

Preparation and Characterization of a Novel Composite Based on Hyperbranched Polysilane and Fullerene

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ABSTRACT: Conjugated polymers doped with fullerenes have shown promising application in photovoltaic cells, in which photoinduced charge transfer takes place. Here, we report a novel composite that was prepared by *in situ* polymerization of σ -conjugated hyperbranched polysilane in the presence of fullerene. Both of the hyperbranched polysilane and fullerene have 3D structures, which are propitious to preparing materials with interpenetrating structure. The resulting composite has good solubility in common organic solvents and the UV spectrum edge suggests a low bandgap. Photoluminescence quenching in the composite is

shown by the PL spectra and is also observed from the fluorescence microscopy images, which may be ascribed to the PCT from the hyperbranched polysilane to the fullerene. The composite was also characterized by GPC, FTIR, NMR, XRD, and TGA. Through further discussion, there may be π - π stacking between hyperbranched polysilane and fullerene, which enhances the photoinduced charge transfer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 821–826, 2007

Key words: charge transfer; hyperbranched; polysilane; fullerene; composite

INTRODUCTION

Photoconducting materials are employed in many applications, including photovoltaic cells. In these materials, researchers used to focus on polymers, especially conjugated polymers that demonstrated easy processibility, low production cost, and flexibility. Now, more and more attentions are paid on this area. Since the discovery of the methods for mass production of fullerene C_{60} ¹ and the observation of photoinduced charge transfer (PCT) from conjugated polymers (electron donor, D) to C_{60} (electron acceptor, A),² conjugated polymers- C_{60} composites have attracted substantial attention as it offers a possible alternative to conventional photovoltaic cell materials.^{3–6}

Generally, the commonly used conjugated polymers are mainly π -conjugated polymers.^{3–6} In recent years, great attention has been paid to the polysilanes, which are a class of σ -conjugated polymers with the backbone consisting of tetrahedrally coordinated silicon atoms and different side-chain substituent groups. Because of extensive delocalization of σ -electrons along the silicon main chain, polysilanes have many interesting electronic properties such as photocon-

ductivity with a high hole mobility of $\sim 10^{-4} \text{ cm}^2/(\text{V s})$ at room temperature.^{7,8} Nevertheless, the photoinduced charge-generation efficiency of polysilanes is low. Wang and coworkers reported that doping of C_{60} into polysilane could greatly enhance its charge-generation efficiency.⁹ It is expected that the combination of high carrier mobility and high charge-generation efficiency may make the polysilanes- C_{60} composites form a new type of polymeric photoconductor and open a new field in material science. It was reported that it is very important to prepare interpenetrating D/A bicontinuous networks to obtain higher conversion efficiency by increasing the interfacial area between the donor/acceptor phases.^{10,11}

The common use of polysilanes as electron donor has been mainly focused on polymethylphenylsilane (PMPS) in which the substituents are methyl and phenyl groups.^{9,12–15} Meanwhile, hyperbranched polysilanes, different from linear polysilanes, have red shift of absorption and emission spectra, and can reduce bandgap due to the extent of σ -conjugation at branching points.^{16–18} And its 3D structure is very propitious to preparing interpenetrating structure that is ideal for photovoltaic cells. But there are few literatures about hyperbranched polysilanes used as electron donor.

Fullerene was chosen as a new three-dimensional efficient acceptor because of its unique delocalization, provided by the three-dimensional structure of the fullerene core. In combination with the small reorganization energy associated with almost all its reactions,

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especially in photoinduced charge transfer (PCT), and absorption spectra extending to most of the visible spectra.^{19–22}

In this article, we select σ -conjugated hyperbranched polysilane as electron donor and C_{60} as electron acceptor. Both have 3D structures, and their ball stick models generated by chemical 3D (Cambridge Soft Corp.) are shown in Figure 1(a). We prepared the composite in a simple one-pot approach, *in situ* polymerization. After means of characterization, we found that there may be π - π stacking between the electron donor and acceptor. And effective photoluminescence (PL) quenching was observed, which indicates the PCT from the hyperbranched polysilane to the C_{60} as shown in Figure 1(b) and the composite may find application in photovoltaic devices.

EXPERIMENTAL

General

High-purity (99.9%) C_{60} was purchased from Peking University, China. Dichloromethylphenylsilane was purchased from Aldrich. Trichloromethylsilane was purchased from Alfa Aesar. Toluene was distilled from sodium immediately prior to use. Analytical grade isopropylalcohol was used to precipitate the products.

The ultraviolet-visible (UV-vis) absorption spectra of the products in toluene solution were recorded using a Labtech-2000. The molecular weight distribution of the obtained products were measured by gel permeation chromatography (GPC) using Waters-1515/2414, calibrated with polystyrene standards and tetrahydrofuran as an effluent at a flow of 1 mL/min. FTIR spectra were measured on a WQF-410 spectrophotometer (KBr). Nuclear magnetic resonance (NMR) spectra were collected using an INOVA-400 spectrometer for $^1\text{H-NMR}$ (400 MHz) spectra with chloroform-*d* as a solvent and tetramethylsilane as an internal standard. The products were also characterized by means of X-ray diffraction (XRD) on Bruker D8 Advanced diffractometer ($\text{Cu } k_\alpha$ 1). The photoluminescence spectra of the products in toluene solution were measured using an F-4500 spectrophotometer. The microscopy images of the products whether in toluene solution or in solid state were directly observed on a NSPL 3488A Zeiss microscopy spectrophotometer, operating in fluorescence mode under UV light. The thermal gravimetric analysis (TGA) was studied on a TA instrument STA449C under nitrogen at a heating rate of $10^\circ\text{C}/\text{min}$.

Synthesis

The composite was prepared in a procedure of *in situ* polymerization, which is in the presence of C_{60} cages

as a former network, then synthesized the latter network, hyperbranched polysilane polymethylphenylsilane-*co*-methylsilane (PMPS-*co*-MS) via Wurtz coupling method using dichloromethylphenylsilane and trichloromethylsilane as monomers at a mole ratio of 3:2 according to the equal activity of Flory.²³

A fine dispersion of sodium (2.07 g, 0.09 mol) was prepared by melting and agitating with a mechanical stirrer in toluene (90 mL) in a three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a nitrogen inlet. Then cooled to room temperature, added 0.2900 g C_{60} with 50 mL toluene and changed mechanical stirring to magnetism stirring. Subsequently, dichloromethylphenylsilane (3.72 g, 0.0195 mol) and trichloromethyl silane (1.94 g, 0.013 mol) in 24 mL toluene was added dropwise using a constant pressure syringe under 65°C within 1 h. After the addition of the monomers, the mixture was refluxed for 3 h and allowed to room temperature and stirred for another 21 h. Then stopped stirring, after filtrated and distilled the filtrate to remove most of the toluene. After cooling to room temperature, the residual solution was added to 200 mL isopropylalcohol under magnetism stirring to precipitate the products. After static laying overnight and removed the supernatant, followed by drying in a vacuum oven (65°C , 24 h), yielded 0.9445 g (29.62%) of the products. Because of good solubility of fullerene in toluene, about 2.15 mg/mL and insolubility in isopropylalcohol, we hold that nearly all of the

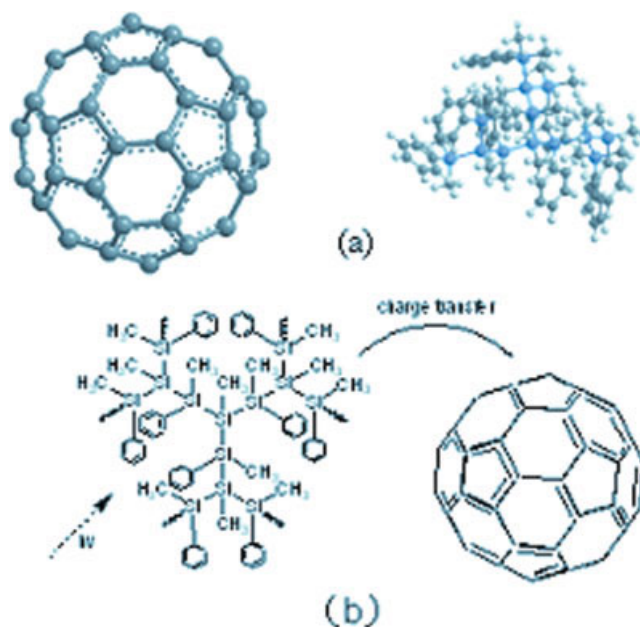


Figure 1 (a) Ball-Stick models of C_{60} and ideal hyperbranched polysilane PMPS-*co*-MS (b) Schematic description of photoinduced charge transfer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

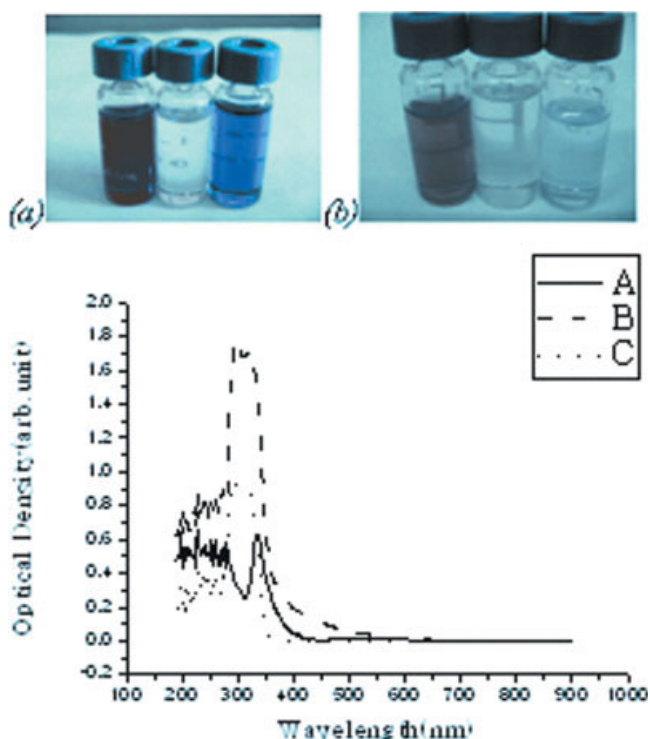


Figure 2 (a) Typical appearances of PMPS-*co*-MS- C_{60} , PMPS-*co*-MS and fullerene in toluene solution and (b) in cyclohexane solution; (c) UV spectra of toluene solution of (A) C_{60} , (B) PMPS-*co*-MS- C_{60} , and (C) PMPS-*co*-MS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fullerenes we added were transferred into the composite in the precipitating process. So the value of the fullerene in the composite is about 30.70%. All operations were carried out under nitrogen atmosphere and light was excluded.

To compare with composite, we also prepared the pure hyperbranched polysilane PMPS-*co*-MS, which is synthesized in the same procedure but in the absence of C_{60} .

RESULTS AND DISCUSSION

The resulting PMPS-*co*-MS- C_{60} composite, at high fullerene C_{60} concentration (about 30.70%), has a brown color, which is different from pure PMPS-*co*-MS (white). When they are dissolved in organic solvents, the pure PMPS-*co*-MS solution is colorless, while the PMPS-*co*-MS- C_{60} composite solution is brown, and the toluene solution of C_{60} is violet. Even the composite can be readily dissolved in cyclohexane with brown color, because of the quite low solubility of C_{60} in cyclohexane and the colorless of the pure PMPS-*co*-MS, the brown color suggested the PMPS-*co*-MS and fullerene are not molecularly dispersed in the solution. This can be directly observed in the digital camera images as shown in

Figure 2(a,b). And this is in agreement with their UV absorption spectra as shown in Figure 2(c). Pure PMPS-*co*-MS has no absorption at wavelength longer than 360 nm corresponding to the values in the literatures.¹⁶ Compared with the pure PMPS-*co*-MS, the PMPS-*co*-MS- C_{60} composite has the similar spectra shape, which indicates that there is no ground-state charge transfer occurring due to the insufficient difference in electronegativity, but extends to a longer wavelength with a long tail that extends to 704 nm. The UV spectrum edge of the composite shows a low bandgap about 1.76 eV, which is much closer to the 1.1 eV of crystalline silicon (c-Si) used in conventional solar cells.¹⁸ Compared with the bandgap of 3.27 eV of the PMPS-*co*-MS, the low bandgap of the composite is achieved by the incorporation of the electron acceptor C_{60} .^{24,25} And the significant difference near 450 nm indicates that the two components are not simply mixed, because both of the PMPS-*co*-MS and the C_{60} nearly have no absorption in this area. This result suggests that there is a specific interaction between the PMPS-*co*-MS and C_{60} , which may be π - π stacking between the curved π surface of the C_{60} cage and the flat π surface of the phenyl ring of the PMPS-*co*-MS.

Gel permeation chromatography (GPC) of the PMPS-*co*-MS- C_{60} composite indicates an $M_w = 11,673$ versus polystyrene, similar to the GPC of PMPS-*co*-MS with an $M_w = 12,093$ versus polystyrene. And we do not find obvious signal near 720 of the free C_{60} in GPC of the PMPS-*co*-MS- C_{60} composite. This result shows that the PMPS-*co*-MS and C_{60} are not simply mixed, there is a specific interaction (may be π - π stacking) between the curved π surface of the C_{60} cage and the flat π surface of the phenyl ring of the PMPS-*co*-MS which is strong enough to make the C_{60} not to be separated from PMPS-*co*-MS in the GPC measuring process.

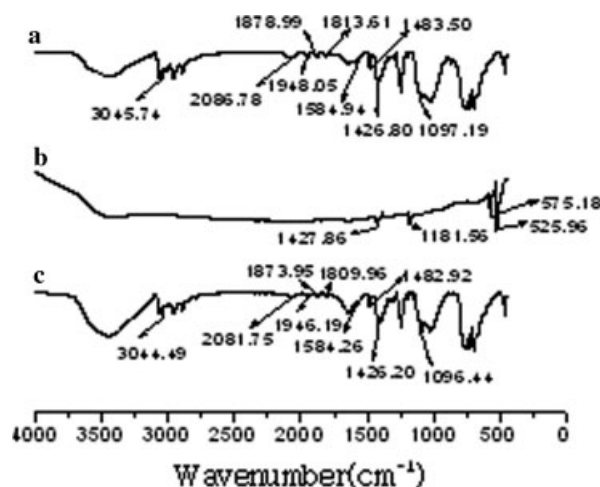


Figure 3 FT-IR spectra of (a) PMPS-*co*-MS, (b) C_{60} , and (c) PMPS-*co*-MS- C_{60} .

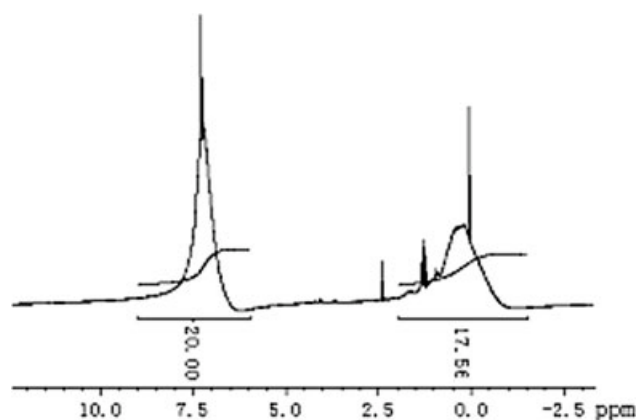


Figure 4 $^1\text{H-NMR}$ spectra of PMPS-*co*-MS- C_{60} .

We also measured the FTIR spectra of the pure PMPS-*co*-MS, C_{60} and the PMPS-*co*-MS- C_{60} composite, as shown in Figure 3. In the FTIR spectra of the PMPS-*co*-MS, absorption at 2954 and 2893 cm^{-1} indicates the existence of the methyl group, absorption at 3045 , 1948 , 1878 , 1813 , and 1483 cm^{-1} indicates the existence of the phenyl group, absorption at 1426 , 1097 , and 1025 cm^{-1} indicates the existence of the Si-Ph, absorption at 1247 and 753 cm^{-1} indicates the existence of the Si- CH_3 , and absorption at 463 cm^{-1} clearly indicates the existence of the Si-Si bond. These results imply the polymerization of the monomers. The spectra of the PMPS-*co*-MS- C_{60} composite look quite similar with the PMPS-*co*-MS, and these are not the specific spectra of C_{60} in the composite, because C_{60} has much weaker absorption than PMPS-*co*-MS. Closer inspection reveals some difference compared with the pure PMPS-*co*-MS, in the FT-IR spectra of the PMPS-*co*-MS- C_{60} composite, all the absorption of the bonds associated with phenyl group are shift to low wavenumber (cm^{-1}). Including, from 3045.74 to 3044.49 ($\nu_{\text{C-H}}$, phenyl group); from 2086.78 to 2081.75 , from 1948.05 to 1946.19 , from 1878.99 to 1873.95 , from 1813.61 to 1809.96 ($\delta_{\text{C-H}}$, phenyl group, comb); from 1584.94 to 1584.26 (γ , phenyl group, overlap); from 1483.50 to 1482.92 (st, phenyl group); from 1426.80 to 1426.20 , and from 1097.19 to 1096.44 ($\delta_{\text{Si-Ph}}$). These results suggest that there is a specific interaction between the phenyl ring of PMPS-*co*-MS and C_{60} cage. And we think that the specific interaction is π - π stacking between C_{60} cage with rich π -electrons conjugation surrounding the quasi-spherical molecule surface and phenyl group with π -electrons conjugation in the flat phenyl ring. The π - π stacking between the electron donor and acceptor may provide interesting properties and potential applications.

The $^1\text{H-NMR}$ spectra of the PMPS-*co*-MS- C_{60} composite are shown in Figure 4. It shows two broad resonances: one near 0 ppm and the other near 7 ppm ,

which are corresponding to the protons of the methyl groups and the phenyl groups attached to silicon, respectively. Through the integration of the $^1\text{H-NMR}$ resonances for the methyl groups and the phenyl groups, we can know that the molar fractions of the CH_3PhSi and CH_3Si units corresponded basically with those of the monomer feed composition ($3:2$). If trichloromethylsilane reacts at two chlorine groups and one unreacted chlorine group remains, a linear structure must be formed regardless of the monomer feed composition.¹⁶ The result confirms that the branched structure is in existence (although not fully branched), and the synthesis was successful. And this 3D structure is very beneficial for preparing interpenetrating composite, which can be suggested from the XRD patterns.

Figure 5 shows the X-ray diffraction (XRD) patterns of C_{60} , PMPS-*co*-MS- C_{60} , and PMPS-*co*-MS. The XRD patterns of C_{60} shows several peaks corresponding to the values in the database of the Bruker D8 Advance diffractometer, indicating the crystalline structures of C_{60} . We also sought to obtain X-ray crystal structure of the PMPS-*co*-MS, but because of the branched structures with large numbers of side chains producing disorder, the PMPS-*co*-MS failed to crystallize, just produced some noncrystalline domain. In the XRD patterns of the PMPS-*co*-MS- C_{60} composite, the peaks of definite crystalline structures of C_{60} disappeared, which suggests a well defined interpenetrating structure with the absence of aggregates or small crystallites of C_{60} that can inhibit the photoinduced charge transfer. The result suggests that the C_{60} and the PMPS-*co*-MS are not simply mixed, and there is a specific interaction between them, which may be π - π stacking between the curved π surface of the C_{60} cage and the flat π surface of the

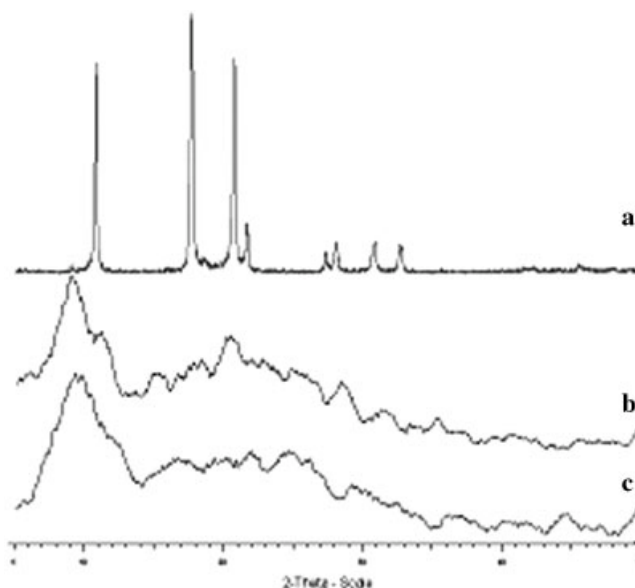


Figure 5 X-ray powder diffraction patterns for (a) C_{60} , (b) PMPS-*co*-MS- C_{60} , and (c) PMPS-*co*-MS.

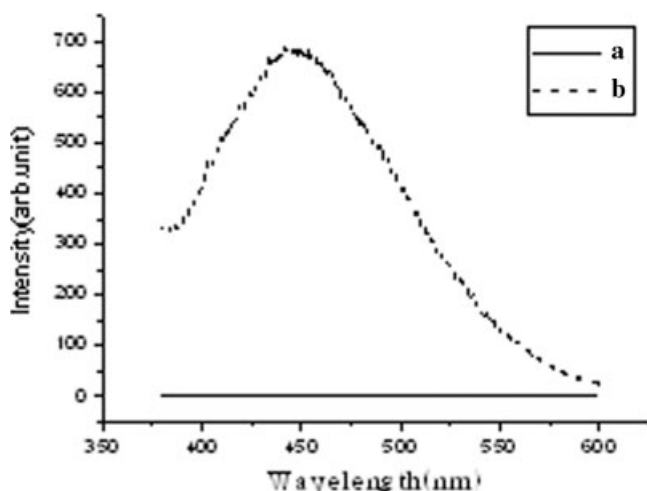


Figure 6 Photoluminescence spectra of toluene solution of (a) PMPS-*co*-MS- C_{60} and (b) PMPS-*co*-MS excited at 358 nm.

phenyl ring of the PMPS-*co*-MS. It is probable that the *in situ* polymerization permits sufficiently close proximity between the PMPS-*co*-MS and C_{60} for π - π stacking to occur. And the specific interaction makes the two compositions prepare a well interpenetrating composite that has been suggested as ideal materials, which is beneficial for PCT process that can occur at the D/A interface of the bulk interpenetrating composite with a high interfacial area.^{26–28}

The photoluminescence (PL) spectra of pure hyperbranched polysilane PMPS-*co*-MS and the PMPS-*co*-MS- C_{60} composite in toluene solution excited at 358 nm are shown in Figure 6. From it, completely PL quenching of the PMPS-*co*-MS can be observed in the PMPS-*co*-MS- C_{60} composite. For the pure PMPS-*co*-MS, it exhibits a broad fluorescence spectrum in the visible region stretching from below 400 nm to over 550 nm with a peak maximum at near 441 nm, which indicates that the pure PMPS-*co*-MS emits blue light. But there is no fluorescence in the composite PMPS-*co*-MS- C_{60} , which reveals that the PL of the PMPS-*co*-MS is significantly quenched by the incorporation of C_{60} . The PL quenching can also be observed directly from the fluorescence microscopy images of the PMPS-*co*-MS and the PMPS-*co*-MS- C_{60} composite whether in solution or in solid state. In the microscopy images of the PMPS-*co*-MS, there is strong blue fluorescence, but there is no fluorescence in the microscopy images of the PMPS-*co*-MS- C_{60} composite. This clearly confirms that the addition of the fullerene quenched the PL of the PMPS-*co*-MS effectively. This result is corresponding to the previous reports that C_{60} can effectively quench the PL of conjugated polymers.^{4,15,29} The PL quenching in solid state can remove the effect of the solvent and it is worth noting that completely PL quenching in solution confirms that PMPS-*co*-MS and C_{60} are not simply mixed.

Otherwise, when they are molecularly dispersed in the solution, the distance between them is not close enough to allow the photoinduced charge transfer.⁶ And this result indicates that the *in situ* polymerization way prepared a well interpenetrating composite with π - π stacking between the hyperbranched polysilane and the fullerene allowing the effective PCT to occur. The completely PL quenching implies the effective photoinduced charge transfer from the PMPS-*co*-MS to C_{60} whose electron affinity is high, due, at least in part, to its 3D structure and low reorganization energy.^{19–22} This implies the composite may find applications in photovoltaic devices.

The thermal stability of the composite was evaluated by the thermal gravimetric analysis (TGA) (Fig. 7). The figure shows that almost no weight loss at temperature below 300°C in nitrogen, indicative of good thermal stability. The good thermal stability may be due to the silicon-silicon main chain and hyperbranched structures.

CONCLUSIONS

In this study, we described a novel composite PMPS-*co*-MS- C_{60} which is prepared in a simple one-pot approach; *in situ* polymerization. Different from previous linear π -conjugated polymer/ C_{60} system, this novel composite is based on σ -conjugated hyperbranched polymer and C_{60} , in which PCT takes place indicated by the PL quenching. Further discussion found that there may be π - π stacking between the curved π surface of the C_{60} cage and the flat π surface of the phenyl ring of the PMPS-*co*-MS, which enhances the charge transfer from PMPS-*co*-MS to fullerene. We believe that this novel composite may find good potential applications in organic photovoltaic devices.

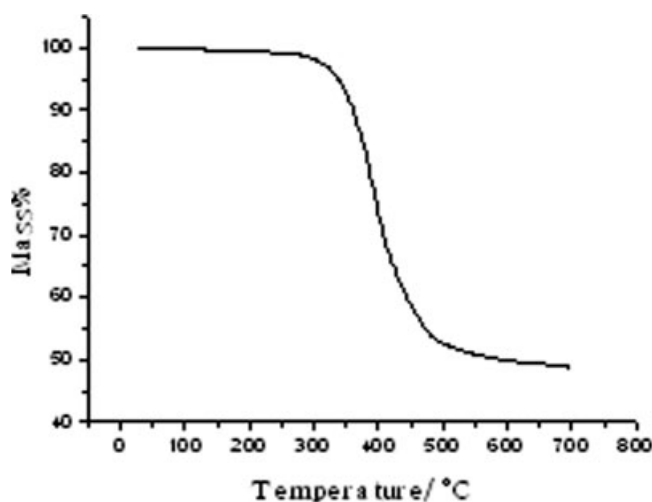


Figure 7 Thermal gravimetric analysis of the PMPS-*co*-MS- C_{60} composite.

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