

Accounts

## Synthesis, characterization and application of soluble fullerene-ated polymer materials

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This article only deals with the topic of intense interest to us and to a considerable extent of our own experimental results on the synthesis, characterization and application of  $C_{60}$ -containing functional polymers such as poly(*N*-vinylcarbazole), polystyrene and polyacrylonitrile-based fullerene polymers. The results demonstrate that [60]fullerene can be directly incorporated into a variety of functional polymers by copolymerization or grafting, but also can be used to modify or improve the electronic, optical and physicochemical properties of polymers. Both the stereo-electronic effect and the steric hindrance of  $C_{60}$  have an important influence on the structure and physicochemical properties of the parent polymer.

**Keywords** Fullerene, functional polymers, preparation, application

### Introduction

Discovery of the fullerenes, a family of carbon cage molecules epitomized by the exquisitely symmetrical  $C_{60}$ , reshaped chemists' understanding of the fundamental properties of carbon and earned Curl, Kroto and Smalley the 1996 Nobel prize in chemistry.<sup>1</sup> As a new form of carbon, [60]fullerene and its organic or polymeric derivatives exhibit a variety of outstanding properties such as superconductivity,<sup>2</sup> ferromagnetism,<sup>3</sup> inhibition of HIV protease,<sup>4</sup> anti-Lou Gehrig's disease,<sup>5</sup> free radical scavenging bioactivity,<sup>6</sup> photoconductivity,<sup>7, 8</sup> non-linear optical (NLO) and optical limiting (OL) properties,<sup>9</sup> thus attracting considerable interest in the fields of physics, chemistry, material science as well as the life sciences.<sup>10-15</sup>

As described in many publications, the spherical [60]fullerene has 12 pentagons, all of which are fully surrounded by hexagons (a total of 20) in a "corannulene-type" fashion.<sup>14</sup> Cyclic voltammetry experiments confirmed that [60]fullerene is a redox-active chromophore which, according to theoretical calculations, exhibits an energetically low-lying, three-fold-degenerate lowest unoccupied molecular orbital (LUMO), and consequently, behaves like an electronegative molecule which could reversibly accept up to six electrons in solution and prefers to react with electron-rich reagents. The possible organic reactions of [60]fullerene mainly include:<sup>10, 14, 16</sup> (1) hydrogenation, (2) oxidation reactions, (3) halogenations, (4) organometallic reactions, (5) cycloadditions, (6) the addition of nucleophiles and (7) the addition of radicals. All these additions are exothermic and are presumably driven by the relief of strain in the  $C_{60}$  cage that largely results from the pyramidalization of its  $sp^2$  carbon atoms.<sup>17</sup> However, unfortunately, the ability to fabricate devices based on  $C_{60}$  has been limited due to its poor processability and its complex nature due to multiaddition of the organic group onto the cage. Monofunctionalized  $C_{60}$  has nine different 6:6 bonds (at the junctions between two hexagons) that can react in a second addition. Therefore, controlling the regiochemistry of the second addition to direct the attack to one desired position poses a considerable challenge.<sup>14</sup> Similar problems arise in the polymeric modification of fullerenes. For this reason, the key to the development of polymer modified fullerene is to form selectively soluble fullerene-ated polymers in high yield under very mild

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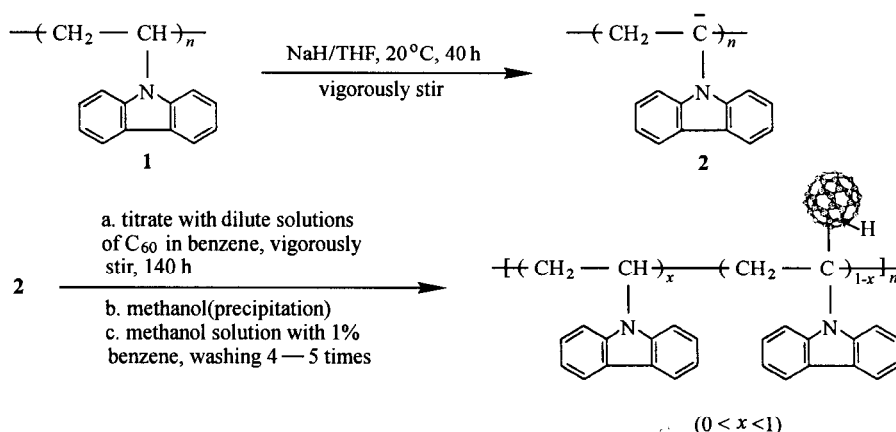
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conditions.<sup>18, 19</sup>

Although [60]fullerene itself and its polyanion salts  $[C_{60}^{n-}(M^+)_n]$ ,  $M = Li, Na, K$  cannot be used to initiate the anionic polymerization of some monomers such as *N*-vinylcarbazole, acrylonitrile and styrene,<sup>19,20</sup>  $C_{60}$  may initiate "charge-transfer" bulk polymerization of some electron-rich monomers under the thermal condition or

the microwave irradiation.<sup>21</sup> In recent years, the polymeric modification of fullerenes has attracted much interest aiming at the utilization of fullerenes. Obviously, the combination of the outstanding characteristics of fullerene with those of the polymeric matrix is very challenging and will probably become of great importance in the future.

Scheme 1



In general, fullerene-based polymer materials may be prepared in four ways:<sup>12,20</sup> (1) the reaction of  $C_{60}$  or a  $C_{60}$  derivative with a preformed polymer or a transition metal complex such as  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ ; (2) polymerization of a monomer containing [60]fullerene functional groups; (3) free radical or, anionic copolymerization of  $C_{60}$  with a monomer; and (4) doping of  $C_{60}$  or  $C_{60}$  derivatives into polymer matrices. This account only deals with the topic of intense interest to us and to a considerable extent of our own experimental results on the "synthesis, characterization and application of soluble fullerenated polymers".

#### *Poly(N-vinylcarbazole)-based fullerene polymers*

Poly(*N*-vinylcarbazole) [PVK] is one of a number of vinyl polymers with aromatic pendant groups that have elicited considerable interest as potential commercial photoconductor systems and exhibit interesting electrical properties.<sup>22-25</sup> The substitution of halogens, nitro, nitroso, chloromethyl, tricyanovinyl, and phosphory groups in the active 3 and 6 positions of the pendant carbazole group has been accomplished by manipulation of the monomer or the polymer, resulting in increased photoconductivity.<sup>22</sup> By the addition of dyes or electron ac-

ceptor molecules, and by the surface or bulk attachment of dyes or electron acceptor functionalities onto the polymer, the spectral range associated with the charge photogeneration process can be controlled. As we described in the introduction section, [60]fullerene is known to be a good electron acceptor ( $E_A = 2.6\text{--}2.8\text{ eV}$ ) and has thus been considered as a host for dopants which are, in most cases, electron donors. Enhanced photoconductivity exhibited by fullerene-doped polymers (a simple blend of fullerene and donor polymer) has been observed.<sup>7,26,27</sup> The photoconductivity exhibited by such fullerene-based polymers is mainly due to the effect of the fullerene on the charge generation and the charge transport process in the polymeric system.<sup>28</sup> Although the doping of hole-transporting, electron donor polymers with fullerenes can result in extended spectral sensitivity as well as enhanced photogenerated efficiency, there are, however, problems associated with this approach. These problems 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.

The first soluble PVK polymer bonded covalently to

various extents with  $C_{60}H$  moieties ( $C_{60}$ -PVK copolymer) was synthesized by direct reaction of [60]fullerene with PVK carbanions (Scheme 1).<sup>8</sup> Fullerene content, which estimated by the thermogravimetry (TG) analysis, is varied from 1.96% to 15.21%.<sup>29</sup> In comparison with pure PVK, this earthy yellow  $C_{60}$ -PVK polymer ( $C_{60}$  modified PVK polymer) has new structure in the UV-Vis absorption spectrum in which the main bands occur at 215, 265, 298, 335, and 345 nm and extends the active range from about 280 nm to 870 nm. The fullerene level in the copolymer essentially determines the absorption degree in the visible region. TG analysis and cyclic voltammetry experiments showed that both the thermal stability and the redox activation of the parent polymer were apparently enhanced by the chemical modification of [60]fullerene.

$C_{60}$ -PVK polymer has intriguing temperature sensitivity and an unusual temperature dependence of the ESR spectrum has been observed.<sup>8,30</sup> At room temperature, the ESR spectrum of this polymer shows two peaks: a narrow peak I ( $g = 2.0028$ ,  $\Delta H_{pp} = 2.2$  G) with respect to the interaction between the pendant  $C_{60}$  molecules and corresponding near-neighbor carbazole groups in the polymer, and a shoulder broad peak II ( $\Delta H_{pp} = 11.2$  G) which is assigned to the interaction between positively charged carbazolyl and the adjacent electron-rich carbazolyl. This implies that two kinds of paramagnetic species occur in the  $C_{60}$  modified polymer. Fig. 1 gives the temperature dependence of the ESR spectrum of the  $C_{60}$ -PVK copolymer. The results show that the unpaired electron spinning concentration in the polymer has a minimum at about 260 K, and both the  $g$ -values and the line width ( $\Delta H_{pp}$ ) of signals I and II are unchanged over the entire temperature range (120–470 K). Perhaps a better rationalization might run as follows. First, if upon addition of a  $C_{60}$  moiety an electron is transferred from the nearby carbazole unit, then both would be in doublet states, which couple to give a close-lying singlet and triplet. With the singlet slightly lower (as can be argued to be plausible), the ESR signal should increase with temperature (as observed at low temperatures). Next, with further increase of temperature one might conceivably imagine a structural change is induced such that further electron transfer occurs from more distant carbazoles to the  $C_{60}$  moieties, where further unpaired electrons might be introduced (again in concert

with observation).<sup>8</sup>

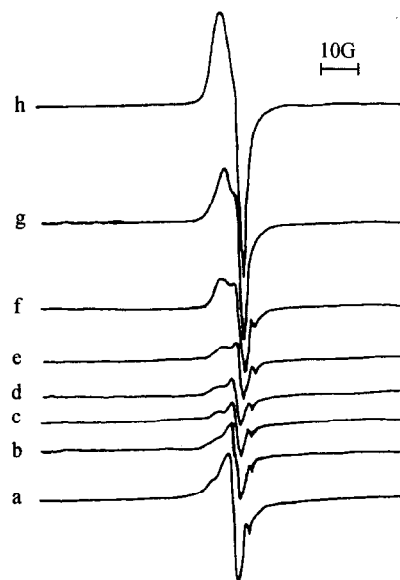
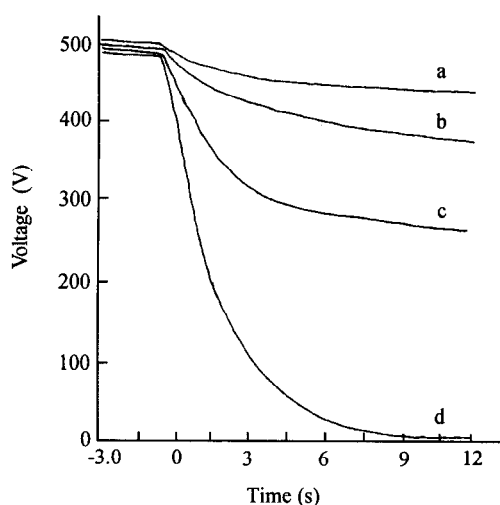


Fig. 1 Temperature dependence of ESR spectra of  $C_{60}$ -PVK copolymer containing 3.85% of  $C_{60}$  over the temperature range 120–470 K. (a) 120 K, (b) 170 K, (c) 220 K, (d) 270 K, (e) 320 K, (f) 370 K, (g) 420 K, and (h) 470 K.

As shown in Fig. 2, addition of  $C_{60}$  moiety to PVK by chemical reaction results in the marked enhancement in photoconductivity relative to pure PVK and  $C_{60}$ -doped PVK.<sup>31</sup> The photoinduced discharge rates for pure PVK,  $C_{60}$ -PVK and  $C_{60}$ -doped PVK under the same experimental conditions are found to be in the following order:  $C_{60}$ -PVK polymer  $\gg$   $C_{60}$ -doped PVK  $>$  pure PVK. A “charge-transfer” interaction between the positively charged carbazole, resulting from charge transfer towards  $C_{60}$ , and near-neighboring 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. The photoconductive performance in the  $C_{60}$ -PVK polymer is closely related to the fullerene level in the polymer.

One unusual feature of fullerene molecules lies in their ability to undergo aggregation from smaller to larger ones in some specific manner, including the growth of fullerene cages by sequential  $C_2$ -capture, the formation of giant fullerenes, multiples of bonded fullerenes, and carbon nanotubes or onions. In our previous experiment,<sup>32</sup> enhanced fullerene cage growth and coalescence

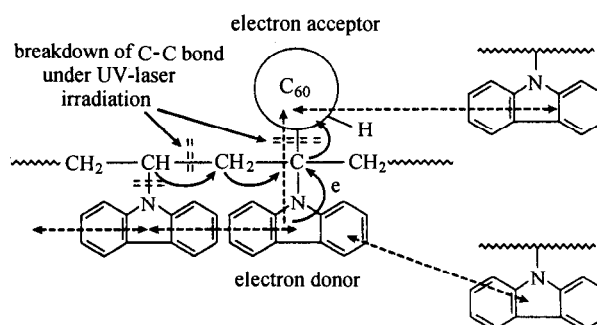


**Fig. 2** A qualitative comparison of the photoinduced discharge curves for (a) pure PVK, (b) 3.85%  $C_{60}$ -doped PVK, (c) 12.28%  $C_{60}$ -PVK copolymer, (d) 3.85%  $C_{60}$ -PVK copolymer under the identical experimental conditions.

were observed in the laser desorption of  $C_{60}$  derivatives ( $C_{60}R_n$ ,  $R_n = C_6H_5CH_2-$  and  $C_9H_7-$ ). The roles played by the radicals in the enhancement, especially in the formation of negative fullerene ions, were discussed. Since such laser-induced reactions may produce new species which are not present in the original sample, some unusual and interesting properties of fullerenes can be revealed.<sup>33</sup> Therefore, the investigation of the photo-physical dynamics for  $C_{60}$  and its derivatives is of significance both in basic research and in exploring applications of fullerenes. The phenomena of aggregation and coalescence of fullerenes in the UV-laser ablation time-of-flight (TOF) mass spectrometric investigation of  $C_{60}$ -PVK polymer and  $C_{60}$ -doped PVK polymer both in the positive and in the negative ion channels have been observed.<sup>34, 35</sup> The results indicate that in  $C_{60}$ -PVK polymer the nascent fullerene fragments ruptured from the main chain can easily coalesce into large fullerenes ( $C_{114}$ ,  $C_{116}$ ,  $C_{132}$ , *etc.*) through collisions, whereas in the  $C_{60}$ -doped PVK the aggregation and coalescence of  $C_{60}$  were relative weak due to non-bonding action and incomplete charge transfer behavior between  $C_{60}$  and PVK. The photoinduced electron transfer between  $C_{60}$  and carbazole units in the  $C_{60}$ -PVK polymer in benzonitrile by laser flash photolysis (it is effective in investigating the initial steps of the charge-generation) at 355 nm has also

been investigated.<sup>34</sup> It was found that efficiency of the anion radical of  $C_{60}$  in  $C_{60}$ -PVK polymer at 1080 nm is higher than that of the  $C_{60}$ -doped PVK polymers apparently. The formation of a  $C_{60}$  radical anion may be ascribed to photoinduced electron transfer between  $C_{60}$  pendanted on the main chain backbone and the inter-, and intrachain carbazole units in the copolymer (Scheme 2).

#### Scheme 2



Since the discovery of superconductivity for  $K_3C_{60}$ , alkali-metal intercalation compounds of  $C_{60}$  have attracted a great deal of interest and have been synthesized by either electrochemical or chemical methods.<sup>2, 36</sup> Electrochemical intercalation of alkali metals into fullerenes and their derivatives not only may provide another synthetic route to alkali-metal-intercalated fullerenes  $M_xC_{60}$  ( $M = K, Na, Rb, Cs$ ), but also may offer an appropriate approach to develop novel and efficient lithium intercalated batteries modified by fullerenes. The first Li-fullerenated PVK battery [ $C_{60}$ -PVK | Li(LiClO<sub>4</sub>/PC)] was prepared at room temperature in an argon-filled glove box in 1996.<sup>37</sup> This battery has a higher open-circuit voltage (*ca.* 3.2 V), and its discharge may be ascribed to the electrochemical intercalation process of lithium in  $C_{60}$ -PVK polymer for positive electrode active materials. Experimental data obtained from FTIR, XRD and ESR showed that the discharge of the electric cell has an apparent effect on the structure and paramagnetic property of fullerenated PVK. One year later, Kawabe *et al.* from Osaka University of Japan also used  $C_{60}$ -PVK polymer as the electrode active material to prepare rechargeable lithium batteries.<sup>38</sup> Their results further demonstrated that the charge capacity, the discharge capacity and Coulombic efficiency increased gradually with repetition of cycles and saturated after about 35 cycles. The Coulombic efficiency reached 93%, which is high e-

nough for practical application. In comparison with the charge-discharge potential of the  $C_{60}$  pellet,  $C_{60}$ -PVK polymer showed lower charge-discharge potential which helps to enhance the cell voltage as well as the energy density.

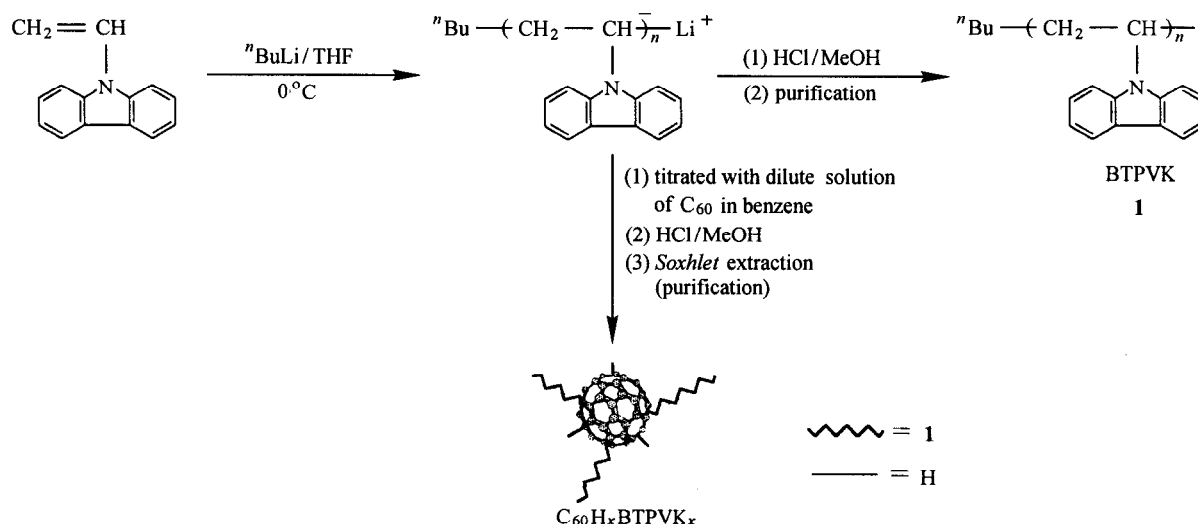
Similarly,  $C_{60}$ -chemical modified bromine-, iodine-, and chloromethyl-substituted PVK polymers were also prepared.<sup>39-42</sup> Unlike  $C_{60}$ -PVK polymer, photoconductivity of the parent PVKBr polymer decreased greatly by the introduction of  $C_{60}$  moiety into this polymer backbone. A possible reason is that in the  $C_{60}$ -PVKBr polymer whose bulky 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, in spite of a favourable energetic relationship between the electron donor and acceptor. The decreased photogeneration efficiency of  $C_{60}$ -PVKBr may be thus linked to this conformational complication.<sup>39</sup>

A potential advantage of the application of polymer chemistry to the functionalization of fullerenes is the encapsulation of fullerene clusters having conducting capabilities by a polymeric insulating layer, which also alters the physical properties and provides novel materials for investigation of the properties of individual isolated carbon clusters.<sup>43</sup> For these reasons, a highly soluble star-shaped  $C_{60}H_x$ BTPVK<sub>x</sub> polymer (BTPVK polymer modified  $C_{60}$ ), which has significantly different spectroscopic properties from both free  $C_{60}$  and *n*-butyl-terminated

poly(*N*-vinylcarbazole) [BTPVK], was synthesized in heterogeneous medium (Scheme 3).<sup>44</sup> The average number of grafted chains and average molecular weight of the resultant  $C_{60}H_x$ BTPVK<sub>x</sub> are roughly calculated as 2.88 and 8085, respectively. <sup>13</sup>C NMR spectra provided strong evidence for the covalent attachment of BTPVK arms onto the  $C_{60}$  core. The six peaks at  $\delta$  110.66, 119.56, 119.93, 120.42, 123.51 and 125.93 may be assigned to the carbazolyl carbons. The three peaks at  $\delta$  76.68, 78.16 and 78.81 correspond to the  $sp^3$  hybridized carbon signals of the substituted  $C_{60}$ . The signal at  $\delta$  29.80 is ascribed to  $\alpha C(-C_{60})$  of *N*-ethyl carbazole units. In the broadened fullerene region  $\delta(130-160)$ , the six new peaks at  $\delta$  141.82, 142.23, 142.46, 144.32, 145.72 and 146.22 were observed and may be assigned to the functionalized  $C_{60}$  cage in the polymer. TG analysis showed that the thermal stability of BTPVK polymer was decreased greatly due to the large steric hindrance effect from the bulky  $C_{60}$  and the corresponding carbazole groups of BTPVK arms causing the highly twist and fold of polymer chain segments, and consequently a striking increase of chain surface tension.

Moreover, a hyperbranched  $C_{60}$ -*N*-vinylcarbazole [ $C_{60}$ -NVC] copolymer was synthesized in lithium naphthalene-initiated anionic polymerization reactions.<sup>20</sup> Like  $C_{60}$ -chemically modified PVK polymer, this layered structure material also exhibits good photoconductivity and temperature sensitivity.

Scheme 3



*Polystyrene-based fullerene polymers*

The fullerene molecule can be incorporated covalently onto the polystyrene (PS) backbone by using of:<sup>12,19</sup> (1) radical-initiated polymerization reactions; (2) alkali-metal naphthalene-initiated anionic copolymerization reactions; (3) cycloaddition reaction of azido-substituted polystyrenes with fullerene; (4) Friedel-Crafts type reactions; (5) amine addition reactions; and (6) reaction of polymeric living carbanions with fullerene. Of all the polymerization methods, the addition of living anionic polymers or polymeric carbanions onto the C<sub>60</sub> core may offer an unique opportunity to control both the number of chains grafted onto the fullerene and the molar mass and polymolecularity of the grafts.

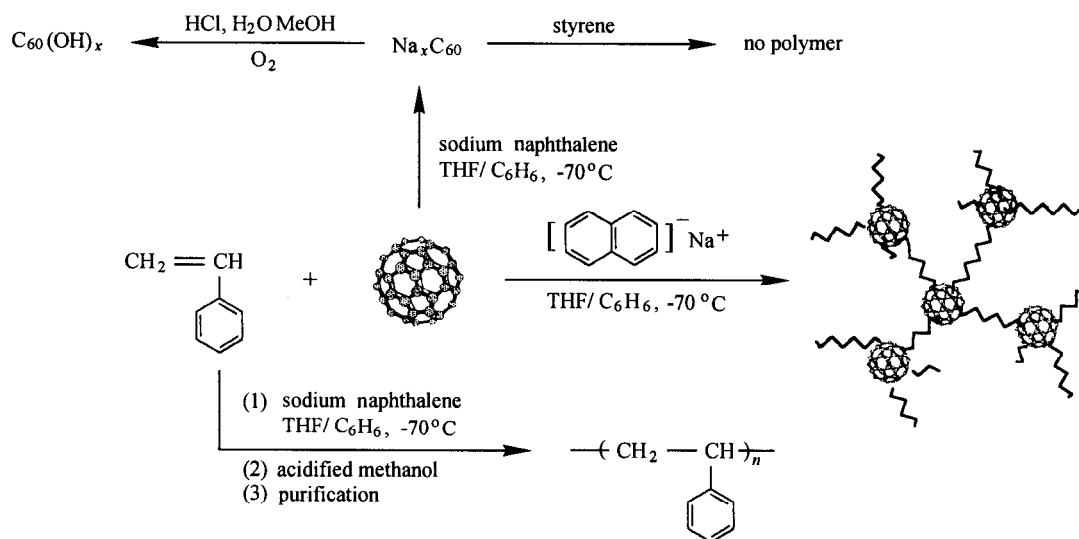
C<sub>60</sub> is an excellent electrophile reacting with a variety of neutral and charged nucleophilic reagents. We reported a new route for the preparation of soluble "charm bracelet" type fullerenated polystyrene through the reaction of fullerene with living polystyrene carbanions obtained by proton abstraction with NaH in 1995.<sup>45(a)</sup> This polymer possesses a new energy band structure with indi-

rect forbidden band when compared with the parent polystyrene. The lattice periodicity of pure polystyrene film is subject to some perturbation or distortion in varying degrees due to the covalent attachment of C<sub>60</sub> moiety to the polymer backbone.<sup>45(b)</sup>

Similarly, C<sub>60</sub>-chemically modified poly(*p*-bromostyrene) [C<sub>60</sub>-PBS polymer] was also synthesized.<sup>46</sup> The product obtained is a "charm-bracelet" non-crosslinked brownish yellow polymer which is easily soluble in many common organic solvents, and has a single glass transition temperature (134.0°C as against 83.2°C for poly(*p*-bromostyrene)), this being congruent with its chemical structure. Both the stereo-electronic effect and the steric hindrance of C<sub>60</sub> have an important influence on the structure and physico-chemical properties of the parent polymer.

Another novel hyperbranched C<sub>60</sub>-styrene polymer (C<sub>60</sub>-PS) was prepared in sodium naphthalene-initiated anionic polymerization reactions.<sup>19(a)</sup> Scheme 4 gives the diagrammatic sketch of the synthetic route. Like pure polystyrene, the C<sub>60</sub>-PS polymers obtained also exhibited high solubility in common solvents, including the

Scheme 4



polymer with high C<sub>60</sub> content. In the polymerization process of C<sub>60</sub> with styrene an important side-reaction, *i. e.*, reaction of C<sub>60</sub> with sodium naphthalene, occurs simultaneously, whereas cross-linking reaction may be negligible. The byproduct, which has an average composition C<sub>60</sub>(OH)<sub>24.5</sub>, obtained from quenching the Na<sub>x</sub>C<sub>60</sub>

with HCl-MeOH-H<sub>2</sub>O, is hardly soluble in any common organic solvents and could thus readily be removed from the resultant polymers by filtration. In the UV-Vis absorption spectra of the C<sub>60</sub>-PS polymers, as the C<sub>60</sub> contents increase gradually, the somewhat structured absorption band of free C<sub>60</sub> is replaced by a steadily de-

creasing curve, typical for substituted [60] fullerene.  $C_{60}$  moieties play not only the chromophoric role but also the somewhat auxochromic role in the UV-Vis absorption. In contrast to the polystyrene reference, the TGA spectrum of  $C_{60}$ -PS containing ~13% of  $C_{60}$  shows two plateaus (Fig. 3). The polystyrene chain segment decomposed first at 300–400°C, its onset temperature for the thermal bond-cleavage is at 402.5°C. Then the fullerene units ruptured from the corresponding polystyrene fragments attached directly to the  $C_{60}$  cores at 500–638°C. XRD evidence indicates that the degree of order of the polymers increases as the fullerene content increased. Incorporation of  $C_{60}$  into polystyrene results in the formation of new crystal gratings or crystallization phases.

The "living" anionic polymeric salts, for example,  $PS^-Li^+$ ,  $PI^-Li^+$ ,  $PS^-K^+$  etc., which were pregenerated by using the anionic polymerization reaction with butyllithium as the initiator, may add to  $C_{60}$  to form fullerene-containing star-shaped polymers. Samulski *et al.* first reported their work, which takes advantage of the  $C_{60}$  reactivity by grafting living anionic polystyrene ( $PS^-$ ) onto the electrophilic  $C_{60}$  core in 1992.<sup>47</sup> The resultant polymer with the formula  $C_{60}(PS)_x$  was obtained by the reaction of living anionic polystyrene with the benzene solution of  $C_{60}$ . The maximum numbers of grafted chains onto the fullerene core mainly depend on the reactivity of the carbanion borne by the chain.<sup>48</sup>

A novel star-shaped  $C_{60}(PMS)_x(CH_3)_x$  ( $x = 1-3$ ) polymer was prepared by reaction of a living anionic poly( $\alpha$ -methylstyrene) ( $PMS^-$ ) with  $C_{60}$ , followed by a capping reaction with methyl iodide.<sup>49</sup> Interestingly, unlike living anionic polystyrene ( $PS^-$ ), at room temperature, the rate of depolymerization for the living anionic PMS was greater than the rate of copolymerization for the living anionic PMS with  $C_{60}$  under the same experimental condition. The above copolymer could not thus be obtained by Samulski's method. This problem can be circumvented by substituting the  $\alpha$ -methylstyrene (MS) solution of  $C_{60}$  for a benzene solution of  $C_{60}$ . The fluorescence quantum yield of this  $C_{60}(PMS)_x(CH_3)_x$  was much smaller than that of pure PMS. This phenomenon can be interpreted as the quenching through intramolecular excited-state energy transfer. The  $C_{60}$ -containing sites may act as energy traps. After multiple PMS arms were grafted covalently onto  $C_{60}$ , the redox activation of the parent polymer was enhanced apparently. Analogously,

highly soluble star-shaped  $C_{60}$ -*p*-methylstyrene copolymers with different  $C_{60}$  contents were also prepared in the toluene-tetrahydrofuran mixed solvents.<sup>50</sup> The average number of grafted polymer chains onto the [60] fullerene was approximately between 1 and 4.

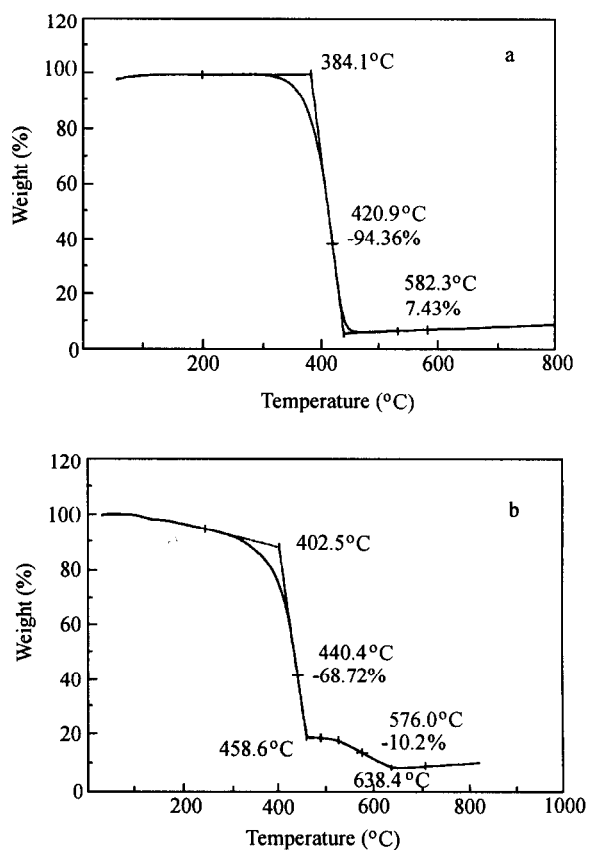


Fig. 3 TG curves at 20 deg/min of (a) PS and (b) 13%  $C_{60}$ -styrene copolymer in flowing (100 mL/min)  $N_2$ .

#### Polyacrylonitrile-based fullerene polymers

The electrical conductivity of polymers such as laterally ordered polyacrylonitrile, polymethacrylonitrile, and poly(copper phthalocyanine) can be controlled by pyrolytic modification and there have been extensive investigations in this field<sup>51,52</sup> due to the potential advantages and applications of the development of functional electrodes, electronic devices, batteries, sensors and so on. In the case of pyrolyzed polyacrylonitrile, the formation of conjugated chain molecules by linking of nitrile groups may be credited with bringing about the enhanced conductivity relative to the parent polymer.

In the search for fullerene-containing polymeric ma-

materials with novel electric, conducting and photophysical properties, a  $C_{60}(CH_3)_x(PAN)_x$  polymer<sup>53</sup> was synthesized by reaction of the living *n*-butyl-terminated polyacrylonitrile (PAN) with  $C_{60}$  in the heterogeneous medium, followed by a capping reaction with  $CH_3I$ . The chemical formulas of PAN and  $C_{60}(CH_3)_x(PAN)_x$  are shown in Scheme 5. The chemical and physical properties of this polymer depend largely on the concentrations of the fullerene covalently bound to the polymer matrix or, on the chain-length of PAN units attached to a  $C_{60}$  core.

In the absorption spectrum of pure PAN polymer ( $PA_0$ ), there are two broad absorption peaks located at 200 nm and 240 nm with a long tail extended to about 400 nm. In the visible region, the absorption of PAN is

weak. Compared with pure PAN film, the  $C_{60}(CH_3)_x(PAN)_x$  polymer films show a new absorption peak in the near ultraviolet region except the intense peak at 200–400 nm. The new absorption peaks locate at 335, 350, 365 and 370 nm for  $PA_1$ ,  $PA_2$ ,  $PA_3$  and  $PA_4$ , respectively. Because there is no characteristic absorption peak at 256 and 328 nm of  $C_{60}$ , the appearance of this new broad peak around 360 nm reveals the interaction of the fullerene molecule with the PAN chain.  $PA_1$  polymer has the shortest chain length among these copolymers, the interaction between  $C_{60}$  and PAN would be significant over the whole chain which results in the shortest wavelength of the new absorption peak. Fig. 4 gives the photoluminescence (PL) spectra of  $C_{60}(CH_3)_x(PAN)_x$  polymers, with the excitation wavelength at (a) 470 nm

Scheme 5

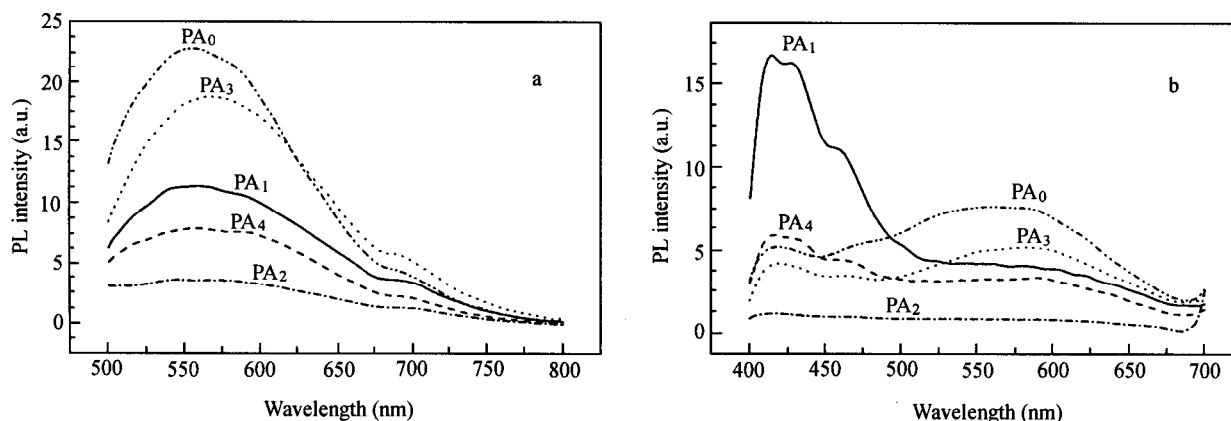
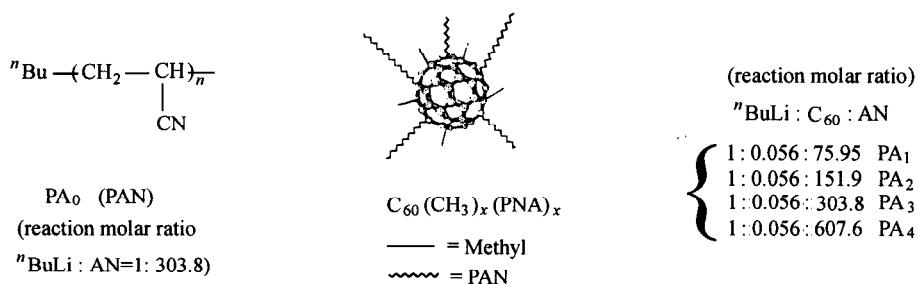


Fig. 4 Photoluminescence spectra of star-shaped  $C_{60}(CH_3)_x(PAN)_x$  copolymers with the excitation wavelength at (a) 470 nm and (b) 370 nm, respectively.

and (b) 370 nm, respectively. It is seen that pure PAN polymer has the most intense PL emission. This wavelength of PL emission should be related to the excited-state of the PAN polymer. All copolymers show the intense PL emission in green region with slight red shift.

PL quenching in the  $C_{60}(CH_3)_x(PAN)_x$  polymers can be explained by the excitation transfer process between  $C_{60}$  cage and PAN polymer chain.

The pure PAN and  $C_{60}(CH_3)_x(PAN)_x$  polymers have been pyrolyzed under vacuum, between 25 and

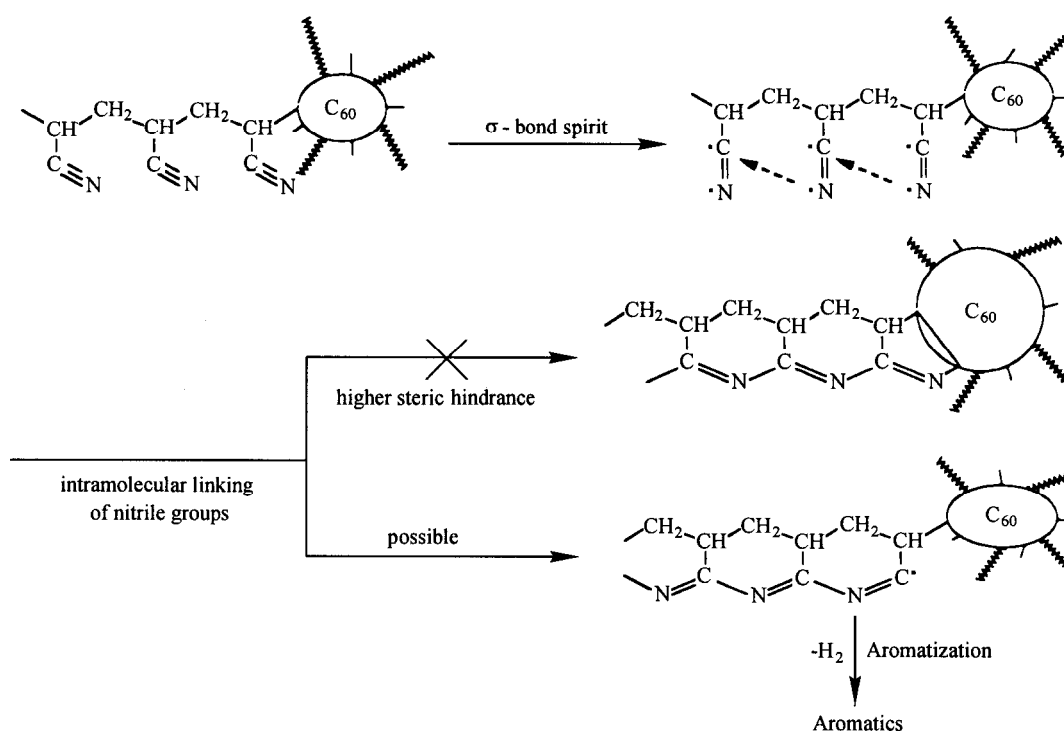


475 °C.<sup>54</sup> It was found that the nitrile groups of the polymers disappear gradually as heating progresses, and C = N linkages appear. As heating is continued, evidence for aromatization is found. Above 350 °C, the most significant changes appear to be the development of broad absorption in the 1200–1700 cm<sup>-1</sup> region. However, interpretation of the peaks that appear during degradation is more difficult. In C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> below 400 °C, linking of CN groups, which would result in the formation of naphthyridine-like structures and C = N conjugated systems, and aromatization by dehydrogen seem to be more difficult than in pure PAN(PA<sub>0</sub>). This might be closely related to enhanced thermal stability and the formation of a larger delocalized electron system in the copolymer. It is interesting that in the copolymer the peak at 540.62 cm<sup>-1</sup> broadens gradually as the temperature is increased and shifts to higher wavenumbers. Because strong steric hindrance, and dipole and electric effects exist in the copolymer, an explanation of the pyrolytic behavior of C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> polymer must, therefore, take into account these contributions as well as experimental observations. A reasonable pyrolysis scheme is suggested (Scheme 6).

The unique temperature dependence of the ESR

spectra of PA<sub>0</sub> and PA<sub>3</sub> has been investigated. Their temperature sensitivities are very intriguing. For PA<sub>0</sub> at lower temperatures, both the linewidth ( $\Delta H_{pp}$ ) and intensity increased dramatically with decreasing temperature. This implies that a reduction of the  $T_2$  value (the transverse spin-spin relaxation time  $T_2$  is inversely proportional to  $g\Delta H_{pp}$ ) resulted in the enhancement of interactions of electrons with other electrons in the polymer. At higher temperature, the shapes of the ESR spectrum are Lorentzian, stemming from homogeneously broadened lines. Meanwhile, the unpaired electron spinning concentration in the polymer increases greatly as pyrolysis proceeds, and the exchange interaction between isotropic electrons strengthens notably, which results in the linewidth of the spectrum narrowing. These experimental facts indicate the delocalization of carriers and the formation of conjugated double bonds by pyrolysis modification. In the case of the copolymer, its ESR spectrum at ambient temperature shows two signals that might result from stronger paramagnetic coupling between the PAN arms and C<sub>60</sub> core, which gives close-lying singlet and triplet states. The temperature sensitivity is similar to that of C<sub>60</sub>-chemically modified poly(*N*-vinylcarbazole) [C<sub>60</sub>-PVK polymer].

Scheme 6



The electrical properties of copolymers and *n*-butyl-terminated PAN were studied. As shown in Table 1, the conduction type for all samples before and after thermal treatment is *N*-type. The effect of pyrolysis modification at 500°C on the electrical properties is not so striking. Above 350°C polynuclear aromatic chains are formed,

while the hydrogen content goes down very steeply. This second conjugation by elimination of one H<sub>2</sub> molecule per monomer unit seems to be the process that really lowers the resistivity.<sup>52</sup> Therefore, additional heat-treatment at higher temperatures would be needed to enhance the conductivity of the polymers.

**Table 1** Electrical properties of *n*-butyl-terminated polyacrylonitrile and C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> copolymers

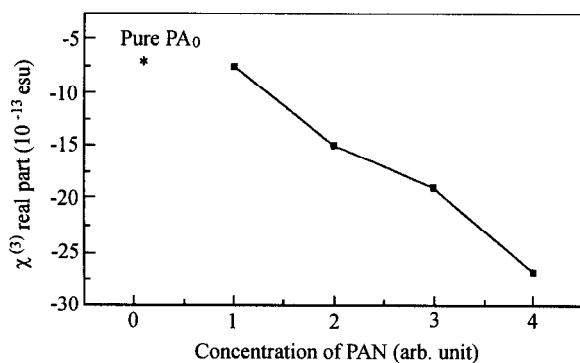
Name	Color	Thickness <i>d</i> (nm)	Resistivity $\rho$ ( $\Omega \cdot \text{cm}$ )	Carrier		Conduction type
				concentration ( $\text{cm}^{-3}$ )	Hall mobility $\mu_n$ ( $\text{cm}^2/\text{V} \cdot \text{sec}$ )	
PA <sub>0</sub>	Light brown-yellow	0.12	$1.59 \times 10^5$	$5.39 \times 10^9$	$0.97 \times 10^4$	N-type
PA <sub>1</sub> <sup>a</sup>	Brown	0.12	$0.75 \times 10^5$	$23.9 \times 10^9$	$0.35 \times 10^4$	N-type
PA <sub>3</sub>	Brown-yellow	0.12	$0.92 \times 10^5$	$4.82 \times 10^9$	$1.50 \times 10^4$	N-type
PA <sub>01</sub> <sup>b</sup>	Black	0.12	$2.20 \times 10^5$	$3.76 \times 10^9$	$0.74 \times 10^4$	N-type
PA <sub>31</sub> <sup>b</sup>	Blue-black	0.12	$0.81 \times 10^5$	$10.6 \times 10^9$	$0.72 \times 10^4$	N-type

<sup>a</sup> The pyrolytic product (PA<sub>11</sub>) of sample PA<sub>1</sub>, which contains a higher fullerene level relative to PA<sub>3</sub>, is very prone to cracking, so that it is difficult to obtain an intact compressed pellet without KBr. <sup>b</sup> PA<sub>01</sub> and PA<sub>31</sub> are obtained by thermal treatment on PA<sub>0</sub> and PA<sub>3</sub>, respectively, at 500°C for 1 h in a flowing nitrogen atmosphere.

Along with metallophthalocyanines and mixed metal clusters, C<sub>60</sub> and other fullerenes have emerged as promising candidate materials for the nonlinear optical applications owing to their intrinsic NLO properties which primarily originate from their large  $\pi$ -electron conjugations and strong electron affinity.<sup>55-57</sup> For pure C<sub>60</sub> and many polymers, the third-order nonlinear optical susceptibility was found around 10<sup>-13</sup> to 10<sup>-12</sup> esu in the near infrared and visible region. Recently, a lot of researches were devoted to modify their structure by adding new radicals to the fullerene cage, generating fullerene anion or polymerizing the fullerene molecule with organic molecules or polymer for getting even better property.<sup>58-60</sup> The results show that modifying the fullerene cage with polymer or other molecule would be an efficient way to improve photoelectric and nonlinear optical response of the fullerene family. However, so far, only a few articles concern the investigations into the third-order nonlinear optical response of C<sub>60</sub>-covalent bonded polymers. For these reasons, we synthesized the novel highly soluble starlike<sup>53</sup> [60] fullerene-based polyacrylonitrile derivatives and described initial results of an investigation into their photoluminescence (PL) spectra, and their third-order nonlinear optical response.<sup>61</sup> As C<sub>60</sub> molecule and PAN have different electron affinity in the star-shaped structure of C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> polymer, there would be the redistribution of the electron cloud along the star-like chain which would certainly change

the energy state and the transition process between the states. This polymer would also have the possibility to show large nonlinear optical susceptibility and fast response. The above analysis was confirmed by femtosecond OHD-OKE (optical heterodyne detected-optical Kerr effect) experiment results. All four C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> polymer films fabricated by the physical jet deposition (PJD) technique at temperature around 360°C exhibit larger OHD-OKE signal than that of pure PAN polymer. The improvement of the ultrafast response of C<sub>60</sub> modified polymer than pure PAN polymer and fullerene logically come from the increase of dipole moment in the copolymer caused by the change of the electron cloud. With the reference of CS<sub>2</sub> ( $\chi_{1111}^{(3)} = 1.0 \times 10^{-13}$  esu), the real part of the third-order nonlinear optical susceptibility of these new materials could be calculated from the measured OHD-OKE signal. Furthermore, it was found that the OKE signal of copolymer film is proportional not only to the thickness of the film which is in agreement with the OKE process, but also to the length of PAN chain. PA<sub>4</sub> film with the longest PAN chain among four copolymers has the largest  $\chi_{1111}^{(3)}$  which is nearly four times larger than that of pure PAN. The relation of the measured third-order nonlinear optical susceptibility of the C<sub>60</sub>(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> copolymer with the content of the PAN is given in Fig. 5. This result proves that the NLO response of these materials depends strongly on the length of the PAN chain in the star-like structure. Similarly,

the femtosecond OHD-OKE response of the hyperbranched C<sub>60</sub>-AN copolymer was also studied.<sup>62</sup> The real part of the third-order nonlinear susceptibility of this polymer was determined to be of  $5.98 \times 10^{-13}$  esu.

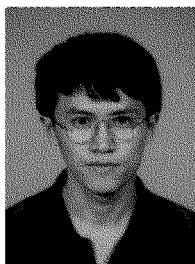


**Fig. 5** Dependence of the third-order nonlinear optical susceptibility on the concentration of PAN in the C<sub>60</sub>-(CH<sub>3</sub>)<sub>x</sub>(PAN)<sub>x</sub> copolymers.

## References and notes

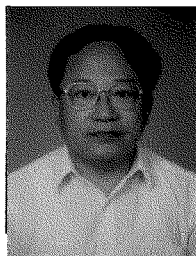
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