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Synthesis and characterization of photoconductive C_{60}–N-vinylcarbazole copolymers

YU CHEN, RUI-FANG CAI, LI-XIANG XIAO, ZU-EN HUANG*
Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China
DAOCHENG PAN
Department of Applied Chemistry, Shanghai Jiaotong University, Shanghai 200240, People's Republic of China

Soluble C_{60}–N-vinylcarbazole copolymers with different C_{60} contents were synthesized in lithium naphthalene-initiated anionic polymerization reactions. ^{13}C nuclear magnetic resonance (NMR) results provided strong evidence for the covalent attachment of poly(N-vinylcarbazole; PVK) units to the C_{60} cores. The chemical shifts located at 142.16, 143.21, 144.70, 145.61, 146.65, 147.09, 149.08 and 170.28 p.p.m. in the ^{13}C NMR spectrum of the copolymer are assigned to the unsaturated carbon signals of the substituted C_{60} cage. Its ultraviolet–visible absorption spectrum tends to move to the longer wavelength compared with those of the N-vinylcarbazole (NVC) monomer and PVK, and the peak range also extended from about 350 to 640 nm due to "charge-transfer" interaction between C_{60} and N-ethylcarbazole units. X-ray diffraction evidence suggests that the structure of the resultant copolymer might be a layered structure. Like the C_{60} chemically modified PVK, this material also exhibits good photoconductivity and temperature sensitivity. An unusual temperature dependence of the ESR spectrum is observed. In addition, it is also found that both [60] fullerene polyanion salts $[(C_{60}^{n-})M_n^+$, M = Li, Na, K] and fullerene itself are unable to initiate the polymerization of such monomers as N-vinylcarbazole, styrene and acrylonitrile, etc.

1. Introduction

Intense interest and activity are currently focused on the combination of unique electronic, conducting, magnetic and photophysical properties of fullerenes with excellent polymer characteristics to develop novel fullerene-containing polymeric materials [1–14], which may be prepared in four ways:

1. polymerization of a monomer containing [60] fullerene functional groups;
2. free radical copolymerization of C_{60} with a monomer;
3. reaction of C_{60} or a C_{60} organic derivative with a preformed "living" polymer or, a polymer with reactive functional groups or, a transition metal complex [15] such as $Pd_2(dba)_3CHCl_3$ (dba = dibenzyldeneacetone); and
4. doping of C_{60} or C_{60} derivatives into polymer matrices.

Of these materials, fullerene-based polymeric photoconductors have attracted much interest [16–24] due to their potential technological applications. The photoconductivity is mainly due to the effect of the fullerene (a good electron acceptor) on charge generation and on the charge transport process in the polymeric system [24]. The enhancement of the photoconductivity of the electron donor poly (N-vinylcarbazole; PVK) films by doping with fullerenes (a mixture of C_{60} and C_{70}) has been reported by Wang [16]. It was said that the performance of this material, with an active spectral range extending from about 280 to 690 nm, is comparable with that of some of the best photoconductors available commercially, such as thiapyrylium dye aggregates. Similar doping effects of fullerene on photoconductivity are also reported on phenylmethylpolysilane [17], zinc phthalocyanine [18], poly [2-methoxy,5-(2′-ethylhexyloxy)-*p*-phenylene vinylene], i.e. MEH-PPV, [19–20] and poly (3-octylthiophene) [21]. However, partial incompatibility of fullerenes and polymer matrices will lead to difficulty in achieving homogeneous dispersions and ultimately phase separation at high loads [25]. Chemical modification of the polymer matrix can circumvent these problems. Chen and co-workers [25–30] first reported the synthesis of C_{60}-chemically modified polymeric photoconductors, such as C_{60}-modified PVK and its bromine- and iodine-modified derivatives, and described the results of an investigation into their electrochemical behaviour and the effect of

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*Author to whom correspondence should be addressed.

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C_{60}-chemical modification on the structure and photoconductivity of the parent polymers. Addition of the C_{60} moiety to PVK by chemical reaction results in marked enhancement in photoconductivity relative to pure PVK and C_{60}–PVK mixtures (C_{60}-doped PVK). 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 enhanced photoconductivity relative to PVK itself via increased photogeneration of charge carriers. It is well known that C_{60} is an excellent electrophile, reacting with a variety of neutral and charge nucleophilic reagents. Carbanions could add across the carbon–carbon double bonds of C_{60} to give alkylated reaction products [31–33]. Similarly, the "living" polymer carbanions, which were pregenerated by using a standard anionic polymerization reaction with butyllithium as the initiator, may also add to the carbon–carbon double bonds of C_{60} to form fullerene-containing polymers [34–37]. However, little information is available on the anionic polymerization of C_{60} and a polymer monomer, for example, N-vinylcarbazole (NVC), styrene, methyl methacrylate (MMA) and acrylonitrile (AN), etc., initiated by lithium (sodium, potassium) naphthalene $[(C_{10}H_8)^-M^+$, $M = $ Li, Na, K] in the presence of C_{60} in the THF–C_6H_6 mixed solvents. This article reports the synthesis of the C_{60}–N-vinylcarbazole (CNVC) copolymers with different [60] fullerene contents and the initial results of an investigation into their structural characteristics and photoconductive performance.

2. Experimental procedure

Fullerenes were generated by arcing of graphic electrodes, and pure C_{60} was isolated by using a method reported by Isaacs *et al.* [38]. High performance liquid chromatography (HPLC) analysis showed C_{60} to be 99.5% pure. The NVC (purity $>98\%$) used was a commercially produced monomer obtained from Tokyo Kasei Kogyo Co. Lithium naphthalene (or lithium naphthalenide) was prepared in tetrahydrofuran (THF) by reacting naphthalene (Aldrich) on a lithium mirror under a purified argon atmosphere, and its molar concentration in THF was about 1.6 M. All solvents including benzene and THF were dried, deoxygenated and distilled before use. Unless noted otherwise, other analytically pure reagents, for example, methanol, hydrochloric acid and trichloromethane, etc., were used as-received.

The operations for synthesis prior to the termination reaction were carried out under purified dry argon by use of standard *Schlenk* tubes. Ultraviolet–visible (u.v.–vis) absorption spectra in THF were measured on a u.v.-240 spectrophotometer. Fourier transform infra-red (FTIR) spectra were recorded on a Nicolet FT-IR-5DX spectrophotometer using KBr pellets. ^{13}C nuclear magnetic resonance (NMR) spectra in $CDCl_3$ were run on a Bruker MSL-600 NMR spectrometer. The chemical shifts are reported in parts per million (δ p.p.m.) downfield from tetramethylsilane, which had been used as an internal standard. X-ray diffraction (XRD) spectra were measured on a Japanese Science D/Max-RB diffractometer (Cu target). The submicro-morphological structures of the samples were studied using a Hitachi HO-IIB scanning electron microscope (SEM). Electron spin resonance (ESR) spectra were recorded on a Bruker ER200D-SRC spectrometer, and g-values were determined by calibration with (α, α'-diphenyl-β-picryl hydrazyl (DPPH)). The photoconductivity [16, 25] of the samples was measured on a Shishido Type S-5109 Static Honestmeter, which is an apparatus for measuring photoconductivity of the materials and was made in Japan. A halotungsten lamp (150 W) was used as the light source. The light intensity used was 180 lm m^{-2}. The sample film, deposited on an electrically grounded aluminum substrate, is first corona-charged (positively or negatively) in the dark. The amount of surface charge is 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. The photoinduced discharge process is the basis of xerography.

In a typical polymerization, x milligrams of C_{60} ($x = 6.67, 20, 40, 80$) and 1000 mg of NVC were dissolved in 80 ml benzene, forming a purple solution, 90 ml of THF solution of lithium naphthalene (2.4 mmol) was slowly added to the above magnetically stirred solution at $-20\,^\circ C$ under purified argon, followed by stirring for 24 h. The solution becomes blackish green. The polymer was precipitated with acidified methanol, redissolved in $CHCl_3$, filtered to remove any insoluable materials, reprecipitated with methanol to give a brownish red solid that was soluable in some common organic solvents. Solvent residues were removed by freeze-drying under slightly higher vacuum for several hours. The pure PVK was synthesized under identical conditions in the absence of C_{60}. In a control experiment, we failed in our attempt to initiate anionic polymerization of NVC monomer using $(C^n_{60})Li^+_n$, which was prepared by the reaction of C_{60} with lithium naphthalene under argon, as initiator. Like our previous unpublished work, which indicated that [60]fullerene polyanion salts $[(C^n_{60})M^+_n$, $M = $ Li, Na, K] and fullerene itself are unable to initiate the polymerization of such monomers as styrene and acrylonitrile, etc., $(C^n_{60})Li^+_n$ is also unstable to initiate the anionic polymerization of NVC monomer. Fig. 1 is a diagrammatic sketch of the synthetic route of the C_{60}–NVC copolymer.

3. Results and discussion

It is well known that C_{60} is an excellent electrophile reacting with a variety of neutral and charged nucleophilic reagents, and readily accepts up to six electrons to form fulleride anions [39, 40]. Since the discovery of superconductivity for K_3C_{60} [41], the [60] fullerene polyanions (C^{n-}_{60}) have attracted considerable interest and have now been synthesized by electrochemical or chemical methods [42–46]. For example, C_{60} can be reduced with lithium metal in THF with the aid of ultrasound to form the fullerene

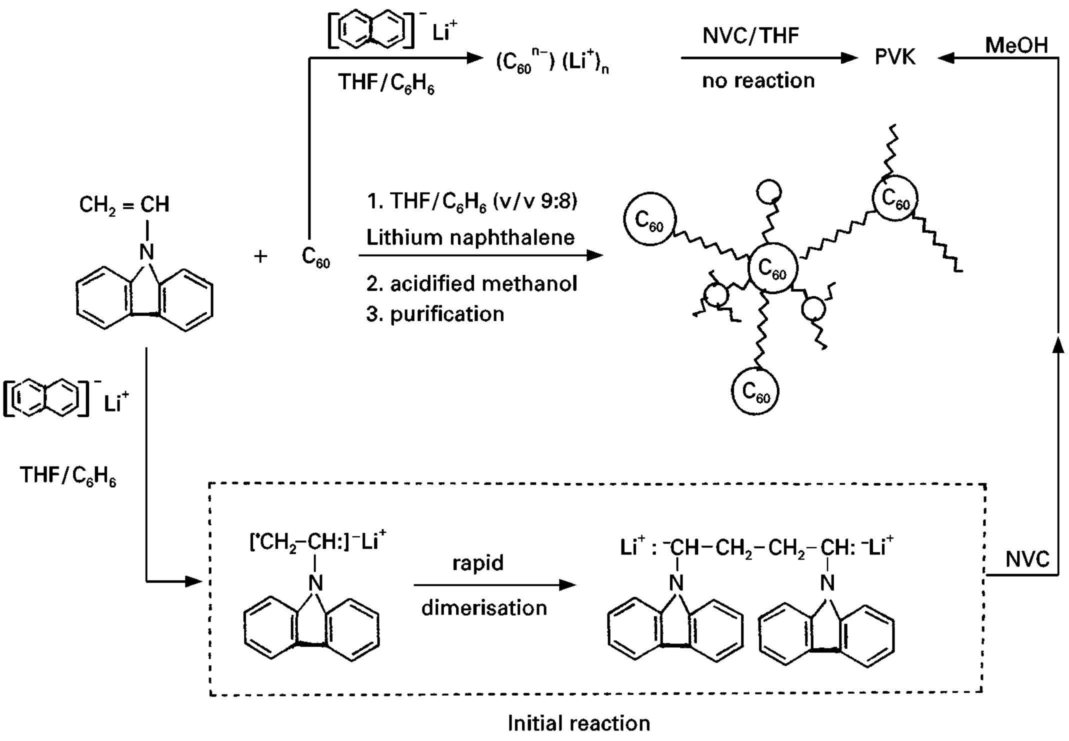


Figure 1 Diagrammatic sketch of the synthetic route of the C_{60}–NVC copolymer.

polyanions $C_{60}^{n-}(Li^+)_n$ [47]. Stoichiometric 1:1 reaction of C_{60} with potassium mediated by 1-methyl naphthalene in THF at room temperature may produce $KC_{60}(THF)$ [45]. These results once prompted us to investigate the possibility that fullerene polyanions initiate the anionic polymerization of some vinyl-containing monomers, however, we failed in our attempt to initiate the anionic polymerization of acrylonitrile or styrene by $C_{60}^{n-}(Li^+)_n$, no polymer was obtained. As we discussed in the experimental section, $C_{60}^{n-}(Li^+)_n$ is also unable to initiate the anionic polymerization of NVC monomer. These observations show clearly that [60] fullerene and its polyanion salts $[C_{60}^{n-}(M^+)_n$, M = Li, Na, K] cannot be used to initiate the polymerization of some monomers such as N-vinylcarbazole, acrylonitrile and styrene, etc. Furthermore, it should be noted that in the polymerization process of C_{60} with NVC an important side-reaction, i.e. reaction of C_{60} with lithium naphthalene, would occur simultaneously. But the hydrolysis product of Li_xC_{60} is hardly soluble in any common organic solvent, such as THF, $CHCl_3$ and C_6H_6, etc. This insoluble hydrolysis product, and other impurities including a small amount of crosslinked product and unreacted C_{60} (if any), could thus readily be removed from the resultant polymers by filtration.

Fig. 2 gives the FTIR spectra of the samples: (a) C_{60}, (b) NVC, (c) PVK (a commercially produced polymer obtained from Tokyo Kasei Kogyo co. Ltd), (d) PVK′ (a product prepared by the anionic polymerization method described in the experimental section), (e) 1.96% C_{60}–NVC copolymer and (f) 7.41% C_{60}–NVC copolymer. The four characteristic infra-red bands of C_{60} at 528, 577, 1183 and 1429 cm^{-1} were observed, this being consistent with the result reported by Suzuki *et al.* [48]. The FTIR spectrum from PVK′ was basically the same as that of the commercially produced PVK. Comparison of Fig. 2d with Fig. 2f indicates that the peak intensity at 528.1 cm^{-1} in C_{60}–NVC copolymer increased dramatically with increasing C_{60} content compared with that at 421.9 cm^{-1}. This may be interpreted as being associated with one of the characteristic vibration modes of C_{60}. The C_{60}–NVC copolymer has a typical polymeric band pattern in the infra-red spectrum, which is similar to that of PVK. Its main bands occur at 1740.6, 1634.4, 1621.9, 1596.9, 1481.2, 1453.1, 1431.2, 1390.6, 1371.9, 1334.4, 1312.4, 1312.5, 1268.7, 1237.5, 1221.9, 1187.5, 1156.2, 1100.0, 1037.5, 1003.1, 959.4, 846.9, 768.8, 746.9, 721.9, 675.0, 578.1, 556.3, 540.6, and 528.1 cm^{-1}. Among these peaks, the peaks at 528.1, 578.1, 1187.5 and 1432.2 cm^{-1} may be assigned to the substituted C_{60}, implying that the carbon-cage framework structure was not broken during polymerization.

The C_{60}–NVC copolymer had a visibly brownish red cast when compared with PVK and NVC monomer, and the reason for this is apparent in the u.v.–vis absorption spectrum in THF shown in Fig. 3. It is seen that both PVK and NVC are essentially transparent at wavelengths longer than 350 nm, their main absorption bands locate at 242, 255, 266, 270, 291, 310, 325 and 338 nm for NVC; 242, 261, 294, 316, 325 and 340 nm for PVK, respectively. In contrast to the NVC monomer and PVK, the copolymer has a new structure in the absorption spectrum in which the main bands occur at 242, 254, 286, 325 and 445 nm, and extends the active range from about 350 to 640 nm due to "charge-transfer" interaction existing between C_{60} and N-ethylcarbazole units. The new absorption at 445 nm may result from the covalent attachment of PVK arms to the C_{60} cores, while the peak at

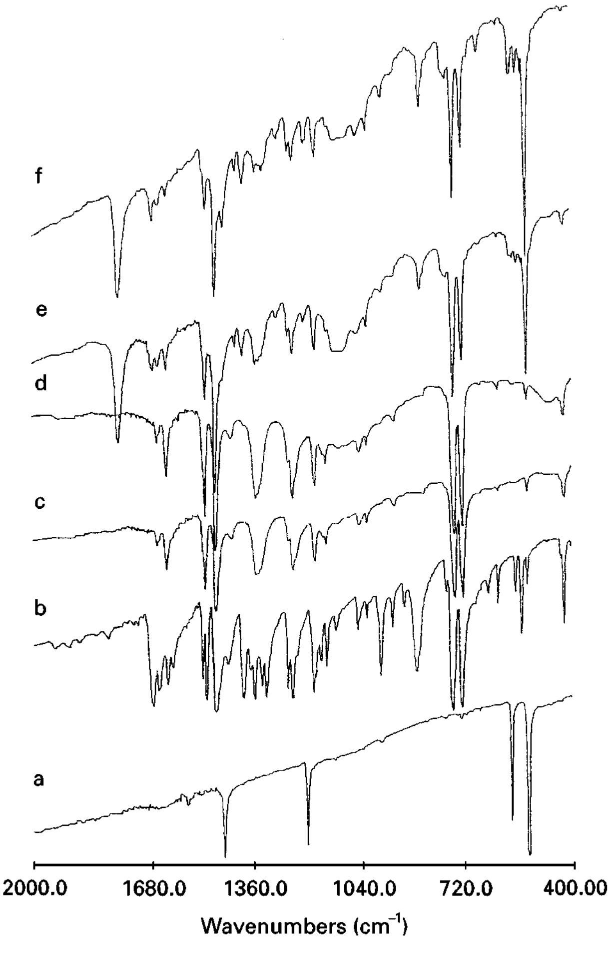


Figure 2 FTIR spectra of (a) C_{60}, (b) NVC, (c) PVK (a commercial product), (d) PVK synthesized by ourselves (PVK′), (e) 1.96% C_{60}–NVC copolymer and (f) 7.41% C_{60}–NVC copolymer.

254 nm (very strong) corresponds to the characteristic absorption for the substituted C_{60}. The other eight peaks at 257 (strong), 330 (strong), 404 (weak), 500 (very weak), 540 (very weak), 570 (very weak), 600 (very weak), and 625 (very weak) nm of pure C_{60} in *n*-hexane [49] were not detected in the copolymer (u.v.–vis spectrum of C_{60} in THF cannot be observed due to its insolubility in tetrafurnan). Furthermore, we have found that the u.v.-vis absorption spectrum of the NVC–C_{60} composite (C_{60}-doped NVC) in benzene is a simple superposition of the components, basically implying relative weak mixing of the ground-state electronic wave functions.

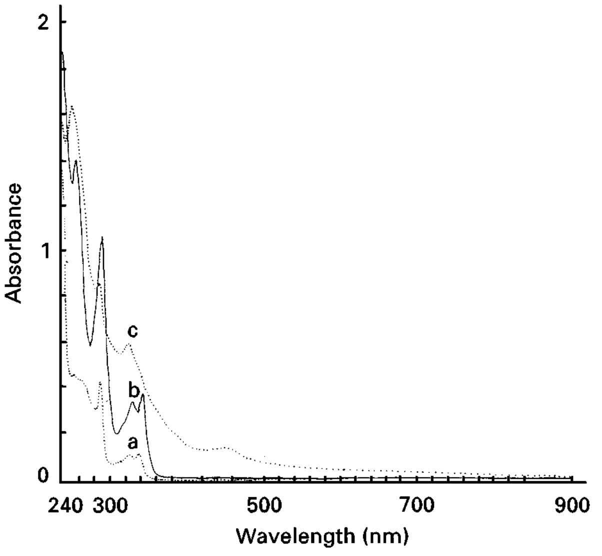


Figure 3 U.V.–visible absorption spectra of the samples in THF: (a) NVC, (b) PVK and (c) 7.41% C_{60}–NVC copolymer.

The structures of the samples have been studied by XRD and are shown in Fig. 4. The XRD pattern from NVC monomer was very complicated and has 52 peaks in which the first eight relatively strong diffraction peaks centred at 2θ are 10.34 ° (0.855 nm), 17.24 ° (0.514 nm), 22.72 ° (0.391 nm), 23.56 ° (0.377 nm), 28.18 ° (0.316 nm), 18.68 ° (0.475 nm), 16.06 ° (0.551 nm), and 11.10 ° (0.796 nm), respectively. The magnitude in the brackets represents the corresponding *d*-values for the 2θ peaks. Like the u.v.–vis spectrum of C_{60}-doped NVC, its XRD spectrum also seems to be a simple superposition of two spectra corresponding to C_{60} and NVC, demonstrating that the doping of C_{60} (electron acceptor) into NVC monomer (electron donor) does not apparently result in the formation of new crystallization phases. The XRD pattern from PVK was similar to that reported by Griffiths [50], Richard [51], and Chen *et al.* [26], two diffraction peaks centred at $2\theta = 20.45°$ (0.432 nm), 7.21° (1.147 nm), respectively, were observed. 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 [52], the nearest chain-to-chain distance being approximately 1.147 nm. In the 7.41% C_{60}–NVC copolymer, five diffraction peaks centred at $2\theta = 8.80°$ [1.004 nm, 48 (I/I_0)], 18.82° [0.471 nm, 100 (I/I_0)], 29.38° [0.304 nm, 22 (I/I_0)], 43.70° [0.207 nm, 10 (I/I_0)], and 55.32° [0.166 nm, 6(I/I_0)], were observed and the curve shape is significantly different from that of pure PVK. This result is very intriguing, suggesting that it might have a layer structural characteristic and requiring further investigation. The XRD spectra of C_{60} and naphthalene were also measured. Their eight relatively stronger sharp diffraction peaks centred at $2\theta = 2\theta 17.54°$ $(I/I_0 = 100)$, 20.58°, 10.60°, 21.56°, 27.98°, 30.74°, 32.66°, and 18.52° for C_{60}; 12.04°$(I/I_0 = 100)$, 19.46°, 25.54°, 21.46°, 26.16°, 29.64°, 23.88°, 18.92°, for napthalene, respectively. Comparison of the XRD results of C_{60} and naphthalene with that of C_{60}–NVC copolymer shows nonexistence of possible trapped C_{60} microcrystals and naphthalene impurities in the copolymers.

^{13}C NMR results also provided strong evidence for the covalent attachment of PVK units to the C_{60} cores (Fig. 5). The resonant peaks at $\delta = 20 \sim 50$ p.p.m. are attributed to saturated carbon, whereas peaks at $\delta = 100 \sim 60$ p.p.m. correspond to the resonant signals of aromatic carbon and olefinic carbon. As shown in Fig. 5, the NVC monomer has eight ^{13}C NMR signals, in which the two peaks at 101.82, 110.38 p.p.m. were assigned to the α-substituted vinyl carbons, while the other six peaks at 120.14, 120.52, 123.89, 126.14, 129.37 and 139.26 p.p.m. corresponded to the carbazyl carbons. The ^{13}C NMR spectrum from pure PVK was similar to that reported by Williams [53]. Its main

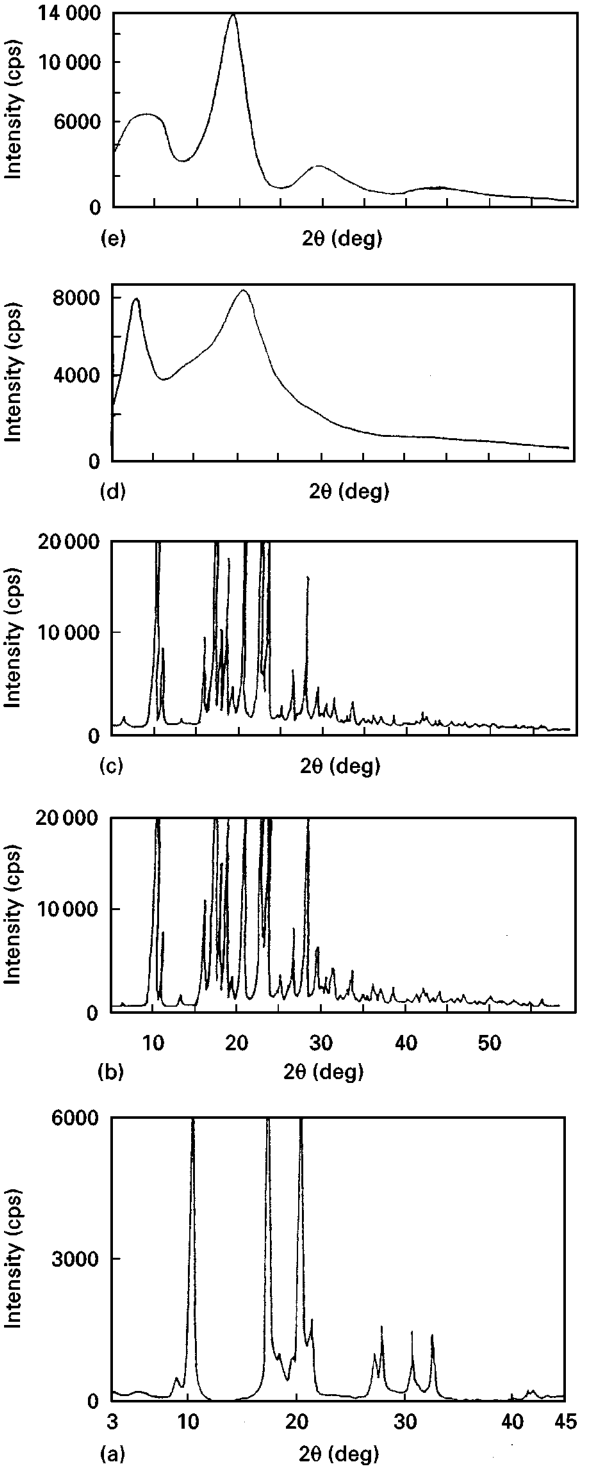


Figure 4 XRD: (a) C_{60}, (b) NVC, (c) C_{60}–doped NVC, (d) PVK and (e) 7.41% C_{60}–NVC copolymer.

peaks are located at 35.58, 48.44, 49.26, 50.07, 107.56, 108.09, 110.37, 118.57, 118.91, 120.24, 121.98, 123.91, 125.03, 137.46, 137.89 and 140.09 p.p.m. In contrast to the NVC monomer and PVK, the ^{13}C NMR spectrum of C_{60}–NVC copolymer shows 25 peaks, which are located at 31.01, 68.4, 71.5, 110.38, 110.66, 119.01, 119.56, 120.02, 120.42, 123.49, 124.16, 125.61, 125.94, 126.42, 128.44, 139.61, 139.81, 142.16, 143.21, 144.70, 145.61, 146.65, 147.09, 149.08, and 170.28 p.p.m., respectively. Among these peaks, the last eight peaks are assigned to the unsaturated carbon signals of the substituted C_{60} cages. The signal at 31.01 p.p.m. is ascribable to $\alpha C(\text{-}C_{60})$ of ethyl units, while the two

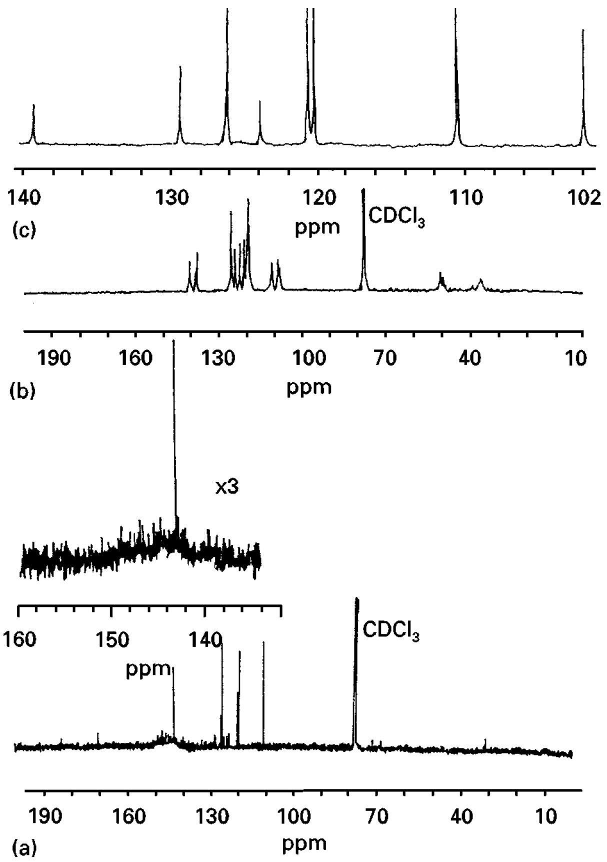
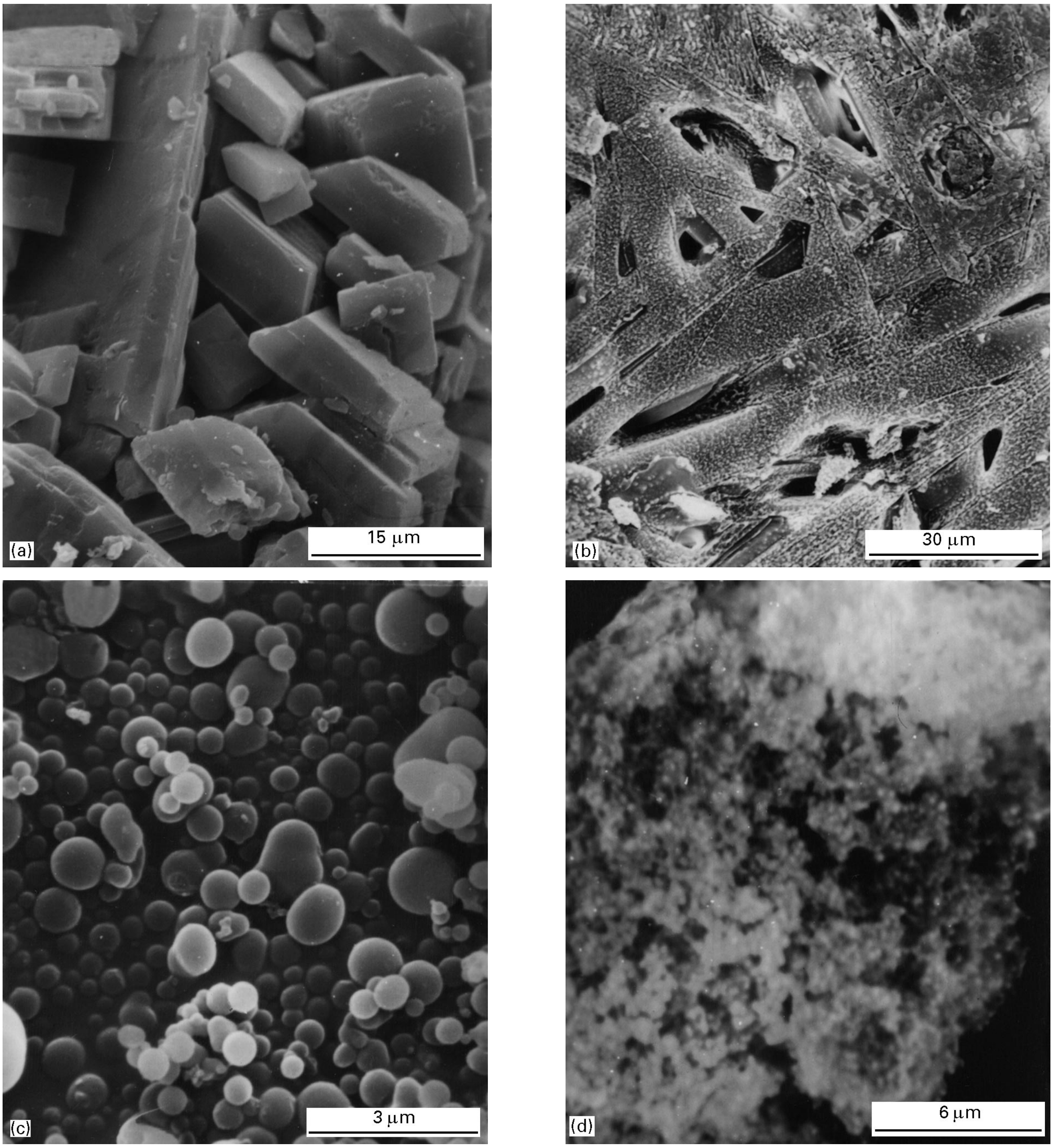


Figure 5 ^{13}C NMR spectra in $CDCl_3$ for: (a) 7.41% C_{60}–NVC copolymer, (b) PVK and (c) NVC.

peaks at 68.4 and 71.5 p.p.m. correspond to sp^3 hybridized carbon signals of the substituted C_{60}. These findings further indicate the covalent attachment of PVK units to the C_{60} cores.

The submicro-morphological structure of the 7.41% C_{60}–NVC copolymer is shown compared with that of the NVC monomer, PVK, C_{60}-doped NVC and C_{60} in Fig. 6 The figure clearly indicates that in PVK a great number of globules, which possess a diameter of 0.3–2.1 μm, were loosely heaped together; whereas in the C_{60}–NVC copolymer, its surface morphology was similar to that of coral reef. The microstructure of C_{60} appeared flakelike as a whole. It is thus obvious that the morphology of C_{60}–NVC copolymer differed greatly from that of the above samples.

As we discussed in the u.v.–vis absorption spectra, there exists considerable difference in electronic structure between pure NVC and C_{60}–NVC copolymer. This difference was further confirmed by ESR techniques. An ESR spectrum is obtained when microwave energy is absorbed by a paramagnetic sample as a consequence of transitions induced between the magnetic Zeeman state. At ambient temperature, no ESR signals for either NVC, PVK or fullerenes were detected, indicating no unpaired electrons or free radicals existed in the above samples. Although lithium naphthalene (in the synthesis procedure, its amount used is only 2.4 mmol) is paramagnetic, it is extremely sensitive to air, water and acidified solvents, and can be readily quenched by acidified methanol in the chain termination reaction. For the 7.41% C_{60}– NVC copolymer,



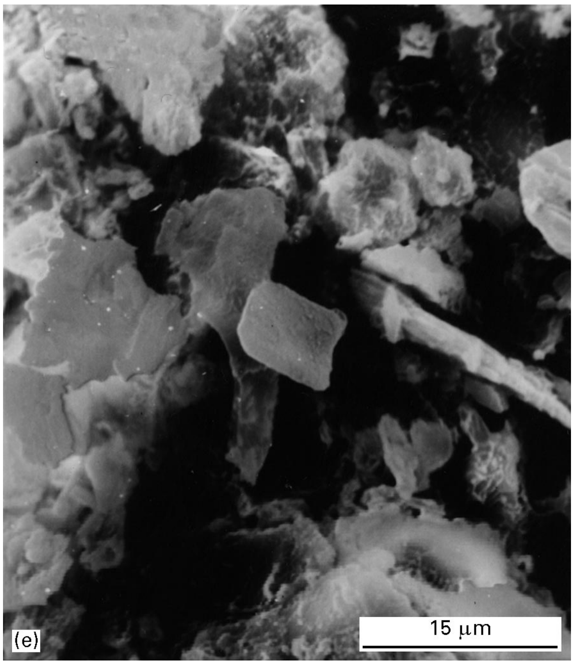


Figure 6 Scanning electron micrographs of: (a) C_{60}, (b) NVC, (c) PVK, (d) 7.41% C_{60}–NVC copolymer and (e) C_{60}–doped NVC.

ESR spectrum show two peaks, a narrow peak, I ($g = 2.0026$; line width, $\Delta H_{pp} = 1.7\,G$) attributed to "charge-transfer" interaction between the C_{60} moieties and the corresponding near-neighbouring carbazole units, and a shoulder broad peak, II ($\Delta H_{pp} = 11.8\,G$) which is assigned to interaction between the positively charged carbazyl and the adjacent relatively electron-rich carbazyl [26]. It is thus clear that two kinds of paramagnetic species occur in the copolymer. The line width, ΔH_{pp}, in the parentheses is generally defined as the distance (in guass) between both peaks of the derivative. Fig. 7 shows the variable-temperature ESR spectra of the 7.41% C_{60}–NVC copolymer. The results show that its temperature sensitivity is very intriguing and closely related to paramagnetism of the polymer. Both the g-values and the line width of signals I and II

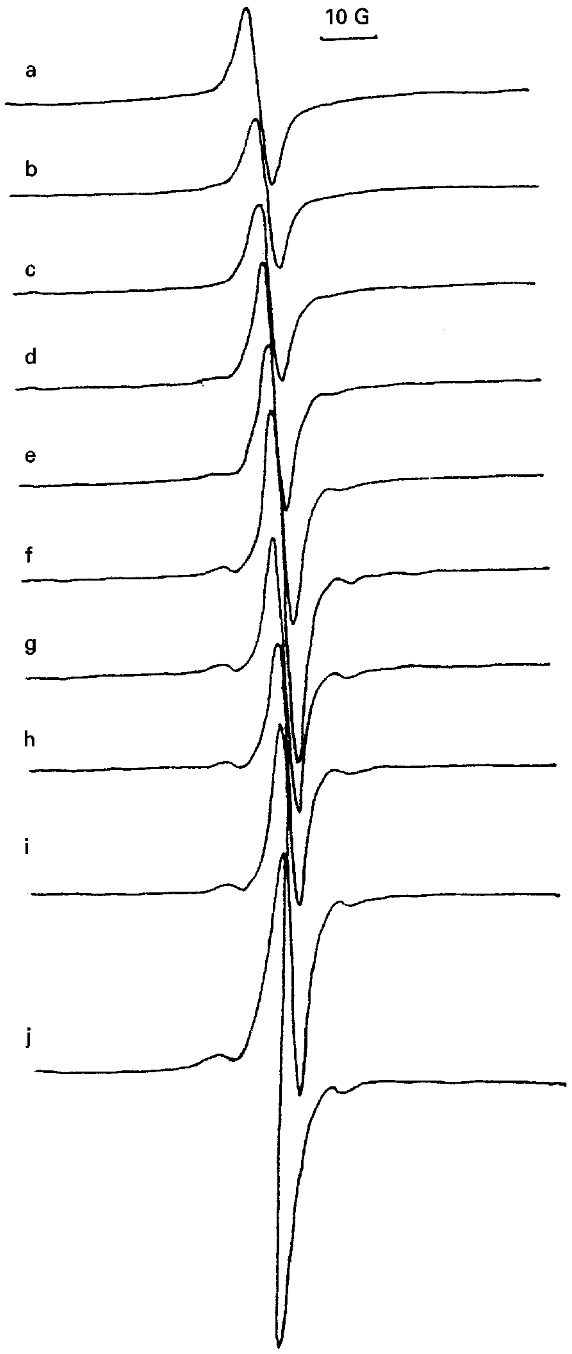


Figure 7 Variable-temperature ESR spectra of the 7.41% C_{60}–NVC copolymer at: (a) 100 K, (b) 140 K, (c) 160 K, (d) 180 K, (e) 200 K, (f) 260 K, (g) 300 K, (h) 350 K, (i) 400 K and (j) 450 K.

remain basically unchanged over the entire temperature range (100–450 K). It is well known that the relative ESR signal intensity is directly proportional to $Y'_{\mathrm{m}}(\Delta H_{\mathrm{pp}})^2$, where Y'_{m} is the amplitude of the peak. Since ΔH_{pp} remains constant, signal intensity is directly proportional to peak height. Therefore, in this case, the unpaired electron concentrations (UEC) in the polymer are only directly proportional to peak height. Fig. 8 gives the temperature dependence of the unpaired electron concentrations in the polymer, which only refers to peak I. The salient features are:

1. a striking increase in UEC above 340 K, and
2. an UEC change taking on the shape of the letter "W" at lower temperature.

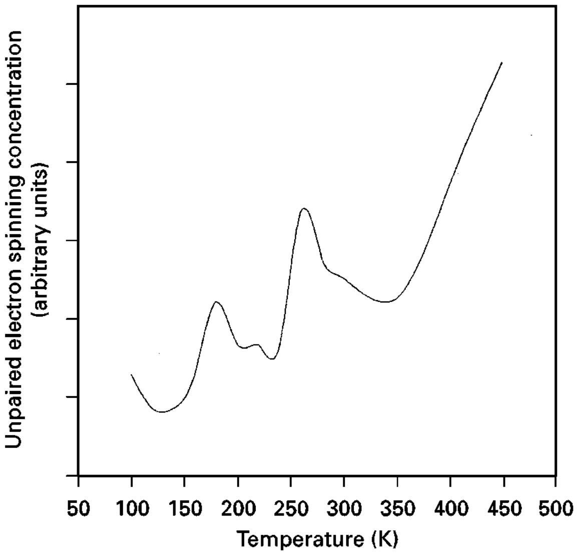


Figure 8 Temperature dependence of the upaired electron concentrations in the 7.41% C_{60}–NVC copolymer over the temperature range 100–450 K.

These findings demonstrate the effect of temperature on the formation or recombination of unpaired electrons in the polymer, and might be closely related to the conformational complexity of the polymer, stemming from a structural change induced by temperature increased. In addition, the effect of u.v. irradiation, with a W-Germany Hereaus-type high-pressure mercury lamp as the light source, on the paramagnetic electronic structure of NVC monomer, PVK and 7.41% C_{60}–NVC copolymer was also studied. u.v. irradiation on the copolymer results in the formation of new paramagentic species, whose ESR signal intensity increases as time of u.v. irradiation increases (Fig. 9). Further investigation of the copolymer shows that this photoinduced ESR enhancement, is reversible, which may be the reason for the resulting marked enhancement in photoconductivity for the copolymer relative to NVC and PVK. The origin, nature and properties of the new paramagnetic centres in this copolymer require further investigation. However, no ESR signals for either NVC or PVK were detected during u.v. irradiation, thus implying that u.v. irradiation has little effect on the NVC monomer and PVK.

A qualitative comparison of the photoinduced discharge curves for pure NVC, PVK, 0.66% C_{60}–NVC copolymer, 3.85% C_{60}–NVC copolymer and 3.85% C_{60}-doped NVC under the same experimental conditions is shown in Fig. 10. The initial results show that addition of multiple PVK arms to the C_{60} cores results in a marked enhancement in photoconductivity relative to pure NVC, PVK and C_{60}-doped NVC. Photoinduced discharge rates of the above samples are found qualitatively in the following order: 3.85% C_{60}–NVC $>$ 0.66% C_{60}–NVC $>$ 3.85% C_{60}-doped NVC $>$ NVC $>$ PVK under the same experimental conditions. Further detailed studies on the photoconductivity properties of C_{60}–NVC copolymer and its derivatives are currently in progress.

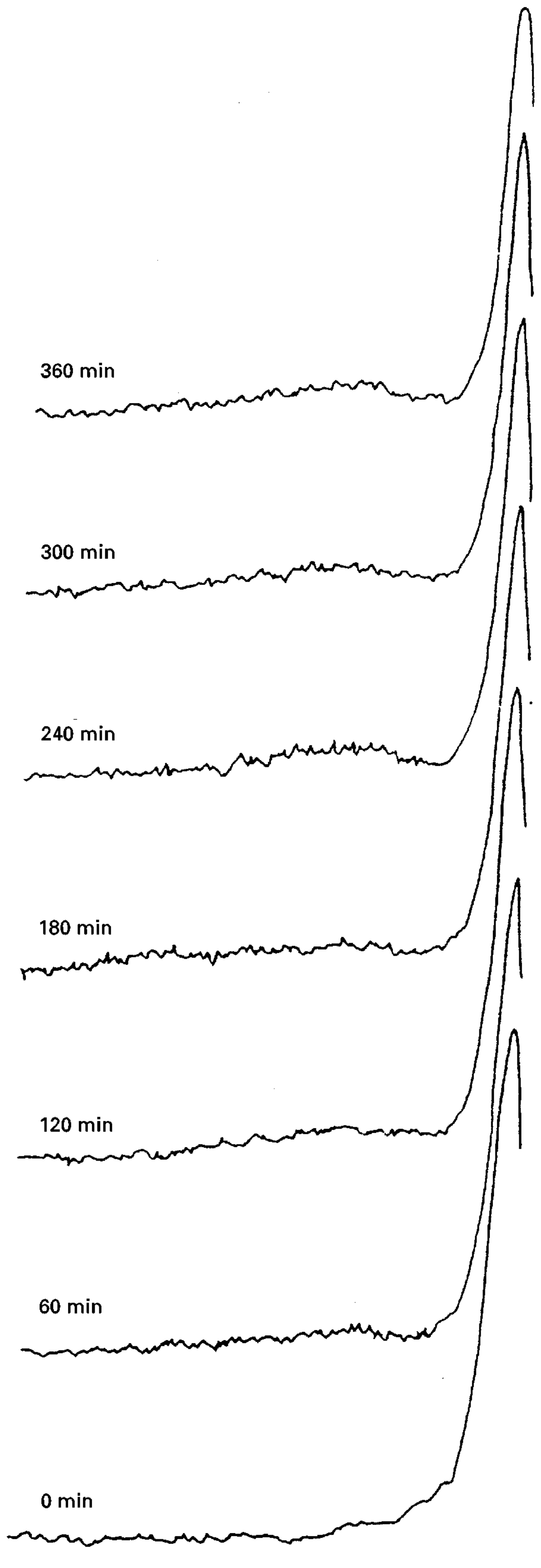


Figure 9 The effect of u.v. irradiation on the paramagnetic structure of the 7.41% C_{60}–NVC copolymer (partial amplified ESR spectra).

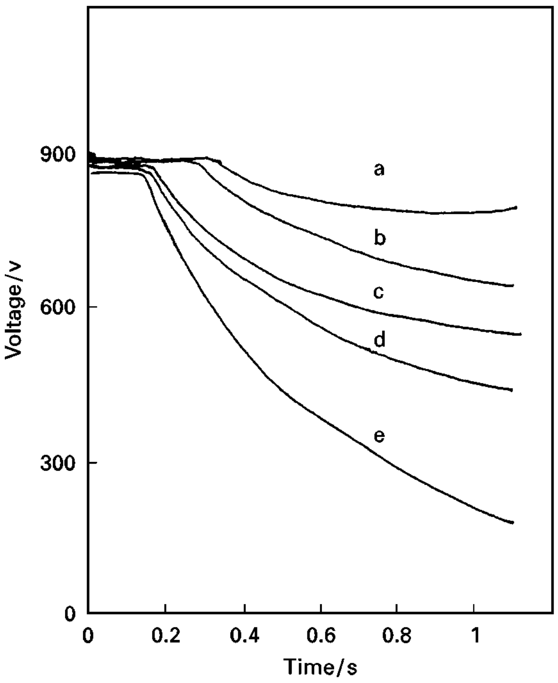


Figure 10 A qualitative comparison of the photoinduced discharge curves for: (a) PVK, (b) NVC, (c) 3.85% C_{60}–doped NVC, (d) 0.66% C_{60}–NVC copolymer and (e) 3.85% C_{60}–NVC copolymer under identical experimental conditions.

4. Conclusions

We have demonstrated the synthesis of a soluble C_{60}–N-vinylcarbazole copolymer and described the results of a preliminary investigation into its structural characterization and photoconductive performance. Both [60] fullerene polyanion salts $[(C_{60}^{n-})M_n^+$, M = Li, Na, K] and fullerene are unable to initiate the polymerization of such monomers as NVC, styrene and acrylonitrile etc. In our experimental condition, the reaction mechanism is more complicated and requires further investigation. The C_{60}–NVC copolymer has a new structure in the u.v.–vis absorption spectrum in which the main bands occur at 242, 254, 286, 325 and 445 nm, and extends the active range from about 350 to 640 nm due to a "charge-transfer" effect existing between C_{60} and N-ethylcarbazole units. XRD evidence shows that this material might have a layer structural characteristic. The surface morphology of this copolymer was similar to that of coral reef. ^{13}C NMR provided strong evidence for the covalent attachment of PVK units to the C_{60} cores. The chemical shifts located at 142.16, 143.21, 144.70, 145.61, 146.65, 147.09, 149.08 and 170.28 p.p.m. in the ^{13}C NMR spectrum of the copolymer are assigned to the unsaturated carbon signals of the substituted C_{60} cage. ESR studies on the copolymer demonstrate that its temperature sensitivity is closely related to polymer paramagnetism; an unusual temperature dependence for the ESR spectrum is observed. u.v. irradiation of the copolymer results in the formation of a new paramagnetic species whose ESR signal intensity increases with increasing time of u.v. irradiation. This photoinduced ESR enhancement is reversible. Finally, qualitative comparison of the photoinduced discharge curves for the samples indicated that addition of multiple PVK arms to C_{60} cores results in marked enhancement in photoconductivity relative to pure NVC, PVK and C_{60}-doped NVC.

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