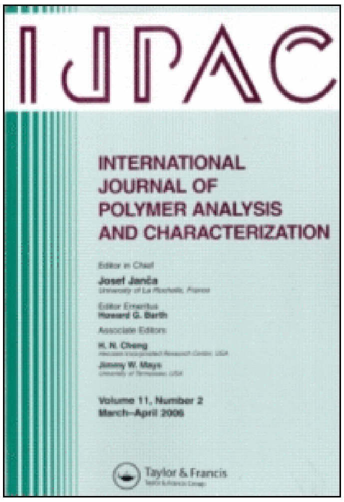

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Preparation and Structural Characterization of C_{60}-bonded Poly(*p*-methylstyrene)

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The soluble fullerenated poly(*p*-methylstyrene) with different C_{60} contents was prepared through the reaction of carbanion intermediates of poly(*p*-methylstyrene)[PPMS], which were obtained by proton abstraction with NaH, with C_{60} in the heterogeneous medium. Covalent grafting of electrophilic C_{60} moieties onto the PPMS backbone resulted in the enhancement of absorption at longer wavelengths and thermal stability of the polymer. The paramagnetic species in the fullerenated PPMS results from the π–π stereo-electron interplay between C_{60} and the adjacent *p*-methylphenyl groups of PPMS.

Keywords: [60]Fullerene; Poly(*p*-methylstyrene); Structural characterization; Polymeric modification

INTRODUCTION

Discovery of the fullerenes, a family of carbon cage molecules epitomized by the exquisitely symmetrical C_{60}, reshaped chemists' understanding of the fundamental properties of carbon and earned Curl, Kroto and Smalley the 1996 Nobel prize in chemistry.[1] The physicochemical properties of C_{60} have demonstrated that it possesses high electron affinity (EA = 2.6–2.8 eV) and three degenerate LUMO levels, which should readily accept up to six electrons in electrochemical reductions or, in chemical conversions.[2,3] Thus, C_{60} is an excellent

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electrophile reacting with a variety of neutral and charged nucleophilic reagents. Organic carbanion adds across the carbon–carbon double bonds of C_{60}, to give alkylated reaction products.[4–6] Likewise, living polymer carbanions pregenerated by proton abstraction with NaH[7–11] or butyllithium[12,13] also will add to C_{60} to form fullerene-containing "charm bracelet" type polymers.

Bergbreiter and Gray[13] took advantage of the C_{60} reactivity by grafting C_{60} molecules onto a pregenerated lithiated polyethylene surface. Polyethylene films functionalized with diphenylmethyl groups were deprotonated to form a nucleophilic lithiated surface which in turn was used to covalently bind C_{60} to polyethylene. Both the steric effects of the diphenylmethyl group and the entropic constraints of the surface should preclude polysubstitution. Dai *et al.*[12] used a similar method to obtain fullerene-functionalized polymers with multiple pendant buckyballs dispersed along the polymer backbone. In our previous papers,[7a,8,9] we have developed a simple and useful method for the synthesis of soluble fullerenated polymers through the reaction of C_{60} with pregenerated carbanion intermediates of such polymers as poly(*N*-vinylcarbazole), polystyrene, etc. Both the stereo-electronic effect and the steric hindrance of the bulky C_{60} molecule have an important influence on the structure and physicochemical properties of polymer. Here we report the preparation and structural characterization of C_{60}-bonded poly(*p*-methylstyrene) copolymer, hereafter referred to as C_{60}-PPMS. The product obtained is a "charm-bracelet" noncross-linked earthy-yellow polymer which is highly soluble in many common organic solvents.

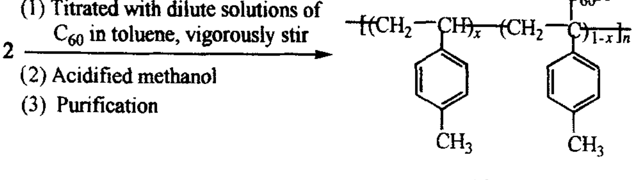
EXPERIMENTAL

Poly(*p*-methylstyrene) [PPMS] was prepared by using standard anionic polymerization reaction with *n*-butyllithium as the initiator. Gel permeation chromatography of the PPMS polymer gave $M_n = 5978$, $M_p = 8655$ and $M_w = 9455$, respectively. C_{60} was synthesized and purified according to the literature.[14,15] HPLC analysis showed C_{60} with a purity of 99.5%.

Both toluene and tetrahydrofuran were dried, deoxygenated and distilled before use. Unless noted otherwise, other analytically pure reagents, for example, methanol, hydrochloric acid, etc., were used as received. The operations for synthesis prior to the termination reaction were carried out under purified dry nitrogen by use of standard *schlenk* tubes.

Ultraviolet–visible absorption spectra in THF were measured on a UV-240 spectrophotometer. Fourier transform-infrared (FTIR) spectra were recorded on a Nicolet FT-IR-5DX spectrophotometer using KBr pellets. ^{13}C NMR spectra in $CDCl_3$ were run on a Bruker MSL-600 NMR spectrometer. X-ray diffraction spectra were measured on a Japanese Science D/Max-RB diffractometer (Cu target). Electron spin resonance spectra were recorded on a Bruker ER200D-SRC spectrometer, and *g*-values were determined by calibration with DPPH (α,α'-diphenyl-β-picryl hydrazyl). Thermal properties of the samples were measured using a DuPont 2000 thermogravimetric analyzer under a nitrogen flow.

The soluble PPMS doped covalently to various extents with $C_{60}H$ moieties (i.e., C_{60}-PPMS) prepared by the following method under a purified nitrogen atmosphere (Scheme 1). The polymers were redissolved in THF, filtered to remove any unreacted C_{60}, and then reprecipitated with methanol to give a earthy-yellow product (3) which was



(0 < *x* < 1)

C_{60}-PPMS copolymer

3

SCHEME 1

highly soluble in many common organic solvents such as THF, $CHCl_3$, etc. Solvent residues were removed by freeze drying under vacuum for several hours. The C_{60} content, which was estimated by the TGA results, were 2.4%, 3.2% and 6.2%.

RESULTS AND DISCUSSION

Figure 1 gives the UV–visible absorption spectra of pure PPMS and C_{60}-PPMS copolymers with C_{60} wt% of ~2.4%, ~3.2%, ~6.2% in THF. The strong absorption bands at 268 and 277 nm corresponding to the copolymers with different C_{60} content are in general agreement with those of the pure PPMS. The covalent attachment of electrophilic C_{60} moieties to the PPMS backbone results in the enhancement of absorption at longer wavelengths; whereas pure PPMS is basically

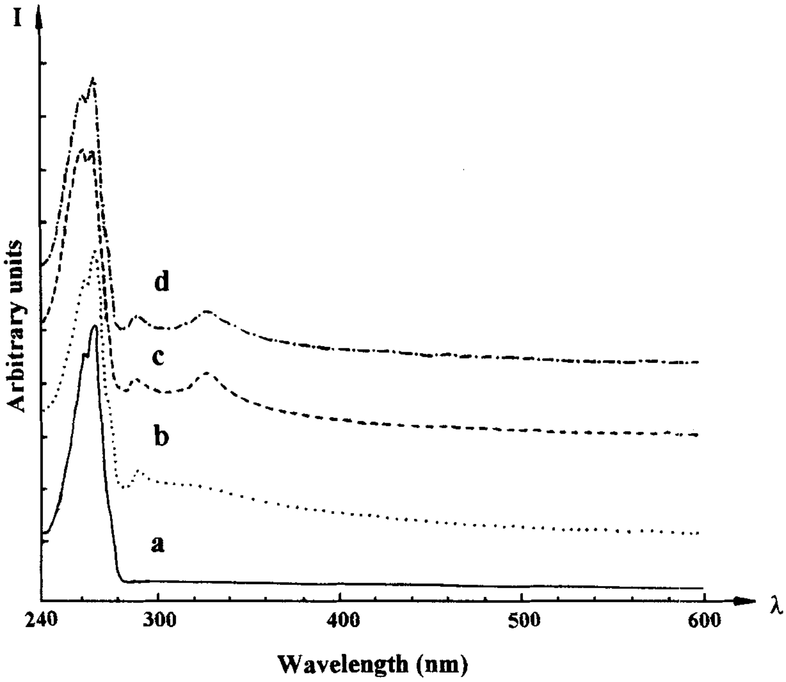


FIGURE 1 UV–vis absorption spectra of the samples: (a) PPMS, (b) 2.4% C_{60}-PPMS, (c) 3.2% C_{60}-PPMS and (d) 6.2% C_{60}-PPMS in tetrahydrofuran.

transparent at wavelengths longer than 290 nm. Two new absorption peaks at 291 and 330 nm were observed in the ultraviolet–visible spectra of the copolymers and may be ascribed to the characteristic absorption for the covalent grafting of C_{60} to the PPMS backbone[8,9] as compared with the ultraviolet–visible absorbances at 213, 254, 257, 329, 404, 500, 570, 600 and 625 nm of pure C_{60} in *n*-hexane. (The ultraviolet–visible spectrum of C_{60} in THF cannot be observed due to its poor solubility in polar solvents.)

The difference between C_{60}-PPMS copolymers and pure PPMS in the absorption spectra are also confirmed by the ESR results (Figure 2). No ESR signal in pure PPMS is detected, indicating the

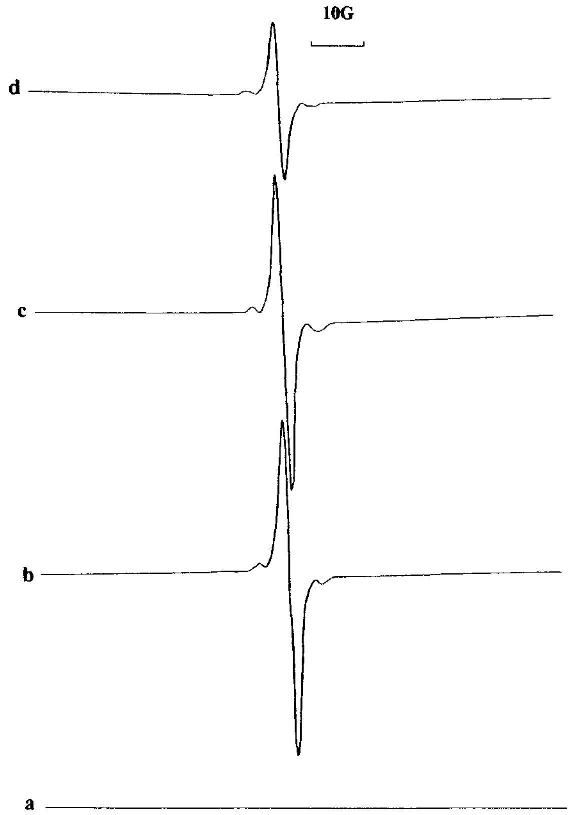


FIGURE 2 ESR spectra of (a) PPMS, (b) 2.4% C_{60}-PPMS, (c) 3.2% C_{60}-PPMS and (d) 6.2% C_{60}-PPMS.

nonexistence of unpaired electrons or free radicals. In the C_{60}-PPMS copolymer, ESR spectrum shows two peaks: a narrow peak ($g = 2.0022$, $\Delta H_{pp} = 1.8\,G$) attributed to the $\pi - \pi$ stereo-electronic interaction between the pendant C_{60} molecule and the near-neighboring flat *p*-methylphenyl rings of PPMS in the copolymer, and a small broad shoulder peak ($\Delta H_{pp} = 12.3\,G$) which is assigned to the interaction between the positively charged *p*-methylphenyl rings and the adjacent relatively electron-rich *p*-methylphenyl rings.[7,9] It is worth noting that the relative intensity of the narrow peak decreased gradually with increasing C_{60} content. A reasonable explanation is that the large steric hindrance effects from the bulky C_{60} molecules and the bulky *p*-methylphenyl groups, and possible resultant barriers to rotation of C–C single-bond links may lead to situations in which the conformational requirements for effective "charge-transfer" complexation are not met, in spite of a favorable energetic relationship between the pendant C_{60} molecule (electron acceptor) and the adjacent relatively electron-rich *p*-methylphenyl groups. These findings further confirm the conclusion that the formation of paramagnetic centers in the C_{60}-based organic polymers may be due to the $\pi - \pi$ stereo-electron interplay between C_{60} and the adjacent relatively electron-rich atomic groups of polymers.

The FT-IR spectrum of C_{60}-PPMS copolymer was essentially the same as that of pure PPMS and gave little additional information concerning the structure of this material. Perhaps a better rationalization might be as follows: The steric restrictions introduced by a bulky *p*-methylphenyl group hinder the carbanion intermediates of PPMS from attacking at C_{60}, resulting in relative lower C_{60} contents in the copolymer. Also, the electron-donating effect of the *p*-methyl groups on the phenyl ring should result in decreased carbanion stability of the polymer. On the basis of the above analysis, because of the overwhelming contributions of unsubstituted *p*-methylstyrene units in the polymer structures, the structure changes cannot be observed by IR spectrum in our experimental conditions. Likewise, ^{13}C NMR spectra of the copolymers are also similar to that of the parent polymer and only give little information concerning structure. In the fullerene region (130–150 ppm), five small new peaks, which located at 143.5, 143.4, 143.2, 142.5 and 142.5 ppm, respectively, were detected and may be assigned to the functionalized C_{60} cage in the copolymer.

Due to the effect of strong electron affinity of C_{60} on the aromatic carbons of PPMS, the ^{13}C chemical shifts of *p*-methylphenyl groups of PPMS move slightly down-field.

Thermogravimetric analysis showed that, for all the polymers, only a distinct stage of weight loss was observed. The maximal thermal decomposition temperatures of the pure PPMS and C_{60}-PPMS copolymers with C_{60} wt% of 2.4%, 3.2%, 6.2% are 360.9, 382.3, 390.2 and 399.4°C, respectively. Obviously, the thermal stability of PPMS was enhanced considerably by C_{60} chemical modification, suggesting that possibly C_{60} may be used as a chemical additive for increasing thermal stability of the polymer.[16,17] Milliken *et al.*[18] indicated that the onset of weight loss for C_{60} in N_2 is about 600°C. Thus, by assuming that before 500°C the other residues remaining in the copolymer have the same weight percent as that of pure PPMS except undecomposed C_{60} residues, the weight percent of C_{60} in the copolymer may be calculated.

The X-ray powder diffraction spectra from the C_{60}-PPMS copolymers with different C_{60} contents are shown compared with that from the parent polymer in Figure 3. For the pure PPMS, eight diffraction peaks, which centered at $2\theta = 8.38°$ (10.54 Å), 18.08° (4.90 Å), 28.52° (3.13 Å), 29.80° (2.99 Å), 45.68° (1.98 Å), 49.96° (1.82 Å), 52.48° (1.74 Å) and 59.46° (1.53 Å), respectively, were observed (the magnitude in parentheses represent corresponding *d*-value for the 2θ peak). It is interesting that, like the XRD spectra of C_{60}-chemically modified poly(*N*-vinylcarbazole),[7] after the electrophilic C_{60} moieties were grafted covalently onto the parent polymer backbone, two main diffraction peak positions centered near $2\theta = 8.38°$ and 18.08° did not vary with increasing fullerene content, indicating that the periodicity of the main arrangement of atoms or atomic groups in the copolymer remains unchanged. However, their diffracted intensities take on regular changes with increasing fullerene content. At first, the diffracted intensity decreased greatly with increasing C_{60} content, and then began to increase as the fullerene level increased up to 6.2 wt%. The position (2θ) of the diffraction line only relates to periodic features of atomic arrangements, whereas diffracted intensity, which is directly proportional to the square of structure factor F depends on properties, such as atomic species, quantity and relative position distribution, etc. In view of this, the introduction of C_{60} moieties into the polymer

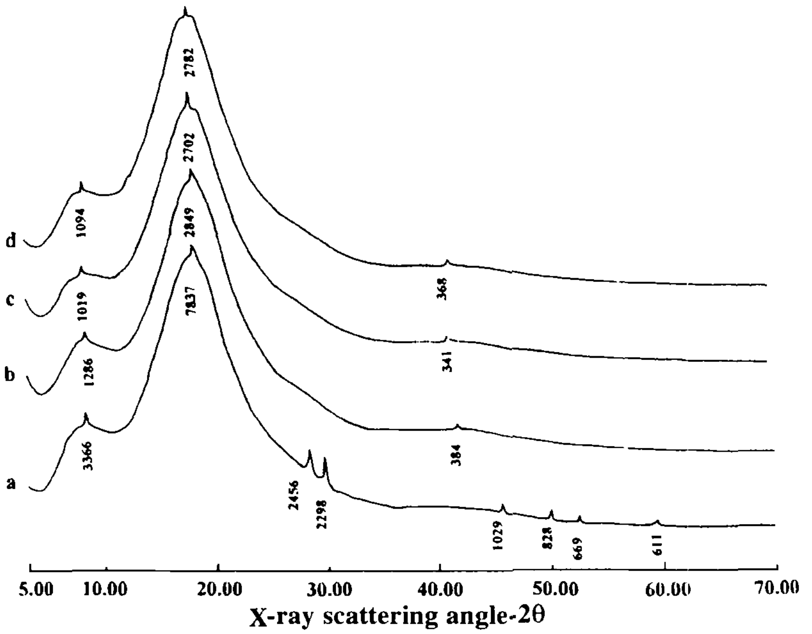


FIGURE 3 X-ray powder diffraction diagrams from (a) PPMS, (b) 2.4% C_{60}-PPMS (c) 3.2% C_{60}-PPMS and (d) 6.2% C_{60}-PPMS. The magnitude in this figure represents diffracted intensity (defined as counts per second (cps) under the identical experimental condition) for the 2θ peak.

therefore results in (a) partial extinction with respect to some distribution of atoms or atomic groups and consequently a decreased diffraction intensity at lower C_{60} contents, and (b) the role of partial extinction is reduced as C_{60} content in copolymer is increased up to some magnitude.[7] In addition, we also find that after C_{60} moieties were attached covalently to the PPMS backbone, the peaks centered at $2\theta = 28.52°, 29.80°, 45.68°, 49.96°$, 52.48° and 59.46° corresponding to the parent polymer vanished completely with the simultaneous presence of a new sharp peak at $2\theta = 41.84°$ (2.16 Å). These results show that in the X-ray diffraction structure of the copolymer, besides having a main diffraction pattern, a new crystal grating or crystallization phase was formed when compared to the XRD spectrum of pure PPMS.

CONCLUSION

The soluble PPMS polymer doped covalently to various extents with $C_{60}H$ moieties (C_{60}-PPMS copolymer) was prepared through the reaction of C_{60} with the carbanion intermediates of PPMS. This fullerenated polymer had a visibly earthy-yellow cast when compared with the unreacted parent polymer. Covalent grafting of electrophilic C_{60} moieties onto the PPMS backbone resulted in the enhancement of absorption at longer wavelengths and thermal stability of the polymer. ESR spectrum of the copolymer showed two peaks: a narrow peak and a small broad shoulder peak. These paramagnetic species in the copolymer may be stemmed from the π–π stereo-electron interplay between C_{60} and the adjacent *p*-methylphenyl groups of PPMS. X-ray powder diffraction demonstrates that after the electrophilic C_{60} moieties were grafted covalently onto the parent polymer backbone, two main diffraction peak positions centered near $2\theta = 8.38°$ and $18.08°$ did not vary with increasing fullerene contents, implying that the periodicity of the main arrangement of atoms or atomic groups in the copolymer remains unchanged. However, their diffraction intensities take on regular changes with increasing fullerene content. Further studies on the physical and chemical properties of the copolymers are currently in progress.

Acknowledgments

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