Photoconductivity of 1,2-(1',1',2',2'-Tetracyanomethanoxymethano)[60]fullerene-Doped PVK

FENGYING LI, YULIANG LI, ZHIXIN GUO, CHENFENG LONG, FENGLIAN BAI, DAOBEN ZHU

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 4 May 1998; accepted 5 June 1998

ABSTRACT: 1,2-(1',1',2',2'-Tetracyanomethanoxymethano)[60]fullerene, a derivative of C_{60} , is a better electron acceptor than the parent C_{60} . The film of PVK doped with 1.6 wt % of this derivative was prepared and characterized. The micromorphology of the film was studied by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). The photoinduced discharge curves and photoconduction spectra of the films were measured. The results showed that PVK doped with the C_{60} derivative displayed more photoconductivity than that of PVK doped with pure C_{60} or a mixture of C_{60} and C_{70} . © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 209–213, 1999

Key words: fullerene, poly(N-vinylcarbazole); photoconductivity; CV; TEM

INTRODUCTION

Fullerenes, in particular the readily available C_{60} , possess a wide range of physical and chemical properties that make them interesting as building blocks for superconductors, photoconductors, semiconductors, ferromagnetic, and new materials.¹⁻⁵ Fullerenes are known to be good electron acceptors. In the presence of electron donors such as aromatic amines, TDAE, tetrathiafulvalene derivatives, and some polymers (PPV, PVK), weakly bonded charge–transfer complexes can be formed.⁶⁻¹² Through the interaction of charge–transfer, the formation of a complex and the stacking form, such as molecules, can exhibit some special optic, electronic, and magnetic properties.

PVK has been investigated extensively due to its photoconductivity after doping, the charge– transfer complex formation with acceptors, and

carrier transport properties, and several publications have illustrated strong interest in its photo-conductive properties. $^{13-17}$ The $\rm C_{60}$ moiety has been found to be a good electron acceptor in photoinduced intramolecular processes such as electron transfer and energy transfer when illuminated by light. Wang¹³ first reported the preparation of photoconducting films of PVK doped with a mixture of C₆₀ and C₇₀ through a liquid phase mechanical mixing and found fullerenes could be doped into PVK to enhance its chargegeneration efficiency. So far, only the photoconductivity of pure C₆₀ and mixtures of C₆₀ and C₇₀ doped into different polymers have been reported. We are interested in using a C_{60} derivative that possesses stronger electron-accepting ability than C₆₀ to dope PVK in an effort to show a new photoconductive phenomenon.

Recently, a C_{60} derivative (TCNEO- C_{60}) was synthesized by N. Jagerovic et al.,¹⁸ as shown in Scheme 1. The compound has two couples of an acceptor CN group. We employed cyclic voltammetry (CV) to study the electrochemical properties of TCNEO- C_{60} , and found that TCNEO- C_{60} exhibited stronger electron-accepting ability than the parent C_{60} . Therefore, we suggested that the

Correspondence to: Y. Li.

Contract grant sponsor: National Natural Science Foundation of China.

Journal of Applied Polymer Science, Vol. 72, 209-213 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/020209-05



photoconductivity of TCNEO- C_{60} -doped PVK could be much better than that of pure C_{60} and a mixture of C_{60} and C_{70} doped into PVK. The photoconductivity of TCNEO- C_{60} -doped PVK has been studied. In fact, it was found that the films of PVK doped with the derivative (TCNEO- C_{60}) showed higher photoconductivity than that of PVK doped with C_{60} . The result indicates that increasing electron-accepting ability of fullerenes is a key factor in the improvement of photoconductivity of polymers doped with fullerenes.

EXPERIMENTAL

Preparation of TCNEO-C₆₀

A mixture of TCNEO and C_{60} (1 : 1 molar equiv.) in dry toluene was stirred and refluxed under an atmosphere of nitrogen for 15 h. Then the solution was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, petroleum ether: chloroform = 2 : 1), yielding 38% of the monoadduct (TCNEO-C₆₀). The FD-mass spectrum shows a peak at 865 (relative intensity 100%, [M + H]⁺) and the peak for fullerene at 721 (relative intensity 9%, [C₆₀ + H]⁺). The FTIR exhibits a typical absorption band at 2245 cm⁻¹ for the CN group.

Cyclic voltammetry (CV) was carried out with an electrochemical instrument consisting of an EG&G Par Model 175 Universal Programmer and Model 174A polarographic analyzer. Absorption spectrum measurement was carried out utilizing a diode-array spectrophotometer HP8452A.

The Photoconductivities of the Samples

PVK and PVK doped with 1.6 wt % TCNEO- C_{60} were measured using the standard photoinduced discharge method on an Electrostatic Paper Analyzer Model sp-428. A Tungsten lamp (30 W) was used as the light source. The light intensity used was 400 lx. The sample film, deposited on an

electrically grounded aluminum substrate, was first corona charged (positively or negatively) in the dark. The amount of surface charge was detected by an electrostatic voltmeter. On exposure to light, the photogenerated electrons and holes migrated to the surface, and discharged the surface potential. This photo-induced discharge process is the basis of Xerography.

Photoconduction Spectra

By casting the toluene solution (1.6 wt % TCNEO-C₆₀-doped PVK) on an ITO (In-Sn Oxide)-coated glass substrate, thin films were prepared. The films were dried in vacuum at 100°C for 2 h. Finally, an Al electrode was vacuum deposited on top of the films. Photoconduction spectra were recorded on combined units of an HITACHI MPF-4 Fluorescence Spectrophotometer and TR8651 Electrometer. The light source was a 150-W Xe lamp. For the spectral response measurement of photoconductivity, the excitation monochromator of MPF-4 was used to disperse light.

TEM

Photoconducting films of PVK doped with 1.6 wt % TCNEO-C₆₀ were exposed to vapor of 0.5 wt % aqueous solution of RuO₄ for 2–3 h at room temperature.¹⁹ It was found that the film-covered grids were darkened slightly, indicating that ruthenium tetraoxide attacked the aromatic moieties in PVK and TCNEO-C₆₀. Electron micrographs were taken with a Hitachi H-800 electron microscope at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

The electrochemical properties of TCNEO- C_{60} were studied by cyclic voltammetry (CV).²⁰ As shown in Figure 1, the half-wave potentials of the product contain three reduction steps (-0.44V, -0.97V, -1.42V vs. SCE) in CH₂Cl₂ with 0.1*M* TBAPF₆ as the supporting electrolyte, while those of C₆₀ are (-0.61V, -1.02V, -1.46V vs. SCE) under the same conditions. The second reduction peak (II) splits into two separate peaks, IIa and IIb. The reason may be that 1a(TCNEO-C₆₀) is reduced to 1a⁻, undergoing a structure change in the sense of isomerization to 1a⁻ and 1b⁻,²¹ which are further reduced at different potentials. Significantly, the first three reduction



Figure 1 The CVs of C_{60} and 1a (TCNEO- C_{60}) in CH_2Cl_2 containing 0.1 mol \cdot L^{-1} TBAPF_6, scan rate: 50 mV \cdot s^{-1}.

peak potentials of TCNEO- C_{60} are positively shifted 170, 50, and 40 mV, respectively, compared with those of C_{60} , reflecting its stronger electron-accepting ability than the parent C_{60} .

The photoinduced discharge curves of pure PVK and PVK doped with 1.6 wt % TCNEO-C₆₀ are shown in Figure 2. As shown in this figure, pure PVK does not show any detectable surface discharge upon illumination with a Tungsten lamp due to its low charge–generation efficiency.



Figure 2 A qualitative comparison of photoinduced discharge curves of a 6.5- μ m-thick PVK film and a 5.9- μ m-thick TCNEO-C₆₀ doped PVK film under the same experimental conditions. A Tungsten lamp (30 W) is used as the light source. The light intensity used is 400 lx.



Figure 3 Photoconduction spectra of a TCNEO- C_{60} -doped PVK film (2.16 μ m): up triangles for positive bias, and circles for negative bias. The field strength is 3×10^{6} V/cm; active area of the cells: 0.12 cm². Absorption spectrum for a 1.9- μ m-thick film is shown for comparison (solid line).

However, it exhibits a remarkable improvement in photosensitivity when doped with 1.6 wt % TCNEO-C₆₀. The photoinduced discharge process is much faster and more complete than that of undoped material and materials of using pure C₆₀ or a mixture of C₆₀ and C₇₀-doped PVK.^{13,22} Together with the low dark conductivity, it possesses three of the most important criteria for electrophotographic applications.

Figure 3 shows the photoconduction spectra of Al/PVK: TCNEO-C₆₀/ITO under both positive and negative bias. The term "positive bias" means that the positive voltage is applied to the ITO electrode. Also displayed is the optical absorption spectrum of the film. As shown in this figure, a larger photocurrent under a more positive bias than that under a negative bias is observed. The photoconduction spectra essentially follow the absorption spectrum, indicating that TCNEO-C₆₀ is the light absorber and functions as the sensitizer for photoconductivity, and it is responsible for the charge generation. However, in the strongly absorbing wavelengths, carriers are generated near the surface and have to migrate through the whole thickness of the PVK polymer film, the result showing that only holes can achieve this. The fact that a larger photocurrent under positive

bias than that under negative bias is observed should be interpreted in terms of photoinduced charge transfer between TCNEO-C₆₀ and PVK. In the case of the positive bias condition, the direction of migration of the charged carriers due to the electric field corresponds with the direction of the photoinduced charge separation, resulting in a photocurrent larger than that in negatively biased case.

Photoconductivity is the convolution of photoinduced charge generation and charge transport processes. Because the concentration of TCNEO- C_{60} in PVK (1.6% weight) is well below the percolation threshold, the transport of carriers has to occur through PVK. TCNEO-C₆₀ serves mainly as a sensitizer for photogeneration of charges, as demonstrated by the photoconduction spectra. The most likely site for hole injection in PVK is the carbazole moiety. Transport of holes can then be accomplished by hopping along the pendant groups (i.e., carbazole). PVK is known to be effective hole transport material.²³⁻²⁵ Moreover, TC- $\rm NEO\text{-}C_{60}$ is an electron acceptor, and the carbazole group in PVK is an electron donor, which leads to the formation of a weakly bonded complex between them and enhances the electron transfer from PVK to TCNEO-C₆₀.

TEM and HRTEM have been used to visualize the micromorphological feature of the films of the charge transfer complex between the poly(N-vinylcarbazole) and TCNEO- C_{60} . It was necessary to enhance image contrast for polymeric materials by use of a staining agent due to the low contrasts between structural details. The electron transmission micrograph and high-resolution transmission electron micrograph of the RuO₄stained film are shown in Figure 4(a) and 4(b), from which can be found the microdomains (dark region) embedded in the PVK continuous matrix. The microdomains appear to be striplike (ribbonlike) and connect to form a network structure. The formation striplike microdomains should correspond to the charge-transfer complex between PVK and TCNEO-C₆₀.

PVK is a member of an interesting family of linear vinyl polymer having large bulky pendant groups. It is a very stiff molecule in dilute toluene solution, and low molecular weight PVK is rod-like. Crystal²⁵ reported rod-type PVK single crystal morphology crystallized from 0.5% *p*-xylene solution at 100°C for 48 h, and pointed out that the rod length approximated the expected molecular chain length from molecular weight data. This suggested that PVK in dilute *p*-xylene solution



<u>25nm</u>,

(b)

Figure 4 (a) Transmission electron microscopy of the RuO_4 -stained film (1.6 wt % TCNEO-C₆₀ doped PVK). (b) High-resolution transmission electron microscopy of the RuO_4 -stained film (1.6 wt % TCNEO-C₆₀ doped PVK).

tion was a very stiff molecule, perhaps in a rod conformation, because of a steric hindrance effect from the bulky pendant groups and possible resultant barriers to rotation.

The planar pendant carbazol groups lie close to and parallel to one another, and could result in charge-transfer interactions with tetracyano methanoxy groups in TCNEO- C_{60} .

This research is supported by the National Natural Science Foundation of China. We wish to thank Prof. D. Y. Ren for technical assistance and helpful discussion.

REFERENCES

- Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. Nature 1991, 350, 600.
- Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. Nature 1991, 352, 222.
- Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. Science 1991, 253, 301.
- Li, Y. L.; Mao, Z.; Xu, J. H.; Yang, J. K.; Guo, Z. X.; Zhu, D. B.; Li, J. W.; Yin, B. Chem Phys Lett 1997, 265, 361.
- 5. Imahori, H.; Sakata, Y. Adv Mater 1997, 9, 537.
- Li, Y.; Gao, Y.; Wu, Z.; Bai, F.; Li, Y.; Mo, Y.; Zhang, B.; Han, H.; Zhu, D. Synth Met 1995, 70, 1459.
- Izuoka, A.; Tachikawa, T.; Sagawara, T.; Suzuki, Y.; Konno, M.; Saito, Y.; Shinchara, H. J Chem Soc Chem Commun 1992, 1472.
- 8. Zhang, B.; Li, Y.; Zhu, D. Synth Met 1995, 70, 1483.
- Kobayashi, H.; Tomita, H.; Moriyama, H.; Kobayashi, A.; Watamabe, T. J Am Chem Soc 1994, 116, 3153.
- Li, Y.; Xu, Y.; Liu, S.; Wu, Z.; Zhu, D. Solid State Commun 1993, 86, 745.
- Stephens, P. W.; Cox, D.; Laug-her, J. W.; Mihaly, L.; Wiley, J. B.; Allemand, P.-M.; Hirsch, A.; Holc-

zer, K.; Li, Q.; Thompson, J. D.; Wudl, F. Nature 1992, 355, 331.

- Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. Science 1992, 258, 1474.
- 13. Wang, Y. Nature 1992, 356, 585.
- Wang, Y.; West, R.; Yuan, C. H. J Am Chem Soc 1993, 115, 3844.
- Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789.
- Watanabe, A.; Ito, O. J Chem Soc Chem Commun 1994, 1285.
- 17. Wang, Y.; Suna, A. J Phys Chem B 1997, 101, 5627.
- Jagerovic, N.; Elguero, J.; Aubagnac, J.-L. J Chem Soc Perkin Trans 1996, 1, 499.
- Trent, J. S.; Scheinbeim, J. I.; Couchman, P. R. Macromolecules 1983, 16, 589.
- 20. Fan, L. Z.; Li, Y. F.; Li, F. Y.; Li, Y. L.; Zhu, D. B. Chin Chem Lett to appear.
- Zhou, J.; Rieker, A.; Gresser, T.; Skiebe, A.; Hirsch, A. J Chem Soc Perkin Trans 2 1997, 2, 1.
- Chen, Y.; Huang, Z.; Cai, R.; Fan, D.; Hou, X.; Yan, X.; Chen, M.; Jin, W.; Pan, D.; Wang, S. J Appl Polym Sci 1996, 61, 2185.
- Regensburger, P. J. Photochem Photobiol 1968, 8, 429.
- 24. Melz, P. J. J Chem Phys 1972, 57, 1694.
- 25. Pfister, G.; Williams, D. J. J Chem Phys 1974, 61, 2416.
- 26. Crystal, R. G. Macromolecules 1971, 4, 379.