

## Preparation of C<sub>60</sub> bonded Poly(N-vinylcarbazole) with C<sub>60</sub>Cl<sub>n</sub>/CuCl/Bpy catalyst system

Hua Jing<sup>1</sup>, Chen Dianbao<sup>2</sup>(✉), Yu Yongliang<sup>2</sup>, Xu Ling<sup>2</sup>, Zhang Yifeng<sup>1</sup>, Jing Xiongke<sup>3</sup>, Wu Aiqin<sup>c</sup>, Shi Lei<sup>3</sup>

<sup>1</sup> Institute of Polymer Science, Zhe Jiang University, P.R.China 310027

<sup>2</sup> Department of Polymer Science and Engineering, Qingdao Institute of Chemical Technology, P.R. China 266042

Tel.:+86-532-402-2926, Fax:+86-532-485-6613, e-mail: chendian@public.qd.sd.cn

<sup>3</sup> Qingdao DIC Fine Chemical Co. LTD., P.R. China 266101

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### Summary

C<sub>60</sub> bonded poly(N-vinylcarbazole) has been synthesized by C<sub>60</sub>Cl<sub>n</sub> (the average value of n is 20)/CuCl/2,2'-bipyridine (Bpy) catalyst system and its structure was analyzed by UV-Vis and proton NMR. The polymerization mechanism was proposed proceeding via an atom transfer radical polymerization (ATRP). The photoconducting properties of C<sub>60</sub> bonded poly(N-vinylcarbazole) was better than poly(N-vinylcarbazole) initiated by AIBN.

### Introduction

Fullerene(C<sub>60</sub>) 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 lot of attempts resulted in polymeric C<sub>60</sub> 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<sub>60</sub>°C 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<sub>60</sub>-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<sub>60</sub>-chemical modification on the structure and photoconductivity of the organic polymers. They also prepared a star-shaped C<sub>60</sub>H<sub>x</sub>BTPVK<sub>x</sub> copolymer<sup>[13]</sup> by addition of “living” n-butyl-terminated poly(N-vinylcarbazole) onto C<sub>60</sub> in the heterogeneous medium.

Our attempt is to incorporate  $C_{60}$  into PVK by atom transfer radical polymerization(ATRP) 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 star-shaped polymer, because of multiple Cl atom 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 which has predictable average molecular weights (e.g. Mn) and narrow polydispersity indices (PDI) . Herein we will report the preliminary 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<sup>[15]</sup> by our own lab. The value of n was decided by elementary analysis and weight method. The absolute value of n can not be decided by mass spectra by FAB (fast atom bombardment), because even under these mild ionization conditions,  $C_{60}Cl_n$  lose chlorine, only peak due to the  $C_{60}$  was observed.

### *Polymerization Procedure*

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, 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°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 hours to remove the unreacted N-vinylcarbazole and  $C_{60}Cl_n$  then pumped overnight in a vacuum oven. The yields were calculated from the weight of recovered polymers.

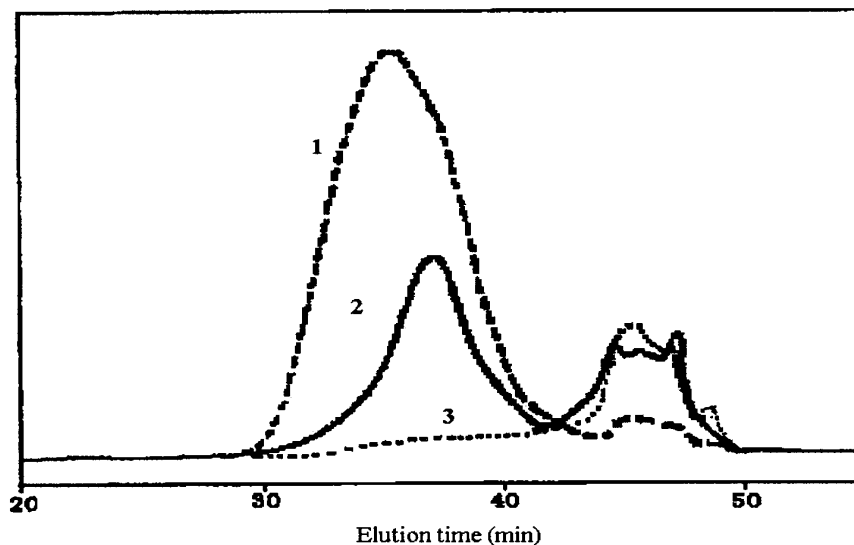
## Characterization

The  $M_{n,GPC}$  of polystyrenes were measured by gel permeation chromatography(GPC) with a SHIMADZU 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

SHIMADZU spectrophotometer.  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectra were taken with an AL-spectrometer 300MHz, FT-NMR systems-Jeol spectrometer in  $\text{CDCl}_3$ , using tetramethylsilane as internal reference. The photoconductivity measurement was according to Ref<sup>[16]</sup>.

## Results and discussion

N-Vinylcarbazole (VK) was polymerized at  $130^\circ\text{C}$  in toluene using 1/20:1:2  $\text{C}_{60}\text{Cln}:\text{CuCl}:2,2'$ -bipyridine(Bpy) and  $[\text{vk}]:[\text{CuCl}]=40:1$ . The conversion of the monomer exceeded 98% after polymerizing for 20 hours. The product's color was reddish-brown. The Gel-permeation chromatography (GPC) curves of PVK initiated by the three initiator systems, azobisisobutyronitrile (AIBN),  $\text{C}_{60}\text{Cln}/\text{CuCl}/\text{Bpy}$  and therm-polymerization, were shown in Figure1. The peak molecular weights of these products and their conversion were summarized in Tab.1. From figure 1 we can find that about 43% (wt%) PVK in GPC curve 2 (the second peak)



**Fig.1** GPC curves of PVK with different catalyst system 1,ordinary polymerization catalyst system. AIBN:[VK]=1:100,T= $130^\circ\text{C}$  2,  $\text{C}_{60}\text{Cln}/\text{CuCl}/\text{Bpy}$  initiator system 3, therm-polymerization, T= $130^\circ\text{C}$

was therm polymerization which GPC curve was similar to the curve 3. The DPI of the first peak in GPC curve2 was 1.33. This part of PVK might be the product of ATRP initiated by  $\text{C}_{60}\text{Cln}/\text{CuCl}/\text{Bpy}$ , because of the small value of DPI. After-N-Vinylcarbazole polymerized completely, by adding methymethacrylate the copolymer

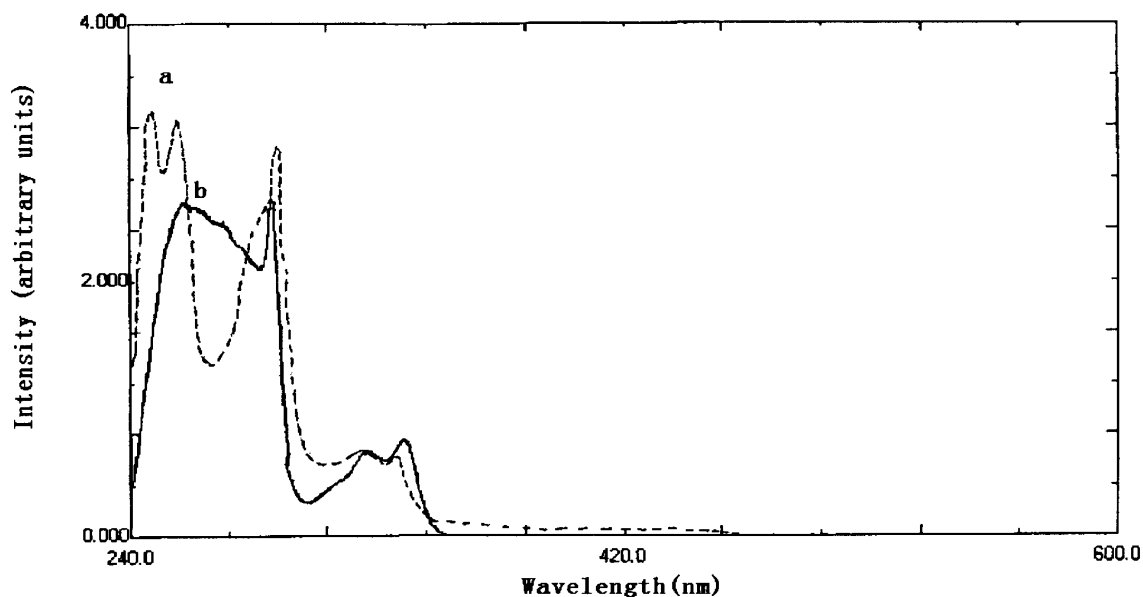
of poly N-Vinylcarbazole -block-polymethylmethacrylate can also be compounded. Which also verified a “living” nature of the polymerization. The PVK samples can be easily dissolved in tetrahydrofuran(THF). The THF solution of PVK- $C_{60}$  is reddish brown. Fig.2 depicts the UV spectra of PVK by therm polymerization and  $C_{60}$ - PVK (a and b). The absorption peak of pure PVK occurs at 259.0,292.0,327.0

**Table 1** The polymerization of the N-vinylcarbazole

Initiator System	Therm-polymerization	Radical Polymerization <sup>a</sup>	$C_{60}Cl_n/CuCl/Bpy$ <sup>b</sup>
Conversion(%)	43.0	88.1	98.1
DPI	2.86	3.73	1.33
$M_n$	367	7064	9972

<sup>a</sup> [vk]=0.25g/ml , solution: toluene a:AIBN:[M]=1:100;

<sup>b</sup> The first peak value of  $C_{60}Cl_n$  initiator system's GPC curve



**Fig.2** UV-visible absorption spectra of the samples (a)PVK , (b) $C_{60}$ -PVK

and 340.0nm, while those of  $C_{60}$ -PVK appear at 248.0,257.5,293.5,323.5 and 336.5nm. Although the absorption spectrum of  $C_{60}$ -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  $C_{60}$  core also results in the

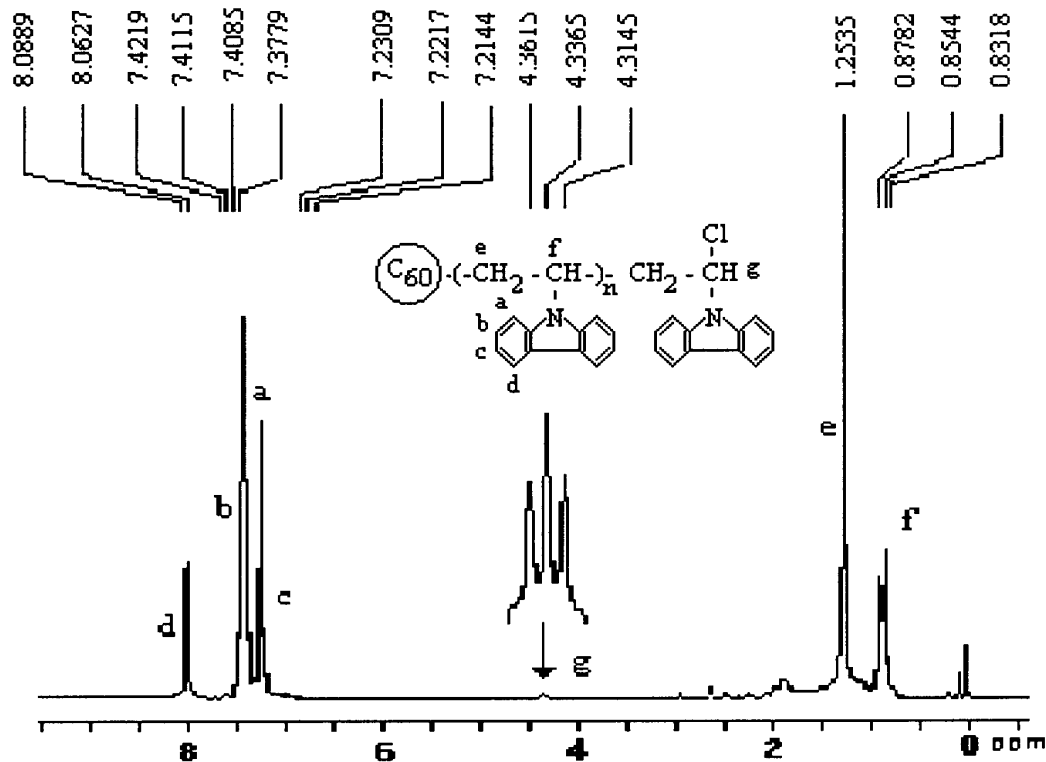


Fig. 3 The  $^1\text{H-NMR}$   $\text{C}_{60}$ -PVK

enhancement of the absorption degree at longer wavelengths. This result shows that it is true that  $\text{C}_{60}\text{Cln}$  has initiated the polymerization of N-vinylcarbazole and bonded in PVK chains.

In Figure 3 of  $^1\text{H-NMR}$  of  $\text{C}_{60}$ -PVK, the signal of g at 4.3 ppm is responding to the one end group, that is,  $\text{CH}_2\text{C}(\text{carbazole})\text{H-Cl}$ , so an  $\omega$ -chlorine atom is an end group. The result combines with the mechanism of ATRP.

So, the mechanism of the preparation of the  $\text{C}_{60}$ -PVK might be deduced tentatively as shown in the following schematic illustration.

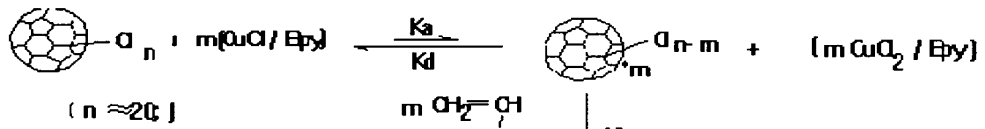
Figure 4 shows the photoinduced discharge curve (PIDC) of P/R from PVK (initiated by AIBN), PVK- $\text{C}_{60}$ . We note that PVK- $\text{C}_{60}$  exhibit a higher charge acceptance ( $V_0=1300$ ) than pure PVK ( $V_0=1200$ ) and  $\text{C}_{60}$ -PVK has a shorter  $t_{1/2}$  (0.71s) than pure PVK (0.89s). So  $\text{C}_{60}$  bonded PVK exhibits better photoconductivity than pure PVK.

However, this paper only presents a preliminary result, more detailed work is needed.

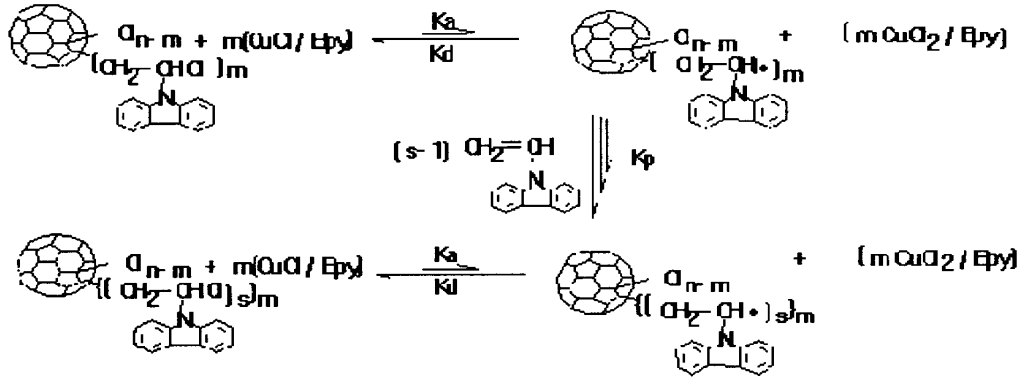
## Conclusion

In conclusion, chemically bonded fullerene  $\text{C}_{60}$  in the main chain of PVK was successfully obtained by a reaction of "living" radical polymerization initiated by  $\text{C}_{60}\text{Cln/Bpy/CuCl}$ . This  $\text{C}_{60}$ -PVK derivative exhibits good photoconductivity. Further study is also being performed now in our laboratory.

[1] Initiate



[2] Propagate



1--PVK  
2--C<sub>60</sub>-PVK

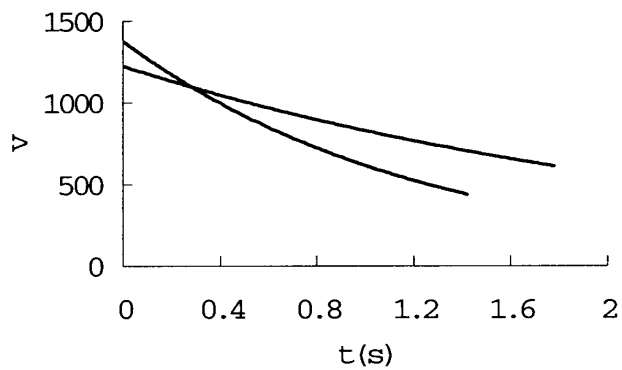


Fig.4 The photoconductivity of pvk and C<sub>60</sub> banded PVK

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