative amount of fullerene of the one-chain peak at 330 nm is the ratio of area percents $[A(1)_{330}/A(2)_{330}]$, the area percent of the 260 nm chromatogram due to fullerene-containing polymer $[F(1)_{260}]$ is given by eq 2, and the percent of the one-chain peak of the 260 nm chromatogram due to fullerene-containing polymer [%F(1)] is given by eq 3. The percent of polymer molecules containing a fullerene (%PS/F) is the sum of the area percents of the two-chain and one-chain peaks in the 260 nm chromatogram that contain fullerene (eq 4). The results of the calculations, which are in Table 3, show wide ranges of percents of fullerene-containing molecules in the one-chain peak and of percents of living polystyrene chains that reacted with C_{60}. Most samples had more than half fullerene-free polystyrene in the one-chain peak.

Table 5. Products from C_{60} and 1-Phenylethyl Living Polystyrenes[a]

sample	methanol insoluble, mg	P_w	P_n	methanol soluble, mg	unreacted C_{60}, mg
P-PS/C_{60}	20.0	1900	1200	48.8	76.6
P-PS-d_8/C_{60}	47.2	3200	2200	25.7	84.1

[a] Each experiment started with 100.0 mg of living polystyrene and 100.0 mg of C_{60}.

$$F(1)_{260} = A(2)_{260}[A(1)_{/330}/A(2)_{330}] \quad (2)$$

$$\%F(1) = 100[F(1)_{260}/A(1)_{260}] \quad (3)$$

$$\%PS/F = A(2)_{/260} + F(1)_{260} \quad (4)$$

Effects of Reaction Conditions on Product Distributions. Tables 2 and 3 report how several experimental parameters affected the compositions of the product mixtures. The major results are as follows. (1) In six different series of experiments the molar ratio of living polystyrene/C_{60} was varied from 1:1 to 2:1 to 4:1. Experiments 16−18 are reported in Tables 2 and 3. More are in the Supporting Information. In every series the greater the living polystyrene/C_{60} ratio, the less the percent of fullerene in the one-chain component [%F(1)] and the less the percent of chains bound to fullerene (%PS/F). (2) In experiments 11, 17, and 20, which all used the same sample of living polystyrene, maximum conversion at 130 °C was reached in 24 h or less. (3) Experiment 4 shows that the rate of dissociation of TEMPO from living polystyrene is fast enough even at 80 °C for 34% of the living polystyrene to add to C_{60} in 24 h. (4) The living polystyrene made by self-initiation of styrene in the presence of TEMPO at 130 °C (experiment 24) gave a percent of chains bound to fullerene similar to those from other sources of living polystyrene, but there was less fullerene in the one-chain components. (5) Experiments 4 and 6 (Tables 2 and 3) show that, without isolation and in the presence of excess styrene monomer, additions of living polystyrene to C_{60} gave higher percents of fullerene-containing polymer but no significant increase in molecular weights of the one- and two-chain adducts. This indicates that polystyryl radicals added faster to fullerenes than to styrene monomer.

NMR Analysis of Polymer End Groups. To obtain polymers for end group analysis, living polystyrene samples with 1-phenylethyl and TEMPO end groups and number-average degree of polymerization = 10 were prepared using 1-phenylethyl-TEMPO with ordinary styrene and with styrene-d_8. The polymers were fractionated into methanol-soluble and methanol-insoluble components (reported in Table 1). The methanol-insoluble components were heated with C_{60} in oDCB at 130 °C and fractionated with methanol to give the polymers reported in Table 5. The chromatograms in Figure 8 show that almost all of the living polystyrene that reacted formed two-chain adducts and that the methanol-soluble polymer contained almost no fullerene.

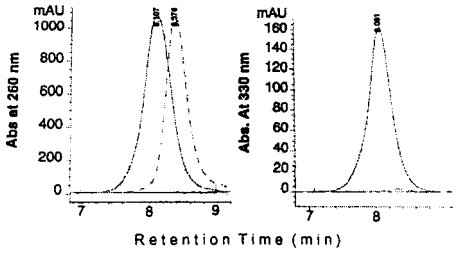

Figure 8. Experimental chromatograms at 260 nm (left) and 330 nm (right) of the fractionated products from 1-phenylethyl living polystyrene and C_{60} (Table 5). Solid lines are from the methanol-insoluble polymer, and dashed lines are from the methanol-soluble polymer. The dashed line of the 330 nm chromatogram is barely distinguishable from the baseline, indicating that the methanol-soluble components contain almost no fullerene.

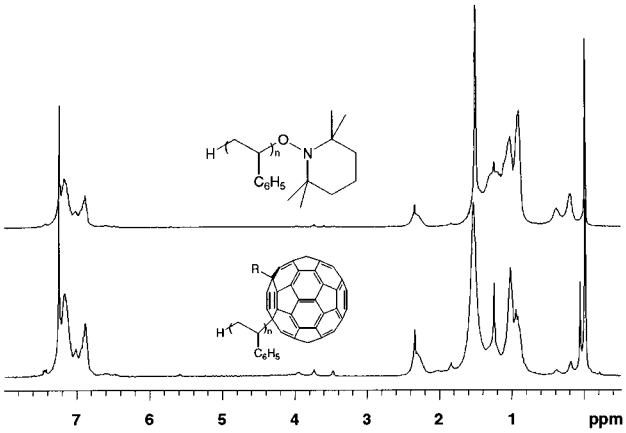

Figure 9. ^{1}H NMR spectra of deuterated living polystyrene (top) and of its adduct with C_{60} (bottom).

Figure 9 shows the ^{1}H NMR spectra of the living polystyrene-d_8 and of the product of its reaction with C_{60} before fractionation into methanol. The only major differences between the spectra are the areas of the signals due to TEMPO end groups at 0.2−0.5 and 0.9−1.6 ppm, which are reduced to about 20% of the original signal area after reaction. Since the unfractionated product contained about 35% of methanol-soluble living polystyrene, starting material, and 65% of methanol-insoluble polystyrene/C_{60} product containing two chains, the spectra prove that the two-chain product does not contain TEMPO groups and that some of the one-chain polymer also lacks TEMPO end groups.

The TEMPO must be liberated into solution during reaction with C_{60}. It does not appear in the ^{1}H NMR spectrum because of its unpaired electron. During isolation of the fullerene polymers by precipitation into methanol, the TEMPO stays in the methanol. In control experiments TEMPO was heated with C_{60} in oDCB at various temperatures as high as 130 °C. Analysis of the resulting solutions at room temperature revealed only unreacted C_{60} and unreacted TEMPO, as reported before.[20,21] TEMPO and C_{60} derivatives also are known not to react at room temperature, because low molar mass compounds containing both C_{60} and TEMPO structural units are chemically stable.[25] We did not try to analyze the amount of free TEMPO in the reaction mixtures from living polystyrene and C_{60}.

Discussion

While our research was in progress, Fukuda and co-workers[20,21] reported the addition of TEMPO-ended living polystyrene to C_{60} under different conditions. They used a 1:4 molar ratio of living polystyrene/C_{60} at 125−145 °C, and we used 1:1 to 4:1 living polystyrene/C_{60} at 80−130 °C. They precipitated unreacted C_{60} into THF and separated the fullerene-containing polymer from fullerene-free polymer by precipitating the fullerene components in benzene/methanol mixtures to get 56−78% yields based on living polystyrene. We removed C_{60} from the polymer by two precipitations into hexane (leaving C_{60} in solution) and two precipitations into methanol. Our procedure left major amounts of both living and dead fullerene-free polystyrene in the product mixtures, whereas theirs did not.

Both we and the Fukuda group find that the major product is an adduct of two polymer chains and one C_{60}, from the approximate doubling of the relative molar mass (P) and UV analysis of the fullerene content of the two-chain product. Our products also contained large amounts of adducts of one polymer chain to C_{60}. Their chromatograms of adducts of living polystyrene (P_n = 5500, P_w/P_n = 1.2) and C_{60} (Figure 4 of ref 20) using 430 and 270 nm UV detection and RI detection also show small amounts of one-chain polymer. A possible reason for the difference of results between the two groups is that their precipitation of C_{60} from THF also removed much of the polymer having only one chain on C_{60}. Since C_{60} is totally insoluble in THF, the polymer with only one chain on C_{60} would probably be less soluble in THF than the polymer with two chains on C_{60}. Also, we may have recovered more of the one-chain polystyrene/C_{60} because its solubility increases with increasing molar mass, and we used higher molar mass living polystyrene.

Some of our products also contained components having at least three polymer chains, as expected from synthesis using a much higher molar ratio of living polystyrene/C_{60}. Moreover, the average number of fullerene units in the ≥3-chain components is more than one and increases with increasing molar mass. These results suggest that the higher molar mass components contain not only adducts of three polystyrene chains to one C_{60} but also components with more than one fullerene unit having fullerene−fullerene bonds. We also found components with multiple fullerenes per macromolecule from polymerization of styrene and C_{60} in oDCB initiated by azo(bis(isobutyronitrile)).[19]

The structures of the one-chain adducts of C_{60} must have a second tetravalent fullerene carbon atom. The NMR spectrum of Figure 9 proves that the second substituent is not TEMPO. We propose, but lack proof, that the structure is $C_{60}H[CH(C_6H_5)CH_2)_nR]$, which has one polymer chain and one hydrogen atom on C_{60}. The likely source of the H atom is polymer. There is no evidence in this research of any product containing a fullerene with an aryl or a chlorine substituent derived from solvent and no such evidence in related research on the structure of dialkyldihydro[60]fullerenes from reaction of C_{60} with azo-initiators.[26,27] Addition of living polystyrene from bromine atom-transfer radical polymerization to C_{60} incorporates a bromine atom as the second substituent.[22]

Fukuda and co-workers assigned the structure of the polymeric diadduct to be the 1,4-isomer from the similarity of its spectra to those of the model diadduct $C_{60}[CH(C_6H_5)CH_2O_2CC_6H_5]_2$, which was obtained from benzoyl peroxide, styrene, and C_{60} under the same conditions used for reactions of living polystyrene with

Scheme 1

$$\text{R-PS-T} \rightleftharpoons \text{R-PS}^{*} + {}^{*}\text{T} \quad (5)$$

$$\text{R-PS}^{*} + C_{60} \longrightarrow \text{R-PS-}C_{60}^{*} \quad (6)$$

$$\text{R-PS-}C_{60}^{*} + \text{R-PS}^{*} \longrightarrow (\text{R-PS})_2\text{-}C_{60} \quad (7)$$

$$2\ \text{R-PS-}C_{60}^{*} \rightleftharpoons (\text{R-PS-}C_{60})_2 \quad (8)$$

$$2\ \text{R-PS}^{*} \longrightarrow (\text{R-PS})_2 \quad (9)$$

$$\text{R-PS-}C_{60}^{*} + {}^{*}\text{T} \rightleftharpoons \text{R-PS-}C_{60}\text{-T} \quad (10)$$

C_{60}.[20] However, the model diadduct is more complex than they reported. Its ^{13}C NMR spectrum[20] has 126 resolved peaks at 120−160 ppm, 4 carbonyl peaks, 4 fullerene sp^3 peaks, 4 methine peaks, and 4 methylene peaks. In every region of the spectrum there are too many peaks for a mixture of one meso and one racemic diastereomers. More recently, we found that additions of 2-cyano-2-propyl and 2-carbomethoxy-2-propyl radicals to C_{60} produce 1,4-adducts, 1,16-adducts, and a small amount of the 1,2-adduct in the cyano case.[26,27] By analogy to these low molar mass adducts, and by the number of peaks in the ^{13}C NMR spectrum, the low molar mass adducts and all of the polymeric diadducts of C_{60} reported by Fukuda, and all of our polymeric diadducts, are mixtures of regio- as well as diastereoisomers.

Our results support the mechanism proposed by Fukuda and co-workers for the reaction of living polystyrene with C_{60}, which is shown in Scheme 1.[20] The activation step, reversible dissociation of TEMPO from polystyrene (eq 5), proceeds at temperatures as low as 80 °C. Once a polystyryl radical forms, it adds to C_{60} (eq 6) at an estimated rate constant of 10^8 M^{-1} s^{-1},[28] much faster than it adds to styrene monomer (estimated rate constant 10^3 M^{-1} s^{-1}).[19] Combination of a fullerene radical with a polystyryl radical (eq 7) accounts for the stable diadducts, but the fullerene radicals may first be diverted to difullerenes (eq 8). Dialkyldi[60]fullerenes [$(RC_{60})_2$] are well-known.[29] If the lifetime of a fullerene radical in solution is substantially longer than that of a polystyryl radical, fullerene radicals may react by dimerization (eq 8) faster than by combination with polystyryl radicals (eq 7). However, eq 8 is reversible, and eq 7 leads to a stable product. Little or no polymer forms by combination of polystyryl radicals (eq 9), because their concentration in solution is much lower than the concentration of C_{60} and C_{60} adducts, and alkyl radicals add to C_{60} and C_{60} adducts (eq 6) with rate constants as high as the rate constants for combination of two radicals (eqs 7−9). If TEMPO ever combines with fullerene radicals (eq 10), the reaction is reversible, because there is no evidence for any adduct of TEMPO and C_{60}.

Conclusion

Polystyryl radicals from TEMPO-terminated polystyrene add to C_{60} at temperatures as low as 80 °C to form mixtures of products containing one and two chains bound to one fullerene. Analyses of product mixtures by molar size exclusion chromatograms prove that when the living polystyrene/C_{60} molar ratio is ≥1, small amounts of macromolecules containing >2 chains and >2 fullerenes form also. Increasing concentration of free TEMPO as the reaction proceeds prevents high conversion of the living polystyrene; in most cases only 30−70% of the polystyrene chains in the product mixtures are bound to fullerenes. The most nearly homogeneous polymer samples that have been obtained so far from polystyryl radicals and C_{60} are isomeric mixtures of adducts with two chains per fullerene, which were isolated as the major products from a living polystyrene/C_{60} molar ratio of 0.25 after use of benzene/methanol to fractionate the product mixtures.[20,21]

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Supporting Information Available: Expanded Tables S2 and S3 of synthetic conditions and analyses of product mixtures from living polystyrene and C_{60}. This material is available free of charge via the Internet at http://pubs.acs.org.

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