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Preparation and photoconductivity of C_{60} chemically modified poly(N-vinylchloromethylcarbazole)

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C_{60} chemically modified poly(*N*-vinyl-chloromethylcarbazole) was synthesized by the reaction of C_{60} with living poly(*N*-vinyl-chloromethylcarbazole) (PVCC) carbanions, which were prepared by α-position proton abstraction with NaH. The structural characterization techniques used were ultraviolet–visible, Fourier transform-infrared spectroscopy, X-ray diffraction, scanning electron microscopy, nuclear magnetic resonance and electron spin resonance, etc. All experimental results proved that C_{60} was covalently attached on the backbone chain of PVCC and consequently causes a remarkable enhancement of the photoconductivity of the parent polymer. Also, it was found that fullerenation of PVCC modified both the electronic structures of the carbazole pendant group and the interchain structure. © *1998 Chapman and Hall*

1. Introduction

In recent years, considerable interest has been shown in the preparation, structural characterization and properties of the novel fullerene-containing polymeric materials [1–10] owing to their potential applications in the fields of photoelectric transform and information engineering, the catalytic industry, medicine treatment and conductive plastics, etc. These materials are often prepared in four ways [11] : (1) reaction of C_{60} or a C_{60} derivative with a preformed polymer or a transition metal complex such as $Pd_2(dba)_3CHCl_3$ [12], (2) polymerization of a monomer containing [60] fullerene functional grous, (3) free radical copolymerization of C_{60} with a monomer, and (4) doping of C_{60} or C_{60} derivatives into polymer matrices.

Fullerenes are known to be good electron acceptors (EA = 2.6–2.8 eV) and have been considered to be hosts for dopants which are, in most cases, donors. Hence various donor dopants were doped into fullerenes and their derivatives. For this reason, both scientists and entrepreneurs are currently focusing their attention on the fullerene-based polymeric photoconductors [7–10, 13–20]. Their photoconductivity, which is one of the commercially significant photoresponses of polymeric systems and is fundamental to photodetection and electrostatic imaging, as well as number of related processes, is mainly due to the effect the fullerene on the charge generation and the charge transport process in the polymeric system [21].

Wang *et al.* [10, 13] first reported the enhancement of the photoconductivity of poly(*N*-vinylcarbazole) (PVK) and polysilanes by doping with fullerenes (a mixture of C_{60} and C_{70}). The wavelength dependence of photoconductivity is essentially determined by the absorption spectrum of the fullerenes. Lee *et al.* [14] have investigated the effect of photoinduced electron transfer on the photoconductivity of conducting polymer-C_{60} films by comparing the photoconductivity (carrier generation and carrier transport) of the conducting polymer sensitized with C_{60} with that of the conducting polymer (MEH-PPV or P3OT) alone. Both the magnitude and the lifetime of the transient photoconductivity increase substantially with increasing concentration of C_{60}.

Evidence for the photoinduced electron transfer from the excited state of MEH-PPV on to C_{60} has also been reported [15, 16]. Photoinduced absorption (PIA) studies demonstrate a different

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excitation spectrum for the composite compared to that for the separate components, and the photoinduced electron resonance signal exhibits the spin-labelled signatures of both the conducting polymer cation and the C_{60} anion. It is interesting that the carrier collection efficiency, η_c, and energy conversion, η_e, of polymer photovoltaic cells can be improved by blending of the semiconducting polymer with C_{60} or its functionalized derivatives [22].

Although the doping of hole transporting, donor polymers with electron acceptors results in extended spectral sensitivity as well as enhanced photogenerated efficiency, there are, however, problems associated with this approach [23]. These stem from the tendency for the dopant molecules to aggregate in the solid state, leading to difficulty in achieving homogeneous dispersions and ultimately phase separation at high loadings. Chemical modification of the polymer matrix can circumvent these problems. Chen *et al.* [17–20] first reported the synthesis of soluble C_{60}-chemically modified polymeric photoconductors such as C_{60}-modified PVK and its bromine- and iodine-modified derivatives. The addition of the C_{60} moiety to PVK by chemical reaction results in a marked enhancement in photoconductivity relative to pure PVK and C_{60}/PVK mixtures (C_{60}-doped PVK) [19]. A "charge-transfer" interaction between the positively charged carbazole resulting from charge transfer towards C_{60}, and near-neighbouring carbazole moieties of the resultant copolymer may be credited with bringing about the enhanced photoconductivity relative to PVK itself via increased photogeneration of charge carriers.

Here, we report the influence of C_{60} chemical modification on the structure and the photoconductivity of poly(*N*-vinyl-chloromethylcarbazole) (PVCC).

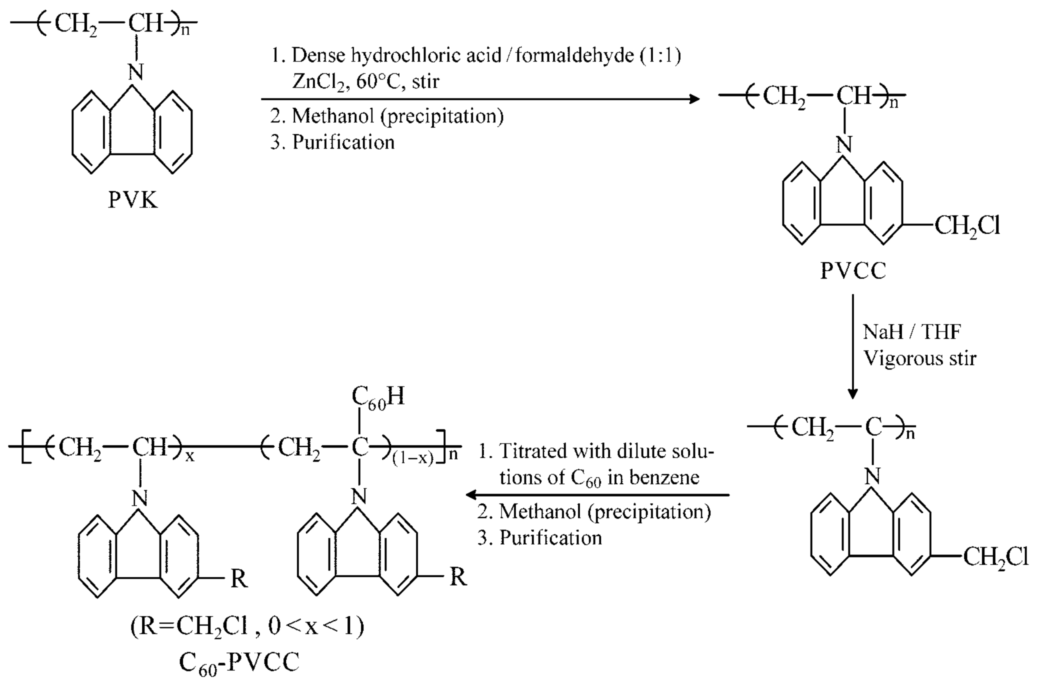
2. Experimental procedure

The poly(*N*-vinylcarbazole) used was a commercially produced polymer obtained from Zhejiang Sanmen Chemical Industry Factory of China, having a number average $M_n = 4 \times 10^5$; this sample was further purified before use. Fullerenes were generated by arcing of graphitic electrodes and pure C_{60} was isolated by using the method reported by Isaacs *et al.* [24]. High performance liquid chromatography (HPLC) analysis showed C_{60} to be 99.5% pure. The operations for synthesis before the precipitation with methanol were carried out under purified nitrogen using standard schlenk tubes. PVCC and fullerenated PVCC containing 3.85% C_{60} (i.e. C_{60}-PVCC copolymer), were synthesized as shown in Scheme I. Fourier transform–infrared FT–IR spectra were recorded on the Nicolet FT–IR-5DX spectrometer. Ultraviolet–visible absorption spectra were measured on a UV-240 spectrophotometer using redistilled paraffin oil as reference standard. Electron spin resonance (ESR) spectra were recorded on Bruker ER 200D-SRC spectrometer, and *g*-values were determined by calibration to α,α''-dephenyl-β-picryl hydrozyl (DPPH). XRD spectra were measured on a Japanese Science D/MAX-RB diffractometer, operation conditions: copper target, tube electric voltage = 40 kV, tube electric current = 80 mA, continuous scanning speed = 4°min^{-1}. The submicromorphological structures of the samples C_{60}, PVK, PVCC, and C_{60}-PVCC were studied using a Japanese Hitachi HO-IIB SEM. ^{13}C CP/MAS NMR spectra were recorded on Bruker MSL-300 NMR spectrometer using TMS as reference standard. The photoconductivity was measured on a Shishido type S-5109 static honenstmeter made in Japan. A halotungsten lamp (150 W) was used as light source. The light intensity used was 180 lux.

3. Results and discussion

In our previous papers [18, 20], we reported that the FT–IR spectra of bromine- and iodine-substituted PVK derivatives were similar to that of pure PVK, and the bromine or iodine substitution on PVK appears randomly in the 3 or the 6 position of the carbazole group. Likewise, the FT–IR spectra from the chloromethylated PVK (PVCC) and the pure PVK were also basically similar (Fig. 1). They differed in the presence of new peaks in the PVCC at 475.00, 571.87, 631.25, 650.00, 773.46, 796.87, 878.12, 962.50, 1625.00, 1687.50, 1765.0, 1884.40 and 1918.70 cm^{-1}. The first four new peaks may be assigned to the stretching vibration of the aromatic carbon-chloromethyl carbon bond, while the weak peak at 773.46 cm^{-1} corresponds to the stretching vibration of the C–Cl bond. The remaining extra peaks are typical of the 1,2, 4 aromatic substitution pattern and are interpreted as indicating chloromethyl substitution in the 3 or the 6 position in the carbazole group. This chloromethyl-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 [25]. Furthermore, the integrated treatment of the spectra shows that chloromethylation of PVK results in considerable increases of the relative intensities of peaks at 721.87, 743.15, 1484.4, and 1596.9 cm^{-1}. This might be interpreted as the association with the influence of the chloromethyl group.

Owing to the overwhelming contributions of the unsubstituted polymer units in the fullerenated polymer structures, the structural changes caused by C_{60} chemical modification on the polymer can hardly be observed except by spectrometric methods [18, 20]. It is thus understandable that the FT–IR spectrum of fullerenated PVCC (Fig. 1d) was also basically the same as that of PVCC and gives only a little information concerning the structure of this material. Because of the strong electron-withdrawing influence of C_{60} on chloromethylated carbazole units in the polymer, the relative intensities of peaks at 571.87, 796.87, 631.25, 650.00, 878.12, 962.50, 1687.5, 1765.6, 1884.4 and 1918.7 cm^{-1} decrease greatly when compared with the corresponding peaks of the parent PVCC polymer. The ^{13}C CP/MAS NMR spectrum from PVK was similar to that reported by Williams [26]. Owing to the intrinsic limitations of the high-resolution



Scheme 1

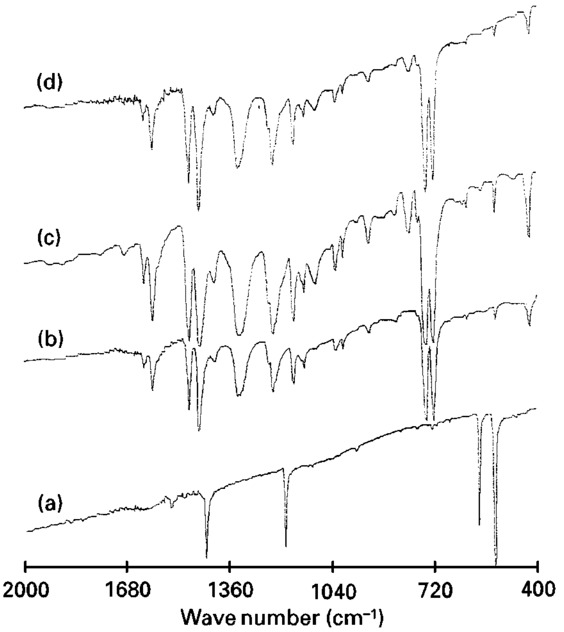


Figure 1 FT–IR spectra of (a) C_{60}, (b) PVK, (c) PVCC and (d) 3.85% C_{60}-PVCC copolymer.

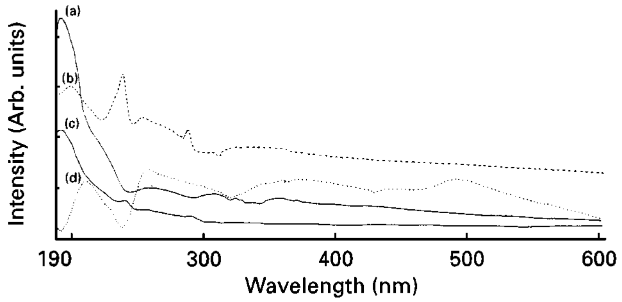


Figure 2 Ultraviolet–visible absorption spectra of the samples: (a) PVK, (b) 3.85% C_{60}-PVCC copolymer, (c) PVCC, and (d) ^{60}C. Redistilled paraffin oil was used as the reference standard.

solid-state nuclear magnetic resonance techniques and the possible reason mentioned above, the spectra of both the resultant C_{60}-PVCC copolymer and the parent PVCC polymer were similar to that of PVK and gave no information concerning structure. The single NMR signal at 143.2 p.p.m. which is attributed to pure C_{60} was not detected, indicating the non-existence of residual pure C_{60} in fullerenated PVCC.

The ultraviolet–visible absorption spectra of PVK, PVCC, C_{60} and fullerenated PVCC are shown in Fig. 2. It is seen that both PVK and PVCC are essentially transparent at wavelengths longer than 350 nm their main ultraviolet–visible bands occur at 195(vs), 225(ms, shoulder peak), 268(vw), 306(vw), 325(vw), 336(vw) and 355(vw) nm for PVK, 192(vs), 220(ms, shoulder peak), 242(w), 290(vw) and 330(vw) nm for the PVCC, respectively. The fullerenated PVCC has a visible deep-earthy yellow cast when compared with the unreacted polymer (PVCC). Its ultraviolet–visible spectrum, in which the main bands are located at 202(ms), 242(s), 255(w), 275(vw, shoulder peak), 292(w) and 345(w, broad peak) nm, tends to move to the longer wavelength in comparison to that of the PVCC polymer. These results demonstrated that addition of C_{60} (a strong electron-acceptor) to the PVCC backbone modified the electronic structure of the parent polymer. This difference in electronic structure between PVCC and C_{60} PVCC is also confirmed by the following ESR results.

ESR results provided strong evidence for the covalent attachment of C_{60} to the polymer backbone. As shown in Fig. 3, an ESR signal for PVK was not detected, indicating that no unpaired electrons or free

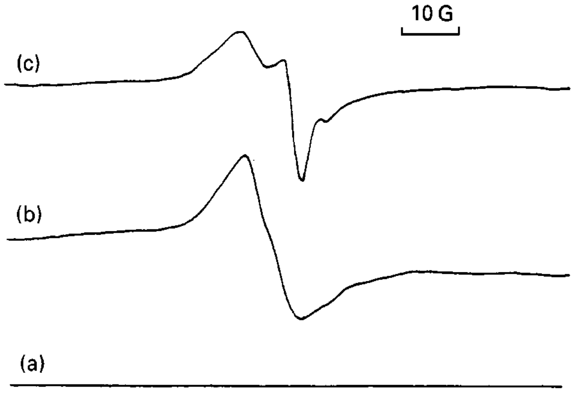


Figure 3 ESR spectra of (a) PVK, (b) PVCC, and (c) 3.85% C_{60}-PVCC copolymer at ambient temperature.

radicals existed in this polymer, whereas in PVCC polymer a broad signal ($g = 2.0052$, ΔH_{pp}, the line width defined as the distance between both peaks of the derivative = 10.25 G, $T_2 = 6.39 \times 10^{-9}$s) was observed at ambient temperature. The origin, nature, and properties of paramagnetic centres in the PVCC polymer require further investigation. T_2 refers to the transverse spin–spin relaxation time from which information can be obtained about interactions of electrons with other electrons. In the C_{60}-PVCC copolymer, its ESR spectrum shows two peaks, a narrow peak I ($g = 2.0028$, $\Delta H_{pp} = 2.54$ G, $T_2 = 2.58 \times 10^{-8}$s) attributed to the "charge-transfer" interaction between the pendant C_{60} molecule and the corresponding near-neighbouring chloromethylated carbazole groups, and a broad peak II ($\Delta H_{pp} = 14.75$ G) which may be assigned to the interaction between the positively charged chloromethylated carbazyl and the adjacent electron-rich chloromethylated carbazyl. It is very clear that in this polymer there are two kinds of paramagnetic species.

The effect of ultraviolet-irradiation (A W-Germany Hereavs type high-pressure mercury lamp is used as the light source) on the paramagnetic electronic structures of the PVCC polymer and copolymer was also studied (Fig. 4). The results show that in the parent PVCC polymer, as the ultraviolet-irradiation time increased, the new paramagnetic species were formed with the simultaneous increase of the relative intensity of the original ESR signal ($g = 2.0025$, $\Delta H_{pp} = 10.25$ G, $T_2 = 6.39 \times 10^{-9}$s), followed by a gradual decrease. However, in the C_{60}-PVCC copolymer, besides the new paramagnetic species formed, the ESR intensity of the narrow peak I increase progressively with increasing ultraviolet-irradiation time. The new paramagnetic species for both PVCC and C_{60}-PVCC copolymer might result from the breakdown of the C–Cl bond of the chloromethyl group under the action of ultraviolet light. Obviously, the effect of ultraviolet irradiation on the paramagnetism of C_{60}-PVCC polymer apparently differs from that of PVCC polymer.

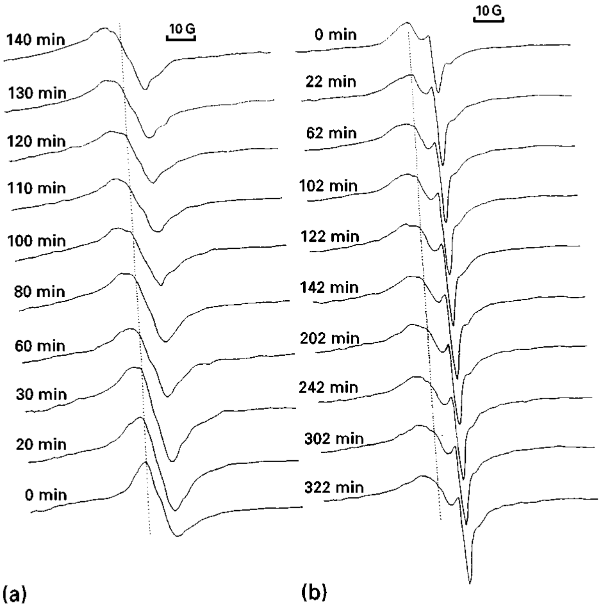


Figure 4 The effect of ultraviolet-irradiation on the paramagnetic electronic structures of (a) PVCC, and (b) C_{60}-chemically modified PVCC containing 3.85% C_{60}.

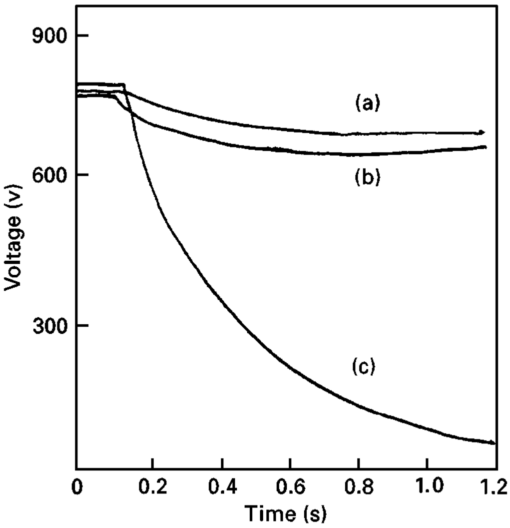


Figure 5 A qualitative comparison of the photoinduced discharge curves for (a) PVK, (b) PVCC, and (c) 3.85% C_{60}-PVCC copolymer under identical experimental conditions.

A qualitative comparison of the photo-induced discharge curves for pure PVK, PVCC and C_{60}-PVCC under the same experimental conditions is shown in Fig. 5. As seen in Fig. 5, addition of C_{60} moieties to the PVCC backbone results in the outstanding enhancement of the photoconductivity relative to pure PVK and PVCC. The photoconductive performance of the fullerenated polymer is closely related to its paramagnetism [20]. Further studies of the photoconductive properties of C_{60}-PVCC and its derivatives are currently being investigated.

Fig. 6 compares the surface topographical structures of the samples: C_{60}, PVK, PVCC and C_{60}-PVCC copolymer. It is seen that the morphology of C_{60} appeared flake-like as whole. A large number of globules of 0.3–2.1 µm diameter were loosely heaped together in the poly (*N*-vinylcarbazole), whereas in the PVCC polymer a honeycomb-like microstructure was observed. Apparently, the morphology of C_{60}-PVCC differed greatly from that of the above samples.

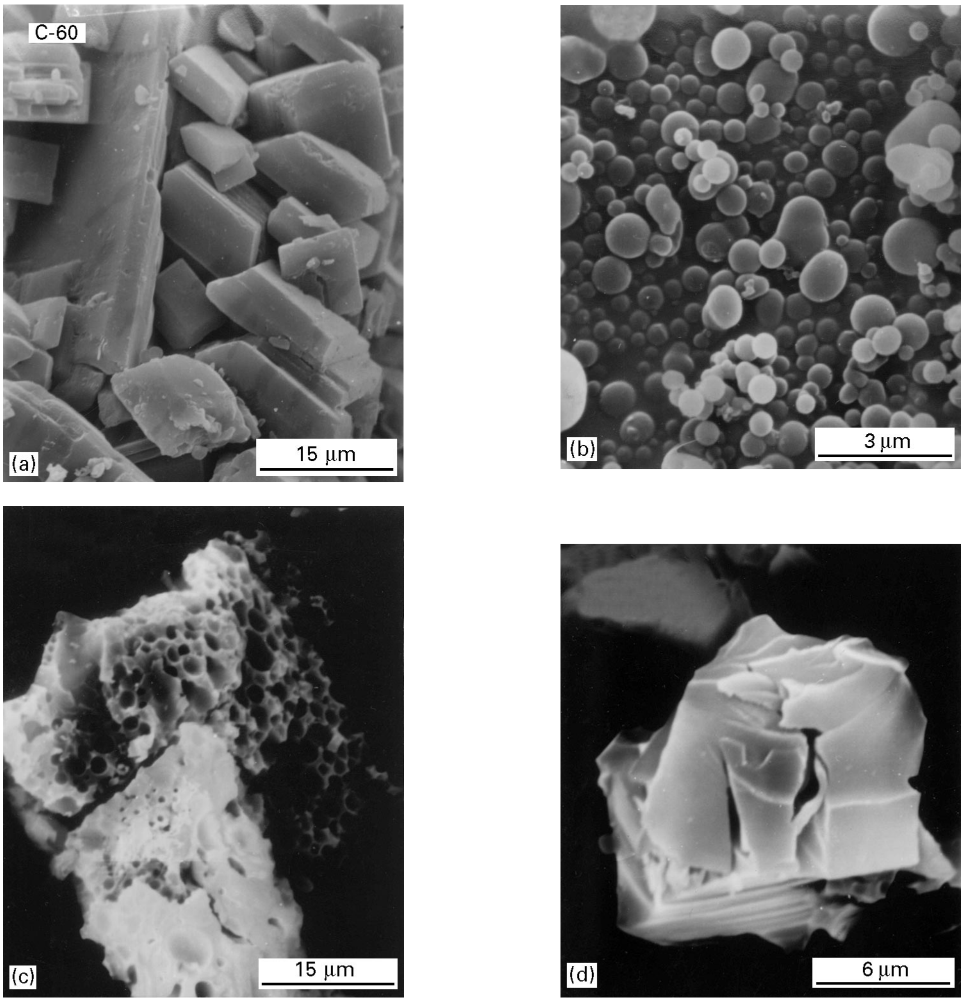


Figure 6 Scanning electron micrographs of (a) C_{60}, (b) PVK, (c) PVCC, and (d) 3.85% C_{60}-PVCC copolymer.

The X-ray diffraction spectra of the samples are shown in Fig. 7. The scattering for pure C_{60} is characterized by eleven peaks centred at 9.02°, 10.60°, 17.54°, 18.52°, 19.74°, 20.58°, 21.56°, 27.30°, 27.98°, 30.74°, and 32.66° 2θ. Among these peaks, those at 10.60° (0.8339 nm), 17.54° (0.5052 nm) and 20.58° (0.4312 nm) 2θ are relatively strong diffraction peaks. The XRD pattern from PVK was similar to that reported by Richard [27], Griffiths *et al.* [25] and Chen *et al.* [17, 18], two diffraction peaks centred at $2\theta = 7.70°$ (1.1472 nm), 20.54° (0.4321 nm), respectively, were observed (the values in parentheses represent corresponding *d*-values for the 2θ peak). The former peak is an amorphous halo which is broad, diffuse and strong, while the latter peak has been shown to be a function of chain parallelism [25], the nearest chain-to-chain distance being approximately 1.1472 nm. As shown in Fig. 7c, the chloromethylation for PVK resulted in a large decrease of the diffracted intensities for both main peaks corresponding to the pure PVK and the marked diffusion effect of the peak at 20.06° 2θ (0.4423 nm). Meanwhile, the diffracted positions of the two main peaks at 7.70° and 20.54° 2θ move slightly to 7.52° (1.1476 nm) and 20.06° (0.4423 nm) 2θ, respectively. Furthermore, the two new peaks at $2\theta = 10.98°$ (0.8051 nm), 15.88° (0.5576 nm) are also observed. These findings demonstrated that like the bromine-substitution on PVK [18], the chloromethyl substitution interferes with the interchain interactions and leads to a partial elimination of the unusual degree of chain parallelism present in the unsubstituted PVK. For the C_{60}-PVCC copolymer, besides the two main peaks whose intensities increase notably, the other two peaks at 10.98° and 15.88° 2θ in the parent PVCC vanished completely with the simultaneous presence of a new peak in the copolymer at $2\theta = 12.20°$ (0.7249 nm). The main diffraction peak at 7.52° (1.175 nm) 2θ tends to move further to the lower X-ray diffraction angle ($2\theta = 7.38°$ (1.1969 nm)), indicating that the average interchain spacing in C_{60}-PVCC might be increased by the introduction of the bulky C_{60} moieties into the polymer. In addition, it was also found that the XRD spectrum of the simple blends of C_{60} and PVCC (C_{60}-doped PVCC) seems to be a simple superposition of two spectra corresponding to C_{60} and PVCC, implying that C_{60} molecules have indeed located on the backbone chain of polymer by chemical reaction.

4. Conclusion

The synthesis of C_{60}-chemically modified poly(*N*-vinylchloromethylcarbazole) by the reaction of C_{60} with living poly(*N*-vinylchloromethylcarbazole) (PVCC) carbanions, which were prepared by α-position proton abstraction with NaH, was investigated.

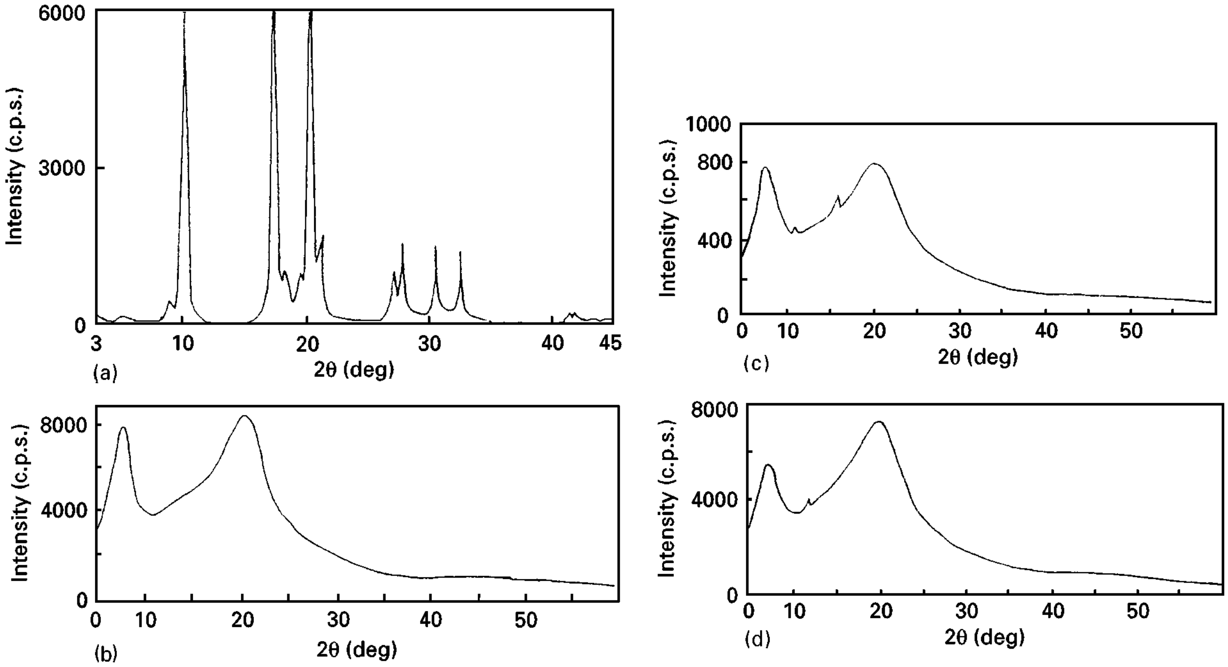


Figure 7 X-ray powder diffraction diagrams from (a) C_{60}, (b) PVK, (c) PVCC, and (d) 3.85% C_{60}-PVCC copolymer.

C_{60} chemical modification of PVCC apparently changes the physical and chemical properties of the polymer and consequently causes a remarkable enhancement of photoconductivity.

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