

# Preparation and Photoconducting Property of $C_{60}Cl_{n-m}$ -Bonded Poly(N-vinylcarbazole) with $C_{60}Cl_n/CuCl/Bpy$ Catalyst System

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**ABSTRACT:**  $C_{60}Cl_{n-m}$  bonded poly(N-vinylcarbazole) ( $C_{60}$ -PVK) has been synthesized by  $C_{60}Cl_n$  (the average value of  $n$  is 20)/CuCl/Bpy (2,2'-bipyridine) catalyst system and its structure was analyzed by UV-Vis and proton NMR. The polymerization mechanism was proposed proceeding via a atom transfer radical polymerization (ATRP). The block copolymer of poly N-vinylcarbazole-*block*-poly-

styrene can also be compounded by adding styrene after N-vinylcarbazole polymerized completely in this polymerization system. The photoconducting properties of  $C_{60}Cl_{n-m}$ -bonded poly(N-vinylcarbazole) was better than poly(N-vinylcarbazole) initiated by AIBN. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 606–609, 2003

## INTRODUCTION

Fullerene ( $C_{60}$ ) and its  $n$ -doped derivatives exhibit a variety of outstanding electronic, conducting, and magnetic properties due to its unusual structure and extended  $\pi$ -electron system.<sup>1</sup> A number of attempts resulted in polymeric  $C_{60}$  derivatives<sup>2</sup> especially functional photoelectrical 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>3–6</sup> In recent years, the enhancement of the photoconductivity of poly(N-vinylcarbazole) (PVK, electron donor) film by doping with fullerene ( $C_{60}$ , electron acceptor,  $EA = 2.6$ – $2.8$  eV) has been reported by Wang et al.<sup>7</sup> Surface-substituted and homogeneous fullerenated PVK were produced by bromination followed by a Friedel-Crafts reaction.<sup>8</sup> Chen et al.<sup>9–12</sup> have reported on the synthesis of “charm bracelet”-type  $C_{60}$ -modified PVK and its bromine- and iodine-modified derivatives, and described the results of an investigation into their electrochemical behaviors and the effect of  $C_{60}$  chemical modifi-

cation on the structure and photoconductivity of the organic polymers. They also prepared a star-shaped  $C_{60}H_xBTPVK_x$  copolymer<sup>13</sup> by addition of “living”  $n$ -butyl-terminated poly(N-vinylcarbazole) onto  $C_{60}$  in the heterogeneous medium.

Our attempt is to incorporate  $C_{60}$  into PVK by atom transfer radical polymerization (ATRP)<sup>14</sup> of N-vinylcarbazole initiated by  $C_{60}Cl_n/CuCl/2,2'$ -Bpy in our laboratory. In this condition, every polymeric chain has been bonded  $C_{60}$  by one step and the production can be a star-shaped polymer, because of multiple Cl atoms in one initiator molecular,  $C_{60}Cl_n$ . This may be a new and promising way to produce a star-shaped poly(N-vinylcarbazole) with a  $C_{60}$  core that has predictable average molecular weights (e.g.,  $M_n$ ) and narrow polydispersity indices (PDI). Herein we will report the results of this initiation system.

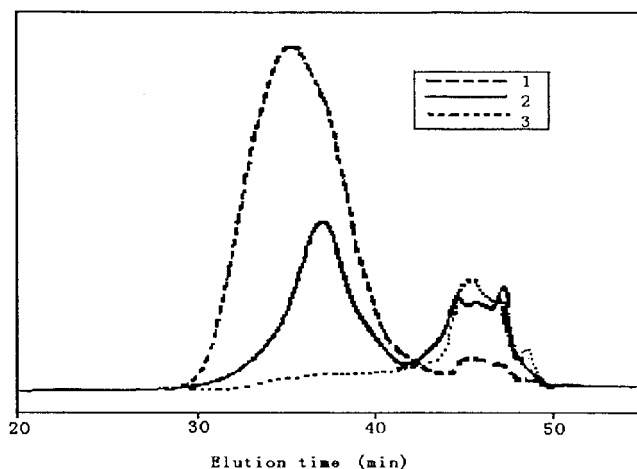
## EXPERIMENTAL

### Materials

N-vinylcarbazole was recrystallized twice from methanol at 40°C, vacuum dried, and stored *in vacuo* in the dark. Copper (I) chloride was purified by washing with acetic acid, acetone, methanol, respectively, and then drying under vacuum. 2,2'-Bipyridine was used as received. Toluene was purified by refluxing over metal sodium in nitrogen atmosphere.  $C_{60}Cl_n$  was synthesized according to ref 15 by our own lab. The value of  $n$  was decided by elementary analysis and

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**Figure 1** The GPC curves of PVK. (1) Ordinary polymerization catalyst system. AIBN : [VK] = 1 : 100,  $T = 130^{\circ}\text{C}$ . (2) C<sub>60</sub>Cl<sub>n</sub>/CuCl/ Bpy initiator system. (3) Therm-polymerization,  $T = 130^{\circ}\text{C}$ .

weight method. The absolute value of  $n$  cannot be decided by mass spectra by FAB (fast atom bombardment), because even under these mild ionization conditions, C<sub>60</sub>Cl<sub>n</sub> lose chlorine, only peak due to the C<sub>60</sub> was observed.

### Polymerization of n-vinylcarbazole

N-vinylcarbazole polymerization was carried out in a 10-mL flask sealed with a rubber plug in an ampule and degassed on a vacuum line. The flask was filled with stoichiometric quantities of N-vinylcarbazole, C<sub>60</sub>Cl<sub>n</sub>, 2,2'-bipyridine (Bpy), CuCl, and then degassed to remove oxygen. Degassed toluene was added using a syringe. The polymerization was carried out in an oil bath at  $130^{\circ}\text{C}$ . The reaction mixture was cooled to room temperature and diluted with THF. The solution was then passed over alumina to remove copper complex, then PVK was recovered by precipitation in hexane and the precipitation was extracted with hexane for 24 h to remove the unreacted N-vinylcarbazole and C<sub>60</sub>Cl<sub>n</sub> then pumped overnight in a vacuum oven. The yields were calculated from the weight of recovered polymers.

### Analysis

The  $M_{n,GPC}$  of polystyrenes were measured by gel permeation chromatography (GPC) with a SHIMADZH system composed of a set of KF-1,KF-2,KF-3,KF-4,KF-6 microstyragel columns and a refractometer detector system in tetrahydrofuran with polystyrene standard calibration.

UV/Vis spectra were obtained in THF using a SHIMADZH spectrophotometer.

<sup>1</sup>H-nuclear magnetic resonance (NMR) spectra were taken with an AL-spectrometer 300 MHz, FT-NMR systems-JEOL spectrometer in CDCl<sub>3</sub>, using tetramethylsilane as internal reference.

The photoconductivity measure was according to ref 16.

## RESULTS AND DISCUSSION

N-vinylcarbazole (VK) was polymerized at  $130^{\circ}\text{C}$  in toluene using 1/20 : 1 : 2 C<sub>60</sub>Cl<sub>n</sub> : CuCl : 2,2'-bipyridine(Bpy) and [vk] : [CuCl] = 40 : 1. The conversion of the monomer exceeded 98% after polymerizing for 20 h. The product's color was reddish-brown. The Gel-permeation chromatography (GPC) curves of PVK initiated by the three initiator systems, azobisisobutyronitrile (AIBN), C<sub>60</sub>Cl<sub>n</sub>/CuCl/Bpy, and therm-polymerization were shown in Figure 1. The peak molecular weights of these products and their conversion were summarized in Table I. From the GPC curve 2 we can find that about 43% (wt %) PVK in GPC curve 2 (the second peak) was therm polymerization which GPC curve was similar to curve 3. The DPI of the first peak in GPC curve 2 was 1.33. This part of PVK may be the product of ATRP initiated by C<sub>60</sub>Cl<sub>n</sub>/CuCl/Bpy, because of the small value of DPI. Partly crosslinking C<sub>60</sub> bonded poly(N-vinylcarbazole) has been synthesized only in present of C<sub>60</sub>Cl<sub>n</sub> in  $120^{\circ}\text{C}$ .

The PVK samples can be easily dissolved in tetrahydrofuran (THF). The THF solution of PVK-C<sub>60</sub> is reddish-brown. Figure 2 depicts the UV spectra of PVK by therm polymerization and C<sub>60</sub>-PVK (a and b). The absorption peak of pure PVK occurs at 259.0, 292.0, 327.0, and 340.0 nm, while those of C<sub>60</sub>-PVK

**TABLE I**  
The Polymerization of the N-Vinylcarbazole

Initiator System	Therm-Polymerization	Radical Polymerization <sup>a</sup>	C <sub>60</sub> Cl <sub>n</sub> CuCl/Bpy <sup>b</sup>
Conversion (%)	43.0	88.1	98.1
DPI	2.86	3.73	1.33
$M_n$	367	7064	9972

[vk] = 0.25g/ml, solution: toluene a: AIBN:[M] = 1:100; b: The first peak value of C<sub>60</sub>Cl<sub>n</sub> initiator system's GPC curve

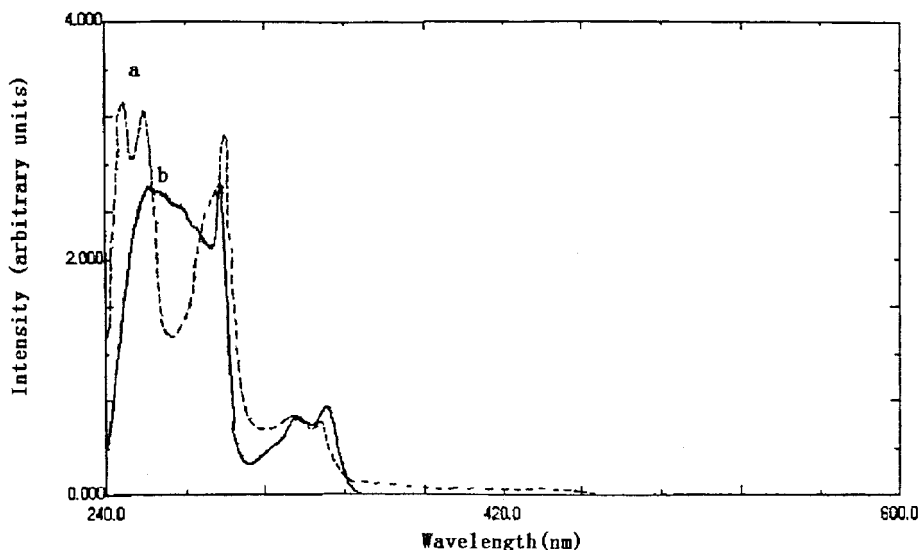


Figure 2 UV-visible absorption spectra of the samples. (a) PVK, (b) C<sub>60</sub>-PVK.

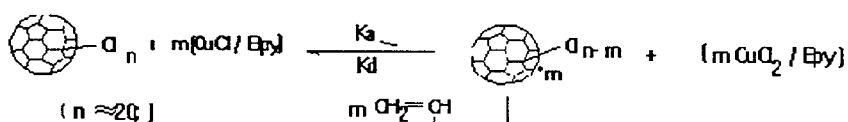
appear at 248.0, 257.5, 293.5, 323.5, and 336.5 nm. Although the absorption spectrum of C<sub>60</sub>-PVK is similar to that of the pure PVK reference, their relatively peak intensities are very different. For the same reason, the covalent attachment of multiple PVK arms onto the C<sub>60</sub> core also results in the enhancement of the absorption degree at longer wavelengths. This result shows that it is true that C<sub>60</sub>Cl<sub>n</sub> has initiated the

polymerization of N-vinylcarbazole and bonded in PVK chains.

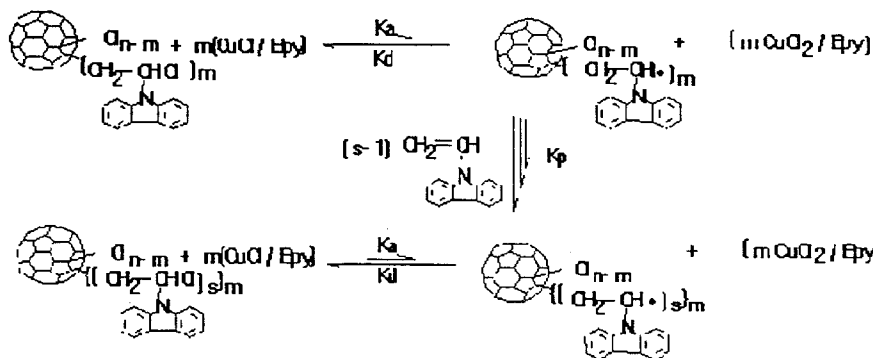
In Figure 3 of <sup>1</sup>H-NMR of C<sub>60</sub>-PVK, the signal of g at 4.3 ppm is responding to the one end group, that is, CH<sub>2</sub>C-(carbazole)H-Cl, so an ω-chlorine atom is an end group.

So, the mechanism of the preparation of the C<sub>60</sub>-PVK might be deduced tentatively as shown in the following schematic illustration.

#### [1] Initiate



#### [2] Propagate



To examine the living nature of the polymerization with the C<sub>60</sub>Cl<sub>n</sub>/CuCl/Bpy catalyst system, a fresh feed of styrene was added to the reaction mixture when the initial N-vinylcarbazole monomer was almost consumed (90% conversion in 20 h). The first peak in GPC curve shift to the left (Fig. 4),

which indicated that the *M<sub>n</sub>* of polymers continued to increase during the second phase, which also verified a "living" nature of the polymerization.

Figure 5 shows the photoinduced discharge curve (PIDC) of P/R from PVK (initiated by AIBN), C<sub>60</sub>-

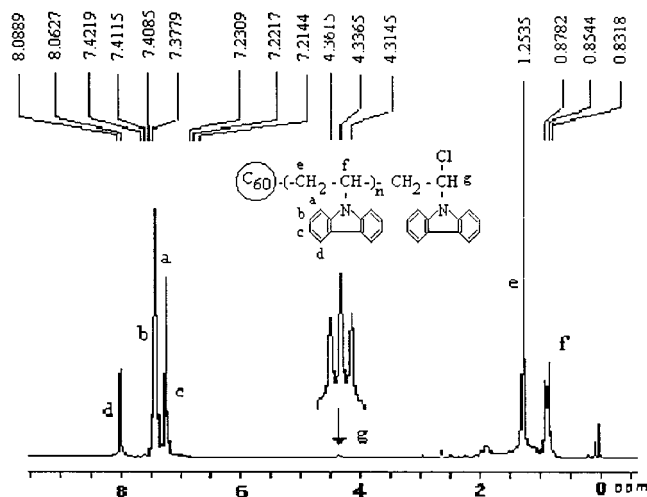


Figure 3 The <sup>1</sup>H-NMR C<sub>60</sub>-PVK.

PVK. We note that C<sub>60</sub>-PVK exhibit a higher charge acceptance ( $V_0 = 1300$ ) than pure PVK ( $V_0 = 1200$ ) and C<sub>60</sub>-PVK has a shorter  $t_{1/2}$  (0.71 s) than pure PVK (0.89s). So C<sub>60</sub>Cl<sub>n-m</sub> bonded PVK exhibits better photoconductivity than pure PVK.

However, this article only presents a preliminary result about the photoconductivity of this polymer; more detailed work is needed.

### CONCLUSION

In conclusion, chemically bonded C<sub>60</sub>Cl<sub>n</sub> in the main chain of PVK was successfully obtained by a reaction of living radical polymerization initiated by C<sub>60</sub>Cl<sub>n</sub>/Bpy/CuCl. The block copolymer of poly N-vinylcarbazole-block-polystyrene can also be compounded by adding styrene after N-vinylcarbazole polymerized completely in this polymerization system. This C<sub>60</sub>-PVK derivative

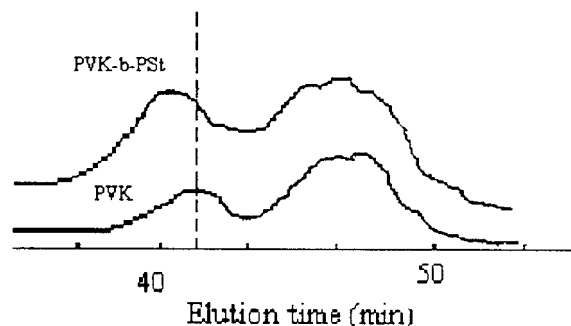


Figure 4 Monomer-addition experiment for polymerization of St with C<sub>60</sub>Cl<sub>n</sub> : CuCl : Bpy in toluene at 120°C.

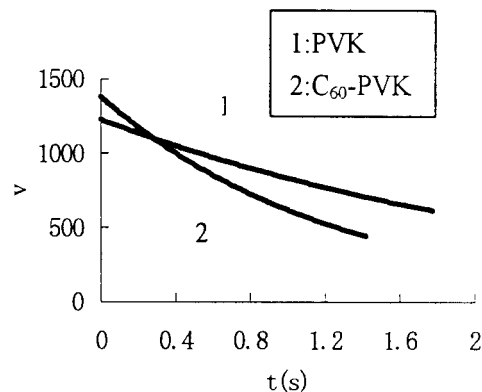


Figure 5 The photoconductivity of pvk and 060-bonded PVK.

exhibits good photoconductivity. Further study is also being performed now in our laboratory.

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