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Preparation and Characterization of Fullerene C_{60} and Phthalocyanine Co-grafted Poly(epoxy propyl carbazole)

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Abatract: The fullerene C_{60} and phthalocyanine co-grafted poly (epoxy propyl carbazole) (C_{60}-CuPC-PEPC) was synthesized by Friedel-Crafts reaction. It was found that C_{60}-CuPc-PEPC had good UV-Vis absorption property, whose active spectral range was expanded from UV to visible spectrum region, and exhibited better photoconductivity than CuPc-PEPC and PEPC. These improvements could be attributed to the interaction between C_{60}, phthalocyanine and PEPC.

Keywords: Fullerene, phthalocyanine, poly (epoxy propyl carbazole), UV-Vis, photocondivity.

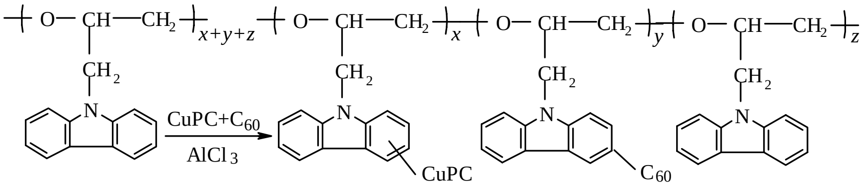
Fullerenes and its derivatives have attracted great interest from the viewpoints of both fundamental science and potential application. Fullerene-doping polymeric photoconductors have been extensively investigated due to their potential technological application. The enhancement of the photoconductivity of the poly (*N*-vinylcarbazole) (PVK) films by dopong with fullerenes (a mixture of C_{60} and C_{70}) was for the first time reported by Wang[1]. He proposed that enhanced photoconductivity was attributed to the electron transfer reaction between fullerenes and PVK[2]. Similar doping effects of fullerenes on photoconductivity have been also reported on phenylmethylpolysilane[3~4] and metal phthalocyanine *et al.*[5]. But fullerenes usually segregates from the polymer matrix because of the intrinsic incompatibility of the two materials, which will lead to difficulty in preparing homogeneous composites of fullerene-containing polymer. Chemical doping can overcome the above shortcoming. Chen *et al.*[6] for the first time reported the synthesis of C_{60} chemically doped PVK and its derivatives, and found this fullerene chemically doped PVK had better photoconductivity than both pure PVK and a mixture of C_{60} and PVK.

Compared with PVK, PEPC has oxyalkyl in main chain which improve its flexibility. C_{60}-chemical doped PEPC was synthesized and characterized in our previous work[7]. Fullerenated PEPC has better UV-Vis absorption spectrum than pure PEPC. On the other hand, the metall opthalocyanine is a kind of good organic photoelectronic material. It was reported that the copolymer of the vinyl carbazole, styrene and acrylamide with pthalocyanine exhibited good photoconductivity[8~9]. PEPC has the active spectrum only in UV region, metal phthalocyanine is active in both UV and visible region. In order to further improve the UV-Vis absorption characteristics and photoconductivity, here fullerene and CuPc co-grafted PEPC was for the first time synthesized and characterized.

C_{60} (99.9%) was purchased from Wuhan University. PEPC, C_{60} and acyl CuPc were dissolved in the mixed solvent of carbon disulfide and nitrobenzene. C_{60}-CuPc-PEPC was synthesized by Friedel-Crafts reaction employing anhydrous aluminium chloride as catalyst as described in the previous work[7]. The final product dissolved in THF and was precipitated by methanol in order to remove the surplus C_{60}. For comparison, CuPc-PEPC was also synthesized.

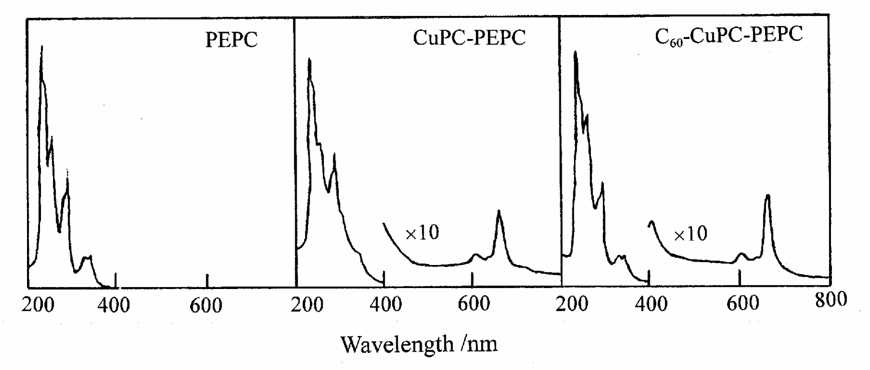
FT-IR spectra shows that C_{60} has four characteristic bands at 527, 576, 1182 and 1429 cm^{-1}, this agrees with the result reported by Suzuki *et al.*[10]. PEPC has the vibration peaks at 1060-1150 cm^{-1} corresponding to C-O. FT-IR spectra of CuPc-PEPC are similar to that of PEPC, except some peaks of CuPc-PEPC has been changed in sizes and proportion. It is noticed that the peaks at 750 and 723 cm^{-1} attributed to the C-H bending vibration in the benzene ring has separated into three sharp peaks at 750, 723 and 704 cm^{-1} in comparison with pure PEPC. The reason for this is that CuPc is grafted to the carbazole of PEPC. Chen *et al.*[8] has demonstrated that the CuPc was covalently grafted to the carbazole groups of PVK, FT-IR of C_{60}-CuPC-PEPC is nearly the same as those of CuPc-PEPC. Though there is also absorption at 527 cm^{-1} in PEPC and CuPc-PEPC, it is noticeable that the relative intensity of 527 cm^{-1} of C_{60}-CuPc-PEPC is obviously larger than that of both PEPC and CuPc-PEPC compared to the nearby peaks. It is due to that 527 cm^{-1} is the strongest characteristic peak of C_{60}, which is survived in fullerenated polymer. In the previous work[7], it has been confirmed that C_{60} was covalently grafted to carbazole groups of PEPC by NMR spectra. Therefore, the molecular structure of C_{60}-CuPc-PEPC can be shown by **Figure 1**. The result of elemental analysis shows that C_{60} moiety in C_{60}-CuPC-PEPC is about 1.95% by mole ratio.

Figure 1 The structure formula of C_{60}-CuPc-PEPC



The UV-Vis absorption spectra of pure PEPC, CuPc-PEPC and C_{60}-CuPc-PEPC are recorded using a Shimadzu UV-240 scanning spectrophotometer, and shown in **Figure 2**. It can be seen that pure PEPC has the absorption bands at 293, 329 and 342 nm, and is transparent completely at over 360 nm, which agrees with result reported in Ref.[11]. CuPc-PEPC remains the Q absorption band of CuPc at 600-700 nm, the maximum absorption peak is at 666 nm. A wide absorption band of CuPc-PEPC is extended from 293 nm to 400 nm in UV region, which is apparently different from the absorption of PEPC at 329 nm and the absorption of CuPc at 345 nm. The fact indicates that the absorption spectrum of CuPc-PEPC is not a simple superimposition of that of CuPc and PEPC. Chen *et al.*[8] proposed the interaction between CuPc and PVK would change its UV-Vis absorption spectrum structure, which was different from the simple overlap of that CuPc and PEPC. Similarly, because of the interaction between CuPc and PEPC, the UV-Vis absorption spectrum of CuPc-PEPC will be different from the simple mixture of that of CuPc and PEPC. **Figure 2** shows that CuPc-PEPC is active in both ultraviolet and visible region. C_{60}-CuPc-PEPC has absorption spectra structure like as pure PEPC in UV region, and visible absorption bands similar as the Q absorption band of CuPc at 600-700 nm. In addition, a little absorption peak contributed to C_{60} is observed, which is different from both pure PEPC and CuPc-PEPC. The active spectral range of C_{60}-CuPc-PEPC in visible region is expanded from 404 nm to Q absorption bands of CuPc. The characteristic diaphanous area of C_{60} does not appear, which shows the UV-Vis absorption spectrum is not a simple mixture of that of C_{60}, CuPc and PEPC. Because that C_{60} and CuPc are covalently grafted to the carbazole ring of PEPC, the interaction of C_{60}, CuPc and PEPC improves the UV-Vis absorption characteristics, and expanded the active spectral range of C_{60}-CuPc-PEPC from UV to visible region. The expanding of absorption spectra over all the sunlight has good potential for developing the novel photoelectric materials for the solar cell.

Figure 2 UV-Vis absorption spectra of PEPC, CuPc-PEPC and C_{60}-CuPc-PEPC



The photoinduced discharge curves were recorded on a photoconductivity testing instrument made by Zhejiang University. The results are summaried in **Table 1**, where *V*c, *V*r and DDRC are charge voltage, residual voltage, dark attenuation rate, respectively. $T_{1/2}$ is half-life time, which can denote the sensitivity of the photoconductor. Among three samples, pure PEPC has lowest charge voltage, CuPc-PEPC has higher charge voltage, but which exhibits the fastest DDRC, longer half-life time as well as residual voltage. The C_{60}-CuPc-PEPC displays a higher charge voltage, lower DDRC and the shortest half-life time. The facts indicate that C_{60}-CuPc-PEPC has better photoconductivity than PEPC and CuPc-PEPC, and so the fullerene chemical modification can significantly improve the photoconductivity of the polymer. It is well known that the enhanced photoconductivity is attributed to the effect of "charge transfer" between fullerene and parent polymer^{2}. C_{60} is a good electron accepter, and hence can form the charge-transfer complexs with electron donor such as carbazole. When the fullerenes are covalently grafted the pendant carbazole groups of PEPC, they would form the charge transfer complex. In addition, CuPc chemical modification can also improve the photoconductivity of parent PEPC polymer because of the overlap of their π-conjugate systems. Therefore, it can be concluded that the improvement in photoconductivity of C_{60}-CuPc-PEPC is chiefly attributed to the interaction between C_{60}, CuPc and PEPC polymer.

Table 1 Results of photoconductivity measurement

Sample	Vc /V	DDRC /V s^{-1}	$T_{1/2}$ /s	Vr /V
PEPC	249	9	0.71	152
CuPc-PEPC	1270	49	0.71	882
C_{60}- CuPc-PEPC	1220	36	0.31	648

(white light and exposure light of 2500 lux)

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References

1. Y. Wang, *Nature,* **1992,** *356,* 585.
2. Y. Wang, A. Suna, *J. Phys. Chem. B,* **1997,** *101,* 5627.
3. Y. Wang, R. West, C. H. Yuan, *J. Am. Chem. Soc.,* **1993**, *115,* 3844.
4. K. G. Kepler, P. A. Gahill, *Appl. Phys. Lett.,* **1993**, *63:* 1552.
5. Z. D. Xu, W. X. Chen, Y. J. Long, Y. Xu, W. Li, M. Wang, *J. Matter. Sci. Lett.,* **1995**, *14,* 1030.
6. Y. Chen, R. F. Cai, Z. E. Huang, X. Bai, B. C. Yu, W. Jin, D. C. Pan, S. T. Wang, *Polym. Bull.,* **1996**, *36,* 203.
7. T. Gu, W. X. Chen, Z. D. Xu, *Polym. Bull.,* **1999**, *42,* 191.
8. H. Z. Chen, M. Wang, L. X. Fang, S. L. Yang, *J. Polym. Sci.,* **1993,** *31,* 1165.
9. H. Z. Chen, M. Wang, L. X. Fang, S. L.Yang, *J. Appl. Polym. Sci.,* **1993**, *43,* 679.
10. T. Suzuki, Q. Li, K.C. Khemani, F. Wudl, *J. Am. Chem. Soc.,* **1992,** *114,* 7301.
11. G. V. Grazulevicius, R. Kublickas, *Eur. Polym.,* **1991**, *27,* 1411.

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