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# Preparation and Characterization of Fullerene−Styrene Copolymers

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ABSTRACT: [60]Fullerene−styrene copolymers with [60]fullerene contents up to 50% (wt/wt) were prepared in radical-initiated polymerization reactions. Molecular weights of different fractions of the copolymers were determined by gel permeation chromatography measurements using chloroform and DMSO as mobile phases. Structures of the copolymers with different [60]fullerene contents were characterized by use of proton and $^{13}$C NMR, FT-IR, and thermal analysis methods. The mechanistic implication of the proposed copolymer structures is discussed.

## Introduction

Recently, fullerene-containing polymeric materials have received attention for their potential technological applications.[1] The fullerene-containing polymers under active investigations can be classified roughly into three categories. One category represents so-called polyfullerenes, which are all-carbon polymers from covalently linking fullerene molecules.[2−5] A preferred linking pattern seems to be [2 + 2] cycloaddition of double bonds on neighboring fullerene molecules, though structural details of the polyfullerenes remain to be understood. The second category includes pendant fullerene polymers, in which fullerene molecules are attached to groups or branches on a polymer chain through so-called “buckyball fishing”.[6] In the absence of multiple functionalization of a single fullerene cage, pendant fullerene polymers are referred to as “fullerene charm-bracelet polymers”.[1] However, extraordinary effort is often required in order to prevent multiple functionalization of a single fullerene cage in buckyball-fishing experiments. The third category consists of copolymers of fullerene and other monomers,[7] such as fullerene−styrene[8−10] and fullerene−methyl methacrylate copolymers.[10] With the use of potentially a variety of comonomers, copolymerization represents an effective method to incorporate a large number of fullerene molecules into polymeric structures. However, fullerene copolymers are typically complicated systems. Their structural characterizations are very challenging.

Polystyrene has been used in the preparation of several fullerene-containing polymeric systems[6a,7a,11−13] including pendant fullerene−polystyrene polymers[6a,11,12] and so-called flagellenes,[13] in which several linear polystyrene chains are covalently attached to a fullerene “sphere”. Fullerene−styrene copolymers were first prepared independently by Cao and Webber,[8] Bunker *et al.*,[9,14] and Camp *et al.*[10] It was shown that the copolymerization can be accomplished by heating a fullerene−styrene mixture or by use of a radical initiator. As with many other fullerene-containing copolymers, the polymeric materials obtained from radical copolymerization of fullerene and styrene are random copolymers. The mechanism of the copolymerization reactions and the structure and properties of the copolymers are being investigated.[10,14,15] In addition, the fullerene−styrene copolymers exhibit interesting optical properties. There is also evidence for efficient photoinduced intramolecular energy transfers in the copolymers.[9]

While a quantitative understanding of fullerene copolymer structures is intrinsically difficult, there are advantages in the characterization of fullerene−styrene copolymers. For many other fullerene-containing copolymers, a major hindrance in their structural characterization has been poor solubilities of the copolymers in common organic solvents, especially for copolymers with high fullerene contents. However, the fullerene−styrene copolymers are reasonably soluble in solvents such as chloroform and dichloromethane, even for copolymers with fullerene contents up to 50% (wt/wt), making it possible to use solution-based instrumental methods in their structural characterizations. In this regard, fullerene−styrene copolymers may serve as a representative system in the study of fullerene-containing copolymers.

In this paper, we report a comprehensive experimental investigation of fullerene−styrene copolymers. In the investigation, copolymers with different fullerene contents were prepared in radical polymerization reactions and characterized using gel permeation chromatography methods. By analyzing the copolymer structures on the basis of the results from proton and $^{13}$C NMR, FT-IR, thermal analysis, and optical spectroscopic measurements, the mechanism of radical-initiated fullerene−styrene copolymerization is discussed.

## Experimental Section

**Materials.** [60]Fullerene ($C_{60}$) was obtained from MER Co. (purity >99.5%) and Southern Chemical Group (purity >99.5%). The sample purity was checked by UV/vis absorption, $^{13}$C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS methods, and the samples were used without further purification. Styrene (Baker Analyzed) was obtained from Baker. It was distilled under reduced pressure to remove stabilizer before use. Benzoyl peroxide was obtained from Mallinckrodt. Toluene, chloroform, methanol, dichloromethane, *o*-dichlorobenzene (all spectrophotometric grade), and DMSO (HPLC grade) were obtained from Burdick & Jackson, and used as received. Deuterated chloroform and tetramethylsilane were obtained from Cambridge Isotope Laboratory.

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**Table 1. Results of Fullerene−Styrene Copolymerization Reactions**

| ID | $C_{60}$:styrene (mg:$\mu$L) | ben. peroxide (mg) | yield (%) | $C_{60}$ wt % | GPC results[a] $M_W$ (UV detector) | $M_W$ ($\Delta RI$) |
|---|---|---|---|---|---|---|
| **I** (bulk)[9,14] | 30:15000 | 200 | ~55 | ~0.4 | | 62000 (~4) |
| **II** (toluene)[9,14] | 50:5000 | 200 | ~65 | ~1.7 | | 79000 (13) |
| **III** (*o*-DCB) | 100:1000 | 200 | ~70[b] | ~14 | | |
| **IIIa** (soluble fraction of **III**) | | | >99 of **III** | | ~37500[c] | ~38000[c] |
| **IIIb** (insoluble fraction of **III**) | | | <1 of **III** | | | |
| **IIIc** (heated) | | | | | ~7500[d] | |
| **IIId** (polystyrene reference) | | | | 0 | 8500 | |
| **IV** (*o*-DCB) | 100:500 | 200 | ~60[b] | ~30 | | |
| **IVa** (soluble fraction of **IV**) | | | 97.8 of **IV** | | ~23200[c] | ~19500[c] |
| **IVb** (insoluble fraction of **IV**) | | | 2.2 of **IV** | | | |
| **IVc** (heated) | | | | | <5000[d] | |
| **IVd** (polystyrene reference) | | | | 0 | 11000 | |
| **Va** (*o*-DCB) | 100:100 | 200 | ~100[b] | ~50 | | |
| **Va** (soluble fraction of **V**) | | | 91.2 of **V** | | 19300 (3.5) | 18700 (2.9) |
| **Vb** (insoluble fraction of **V**) | | | 8.8 of **V** | | 8500 (5.5), 13000 at peak max.[e] | |
| **Vc** (heated) | | | | | <5000[d] | |
| **Vd** (polystyrene reference) | | | | 0 | ~3000 | |

[a] Shown in parentheses are polydispersity values. [b] Calculated without considering the contribution of initiator fragments. [c] Calculated by considering the main GPC peak only. [d] A small fraction of the sample that can be extracted by chloroform. [e] DMSO with 0.2% LiBr as mobile phase and linear poly(2-vinylpyridine) as standard.

**Copolymerization.** $C_{60}$−styrene copolymers with high $C_{60}$ contents were prepared in *o*-dichlorobenzene (*o*-DCB) using benzoyl peroxide as a radical initiator. Copolymerization reactions were carried out for three different initial $C_{60}$:styrene reactant ratios, 1:1, 1:5, and 1:10 (mg:$\mu$L) (Table 1).

In the copolymerization with the initial $C_{60}$:styrene reactant ratio of 1:1, a solution of 100 mg of $C_{60}$ in 3 mL of *o*-DCB was mixed with 100 $\mu$L of styrene. The mixture (dark red color) was deoxygenated by bubbling dry nitrogen gas for ~15 min, followed by the addition of 200 mg of benzoyl peroxide. The polymerization reaction was carried out in a sealed glass bottle at 65 °C for 32 h. The reaction products were precipitated from the *o*-DCB solution into methanol. The precipitation procedure was repeated several times, yielding a solid sample with almost black color. The solid sample was further purified by washing with methanol. After drying under vacuum, ~200 mg of the final copolymer sample (**V**) was obtained. Because the precipitated solutions were colorless, it seems reasonable to assume a complete consumption of $C_{60}$ in the polymerization reaction. Thus, the $C_{60}$ content of ~50% (wt/wt) in the copolymer can be estimated in terms of mass balance. The copolymer sample was fractionated on the basis of solubility in chloroform, yielding 91.2% of soluble (**Va**) and 8.8% of insoluble (**Vb**) materials (Table 1).

$C_{60}$−styrene copolymers with other initial $C_{60}$:styrene reactant ratios of 1:5 and 1:10 were prepared in a similar fashion. The copolymers (**IV** and **III**, Table 1) thus obtained also have dark colors. As the initial $C_{60}$:styrene reactant ratio decreases, the $C_{60}$ content in the final copolymer becomes lower, and the fraction that is insoluble in chloroform becomes less significant (Table 1). In fact, the copolymer prepared with the initial $C_{60}$:styrene reactant ratio of 1:10 is close to being completely soluble in chloroform.

Solubilities of the copolymer samples are strongly dependent on workup procedures. If the copolymer samples were subject to an oven-drying process at 80 °C overnight, the copolymer solubilities became very low. The heated copolymer samples, especially **IVc** and **Vc** (Table 1), are practically insoluble in chloroform, even with soaking for extended period of time. Thus, the oven-drying process was avoided for all of the copolymer samples used in characterizations. Instead, the copolymer samples were repeatedly washed with organic solvents by adding hexane or chloroform and then evaporating under vacuum to remove residual *o*-DCB.

The chloroform insoluble fractions obtained with different initial $C_{60}$:styrene reactant ratios (**IIIb**, **IVb**, and **Vb**) behave differently. The chloroform insoluble sample corresponding to the initial $C_{60}$:styrene reactant ratio of 1:1 (**Vb**) is somewhat soluble in DMSO, while the other two chloroform insoluble samples (**IIIb** and **IVb**) do not dissolve in DMSO at all.

Polystyrene references containing no $C_{60}$ were prepared in *o*-DCB under the same conditions as those for the $C_{60}$−styrene copolymers. For example, in the preparation of the polystyrene reference for the copolymer with initial $C_{60}$:styrene reactant ratio of 1:10, 1 mL of styrene and 200 mg of benzoyl peroxide were reacted in 3 mL of *o*-DCB at 65 °C for 32 h. The polystyrene samples thus obtained are white solids, which are easily soluble in common organic solvents.

**Measurements.** Two gel permeation chromatography (GPC) setups were used in the analyses of $C_{60}$−styrene copolymers. One setup using chloroform as mobile phase consists of a Waters 510 analytical HPLC pump and Waters UV/vis and refractive index detectors. GPC separations were achieved by use of three Waters HT-6E linear Styragel columns connected in a serial fashion. Unless specified otherwise, the chloroform flow rate was 1 mL/min. Polystyrene standards with $\bar{M}_w$ of 3900~965 600 and polydispersity of 1.15 and less were obtained from Polymer Source Inc. and used as molecular weight references. The other GPC setup uses DMSO as mobile phase. It consists of a Shimadzu LC-10AS analytical HPLC pump and a Rainin Instrument UV-1 UV/vis detector. A Waters HT-6E linear Styragel column prepared in DMF was converted to DMSO by pumping a low volume of DMSO (0.1 mL/min) for 24 h at 75 °C. The temperature of the DMSO column and a precolumn loop was maintained by use of a tube oven made in-house. Unless specified otherwise, the column temperature of 75 °C was used in the analyses. The mobile phase DMSO consisting of 0.2% lithium bromide salt was pumped at 0.75 mL/min. Poly(2-vinylpyridine) standards with $\bar{M}_w$ of 9100, 50 000, and 243 000 and polydispersity of 1.18 and less were obtained from Polymer Source Inc. and used as molecular weight references.

Proton and $^{13}C$ NMR measurements were performed on a Bruker 300-MHz NMR spectrometer. Deuterated chloroform was used as solvent, and tetramethylsilane (TMS) was used as an internal standard.

FT-IR spectra were obtained on a Nicolet Magna-IR 550 FT-IR spectrometer. Samples for measurements were mixed with carefully dried KBr solid, and the solid mixture was then made into pellets using a 13-mm die and a hydraulic press. All measurements were carried out under the protection of dry nitrogen gas.

UV/vis absorption spectra were obtained using a computer-controlled Shimadzu UV2101-PC UV/vis spectrophotometer.

Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments 910 calorimeter. Glass transition temperature measurements were carried out under the protection of nitrogen gas in the temperature range of 30−280 °C with a heating rate of 50 °C/min.

## Results

**GPC Analyses.** Chloroform soluble fractions of the copolymers were analyzed by GPC using chloroform as

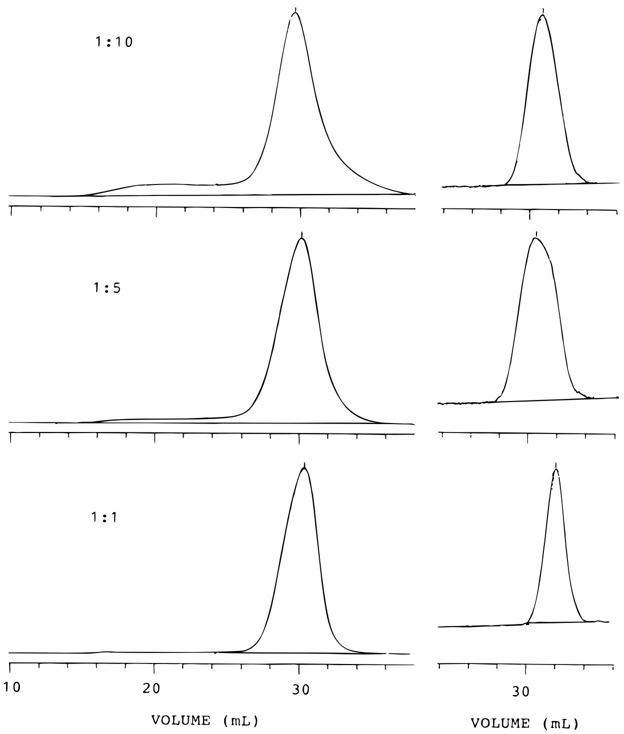


**Figure 1.** GPC results (UV detector at 350 nm) of the chloroform soluble fractions of the $C_{60}$−styrene copolymer samples prepared with initial $C_{60}$:styrene reactant ratios of 1:10 (**IIIa**), 1:5 (**IVa**), and 1:1 (**Va**). The results of neat polystyrene samples prepared under the same experimental conditions are shown at the right for comparison.

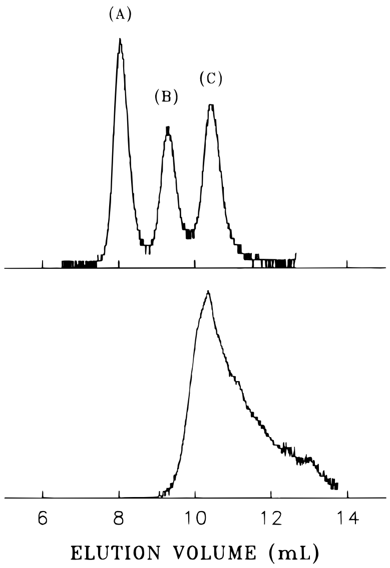


**Figure 2.** GPC results of the linear poly(2-vinylpyridine) standards ($M_w$ and polydispersity: A, 243000 and 1.18; B, 50000 and 1.04; and C, 9100 and 1.09) and the chloroform insoluble fraction of the $C_{60}$−styrene copolymer containing ~50% (wt/wt) of $C_{60}$ (**Vb**) in DMSO with 0.2% lithium bromide at 75 °C.

mobile phase and linear polystyrene standards as molecular weight references. The observed GPC traces are illustrated in Figure 1 and the results of molecular weight calculations are shown in Table 1. There are systematic variations in observed average molecular weights and weight distributions of the copolymers with changes in the initial $C_{60}$:styrene reactant ratio. For the copolymer with ~14% (wt/wt) of $C_{60}$ (**IIIa**), the observed GPC trace exhibits some interesting features. In addition to a main GPC peak that corresponds to the peaks observed in the GPC traces of the copolymers **I** and **II**,[9,14] there is a very broad shoulder with the onset at a much lower elution volume. As a result, the calculated molecular weight distribution is extremely broad. However, if only the main GPC peak is considered, the average molecular weight ($\bar{M}_w$) and polydispersity results of the copolymer **IIIa** are comparable with those of the copolymer **I** and **II**, as shown in Table 1. The observed GPC trace of the copolymer with ~30% (wt/wt) of $C_{60}$ (**IVa**) shows similar features, but the relative contribution of the extremely broad shoulder becomes somewhat smaller (Figure 1). Again, the average molecular weight $\bar{M}_w$ and polydispersity results obtained by considering the main GPC peak only are comparable with those of the copolymers **I** and **II** (Table 1). Interestingly, for the copolymer with even higher $C_{60}$ weight percent of ~50% (**Va**), the observed GPC trace becomes similar to those of the copolymers **I** and **II**. The extremely broad shoulder observed in the GPC traces of the copolymers **IIIa** and **IVa** is absent (Figure 1). With the well-defined main GPC peak, an $\bar{M}_w$ of 19 300 and polydispersity of 3.5 can be calculated. The GPC results obtained by using UV and refractive index detectors are very similar, though only the UV results are shown in Figure 1. It appears that when only the main GPC peaks are considered, $\bar{M}_w$ increases as the initial $C_{60}$:styrene reactant ratio decreases (Table 1).

Upon heating the polymers in an oven at 80 °C in a routing drying process, the copolymers with $C_{60}$ contents of ~14% (wt/wt) and higher became practically insoluble in chloroform. Only a very small portion of a copolymer sample could be extracted with chloroform. These extractants were also analyzed by GPC using chloroform as mobile phase. For the extractants from the copolymers with higher $C_{60}$ contents (**IVc** and **Vc**), GPC results show only oligomeric species. For the extractant from the copolymer with a lower $C_{60}$ content (**IIIc**), the GPC trace shows that in addition to the predominating oligomers there are some contributions from polymeric species with molecular weights comparable to those in an unheated copolymer sample.

GPC analyses were also performed for the neat polystyrene samples that were prepared in *o*-DCB in the absence of $C_{60}$, but under the same conditions as those for the $C_{60}$−styrene copolymers. As shown in Figure 1 and Table 1, weight distributions of the polystyrene references are relatively narrow. For all neat polystyrene samples, there are no broad signals before the main GPC peaks (Figure 1).

The chloroform insoluble fraction of the copolymer with initial $C_{60}$:styrene reactant ratio of 1:1 (**Vb**) is slightly soluble in DMSO, making it possible to carry out GPC characterization using DMSO as mobile phase. It is somewhat surprising that in neat DMSO the copolymer shows behavior typical to a polyelectrolyte.[17] The observed GPC peak is at a lower elution volume than that of the largest poly(2-vinylpyridine) standard ($\bar{M}_w$ of 243 000). The GPC trace was hardly changed upon substantial dilutions of the copolymer solution in DMSO for GPC injection. However, a dramatically different GPC trace was obtained after lithium bromide salt was added to the mobile phase DMSO. Shown in Figure 2 is the result obtained at a lithium bromide concentration of 0.2%. For the poly(2-vinylpyridine) standards, the presence of lithium bromide salt resulted in much less significant changes, with the GPC peaks shifted systematically to somewhat larger elution vol-

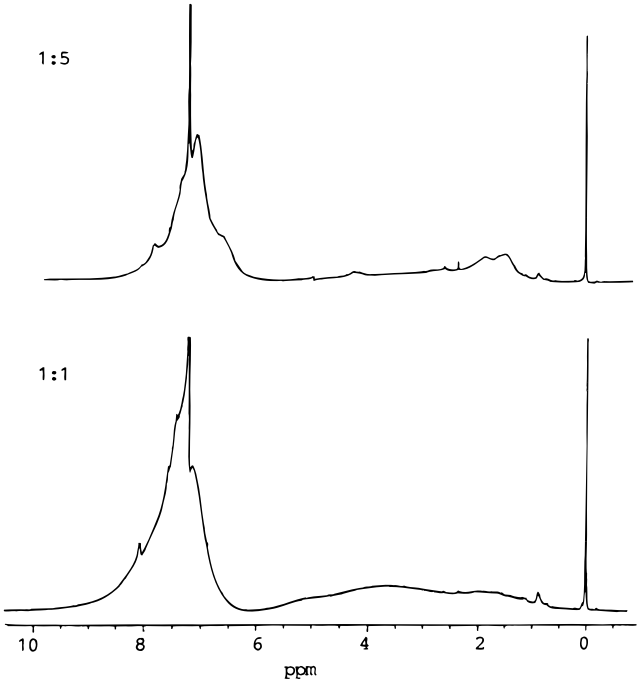


**Figure 3.** Proton NMR spectra ($CCl_3D$ as solvent and TMS as an internal standard) of the chloroform soluble fractions of the $C_{60}$−styrene copolymer samples prepared with initial $C_{60}$: styrene reactant ratios of 1:5 (**IVa**) and 1:1 (**Va**).

umes. Based on the GPC result shown in Figure 2, an $\bar{M}_w$ of 8500 and polydispersity of 5.5 can be calculated for the chloroform insoluble copolymer **Vb**. The molecular weight corresponding to the GPC peak maximum is 13 000 (Table 1). An increase in lithium bromide concentration in the mobile phase DMSO to 0.5% resulted in only minor shifts in GPC peaks of the sample and standards. Thus, the effect on molecular weight calculations is relative small. A comprehensive account of the polyelectrolyte effect in GPC analyses of fullerene-containing polymers with high fullerene contents will be reported separately.

**Characterization.** The $C_{60}$−styrene copolymers were characterized by use of proton and $^{13}C$ NMR methods. For copolymers with $C_{60}$ weight percents of ~0.4% (**I**) and ~1.7% (**II**), both proton and $^{13}C$ NMR spectra are dominated by signals due to polystyrene structures. In fact, the observed NMR spectra are indistinguishable from those of the neat polystyrene references prepared under the same experimental conditions.

For the copolymers with higher $C_{60}$ contents, the proton NMR spectra obtained in deuterated chloroform are shown in Figure 3. The proton signals of the copolymer containing ~14% (wt/wt) of $C_{60}$ (**IIIa**) are still due largely to polystyrene structures, with broad peaks in aliphatic (1−2.5 ppm) and aromatic (6.5−7.5 ppm) regions. Relative populations of aliphatic and aromatic protons are also consistent with those of polystyrene. However, for the copolymer with a higher $C_{60}$ weight percent of ~30% (**IVa**), both aliphatic and aromatic proton signals become broader. While broad peaks in the aliphatic region are still somewhat separated, the aromatic peaks observed in the spectrum of polystyrene are replaced by an extremely broad band centered at ~7.2 ppm (Figure 3). In addition, relative populations of the aromatic and aliphatic protons become very different, with the ratio of integrations of aromatic vs aliphatic protons in the copolymer larger than that in polystyrene. As the $C_{60}$ weight percent in the copolymer increases further to ~50% (**Va**), the observed proton NMR spectrum shows even more dramatic changes. The well-defined aliphatic peaks observed in the spectra of polystyrene and $C_{60}$−styrene copolymers with lower $C_{60}$ contents are absent. Instead, there are weak and extremely broad proton signals spread over almost the entire aliphatic region, indicative of very inhomogeneous environments for aliphatic protons. The aromatic signals are also extremely broad. Moreover, the results in Figure 3 show that the center of the aromatic proton signals shifts slightly downfield as the $C_{60}$ content in the copolymers increases.

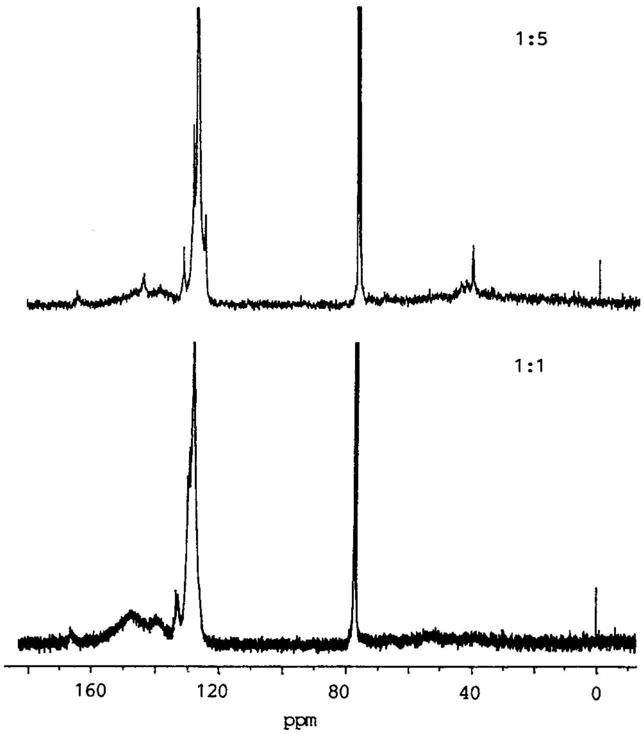


**Figure 4.** $^{13}C$ NMR spectra ($CCl_3D$ as solvent and TMS as an internal standard) of the chloroform soluble fractions of the $C_{60}$−styrene copolymer samples prepared with initial $C_{60}$: styrene reactant ratios of 1:5 (**IVa**) and 1:1 (**Va**).

$^{13}C$ NMR results of the $C_{60}$−styrene copolymers obtained in deuterated chloroform (Figure 4) are also characteristic, consistent with the trend observed in the proton NMR spectra. For the copolymers with $C_{60}$ contents of ~14% (wt/wt) and less (**I**, **II**, **IIIa**), the observed $^{13}C$ NMR spectra are essentially the same as that of neat polystyrene. However, the $^{13}C$ NMR spectrum of the copolymer with $C_{60}$ weight percent of ~30% (**IVa**) is apparently different. There is an extremely broad peak in the so-called fullerene region (135−160 ppm) which can be assigned to functionalized $C_{60}$ cages in the copolymer. The aromatic carbon signals in the 125−130 ppm region observed in the spectrum of polystyrene become broader. In addition, the relative intensity of the peak at ~145 ppm due to the first carbon on phenyl rings apparently becomes smaller. These new $^{13}C$ NMR features become more evident in the spectrum of the copolymer with an even higher $C_{60}$ weight percent of ~50% (**Va**). Contributions of functionalized $C_{60}$ cages in the 135−160 ppm region are more significant. The signal due to the first carbon on the phenyl rings is not visible in the spectrum, and the signals in the 125−130 ppm region become even broader. A more significant difference is the absence of the aliphatic peaks around 40 ppm observed in the spectra of polystyrene

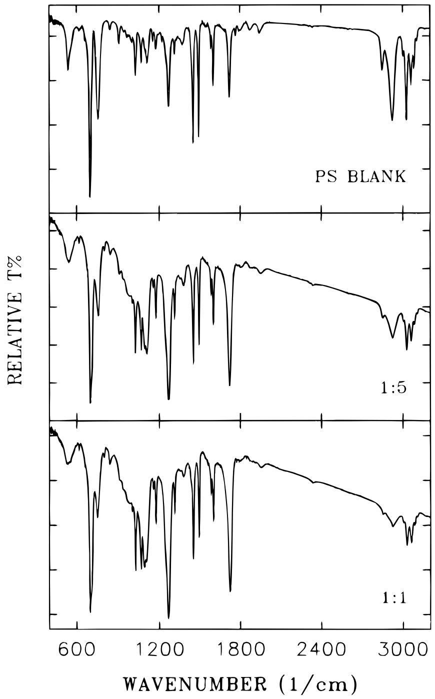


**Figure 5.** FT-IR spectra (in KBr matrix) of the chloroform soluble fractions of the $C_{60}$−styrene copolymer samples prepared with initial $C_{60}$:styrene reactant ratios of 1:5 (**IVa**) and 1:1 (**Va**). The spectrum of the polystyrene blank is also shown for comparison.

and the copolymers with lower $C_{60}$ contents. Instead, there are weak and broad signals in a much wider region of 35−70 ppm (Figure 4).

FT-IR spectra were measured for chloroform soluble (**I**, **II**, **IIIa**, **IVa**, **Va**) and insoluble (**IIIb**, **IVb**, **Vb**) $C_{60}$−styrene copolymers in KBr matrices, and the results were compared with those of neat polystyrene samples prepared under the same experimental conditions. As shown in Figures 5 and 6, observed FT-IR spectra of both chloroform soluble and insoluble fractions of $C_{60}$−styrene copolymers are somewhat dependent on $C_{60}$ contents.

For chloroform soluble $C_{60}$−styrene copolymers, there are systematic changes in observed FT-IR spectra as a function of $C_{60}$ contents. FT-IR spectra of the copolymers with $C_{60}$ contents ~14% (wt/wt) and less are very similar to that of neat polystyrene, as shown in Figure 5. However, for copolymers with higher $C_{60}$ contents, there are apparently different features in the observed FT-IR spectra. The bands in the 2800−3100 $cm^{-1}$ region due to aliphatic and aromatic C−H stretch absorptions become broader and relatively weaker, the ratio between absorptions at 759 $cm^{-1}$ (out-of-plane hydrogen) and 698 $cm^{-1}$ (out-of-plane phenyl ring) is smaller, and the peak at 541 $cm^{-1}$ also becomes broad (Figure 5). In addition, a peak at ~527 $cm^{-1}$ due to functionalized $C_{60}$ cages can be identified in the spectrum of copolymer sample **Va**.

There are obvious differences between the FT-IR spectra of chloroform soluble and insoluble fractions of a copolymer sample. The aliphatic and aromatic C−H stretch bands are relatively weaker in the chloroform insoluble fractions (**IIIb**, **IVb**) than in their corresponding chloroform soluble fractions (**IIIa**, **IVa**), and the ratio of 759 and 698 $cm^{-1}$ bands is also smaller in the insoluble fraction **IIIb** than in the soluble fraction **IIIa**. However, the 527 $cm^{-1}$ peak due to functionalized $C_{60}$ cages becomes evident in the spectra of all three chloroform insoluble samples (Figure 6). In a general comparison of Figure 5 and 6, the spectrum of the soluble fraction of the copolymer sample with ~50% (wt/wt) of $C_{60}$ (**Va**) is very similar to that of the insoluble fraction of the copolymer with ~14% (wt/wt) of $C_{60}$ (**IIIb**).

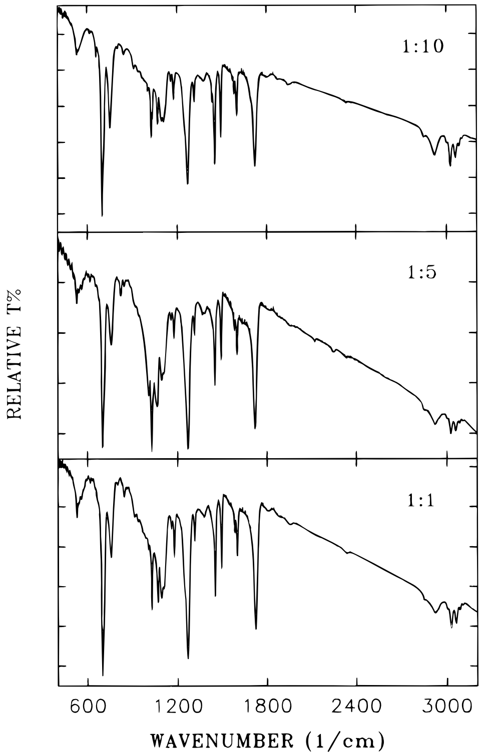


**Figure 6.** FT-IR spectra (in KBr matrix) of the chloroform insoluble fractions of the $C_{60}$−styrene copolymer samples prepared with initial $C_{60}$:styrene reactant ratios of 1:10 (**IIIb**), 1:5 (**IVb**), and 1:1 (**Vb**).

FT-IR spectra of the $C_{60}$−styrene copolymers that become insoluble as a result of heating (**IIIc**, **IVc**, **Vc**) are essentially the same as those of unheated copolymer samples (**III**, **IV**, **V**).

Thermal properties of $C_{60}$−styrene copolymers are different from those of neat polystyrene references. Differential scanning calorimetry (DSC) results show no glass transitions for the copolymers in a wide temperature range of 30−280 °C. However, glass transitions were observed at 80−100 °C for the neat polystyrene samples prepared under the same conditions as those for the $C_{60}$−styrene copolymers.

**Electronic Absorption.** The electronic absorption spectra of the $C_{60}$−styrene copolymers shown in Figure 7 are very different from that of monomeric $C_{60}$.[8,9,14,15] Apparently, the absorptivities per unit weight concentration of the copolymers increase with increasing $C_{60}$ contents in the copolymers. By normalizing the observed absorption spectra at 350 nm with factors $\epsilon_{W,i}$, where $\epsilon_W$ represents absorptivities in units of $(mg/mL)^{-1}$ $cm^{-1}$ and $i$ denotes different copolymers with different $C_{60}$ contents, the spectral profiles are similar for different $C_{60}$−styrene copolymers (Figure 7). A linear plot is shown in Figure 8 for the $\epsilon_{W,i}$ values as a function of $C_{60}$ weight percents in the copolymers.

## Discussion

The results presented here clearly show that $C_{60}$ and styrene can be copolymerized under different conditions. According to GPC analyses using both UV and refractive

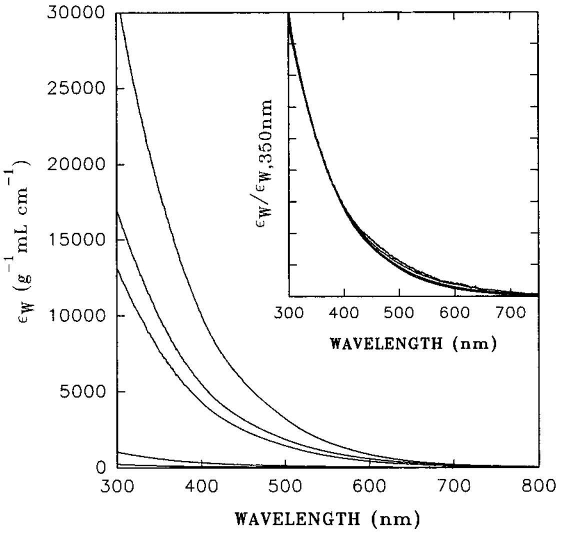


**Figure 7.** Absorption spectra of the $C_{60}$–styrene copolymers containing (in the direction of increasing $\epsilon_W$ values) ~0.4%, ~1.7%, ~14%, ~30%, and ~50% (wt/wt) in dichloromethane. Shown in the insert are the spectra normalized at 350 nm.

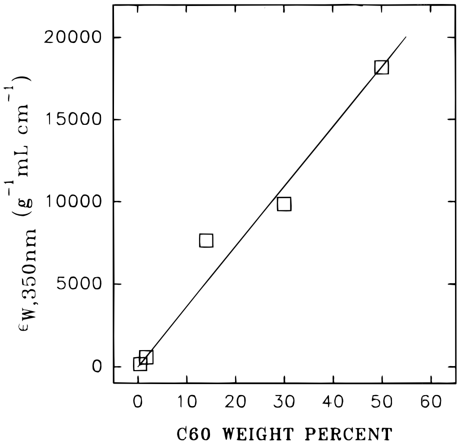


**Figure 8.** A plot of absorptivities per unit weight of the $C_{60}$–styrene copolymers at 350 nm as a function of $C_{60}$ contents in the copolymers.

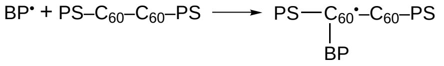
index detectors, $C_{60}$ molecules are covalently incorporated into the polymer structures. With a constant benzoyl peroxide amount, $C_{60}$ contents in the copolymers increase with increasing initial $C_{60}$:styrene reactant ratio (Table 1). There is no apparent reduction in the polymer yield at high initial $C_{60}$:styrene reactant ratios, which is probably due to relatively small [$C_{60}$]/[initiator] values. According to the recent results of Cao and Webber,[15] substantial reductions in polymer yields occur at the [$C_{60}$]/[initiator] ratios of ~0.12 and higher. In addition, molecular weights and weight distributions of the copolymers prepared with different initial $C_{60}$:styrene reactant ratios are not significantly different (Table 1), except for some higher molecular weight species in the copolymer samples prepared with the initial $C_{60}$:styrene reactant ratios of 1:5 and 1:10 (mg:$\mu$L). Since there are no such high molecular weight species in the polystyrene references prepared under the same experimental conditions without $C_{60}$, the presence of high molecular weight species in some copolymer samples may be regarded as evidence for a somewhat different mechanism of radical-initiated $C_{60}$–styrene copolymerization from the classical mechanism of styrene polymerization.

In a classical mechanism of radical polymerization, propagation of $C_{60}$ radicals is critical to the formation of true $C_{60}$–styrene copolymers.[8–10,14,15]

$$\mathrm{PS{-}C_{60}^{\bullet} + S \longrightarrow PS{-}C_{60}{-}S^{\bullet}} \qquad (1)$$

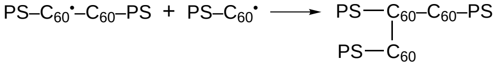
However, it has been suggested[10,15] that propagation of $C_{60}^{\bullet}$ radicals is slow in general because of their relatively high stability.[20,21] It has also been suggested[15] that $C_{60}$ competes effectively with styrene for initiator radicals and, as a logical extrapolation, for $PS^{\bullet}$ radicals as well. In this regard, $C_{60}$ may act as a radical inhibitor in the copolymerization reaction. Evidence for the inhibiting effect includes the observation[15] that at high [$C_{60}$]/[initiator] ratios polymerization yields are low in comparison with those in neat styrene polymerization. Thus, the mechanism of $C_{60}$–styrene copolymerization may be different from the classical mechanism of radical polymerization of styrene such that there is a significant population of $C_{60}$ radicals and their propagation is relatively slow. However, even with the suggested inhibiting effect of $C_{60}$ in the copolymerization reaction, contributions of polystyrene structures are substantial even in the copolymers with high $C_{60}$ contents, as shown in the observed FT-IR spectra of the copolymers (Figures 5 and 6).

By assuming that $C_{60}$ radicals participate in termination processes only, the average number of $C_{60}$ cages per polymer ($N_{C60}$) should be 1–2. However, in the copolymers with high $C_{60}$ contents (Table 1), the estimated $N_{C60}$ values are apparently larger. The high $C_{60}$ populations might be explained by considering the possibility that functionalized $C_{60}$ cages may also compete for initiator radicals.

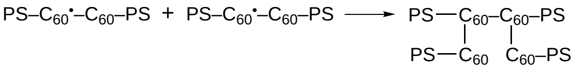

$$\mathrm{BP^{\bullet} + PS{-}C_{60}{-}C_{60}{-}PS \longrightarrow PS{-}\underset{\displaystyle BP}{\underset{|}{C_{60}^{\bullet}}}{-}C_{60}{-}PS}$$

(2)

As a result, copolymers containing more than two $C_{60}$ cages may also be generated in essentially termination reactions.


$$\mathrm{PS{-}C_{60}^{\bullet}{-}C_{60}{-}PS + PS{-}C_{60}^{\bullet} \longrightarrow PS{-}\underset{\displaystyle PS{-}C_{60}}{\underset{|}{C_{60}}}{-}C_{60}{-}PS}$$

(3a)


$$\mathrm{PS{-}C_{60}^{\bullet}{-}C_{60}{-}PS + PS{-}C_{60}^{\bullet}{-}C_{60}{-}PS \longrightarrow PS{-}\underset{\displaystyle PS{-}C_{60}}{\underset{|}{C_{60}}}{-}\underset{\displaystyle C_{60}{-}PS}{\underset{|}{C_{60}}}{-}PS}$$

(3b)

It is not necessary for each $C_{60}$ cage to have only one polystyrene arm. The copolymers thus obtained may have a starlike structure which is conceptually similar to that of the so-called flagellenes, namely multiple polystyrene arms are attached to a core of fullerene cages. Because of different hydrodynamic properties, linear polystyrene standards are not good molecular weight references for the copolymers with high $C_{60}$ contents in GPC analyses. It might be expected that the copolymer molecular weights are underestimated.

There are also fragments of the radical initiator on $C_{60}$ cages, consistent with FT-IR results. The structural implications of the fragments are similar to those of the polystyrene arms. In this regard, the fullerene cage-bound benzoyl peroxide fragments may be considered as the shortest arms without styrene units.

It seems that the $C_{60}$–styrene copolymerization processes and, consequently, the copolymer structures are dependent on the initial $C_{60}$:styrene reactant ratios. For the copolymers with low $C_{60}$ contents (**I** and **II**, Table 1), the $N_{C60}$ values are small and the copolymers are likely generated predominantly in termination processes. Because $C_{60}$ populations in the copolymers are very low, the observed NMR and FT-IR spectra are dominated by contributions of polystyrene structures. At higher $C_{60}$:styrene ratios, $C_{60}$ populations in the copolymers $N_{C60}$ become larger. The NMR and FT-IR results of these copolymers are different, with prominent $^{13}C$ signals in the fullerene region (135−160 ppm, Figure 4) and IR absorption at 527 $cm^{-1}$ (Figures 5 and 6). The observed NMR and FT-IR spectra also show increasing effects of $C_{60}$ cages on polystyrene structures in the copolymers. As $C_{60}$ weight percents in the copolymers increase from ~14% (**IIIa**) to ~30% (**IVa**) and to ~50% (**Va**), the aliphatic proton and carbon signals in observed NMR spectra become broader, indicative of increasingly inhomogeneous environments for aliphatic moieties in the copolymers. The inhomogeneity becomes extreme in the copolymer with ~50% (wt/wt) of $C_{60}$ (**Va**), resulting in extremely broad aliphatic signals in the observed NMR spectra (Figures 3 and 4). In the context of a predominantly starlike copolymer structure, the NMR results of the copolymers with high $C_{60}$ contents are consistent with random multiple substitutions of $C_{60}$ cages by short polystyrene arms. The relative contributions of aliphatic vs aromatic proton signals in the copolymers with high $C_{60}$ contents are apparently smaller. However, because the initiator fragments in the copolymer structures also have aromatic protons, a quantitative evaluation of the fullerenation of polystyrene structures in terms of the copolymer proton NMR spectra is not practical.

With high $C_{60}$ contents, either in the copolymers **IV** and **V** or in the chloroform insoluble fraction **IIIb**, the observed FT-IR spectra are apparently different from those of polystyrene and copolymers with lower $C_{60}$ contents. While the differences seem rather characteristic, their structural implications are not clear. It is possible that the different features in the 2800−3100 and 500−800 $cm^{-1}$ regions are associated with different morphologies of the copolymers with high $C_{60}$ contents from those of polystyrene and the copolymers with lower $C_{60}$ contents. The copolymers with high $C_{60}$ contents have broader IR bands in the spectral regions, which might be related to the proposed copolymer structures in which multiple short polystyrene arms are inhomogeneously attached to a core of fullerene cages. It is known[22,23] that IR absorptions of neat polystyrene can be affected by polymer morphology changes in a relatively significant fashion.

Propagation of $C_{60}$ radicals (eq 1) may indeed be slow due to relatively high radical stability. However, there is not enough evidence for a complete elimination of the possibility of such processes (eq 1). Minor contributions of $C_{60}$ radical propagation may produce some copolymers with a structure in which starlike species are connected by polystyrene segments. It might be a possibility that copolymers with this kind of structure are responsible for the broadly distributed high molecular weight species observed in the GPC analyses of the copolymer samples **IIIa** and **IVa**. Formation of the high molecular weight species is unique to the copolymerization reactions because no such species were observed in the GPC traces of the neat polystyrene references prepared under the same experimental conditions. It is also interesting that the high molecular weight species are only found in the copolymer samples prepared with intermediate initial $C_{60}$:styrene reactant ratios of 1:5 and 1:10 (Figure 1).

The solubilities in common organic solvents exhibited by the copolymers containing as high as 50% (wt/wt) of $C_{60}$ are somewhat surprising. It might be speculated that the proposed starlike polymer structure, in which the core of fullerene cages is surrounded by polystyrene arms, is favorable to the solvation of the copolymers. For the copolymers with $C_{60}$ contents of ~14% (wt/wt) and higher, there are minor fractions that are insoluble in chloroform. The insolubilities are probably due primarily to structural factors, to which vibrational spectra are insensitive. The FT-IR results show no fundamental differences between chloroform soluble and insoluble copolymer samples in the sense that the FT-IR spectra of the insoluble sample **IIIb** and soluble sample **Va** are very similar (Figures 5 and 6). However, the chloroform insoluble fractions apparently have somewhat higher $C_{60}$ contents than their corresponding soluble fractions in terms of the IR absorption at 527 $cm^{-1}$. Interestingly, the chloroform insoluble fraction of the copolymer with highest $C_{60}$ content (**Vb**) is somewhat soluble in DMSO, while the insoluble fractions of the other copolymers (**IIIb** and **IVb**) do not dissolve in DMSO at all. It is known that monomeric $C_{60}$ has no solubility in DMSO, but oligomeric and polymeric species containing high compositions of linked fullerene cages are somewhat soluble in DMSO.[4,24,25] Therefore, the different solubilities in DMSO for the chloroform insoluble fractions of different $C_{60}$−styrene copolymers may be attributed to their somewhat different polymer structures, namely different arrangements of $C_{60}$ cages and polystyrene arms of various sizes.

For the copolymer with ~50% (wt/wt) of $C_{60}$, the GPC results of the chloroform soluble and insoluble fractions obtained by use of chloroform and DMSO as mobile phases, respectively, appear to be somewhat different. However, the difference should be considered in the context that the qualities of the results obtained in the two different GPC solvents are different. Linear poly(2-vinylpyridine) standards may not be suitable as molecular weight references for the copolymer, which presumably has a starlike structure, especially in the presence of polyelectrolyte effect. The tailing in the observed GPC trace of the copolymer may be an indication for the presence of non-GPC interactions. In this regard, the GPC result in DMSO is only qualitative, simply illustrating that the chloroform insoluble fraction also consists of $C_{60}$-containing polymeric species.

The dramatic reduction in solubilities of the copolymers upon heating in a routing drying process is typical to fullerene-containing polymers with high fullerene contents. The same behavior has also been observed in the pendant $C_{60}$−polystyrene[12] and pendant $C_{60}$−polyethylenimine[25] polymers. In fact, for the pendant polymers, their solubilities are also reduced substantially upon only a complete removal of solvent using a rotary evaporator at room temperature.[12,25] There are small amounts of oligomeric species (according to GPC) in the heated copolymer samples that can be extracted by chloroform. For the heated copolymer sample containing ~14% of $C_{60}$ (**IIIc**), a small fraction of polymeric species, presumably with lower $C_{60}$ populations, can also be extracted by chloroform. The much lower solubilities of the heated copolymer samples are unlikely due to significant polymer structural changes as a result of the heating process. A more likely cause may be related to the kinetic factors in the solvation of fullerene-containing polymers. The FT-IR spectra of the heated and unheated copolymer samples are essentially the same.

The glass transitions observed in neat polystyrene samples are absent in $C_{60}$−styrene copolymers. A rationalization might be that the incorporation of $C_{60}$ cages into polystyrene structures has similar effects on the thermal properties as in the cross-linking of polystyrene polymers.[26]

The absorptivities per unit weight of the $C_{60}$−styrene copolymers $\epsilon_W$ increase with increasing $C_{60}$ contents in the copolymers (Figure 7). The molar absorptivities of $C_{60}$ units in the copolymers ($\epsilon_{M,C_{60}}$) are related to $\epsilon_W$ as follows:

$$\epsilon_W = (\epsilon_{M,C_{60}}/M_{C_{60}})\chi_{W,C_{60}} \tag{4}$$

where $M_{C_{60}}$ is the molecular weight of $C_{60}$ and $\chi_{W,C_{60}}$ represents $C_{60}$ weight percents in the copolymers. As shown in Figure 8, the plot of $\epsilon_W$ vs $\chi_{W,C_{60}}$ for the $C_{60}$−styrene copolymers is approximately linear. A $\epsilon_{M,C_{60}}$ value of 26 000 $M^{-1}$ $cm^{-1}$ at 350 nm can be obtained from the slope. This is an average molar absorptivity of $C_{60}$ units in all of the $C_{60}$−styrene copolymers with different $C_{60}$ contents. With a common $\epsilon_{M,C_{60}}$ for different $C_{60}$−styrene copolymers, eq 4 can be used to calculate $C_{60}$ contents from observed $\epsilon_W$ values. The result in Figure 8 indicates that such calculations performed previously[8,9] were reasonable approximations. It should be pointed out that the plot shown in Figure 8 is an approximation itself. The $C_{60}$ weight percents obtained from mass balance are total $C_{60}$ contents in chloroform soluble and insoluble samples. According to FT-IR results, the $C_{60}$ contents in chloroform soluble fractions, for which $\epsilon_W$ values were determined, are lower than those in the corresponding insoluble fractions. However, since the chloroform insoluble fractions are minor (Table 1), the true $C_{60}$ weight percents in the soluble fractions should be close to the total $C_{60}$ contents calculated on the basis of mass balance.

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