

Photoconductivity and Paramagnetism of Fullerene Chemically Modified Polymers

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SYNOPSIS

Addition of the C₆₀ moiety, a powerful electron acceptor, to iodinated poly(*N*-vinylcarbazole) (PVKI) by chemical reaction modifies considerably the photoconductive property of PVKI. The photoinduced discharge rates for pure PVK, PVKI, C₆₀-chemically modified PVKI (C₆₀-PVKI copolymer), and C₆₀-doped PVKI (a simple mixture of the component) under the same experimental conditions are found in the following order: C₆₀-PVKI copolymer > C₆₀-doped PVKI > PVKI > PVK. The fullerenated PVKI has a visibly brownish yellow cast when compared with the unreacted polymer. The UV-vis absorption spectrum in which the main bands occur at 220, 230, 252, 268, 300, 332, and 346 nm extends the active range from about 300 to 860 nm. Also, its apparent temperature sensitivity is very intriguing, and an unusual temperature dependence for the ESR spectrum is observed. The photoconductive performance of the fullerenated polymer is closely related to its paramagnetism. A considerable difference of electronic structure between pure PVKI and the C₆₀-PVKI copolymer is indicated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Fullerene-based polymeric photoconductors^{1,2} are of considerable interest owing to their potential applications in many technological applications, such as electrostatic imaging and photodetection. The photoconductivity is due to the effect of the fullerene on the charge generation and the charge-transport process in the polymeric system.³ To date, all researchers have focused their attention only on photoconductive investigations for simple blends of fullerene and polymers. However, there are some serious problems associated with this approach.⁴ Chemical modification of the polymer matrix can circumvent these problems and further improve the photoresponses of polymers. We report here the marked photoconductivity and the unusual paramagnetism of C₆₀-chemically modified iodo-poly(*N*-vinylcarbazole) (C₆₀-PVKI). Its active range in the

UV-vis spectrum extends from about 300 to 860 nm. The photoconductive performance of the fullerenated polymer is closely related to its paramagnetism and fullerene level in the polymer.

EXPERIMENTAL

Fullerenes were generated by arcing of graphite electrode and pure C₆₀ was isolated using the IL method.⁵ HPLC analysis showed C₆₀ in a purity of 99.5%. The synthesis of iodo-poly(*N*-vinylcarbazole) (PVKI) is similar to that of iodo-polystyrene.⁶ Iodine has been randomly substituted in the 3 or 6 position of the pendant carbazole group of poly(*N*-vinylcarbazole).⁷ The soluble PVKI polymer doped covalently to various extends with C₆₀H moieties (C₆₀-PVKI) was prepared by the following method described in more detail previously^{2b,8,9} under a purified nitrogen atmosphere (shown in the Scheme I):

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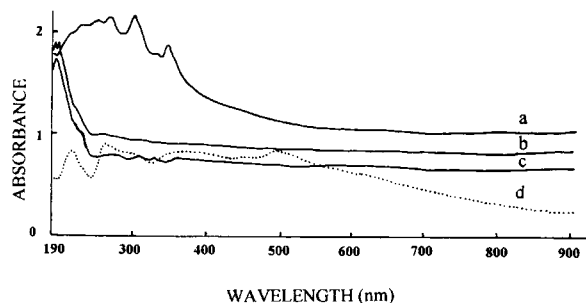
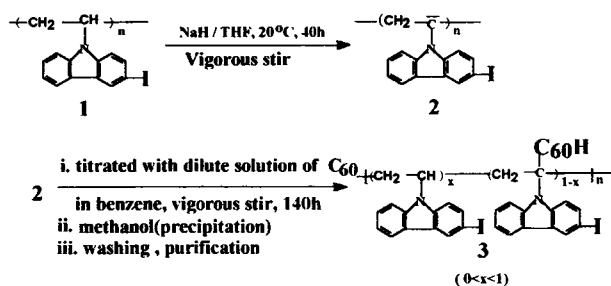


Figure 1 UV-vis absorption spectra of (a) C_{60} -PVKI containing 4% of C_{60} , (b) PVKI, (c) PVK, and (d) C_{60} . UV-vis spectra were measured on a UV-240 spectrophotometer using redistilled paraffin oil as the reference standard.



The structure of the fullereneated PVKI copolymer was confirmed by a variety of techniques such as UV-vis, FTIR, ESR, XRD, ^{13}C -NMR, TGA, and SEM and will be considered for publication elsewhere.

UV-vis absorption spectra were measured on a Shimadzu UV-240 spectrophotometer using a redistilled paraffin oil as the reference standard. FTIR spectra were recorded on a Nicolet FTIR-5DX spectrophotometer using KBr pellets. ESR spectra were recorded on Bruker ER200D-SRC spectrometer, and g -values were determined by calibration to DPPH. The photoconductivity of the samples was measured on a Shishido Type S-5109 static honestmeter made in Japan. A halotungsten lamp (150 W) was used as the light source. The light intensity used was 180 lux. The sample film, deposited on an electrically grounded aluminum substrate, was first corona-charged (positively or negatively) in the dark. The amount of surface charge was detected by an electrostatic voltmeter. On exposure to light, the photogenerated electrons and holes migrate to the surface, recombine with surface charges, and discharge the surface potential. This photoinduced discharge process is the basis of xerography.

RESULTS AND DISCUSSION

The fullereneated PVKI has a visibly brownish yellow cast when compared with the unreacted polymer and the reason for this is apparent in the UV-vis absorption spectrum shown in Figure 1. It is seen that PVKI is essentially transparent at wavelengths longer than 400 nm. Its main UV-vis bands occur at 191 (s), 195 (s), 225 (ms, shoulder peak), 255 (w), 300 (vw), and 320 (vw) nm. However, the fullereneated polymer has a new structure in the absorption spectrum in which the main bands occur at 220, 230, 252, 268, 300, 332, and 346 nm. The active range extends from about 300 to 860 nm. The absorbance in the visible region is essentially determined by the fullerene level in the polymer (i.e., increasing the fullerene level should further enhance the absorption degree at longer wavelengths^{1,9}). Furthermore, we also found that the UV-vis absorption spectrum of the PVKI/ C_{60} composite is a simple superposition of the two components basically, implying relative weak mixing of the ground-state electronic wave functions.

The FTIR spectra from the iodo-substituted PVK and the pure PVK were basically similar. As shown in Figure 2, they differed in the presence of new peaks in the PVKI at 575, 631, 787.50, 872.2, 1002, 1016.5, 1056, 1284.4, and 1468.7 cm^{-1} . The peaks at 575 and 631 cm^{-1} may be assigned to the stretching vibration of the aromatic C—I bond. The remaining extra peaks are typical of the 1, 2, 4 aromatic substitution pattern and are interpreted as indicating iodine substitution in the 3 or 6 position in the car-

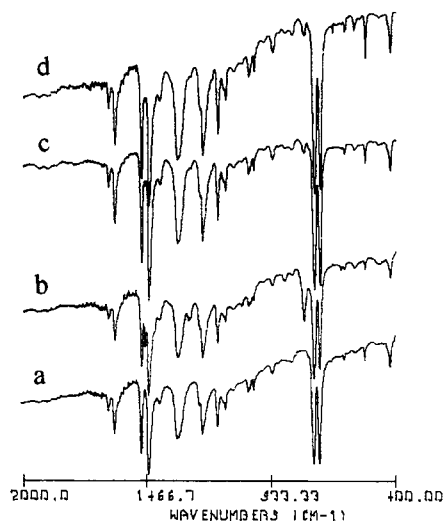
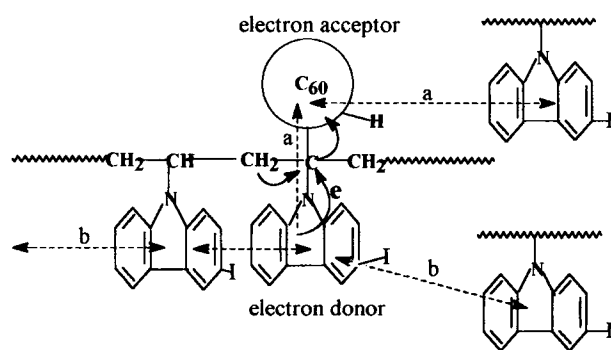


Figure 2 FTIR spectra of the samples: (a) PVK; (b) PVKI; (c) 4% C_{60} -PVKI; (d) 8% C_{60} -PVKI copolymer.

bazole group. This iodine substitution on PVK appears randomly in the 3 or the 6 positions of the carbazole group. These positions are not equivalent in the polymer due to restricted rotation about the backbone C—N bond.⁷ The FTIR spectrum of fullerenated PVKI shows that the peak intensity at 528.12 cm^{-1} increased dramatically with increasing C_{60} content compared to the peak intensity at 421.87 cm^{-1} . This may be interpreted as being associated with one of the characteristic vibration modes of C_{60} . At higher fullerene levels, four new peaks of weaker relative intensities were observed at 472.65 , 556.30 , 647.0 , and 671.85 cm^{-1} . Furthermore, the integrated treatment on the spectra shows that the relative intensities of peaks at 1484.4 , 1453.1 , 743.75 , and 718.75 cm^{-1} also increased considerably, particularly at 1453.1 and 718.75 cm^{-1} .

An ESR spectrum is obtained when microwave energy is absorbed by a paramagnetic sample as a consequence of transitions induced between the magnetic zeeman states. The paramagnetisms of poly(*N*-vinylcarbazole) (PVK), PVKI, and C_{60} -PVKI were studied. The ESR spectra of the above materials at ambient temperature are shown in Figure 3. In the PVKI polymer, only a broad ESR signal ($g = 2.0040$, $\Delta H_{pp} = 8.5\text{ G}$, $T_2 = 0.77 \times 10^{-8}\text{ s}$) is observed, whereas no ESR signal in pure PVK is detected and, thus, indicates the nonexistence of an unpaired electron or free radical in this polymer. For the C_{60} -PVKI polymer containing 4% of C_{60} , the ESR spectrum shows two peaks: a narrow peak I ($g = 2.0026$, $\Delta H_{pp} = 1.8\text{ G}$, $T_2 = 3.6 \times 10^{-8}\text{ s}$) attributed to the "charge-transfer" interaction between the pendant C_{60} molecule and the corresponding near-neighboring iodo-carbazole groups in the polymer^{9,10} and a shoulder broad peak II ($\Delta H_{pp} = 12\text{ G}$) which is assigned to the interaction between the positively charged iodo-carbazyl and the adjacent electron-rich iodo-carbazyl (see Scheme II):



It is obvious that in this polymer there are two kinds of paramagnetic species. The line width ΔH_{pp} in

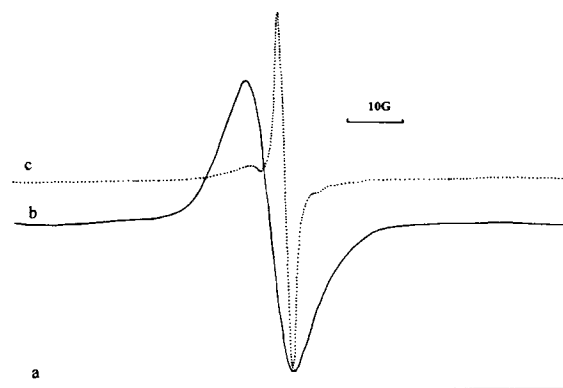


Figure 3 ESR spectra of the following samples at ambient temperature: (a) PVK; (b) PVKI; (c) 4% C_{60} -PVKI copolymer.

the parentheses is generally defined as the distance (in Gauss) between both peaks of the derivative. T_2 refers to transverse spin-spin relaxation time from which information can be obtained about interactions of electrons with other electrons.¹¹

Figure 4 shows the variable-temperature ESR spectra of the samples. The results show that both the g -values and the line width (ΔH_{pp}) of the ESR spectra from C_{60} -PVKI and pure PVKI remain unchanged over the entire temperature range (100–450 K). It is well known that the relative ESR signal intensity is directly proportional to $Y'_m(\Delta H_{pp})^2$, where Y'_m is amplitude of the peak and ΔH_{pp} is the peak-to-peak width. As ΔH_{pp} remains constant, the signal intensity is directly proportional to the peak height. Therefore, in this case, the unpaired electron spinning concentrations in the polymer is only directly proportional to peak height.

Figure 5 gives the temperature dependence of the unpaired electron spinning concentrations in polymers. As shown in Figure 5, the apparent temperature sensitivity is very intriguing. It was found that the unpaired electron spinning concentrations in PVKI and C_{60} -PVKI have a minimum at about 158 and 138 K and a maximum at about 220 and 234 K, over the temperature range of 100–300 K, respectively. At low temperatures, curve a and curve b are similar due to the overwhelming contributions of unsubstituted PVKI units in C_{60} -PVKI polymer. Perhaps a better rationalization on curve a might run as follows: First, if upon addition of a C_{60} moiety an electron is transferred from the nearby iodo-carbazole unit, then both would be in doublet states which couple to give a close-lying singlet and triplet. With the singlet slightly lower (this can be argued to be plausible), the ESR signal should increase with temperature (as observed at low temperatures).

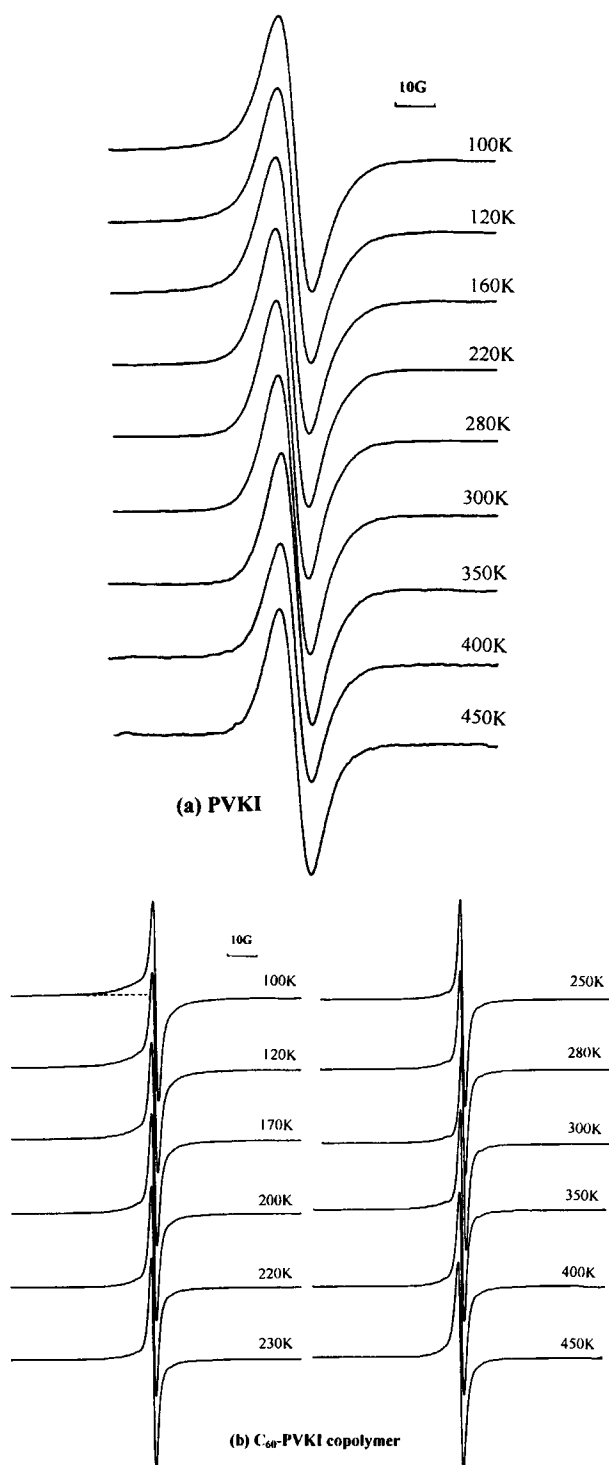


Figure 4 Variable-temperature ESR spectra of the samples: (A) PVKI; (B) C_{60} -PVKI containing 4% of C_{60} .

Next, with further increase with temperature, one might conceivably imagine that a structural change is induced such that further electron transfer occurs from more distant iodo-carbazoles to the C_{60} moi-

eties; hence, further unpaired electrons might be introduced (again in concert with observation at the temperature range of 138–234 K). Williams' NMR measurements¹² indicated that hindered rotation exists in PVK, resulting from the steric restraints of the polymeric environment. As the barriers to rotation are overcome with further increasing temperature, the flexibility of the molecule increases to a sufficient level to accommodate chain folding. In this case, some of the unpaired electrons in the polymer should recombine with each other (as observed at higher temperatures). When the temperature is higher than 350 K, the flexibility of the molecule increases and the thermal motion becomes more drastic. Consequently, the number of the conformation of each polymer chain increases dramatically, and the conformation entropy also increases.¹⁰ In this case, the charge-transfer interaction of the C_{60} moiety with the corresponding iodo-carbazole groups is strengthened. For this reason, the unpaired electron spinning concentration in the C_{60} -PVKI copolymer increases with increasing temperature. However, when the temperature is higher than 300 K, the unpaired electron spinning concentration in the PVKI polymer decreases continuously with the temperature increase. The effect of the UV-irradiation with a W-Germany Hereavs-type high-pressure mercury lamp as the light source on the paramagnetic electronic structures of the PVKI and C_{60} -PVKI was also studied (see Fig. 6). The results show that UV-irradiation has hardly an apparent effect

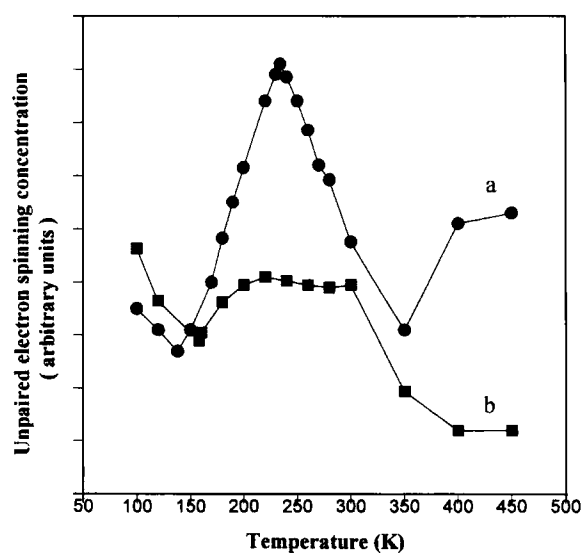


Figure 5 Temperature dependence of the unpaired electron spinning concentrations in the polymers (a) C_{60} -PVKI and (b) PVKI over the temperature range 100–450 K.

on the pure PVKI and its g -values, line width, and the ESR signal intensity remain unchanged. As might be expected, in this iodinated polymer whose active chromophores are close to the backbone, steric interplay may lead to situations in which the conformational requirements for effective charge-transfer complexation are not met under UV-irradiation, in spite of a favorable energetic relationship between the donor and acceptor. This might be associated with the lower photoconductivity of PVKI. In the C_{60} -PVKI copolymer, the UV-irradiation results in the formation of the new paramagnetic species whose ESR signal intensity increases linearly as the time of UV-irradiation increases. This new signal may be interpreted as resulting from the enhancement of the polarity of the carbon-iodine chemical bond and the consequent breakdown of the C—I bond under UV-irradiation; hence, further unpaired electrons or free radicals might be introduced. These might be the important reasons for the resulting marked enhancement in photoconductivity for C_{60} -chemically modified PVKI relative to PVK and PVKI described as follows:

A qualitative comparison of the photoinduced discharge curves for pure PVK, PVKI, the C_{60} -PVKI copolymer, and C_{60} -doped PVKI under the same experimental conditions is shown in Figure 7. The photoconductivity of the parent polymer (PVKI) was enhanced markedly by the covalent attachment of C_{60} to the PVKI backbone. The photoinduced dis-

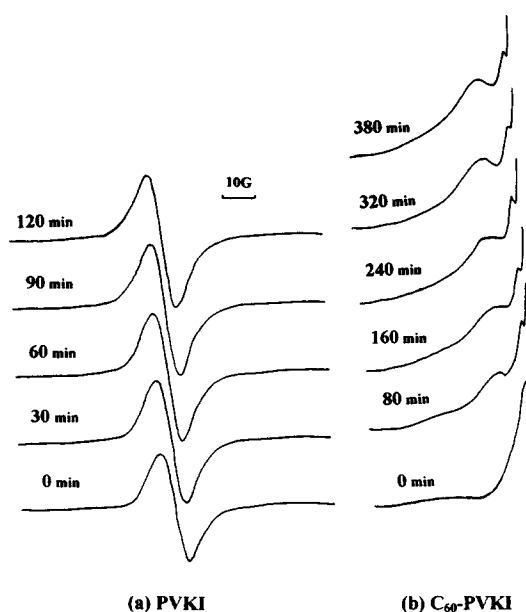


Figure 6 The effect of UV-irradiation on the paramagnetic electronic structure of polymers. (a) PVKI; (b) 4% C_{60} -PVKI copolymer, partial amplified spectrum.

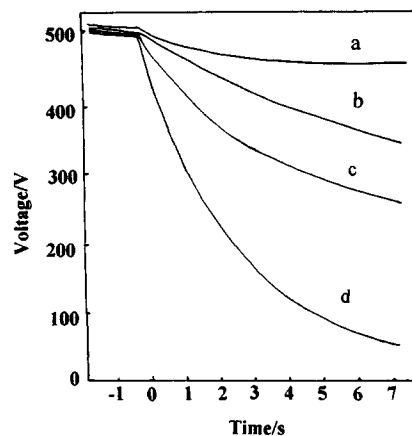


Figure 7 A qualitative comparison of the photoinduced discharge curves for (a) pure PVK; (b) PVKI; (c) 4% C_{60} -doped PVKI (a simple blends), and (d) C_{60} -PVKI copolymer containing 4% of C_{60} under identical experimental conditions.

charge rates for pure PVK, PVKI, C_{60} -chemically modified PVKI (C_{60} -PVKI copolymer), and C_{60} -doped PVKI under the same experimental conditions are found in the following order: C_{60} -PVKI copolymer > C_{60} -doped PVKI > PVKI > PVK. It is worthy to note that the doping of the hole-transporting, donor polymer (PVKI) with the electron acceptor (C_{60}) also results in enhanced photogeneration efficiency. There are, however, problems associated with this approach.⁴ A partial incompatibility of the dopant (C_{60}) and matrix will lead to difficulty in achieving homogeneous dispersions and, ultimately, phase separation at high loadings.^{2b} This was confirmed by the SEM technique. This might be one of the important reasons for the resulting difference in the photoconductivity for copolymer and mixtures. Chemical modification of the polymer matrix can circumvent these problems. As discussed above, the photoconductive performance in the C_{60} -PVKI copolymer should be closely related to its paramagnetism. Further studies on the photoconductive properties of C_{60} -PVKI and its derivatives are currently being investigated.

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