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First Endohedral Metallofullerene-Containing Polymer: Preparation and Characterization of Gd@C₈₂-Polystyrene

Dongmei Yue,^{†,‡} Xiaojuan Bai,^{†,‡} Shixiong Zhao,[†] Xiaopei Miao,[§] Meixian Li,[§] Jinquan Dong,[†] Kurash Ibrahim,^{||} Jiaou Wang,^{||} Yuliang Zhao,^{*,†} Hui Yuan,[†] Gengmei Xing,[†] and Baoyun Sun^{*,†}

CAS Key Lab for Biomedical Effects of Nanomaterials and Nanosafety, Institute of High Energy Physics, Chinese Academy of Sciences, and National Center for Nanoscience and Technology of China, Beijing 100049, China, Beijing University of Chemical Technology, Beijing 100029, China, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China, and Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, CAS, Beijing 100049, China

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Metallofullerene-containing copolymers (0.12, 0.20, 0.40, and 0.60 wt % Gd@C₈₂) were first synthesized via radical bulk copolymerization. The structures and the properties of the new polymers, Gd@C₈₂-PS, were investigated by GPC, UV–vis spectroscopy, FTIR, ¹³C NMR, CV/DPV, and XPS. The polymerization behavior of the metallofullerene and the properties of the Gd@C₈₂-PS polymers were different from those of C₆₀-PS and PS. Gd@C₈₂ exhibited a stronger radical-scavenging ability than that of hollow fullerenes in the polymerization. Molecular weights and the electron-accepting ability of the polymers were discussed and possible mechanisms of the influences were proposed.

Introduction

Fullerene-containing polymers, which have been an increasing interest for many years, are expected to have potential applications, such as effective solar cells,¹ photovoltaic devices,^{2,3} conductive materials, optical devices,⁴ chemical sensors, electroluminescent cells,⁵ polymer grid triodes,⁶ photolithography, and so on.⁷ Huang et al.⁸ revealed that the photocurrent increased with the content of the fullerene in the polymers due to the good electron-accepting ability of fullerene. Tang et al.⁹ reported that C₆₀-containing polyacetylenes exhibited unique optical properties as the C₆₀-PPBs emitted strong blue light upon photoexcitation, representing the first example of highly luminescent fullerene polymers. Enhanced optical limiting properties were detected on polystyrene-bound C₆₀ solids,¹⁰ and poly(3-octylthiophene) solid films were sensitized with methanofullerene.¹¹ One of the most studied physical properties of the C₆₀-containing or C₆₀-doped polymer matrixes may be the photoinduced charge transfer from the polymers to the C₆₀ molecules. Electron transfer from electron donors to C₆₀ resulted in the anionic C₆₀ species, which exhibited superconductivity, semiconductivity, or optical properties.¹ Bunker et al. attached C₆₀ to polystyrene by radical bulk copolymerization and confirmed them by UV and fluorescence spectra.¹² Ya-Ping Sun et al. reported that C₆₀-PS copolymers that were prepared by radical solution copolymerization exhibited interesting optical properties and gave evidence of efficient photoinduced intramolecular energy transfer in the copolymers.¹³ Scientists choose the C₆₀-polymer system not only due to the good electron-accepting ability of C₆₀, sometimes, but also due to the small reorganiza-

tion energy, significant acceleration of the charge separation step, and effective deceleration of the energy-wasting charge recombination step.⁸ C₆₀ has emerged as a novel three-dimensional acceptor and has been extensively studied for the construction of efficient electron-transfer model systems.

So far, the donor–acceptor (D–A) systems based on fullerene and PS, PPV, or other molecules have been observed. However, little attention was paid to the polymers containing metallofullerenes. To our knowledge, the metallofullerene-containing polymer has indeed not been reported by now. Compared to C₆₀, endohedral metallofullerenes have attracted considerable interest as promising spherical molecules for material and biomedical applications because of their unique properties that are unexpected from empty fullerenes.¹⁴ Metallofullerenes are generally more reactive, either thermally or photochemically, than empty fullerenes.^{15–17} They will also become an important nanostructure material for future nanoscaled electronic devices because the band gaps of metallofullerenes can be varied between 1.0 and 0.2 V, depending on the fullerene size, the kind of metal atoms, and the number of metal atoms encapsulated.¹⁸ Yin et al. have demonstrated that Gd@C₈₂(OH)₂₂ has efficiently scavenged superoxide radical anions, hydroxyl radicals, and singlet oxygen.¹⁹ This ability may be attributed to the larger electron affinity. For instance, the electron affinity for C₆₀ and Gd@C₈₂ was proved to be 2.7 and 3.3 ± 0.1 eV, respectively. Therefore, endohedral metallofullerenes have shown greater promise for use as “radical sponges”.²⁰ However, the radical-scavenging ability of metallofullerenes during the polymerization has never been reported.

Importantly, a number of conjugated fullerene–polymers are known to exhibit ultrafast photoinduced charge transfer, with a back transfer that is orders of magnitude slower.²¹ C₆₀ has shown very high electron mobility of up to 1 cm² V^{−1} s^{−1} in field-effect transistors.²² As to metallofullerenes, the similar spherical structure enables these materials to possess similar properties with those of C₆₀. However, compared with empty fullerenes,

* To whom correspondence should be addressed. Tel: 86-10-8823-3595. E-mail: Sunby@ihep.ac.cn (B.S.), zhaoyuliang@ihep.ac.cn (Y.Z.).

[†] CAS Key Lab for Biomedical Effects of Nanomaterials and Nanosafety, CAS.

[‡] Beijing University of Chemical Technology.

[§] Peking University.

^{||} Beijing Synchrotron Radiation Facility, CAS.

the higher electron affinity and superior ability to transport charges make metallofullerenes the best acceptor component currently available for fullerene-containing polymers. Therefore, these properties might make metallofullerene-containing polymers more important candidates for novel solar cells, photo-voltaic devices, and data memory devices.

In this paper, we carried out metallofullerene Gd@C₈₂ as an acceptor together with the donor styrene to investigate the polymerization behavior of this material and synthesized a series of metallofullerene-containing polymers. The properties of the new polymers were investigated by UV-vis spectroscopy and cyclic voltammetry. The structures were measured by using gel permeation chromatography (GPC), FTIR, ¹³C NMR, and XPS.

Experimental Section

Endohedral metallofullerene Gd@C₈₂ (99.5%) and C₆₀ (99.9%) were prepared according to previous methods.^{23–25} Styrene (analytical grade, Sigma) was distilled under pressure to remove stabilizer before use. Benzoyl peroxide was purified according to the traditional method. Toluene, methanol, et al. were used as received.

Gd@C₈₂ (5, 8, 16, and 28 mg, corresponding to the weight percents of 0.12, 0.20, 0.40, and 0.60 wt %, respectively) was dissolved in 5 mL of styrene with benzoyl peroxide as the radical initiator. The polymerization reaction was carried out at 65 °C for 24 h, and a dark brown precipitate was obtained. It was dissolved in 60 mL of hot toluene, cooled to room temperature, and then reprecipitated with 200 mL of methanol. Afterward, we dissolved the polymer in THF, a good solvent of PS but a poor one of Gd@C₈₂, and the THF solutions were ultrasonicated, centrifuged, filtered, and then the homogeneous and transparent filtrate was added into methanol. All the processes were repeated three times to ensure that the unreacted metallofullerene and styrene were removed completely. The precipitates were dried, and black Gd@C₈₂-styrene copolymers were obtained.

The synthesis of PS and C₆₀-PS (with the C₆₀ weight percents of 0.20 and 0.37 wt %) were carried out in a similar fashion.

Gel permeation chromatography (GPC) analyses were conducted on a Waters 515-2410 separation module at 30 °C with the concentration of 2 mg/mL (Waters Ltd., America) using polystyrene as a standard and THF as an eluent. The ¹³C NMR was taken on a Bruker-AV-600 M spectrometer. CDCl₃ was used as the solvent and an internal standard. FTIR was performed on an FT-IR-TENSOR 27 spectrometer by KBr membrane casting solution. The UV-vis absorption spectra were measured with a TU-1901 double-beam UV-vis spectrophotometer in toluene solutions.

A CHI 660A electrochemical workstation (CH Instruments) with a conventional three-electrode cell was used to perform electrochemical measurements. All the experiments were conducted in MeCN/C₆H₅CH₃ (1:4 V/V) containing 0.1 M (*n*-Bu)₄NClO₄ at room temperature. The working electrode was a 4 mm diameter glassy carbon electrode. A Ag wire coated with AgCl was used as the reference electrode and a platinum electrode as the auxiliary electrode. Cyclic voltammograms (CVs) were recorded at 100 mV/s, and differential pulse voltammograms (DPVs) were obtained at 20 mV/s by using a pulse amplitude of 50 mV, a pulse width of 60 ms, and a pulse period of 200 ms. Prior to electrochemical experiments, the solutions were routinely deaerated by purging with high-purity nitrogen. All the potentials in this report were with respect to the ferrocene/ferrocenium redox couple.

XPS spectra were taken at the Photoelectron Spectroscopy Station of the Beijing Synchrotron Radiation Facility, Chinese

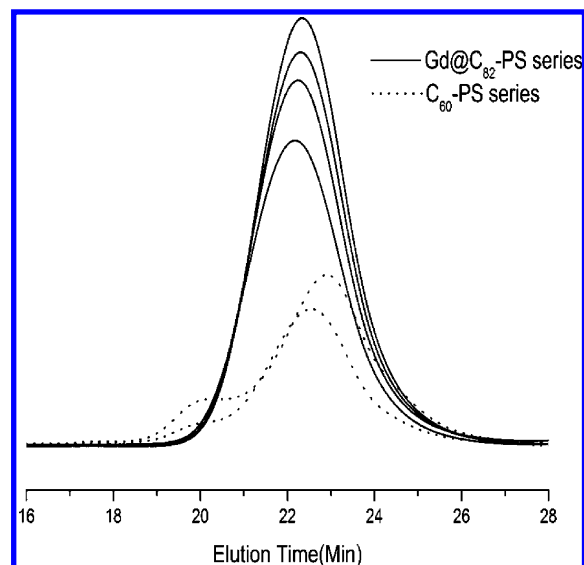


Figure 1. GPC curves of the Gd@C₈₂-PS series (0.12, 0.20, 0.40, and 0.60 wt % Gd@C₈₂) and the PS-C₆₀ series (0.20 and 0.37 wt % C₆₀) by bulk polymerization.

TABLE 1: Polymerization Results for Gd@C₈₂-PS and C₆₀-PS by Bulk Polymerization

no.	Gd@C ₈₂ (wt %)	C ₆₀ (wt %)	yields (%)	<i>M_n</i> (× 10 ⁵)	<i>M_w</i> / <i>M_n</i>
Gd@C ₈₂ -PS-1	0.12		74.5	1.43	1.84
Gd@C ₈₂ -PS-2	0.20		71.2	1.56	1.87
Gd@C ₈₂ -PS-3	0.40		69.5	1.51	1.82
Gd@C ₈₂ -PS-4	0.60		66.4	1.41	1.81
C ₆₀ -PS-1		0.20	62.5	0.99	2.09
C ₆₀ -PS-2		0.37	50.7	1.27	2.00

Academy of Sciences. The films of the samples were prepared on high-purity Au substrates. For example, several drops of polymer toluene solution were dropped on the Au surface to obtain a uniform film after removing the solvent by vacuum evaporation carefully, and the possible absorbed air was removed at about 10^{−8} Torr ultrahigh vacuum for several hours. The gold 4f_{7/2} line at 84.0 eV was used as the reference for the measurement of the binding energy.

Results and Discussion

The GPC traces are illustrated in Figure 1, and the molecular weight calculations are shown in Table 1. The average molecular weights and their distributions displayed regular variation among the copolymers.

The *M_n* and polydispersity (PDI) of Gd@C₈₂-PS and C₆₀-PS were located in the same order of magnitude, whereas Gd@C₈₂-PS exhibited differently. First, compared with C₆₀-PS, the Gd@C₈₂-PS series showed relatively higher *M_n* and narrow polydispersity, yielding 74.5–66.4% of Gd@C₈₂-PS with different weight percents (0.12–0.60 wt %) of metallofullerenes. As mentioned above, the fullerene molecule exhibits high electronegativity. The electron affinity of Gd@C₈₂ was found to be 3.3 ± 0.1 eV, higher than that of C₆₀ (2.7 eV). These suggest that Gd@C₈₂ provides more possibility to absorb multiple electrons and has stronger radical-scavenging ability. The addition of Gd@C₈₂ to the polymerization reaction has effectively depressed the formation of the oligomeric species more than C₆₀. The lower viscosity and hence higher mobility of the shorter chains confer on the oligomers higher chances to combine with the Gd@C₈₂ cages. Tang et al.⁹ have reported

that the C₆₀-containing polymer has a higher and narrow M_w/M_n relative to the parent PPB and one C₆₀ cage may link several oligomers together, effectively consuming the oligomeric species and generating a high molecular weight region. Compared with C₆₀, Gd@C₈₂ has stronger radical-scavenging ability and is more reactive in the polymerization. Therefore, the relatively higher molecular weight was observed. Second, the Gd@C₈₂-PS series showed single peaks, different from those in C₆₀-PS. As to all of the C₆₀-containing polymers, weak shoulder peaks were observed, as seen in Figure 1. This peak might be attributed to the following reasons: (1) THF was used to be the mobile phase when the gel permeation chromatography was carried out to measure the molecular weight. THF is a poor solvent to C₆₀ so that a macromolecular chain with C₆₀ end-capping has been aggregated. (2) Wu et al. have changed the mobile phase to chlorobenzene and the shoulder peak disappeared.²⁶ The shoulder peaks in Gd@C₈₂-PS were not observed, perhaps due to the better dispersal of metallofullerenes in THF.

During the polymeric process of Gd@C₈₂-PS series, the colors of the reactant and the product were different from those of PS but similar to those of C₆₀-PS. As the reaction proceeded, the color of the mixture changed from dark green to dark brown and then to dark. It showed significant difference from the pure PS, which was still colorless, and no change was observed during the whole polymerization. The pure polystyrene was colorless, but the Gd@C₈₂-containing polymers isolated from the product were black. Because the unreacted metallofullerene and styrene had been removed carefully, the dark color undoubtedly came from the influence of the attached Gd@C₈₂ molecules in the polymer chains. Gd@C₈₂ molecules had undergone chemical reactions with the styrene. C₆₀-PS had been synthesized under the same condition, whose color was similar to that of Gd@C₈₂-PS and the same as reported before.¹³ Remarkably, the Gd@C₈₂-PS polymer was soluble in common organic solvents, such as THF, chloroform, and toluene. This implied that there was no cross-linking product left in the polymerization system. The good solubility makes the polymers promising candidates for advanced materials for future applications.⁹

UV-vis absorption spectra of the copolymers in toluene are shown in Figure 2a,b. As it is well-known, Gd@C₈₂ shows its characteristic peaks at 400 and 620 nm in the UV-vis region. However, the Gd@C₈₂-PS series with different contents of metallofullerenes exhibited featureless spectra. A similar tendency had been observed for C₆₀-PS. The C₆₀-PS displayed no absorption peak in the UV-vis region without the special broad bands of C₆₀ around 530 and 600 nm. This might be attributed to the range of weight distributed derivatives of these materials and the nature of the complex. To confirm the structure, a measurement was performed on the mixture of Gd@C₈₂ (in the same ratio) and PS (Gd@C₈₂/PS), which showed almost the same feature as that of Gd@C₈₂. This indicated that Gd@C₈₂ had integrated with PS and the connection between the metallofullerene unit and PS increased the conjugation and the formation of a π -stacked structure.²⁷

The UV measurement was performed on all of the four Gd@C₈₂-PS samples (Figure 2b). As the amount of Gd@C₈₂ increased from 0.12 to 0.6 wt %, the Gd@C₈₂-PS series exhibited featureless spectra, but the absorption around the 300 nm region became higher and higher. The sharp increase around 300 nm mainly came from the high conjugate system. Therefore, we thought that the increase was dependent on the amount of metallofullerene left in the product. A similar phenomenon was observed as the amount of C₆₀ increased from 0.4 to 17%.¹²

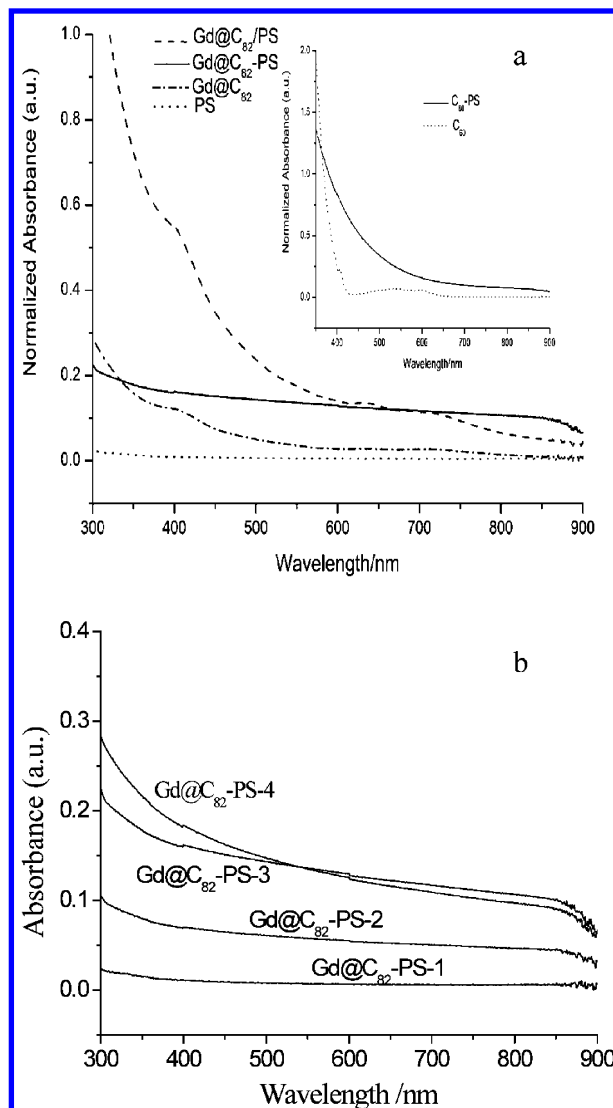


Figure 2. (a) UV-vis spectra of the Gd@C₈₂-PS copolymers (0.40% Gd@C₈₂), the mixture of Gd@C₈₂ (0.40%) and PS (Gd@C₈₂/PS), PS, and Gd@C₈₂ in toluene solution. The spectra of C₆₀-PS (0.37% C₆₀) and C₆₀ were inserted. (b) UV-vis spectra of the four Gd@C₈₂-PS copolymers (0.12, 0.20, 0.40 and 0.60 wt % Gd@C₈₂).

Different from C₆₀-PS, Gd@C₈₂-PS showed a flatter spectrum around 300 nm without a sharp increase as observed with C₆₀-PS, even though the fullerene content was almost the same (Figure 2a). As mentioned above, metallofullerene Gd@C₈₂ was generally more reactive and showed higher radical-scavenging ability than C₆₀. It allowed the radicals to react with metallofullerenes in a faster reaction rate than with C₆₀. Fullerene radical intermediates could continuously be connected with an other radical initiator, fullerene cage, or styrene monomer.¹⁸ The insoluble fullerene-cross-linked polymer was formed, but they had been removed carefully. The content of Gd@C₈₂ left in the product decreased compared with that in C₆₀-PS, and thus, the spectrum exhibited the weak absorption. This further confirmed the better radical-scavenging ability of Gd@C₈₂.

The FTIR spectra (Figure 3) showed similar features, compared with those of neat polystyrene prepared under the same condition, though the amount of Gd@C₈₂ in the polymerization process had been increased to 0.6 wt %. The skeletal vibration bands for the benzene ring portion of Gd@C₈₂-PS at the 3000–3100 cm⁻¹ region (the aromatic C–H stretch) and at 2800–2970 cm⁻¹ (the aliphatic C–H stretch) and the peaks

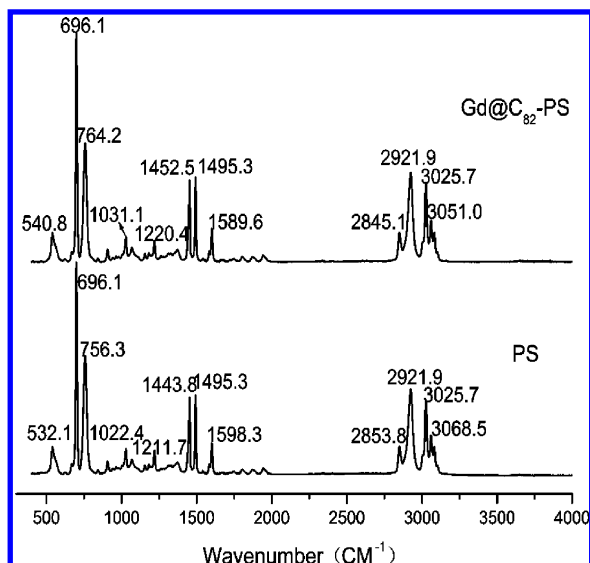


Figure 3. FTIR spectra (in KBr matrix) of Gd@C₈₂-PS (Gd@C₈₂ 0.6 wt %) and PS.

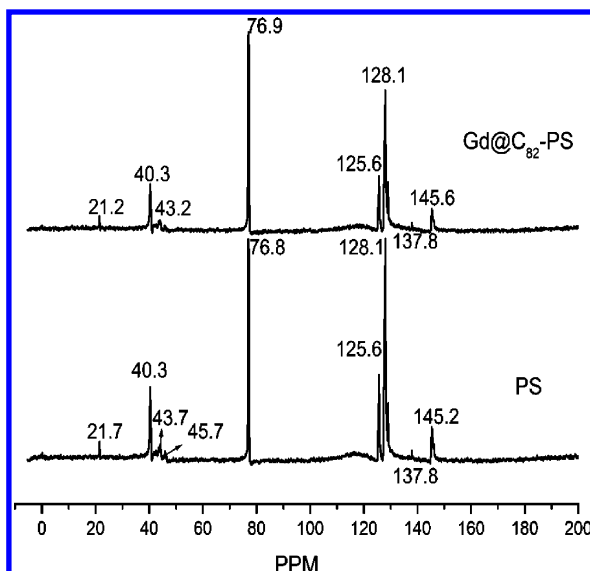


Figure 4. ¹³C NMR of Gd@C₈₂-PS (Gd@C₈₂ 0.6 wt %) and PS in deuterated chloroform.

at 699 and 757 cm⁻¹ (the out-of-plane phenyl ring and out-of-plane hydrogen) could be seen obviously.²⁸ The aromatic C=C stretch of Gd@C₈₂-PS was also obvious at the 1500–1600 cm⁻¹ region. FTIR spectra were nearly the same as those of neat polystyrene, which was in good agreement with the C₆₀-PS results that have been reported before.^{9,29,13,12} However, different from C₆₀-PS, the slight change, such as the peak at 520–530 cm⁻¹, which was ascribed to the functionalized C₆₀ cages, cannot be identified clearly in the spectra of the Gd@C₈₂-PS copolymer. The amount of metallofullerene cages combined with PS was not enough and Gd@C₈₂ molecules embed in the interchain space so that its function, perhaps, was only to loosen the chain links and lead to a large surface area due to its large density of conjugated bonds.^{26,29}

The ¹³C NMR (150 MHz, CDCl₃) spectra of Gd@C₈₂-PS copolymers and PS are shown in Figure 4. The signal of Gd@C₈₂ was practically indistinguishable against the background of the intense signal from the carbon in the PS. The bands at 125–130 ppm and around 40 ppm regions were assigned to the aromatic carbon signals and aliphatic peaks of

the Gd@C₈₂-PS, respectively, which were very similar to those of neat polystyrene. There were no clearly observable peaks originating from the resonance of the C₈₂ moieties in the polymer. The result was in good agreement with that of C₆₀-PS.^{12,13} In contrast to C₆₀ with *I_h* symmetry, which shows only a single peak in the fullerene region, the ¹³C NMR spectrum of C_{2v} Gd@C₈₂ used in this experiment should exhibit 24 distinct lines.^{30,31} The poor symmetry was supposed to be weakly resonated. The amount of the metallofullerene was very small, and it became the other reason that carbon signals of the Gd@C₈₂ cage were lost, even if it had been chemically attached to the PS chains.

Electrochemical methods are powerful in providing direct information of the electronic structure and property of the material. The electrochemical properties of the Gd@C₈₂-PS copolymers with different weight percents of Gd@C₈₂ were investigated by using cyclic voltammetry and differential pulse voltammetry. Detailed analysis of the CV and DPV results indicated that the electrochemical properties of the four Gd@C₈₂-PS polymers displayed different redox characteristics from that of PS. As shown in Figure 5, a broad reduction peak at around -1.0 V and a sharp reduction process at -3.0 V were identified, versus Fc⁺/Fc. The broad reduction peaks were PS-based reductions whose potentials were similar to that of neat PS. The unusual height of the peak at -3.0 V cannot be explained. The unusual peak appeared and was located at the same position in all the polymers. We had to ascribe it to the irremovable impurity produced during the polymerization. As to the second reduction peak at -2.3 V, it was difficult to be designed because it did not exhibit any regularity. However, as indicated in Table 2, the maximum of the broad peak was -1.12, -1.13, -1.29, and -1.35 V, respectively, for the four polymers (0.12, 0.2, 0.4, and 0.6 wt % Gd@C₈₂). Obviously, the broad reduction showed a shift to more negative potential. This indicated that the polymer became more difficult to be reduced as the amount of Gd@C₈₂ increased.^{32,33} Therefore, the substitution of Gd@C₈₂ with varied percentages had an obvious effect on the reduction potentials of the copolymers. All reductions were irreversible, but the oxidation process of the polymers was not observed, even if the potential was scanned up to 0.5 V.

The differences of electrochemical behavior between the copolymer Gd@C₈₂-PS and the mixture Gd@C₈₂/PS with the same content of metallofullerenes (0.4 wt %) were studied under the same experimental condition. The characteristic reduction peaks of Gd@C₈₂ were observed in the mixture Gd@C₈₂/PS along with those of PS. Besides, Gd@C₈₂-PS and Gd@C₈₂/PS all exhibited the irreversible reduction behavior of PS. In contrast to the Gd@C₈₂-PS polymer, three reduction potentials (-0.26, -1.30, and -2.22 V) of Gd@C₈₂ cages^{33,34} were evident in the mixture of Gd@C₈₂ and PS. All of these indicated that Gd@C₈₂ had interacted with the PS chain in the polymer and this attachment influenced the electron-accepting ability of the polymer significantly.

To confirm this conclusion, we investigated the electrochemical behavior of C₆₀-PS (0.37 wt % C₆₀). It is worth mentioning that the characteristic six couples of reversible reduction/oxidation peaks of the C₆₀ cage³⁵ cannot be observed at all. Similar to those of Gd@C₈₂-PS, a negative shift of the broad peak was observed obviously. The maximum of the broad peak was -1.26 V, whereas it was located at -1.22 V for the neat PS. The potential of fullerene-containing polystyrene exhibited a negative shift significantly, indicating that they can be used as a better insulator.

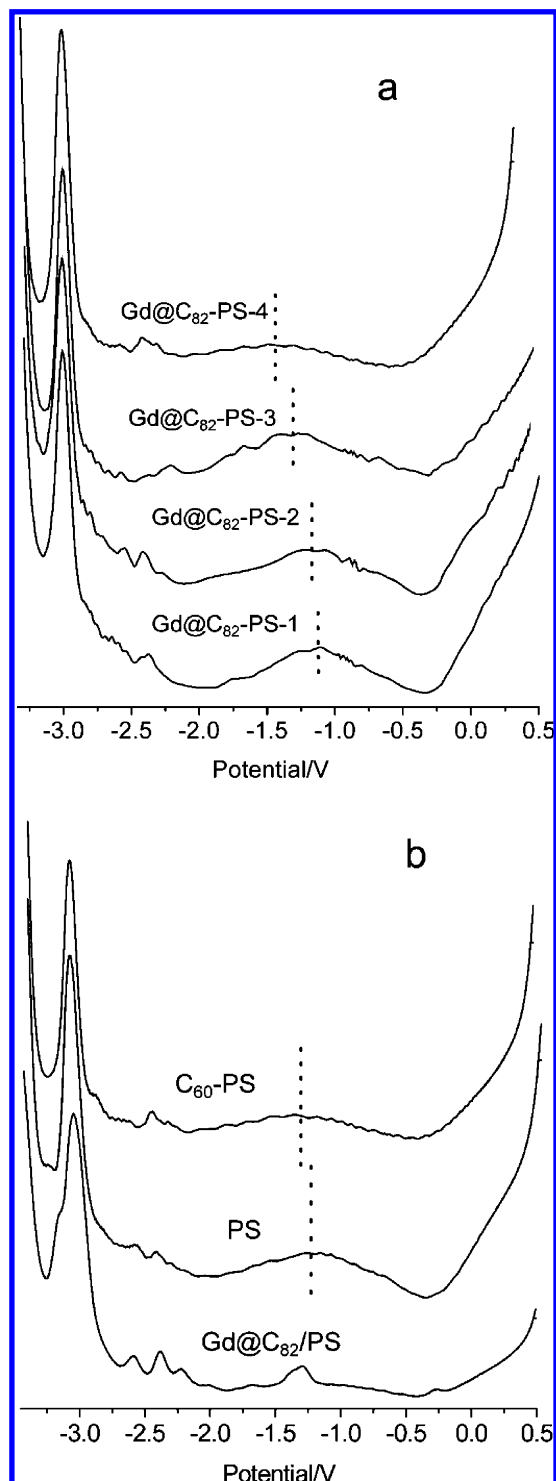


Figure 5. (a, b) Differential pulse voltammograms of copolymers Gd@C₈₂-PS-1 to Gd@C₈₂-PS-4, the mixture Gd@C₈₂/PS, PS, and copolymers C₆₀-PS in MeCN/C₆H₅CH₃ (1:4, V/V) containing 0.1 M (*n*-Bu)₄NClO₄ at a scan rate of 100 mV/s.

TABLE 2: Electrochemical Properties (DPV Peak Potentials) of the Copolymers

	red E_1	red E_2	red E_3	red E_4	red E_5	red E_6
Gd@C ₈₂ -PS-1	-1.12	-2.38	-3.01			
Gd@C ₈₂ -PS-2	-1.13	-2.20	-3.00			
Gd@C ₈₂ -PS-3	-1.29	-2.39	-3.00			
Gd@C ₈₂ -PS-4	-1.35	-2.36	-3.01			
PS	-1.22	-2.36	-3.01			
C ₆₀ -PS	-1.26	-2.36	-3.01			
Gd@C ₈₂ /PS	-0.26	-1.30	-2.22	-2.38	-2.59	-3.04

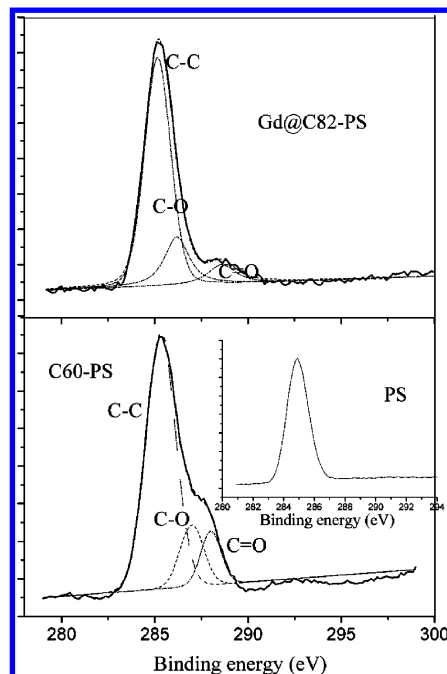


Figure 6. C 1s XPS spectra for Gd@C₈₂-PS, C₆₀-PS, and PS.

XPS was used to derive more information on the structure of the polymers. (Figure 6) A simple curve-fitting analysis demonstrated that there existed different types of carbons in the polymers. The peak at a binding energy of 285 eV was assigned to the nonoxygenated carbons (C–C), whereas the peak at a binding energy of 286 eV was assigned to the carbons linked with a single oxygenated group (C–OR). Another peak was located at a binding energy of 288 eV, suggesting the existence of dioxygenated carbons. Comparing the XPS spectra of Gd@C₈₂-PS, C₆₀-PS, and pure PS, we can see that there existed different types of carbons in the fullerene-containing polymer but oxygenated functionalities could almost be neglected in PS.

More oxygenated groups proved that fullerenes exhibited high electronegativity, which made the radicals react with fullerenes more rapidly than the styrene monomer. These groups can be introduced into the fullerene cage in the polymers by the initiator benzoyl peroxide (C₁₄H₁₀O₄), and one fullerene cage can be connected with more radical initiators.¹⁸ Oxygen with high electronegativity can donate electrons toward the “ π ” orbital of the carbon cage and thus to the PS chain. The process altered the fine electronic structures of the polymers, and as the amount of the fullerene increased, more oxygenated groups were introduced into the systems and made the polymer more difficult to be reduced.

Conclusions

In this paper, a series of novel Gd@C₈₂-PS copolymers have been successfully synthesized via radical bulk polymerization. The behavior of the metallofullerene during the polymerization and the properties of the new polymers were much different from those of C₆₀-PS and PS. It showed a relatively higher M_n and more narrow polydispersity compared with C₆₀-PS, indicating that Gd@C₈₂ possessed a stronger radical-scavenging ability than that of hollow fullerenes. UV, FTIR, and ¹³C NMR gave the confirmation that Gd@C₈₂ molecules have been attached to the polymer chains. As the amount of Gd@C₈₂ increased, the reduction of the copolymers exhibited a regular negative shift, indicating that the attachment of Gd@C₈₂ influenced the electron-accepting ability of the polymer significantly and made

the PS polymer a better insulator. More oxygenated groups were introduced into the polymer, which proved the better radical-scavenging ability of fullerenes and was thought to be the reason for the regular shift of the polymer reduction. Undoubtedly, the new properties of the metallofullerene-containing polymer make it a promising candidate for advanced materials for future applications.

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