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Preparation and characterization of the fullerenated polymers

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Summary

The fullerenated PEPC (Poly(epoxy propyl carbazole)) was synthesized in Friedel-Crafts type reactions. Molecular weights of the polymers were determined by gel permeation chromatography. Structures of the polymers were analyzed and characterized by use of ^{1}H and ^{13}C NMR, FT-IR, thermal analysis and spectroscopic methods. The ^{13}C NMR spectrum of fullerenated PEPC exhibits structured peaks in the fullerene region. Compared with pure PEPC, fullerenated PEPC has the same structure in UV region of the absorption spectrum and extends the active range to longer wavelength. The apparent quenching of PEPC fluorescence was observed in the fullerenated polymer and it can be attributed to intramolecular excited state energy transfer. The fullerenated PEPC is soluble in common organic solvents such as THF and chloroform. The process can be generalized to other polymers having phenyl groups to produce a series of fullerenated polymers.

Introduction

Since the development of methods for mass production of fullerenes(1), there has been great interest in fullerene studies. The physical properties of C_{60} have been extensively investigated(2), and a variety of interesting conducting, magnetic, photochemical and electrical properties have been observed. In 1992, Y. Wang firstly discovered that fullerene-doped PVK (polyvinylcarbazole) has an apparently increased photoconduction compared with pure PVK(3). Since then much attention has been paid to the investigation of the fullerene-doped polymers(4). However, in the preparation of composite films of C_{60}-doped polymers, C_{60} phase usually segregates from the polymer matrix showing a tendency to

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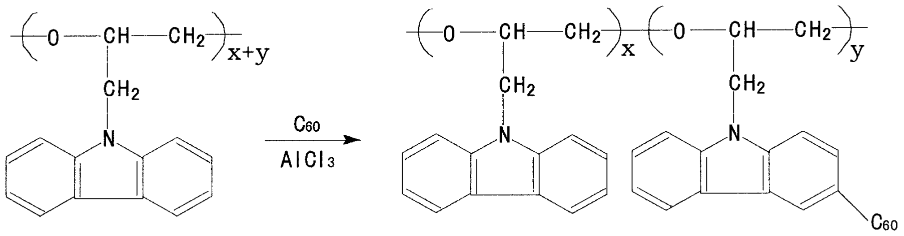
crystallize at higher concentrations because of the intrinsic incompatibility of the two materials. Incorporation of C_{60} into macromolecule architectures offers an attractive possibility to combine the unique electronic and magnetic properties of C_{60} with the advantage of polymeric characteristics such as facility of processing. As we know, PVK is the first organic polymer used for electrophotography. But it possesses some shortcomings such as bad adhesion to metallic substrates and high glass transition temperature caused by the stiffness of its polymeric chain. Compared with PVK, PEPC (Poly(epoxy propyl carbazole)) has oxyalkyl in the main chain which increases the polymer flexibility. Moreover, PEPC exhibits excellent chemical stability in air, water and organic solvents in terms of both its neutral undoped state and the oxidized doped state. Here we reported the attachment of C_{60} cages to the carbazole groups on PEPC chains by Friedel-Crafts type reaction(5) using $AlCl_3$ as the catalyst. The fullerenated PEPC was further characterized by a series of analytical methods. The fullerenated PEPC was proved to be extremely soluble in a variety of organic solvents such as $CHCl_3$, THF, etc. This solubility behavior which is similar to that of PEPC itself demonstrates the polymer attachment has dramatic effect on the processibility of fullerene derivatives. In general, this reaction process may be applied to other polymers with phenyl groups to produce new fullerenated polymers.

Experimental

Synthesis of fullerenated PEPC was accomplished by C_{60} reaction with PEPC in CS_2 according to scheme **I**. Typically, 0.3g PEPC was dissolved in 25ml CS_2 in a vial, then 20mg C_{60} in 10ml CS_2 was added, forming a purple solution. After stirring for half an hour, the solution was mixed with 20mg of anhydrous $AlCl_3$ as the catalyst. The mixture was reacted at room temperature with agitation for 20 hours, a deep brown solution was obtained, then washed with water for 3 times to remove the residual catalyst. Evaporation of the solvent CS_2 yielded red black solids which were mixtures of C_{60}-PEPC and unreacted C_{60}. The solids were dissolved in $CHCl_3$ and precipitated in methanol through a filter paper. The products were redissolved in THF, which has very low solubility of C_{60}, and the brown solution was reprecipitated in methanol and filtered. The finally purified product was thoroughly dried at room temperature under high vacuum to a constant weight to give earth yellow powders. As the element C opposite to the N element in PEPC polymer is an active site, and has a little steric effect, C_{60}, we think, is connected to this site. The structural formula of C_{60} - PEPC polymer is shown in scheme **I**.

Molecular weights of the polymers were analyzed on a Waters 208 LC/GPC apparatus in THF solution with linear polystyrene calibrator. ^1H and ^{13}C NMR spectra were determined in CCl_3D solution using TMS as an internal standard with a Bruker ARX-30 NMR spectrometer. FT-IR spectra of samples were recorded on the Nicolet-FT-IR-5DX

Scheme I :



spectrometer. Thermal analysis was performed on the Perkin Elmer DSC-7 instrument. UV/Vis absorption spectra were obtained using Shimadzu UV-265 spectrophotometer and fluorescence spectra were measured on a Hitachi 850 apparatus, with solvents of THF and toluene.

Results and Discussion

Molecular weights of the polymers measured by gel permeation Chromatography (GPC) is shown in Figure 1. From the figure 1, an essential overlapping of the GPC traces for pure PEPC and fullerenated PEPC was observed. The fullerenated PEPC has almost no shift in the peak maximum but only a somewhat broadening in molecular weight distribution compared with pure PEPC. The slightly reduced average Mw for the fullerenated PEPC might be the result of the smaller hydrodynamic volume in GPC analysis due to conformational changes upon the incorporation of C_{60} into polymers.

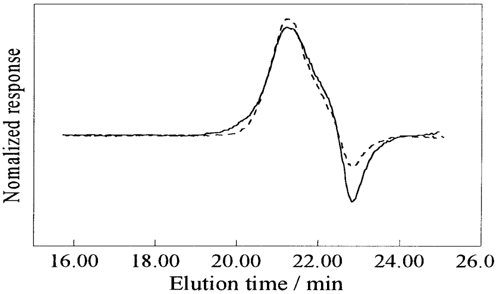


Figure 1 Gel permeation chromatography for pure PEPC (—) and fullerenated PEPC with C_{60} weight percent of 7.2% (----); solvent: THF; flow rate: 1.5ml / min.

The fullerenated PEPC was characterized by spectroscopic methods. The spectrum confirms that C_{60} is covalently attached to the PEPC. The ^{1}H NMR spectrum of fullerenated PEPC is essentially the same as the corresponding pure PEPC. The results are understandable because the loading of C_{60} in the fullerenated PEPC is relatively low. The mole fraction of the fullerenated carbazole units is rather small and difficult to be detectable. It also confirms that the polymer has not suffered from catastrophic degradation during the fullerenation reaction and maintained its basic structure.

The ^{13}C NMR spectrum of the fullerenated PEPC shown in Figure 2 is most informative and all resonance was assigned unambiguously. In addition to the signals from

PEPC, it exhibits structured peaks in the fullerene region while pure C_{60} only shows a singlet (143.2 ppm)(6). This is different from the spectra of other fullerenated polymers in which the fullerene signals show up as an extremely broad peak(7). It seems that in the fullerenated PEPC, the environment surrounding fullerene units is relatively homogeneous.

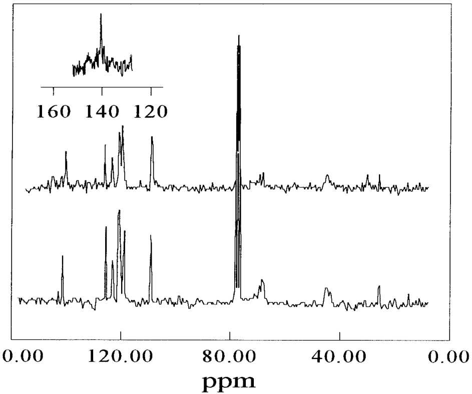


Figure 2 ^{13}C NMR spectra of fullerenated PEPC with C_{60} weight percent of 7.2%(above) and pure PEPC (below). In the left corner is the partly magnified figure for the fullerenated PEPC with C_{60} weight percent of 7.2%.

Due to substantial contributions of unsubstituted carbazole units in the polymer structures, the FT-IR spectra of fullerenated PEPC are nearly the same as those of pure PEPC. However, an apparently change of the relative peak intensity at 527cm^{-1} compared to the nearby peak can be observed in the spectra of the fullerenated PEPC. The peak of 527cm^{-1} corresponds to the most intense band in C_{60} IR spectrum and this absorption band often survives in the functionalization of C_{60}(8). Because the pure PEPC itself has a peak at 527cm^{-1}, the extent of C_{60} incorporation can not be determined by this peak. However, the relative intensity of 527cm^{-1} peak in the fullerenated polymer is apparently larger than that in the pure polymer compared to the nearby peaks. Also the relative intensity is enhanced with the increasing C_{60} content.

The thermal behavior of samples analyzed using Differential Scanning Calorimetry (DSC) shows only a single glass transition temperature(Tg) in fullerenated PEPC, indicating that phase separation is not occurring in this system. Also the Tg values were found to be increased from 81 °C to 85 °C on going from pure PEPC to fullerenated PEPC respectively. Since the molecular weights of PEPC and fullerenated PEPC are similar, this slightly increase can only be attributed to the attachment of C_{60} in the polymer.

The fullerenated PEPC had a visibly earthy yellow color while pure PEPC is nearly colorless. The reason for this is obvious in the UV/Vis absorption spectrum (Figure 3). It is found that PEPC is essentially transparent at wavelength longer than 360nm with the main UV-Vis bands occur at 293, 329 and 342nm corresponding to the value of the literature(9). Compared with pure PEPC, fullerenated PEPC has a similar structure in UV region, but extends the active range to longer wavelength. Moreover, the absorption tail in the visible region is strongly influenced by the amount of fullerene contents in fullerenated PEPC. By comparing the

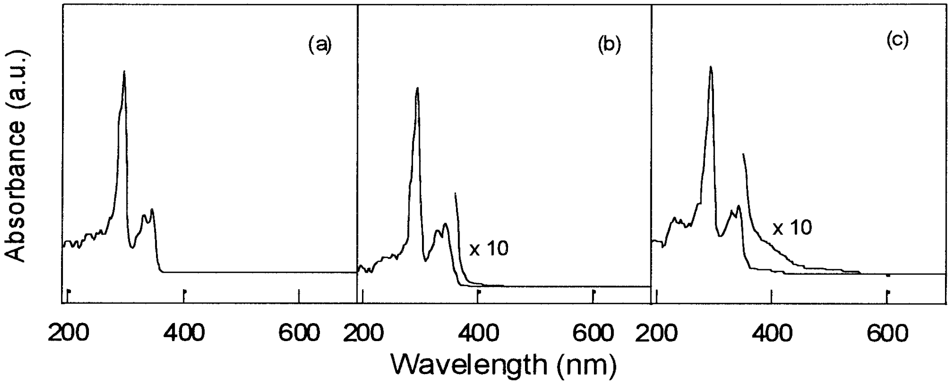


Figure 3 Absorption spectra of pure PEPC (a) and the fullerenated PEPC with C_{60} weight percent of 2.3% (b) and 7.6% (c), respectively.

relative intensity of absorption peak at 342 and 329 nm of physically C_{60}- doped PEPC with the content of C_{60}, we can deduce the C_{60} weight percent of fullerenated samples **I**, **II** and **III** (according to the different reactant ratios of C_{60} and PEPC) are 2.3%, 7.2% and 7.6%, respectively. It can be seen from the structural formula of fullerenated PEPC polymers shown in scheme **I** that the structural differences in these three C_{60}-PEPC polymers are that the x value is changeable.

From the fluorescent emission spectra of samples (Figure 4), we found that the fluorescence spectra of fullerenated PEPC are similar to those of the PEPC reference, which consists of emissions from only the non-interacting monomeric carbazole unit$^{(10)}$. But the fluorescence yields in the fullerenated PEPC are smaller than those in pure PEPC. The decrease of the yields in the fullerenated polymers can be attributed to quenching through intramolecular excited state energy transfer because the C_{60}-containing sites in fullerenated polymers may act as energy traps. Besides, the quenching of PEPC fluorescence is more pronounced when the fullerenated PEPC contain more C_{60}. In addition, the same emission and excitation spectra in both toluene and THF solutions show that effect of solvent can be excluded. Also, the emission attributed to intermolecular carbazole units with parallel arrays can not be observed because of the dilute

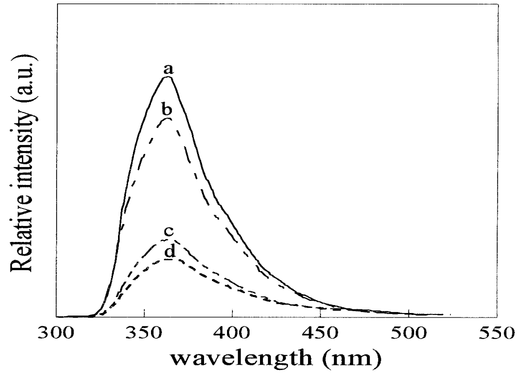


Figure 4 Fluorescent emission spectra of pure PEPC (a) and fullerenated PEPC with C_{60} weight percent of 2.3% (b), 7.2% (c) and 7.6% (d) respectively in toluene, with the same optical density of 308 nm excited at room temperature.

solution. It has been reported that the fluorescence spectra of C_{60} can be observed in C_{60} chemically modified polystryrene and poly(methyl methacrylate)(8,11). (But in our experimental conditions the fluorescence spectra of C_{60} in the fullerenated PEPC are not observed.

Acknowledgment

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