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Development of Carbazole and Bipyridine Copolymers as Novel Photovoltaic Materials

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Summary: A novel acrylate polymer with a carbazole pendant group and bipyridine derivatives as side chains was synthesized, in which derivatives of bipyridine as electro-optic chromophores and carbazole as photoconductive moiety were covalently linked to the acrylate backbone. 2–(Carbazol-9-yl)ethyl methacrylate (CEM) and methacrylic 2-[5-(2-{5,5′-dimethyl-6′-[2-(5-pentylthiophen-2-yl)vinyl]-3,3′-bipyridin-6-yl}vinyl)thiophen-2-yl]ethyl methacrylate (BiPy) were synthesized and then copolymerized to give 99:1, 98:2, 92:8 (mol/mol) CEM/BiPy copolymers. Films of the copolymers blended with poly(3-octylthiophene) (P3OT) or poly(3-decylthiophene) (PDT) and sandwiched between the transparent ITO and Al electrode were examined for photovoltaic properties.

Keywords: bipyridine; carbazole; methacrylates; photovoltaic properties

Introduction

Organic materials have recently attracted interest due to application in photovoltaic solar cells.[1–4] The most widely used design of organic solar cells that exhibit relatively high efficiencies have been reported.[4–7] Out of a number of polymers, poly(*N*-vinylcarbazole), PVK, and other carbazole-containing compounds may play an important role in organic photovoltaic devices owing to their hole-transporting nature; carbazole-based photovoltaic devices have been reported.[8–11] In this context, we were interested in synthesizing the copolymers containing 2-(carbazol-9-yl)ethyl methacrylate (CEM) and 2-[5-(2-{5,5′-dimethyl-6′-[2-(5-pentylthiophen-2-yl)vinyl]-3,3′-bipyridin-6-yl}vinyl)thiophen-2-yl]ethyl methacrylate (BiPy). The synthesis of monomers and their polymerization as well as the properties of the devices are presented.

Experimental Part

Monomer Synthesis

9-(2-Chloroethyl)carbazole (I) was prepared using a modification of the procedure described by Bogdal and Jaskot.[12] A mixture of carbazole (2.5 g, 0.015 mol), potassium hydroxide (8.4 g, 0.15 mol), potassium carbonate (20 g, 0.15 mol), and tetrabutylammonium bromide (TBAB) (0.48 g, 0.0015 mol) was stirred in 1,2-dichloroethane (100 ml) at 45 °C for 5 h. After cooling, the mixture was filtered and the solid was washed with 1,2-dichloroethane. Then, the two organic solutions were combined, washed twice with water (2 × 50 ml), and dried over anhydrous $MgSO_4$. The solvent was evaporated to give a solid, which was recrystallized twice from an ethanol solution to afford 2.5 g of 9-(2-chloroethyl)-carbazole. Yield: 75%, m.p., 129–130.5 °C (Scheme 1).

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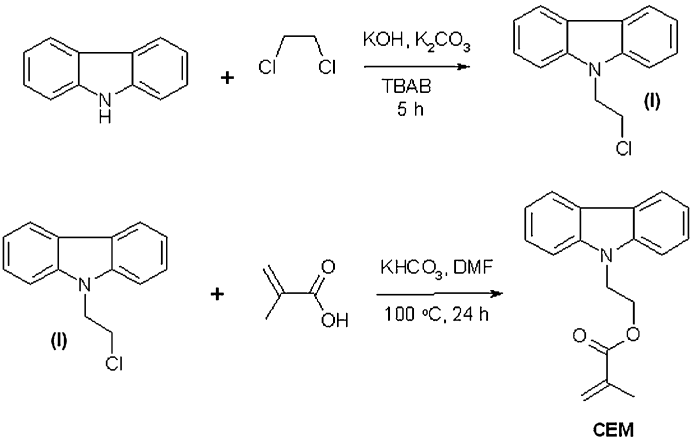


Scheme 1.
The synthesis of 2-(carbazol-9-yl)ethyl methacrylate (CEM).

2-(Carbazol-9-yl)ethyl methacrylate (CEM) was prepared according to the modified procedure described by Nakano et al.[13] Thus, methacrylic acid (1.0 g, 0.012 mol) was stirred with potassium hydrogencarbonate (1.4 g, 0.014 mol) at room temperature for 5 min to form potassium methacrylate. Then, 9-(2-chloroethyl)carbazole (2.3 g, 0.010 mol) and hydroquinone (0.016 g, 0.0015 mol) in a dimethylformamide (DMF) solution (70 ml) were added to the salt and the mixture was stirred at 100 °C for 24 h. The reaction mixture was allowed to cool, and the solvent was evaporated. The resulting solid was dissolved in methylene chloride (80 ml) and poured into water (ca 300 ml). The organic layer was separated, washed with 5% aqueous NaOH and then with water. The organic solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was recrystallized twice from ethanol to afford 2.40 g of CEM. Yield 86%; m.p. 81.5–82.5 °C (Scheme 1).

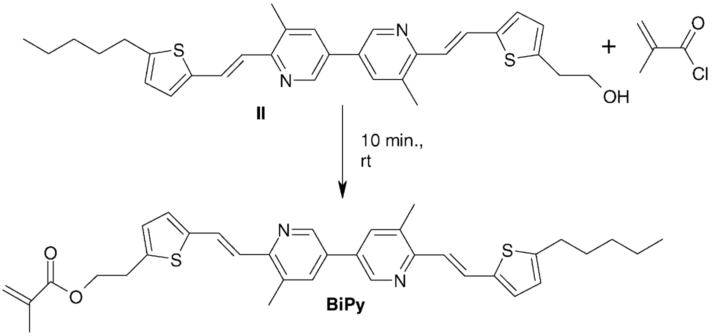
2-[5-(2-{5,5′-dimethyl-6′-[2-(5-pentylthiophen-2-yl)vinyl]-3,3′-bipyridin-6-yl}vinyl)thiophen-2- yl]ethan-1-ol (II), the starting material for the synthesis of BiPy was prepared according to the method given of Attias et al.[14,15]

Methacrylic acid 2-[5-(2-{5,5′-dimethyl-6′-[2-(5-pentylthiophen-2-yl)vinyl]-3,3′-bipyridin-6-yl}vinyl)thiophen-2-yl]ethyl methacrylate (BiPy) was prepared by the method Chen et al.[16] (0.1 g, 0.0004 mol), methacryloyl chloride (0.044 g, 0.0004 mol), and triethylamine (0.043 g, 0.0004 mol) as a catalyst, and 1,2-dichloroethane (10 ml) were stirred for 10 min at room temperature. Yield 89%; m.p. 123–125 °C (Scheme 2).

Polymerization

Preparation of PCEM: A mixture of 2-(carbazol-9-yl)ethyl methacrylate (CEM; 0.2 g) and 2,2′-azobis(2-methylpropanenitrile) (AIBN) (0.01 mol) was dissolved in toluene (10 ml). The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60 °C to initiate polymerization. After 48 h the reaction was terminated by adding THF (15 ml) and the polymer was precipitated into a large amount of methanol. The crude product was several times redissolved in THF and reprecipitated into methanol to afford 0.18 g of PCEM.

Copolymerization of CEM and BiPy: The monomers (total amount 0.2 g) taken in the desired molar ratio were dissolved in toluene (10 ml) together with AIBN (1 mol %). The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60 °C to initiate polymerization. After 48 h the reaction was terminated by adding tetrahydrofuran (THF) (15 ml)



Scheme 2.
The synthesis of 2-[5-(2-{5,5′-dimethyl-6′-[2-(5-pentylthiophen-2-yl)vinyl]-3,3′-bipyridin-6-yl}vinyl)thiophene-2-yl]ethyl methacrylate (BiPy).

Table 1.
Molecular weights of the copolymers of CEM and BiPy.

Polymer/copolymer code	BiPy content [mol %]	M_n	M_w	M_w/M_n
PCEM	0	4 970	11 540	2,32
PCEM1BiPy	1	4 360	8 520	1,95
PCEM2BiPy	2	5 020	10 110	2,01
PCEM8BiPy	8	4 160	8 620	2,07

and the polymer was precipitated into a large amount of methanol. The product was redissolved in THF several times and reprecipitated into methanol (Table 1). The molecular weights of the copolymers were estimated in THF by GPC.

Absorption spectra were obtained in solution with an Ocean Optics spectrometer. Photoluminescent properties were investigated using an Ocean Optics spectrometer with fiber optics. A xenon lamp was used as the source of light.

Results and Discussion

UV-Vis absorption spectra of the copolymers and PCEM solutions are presented in Figure 1. The absorption spectra of copolymers and PCEM are quite similar.

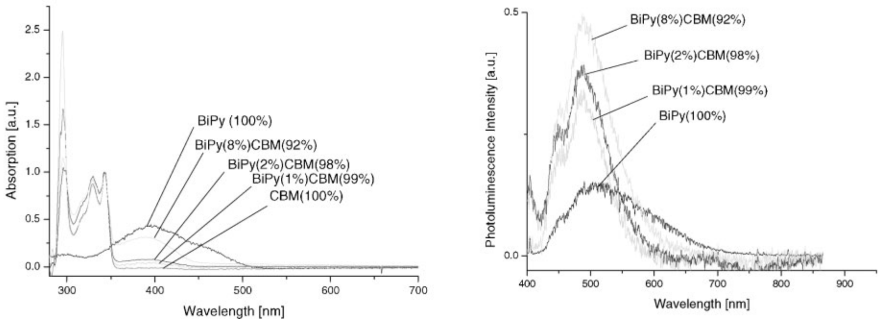


Figure 1.
Absorption spectrum of the copolymers and PCEM and photoluminescence spectrum of the copolymers and PCEM in chloroform solution.

Table 2.
Photovoltaic properties of solar cells with the copolymers as active layers.

Copolymer/polymer[a]	V_{oc}[V]	J_{sc}[A/cm^2]	FF	R_{sh} [Ω]	R_s [Ω]
PCEM1BiPy:P3OT	1.174	-2.98×10^{-6}	0.279	2.69×10^5	1.05×10^5
PCEM1BiPy:PDT	1.270	-2.66×10^{-6}	0.302	8.92×10^5	2.59×10^5
PCEM2BiPy P3OT	1.174	$-2{,}23 \times 10^{-6}$	0.309	5.52×10^5	1.68×10^5
PCEM2BiPy:PDT	0.891	$-1{,}55 \times 10^{-6}$	0.227	9.12×10^6	1.68×10^5
PCEM8BiPy:P3OT	1.074	-6.20×10^{-6}	0.254	2.05×10^5	1.80×10^5
PCEM8BiPy PDT	0.779	-1.22×10^{-7}	0.217	5.17×10^6	2.97×10^7

[a] P3OT – poly(3-octylthiophene); PDT - poly(3-decylthiophene) (Aldrich)

Comparing the spectra of PCEM and BiPy as well as of PCEM1BiPy, PCEM2BiPy, and PCEM8BiPy copolymers, one can observe that the spectra of the copolymers are the sum of PCEM and BiPy monomer spectra depending on the BiPy units content in the copolymer. In the range 360–440 nm there is a clear absorption increase associated with the increase in the molar fraction of the BiPy unit in the copolymer. The absorption is growing linearly when increasing the molar fraction of BiPy.

The photoluminescence spectra recorded in solutions are presented in Figure 1. A profound influence of the BiPy units is observed despite its low content in the copolymers. In solution, photoluminescence spectra of the copolymers can be treated as a sum of the emission spectrum of PCEM and BiPy. A higher content of BiPy in the copolymer causes a clear increase in the emission maximum derived from this group.

The intensity of the photoluminescence in the range 420–600 nm is not proportional to the content of BiPy units, which changes the light emission spectra measured at the excitation wavelength 340 nm (e.g., excitation of the CEM groups). The emission maximum of the BiPy unit in solution is at 490 nm. The position of the emission maximum derived from the BiPy groups does not change.

For the study of photovoltaic properties, we fabricated devices of double-layer structure. Such architecture has two active materials: an electron donor (D) and electron acceptor (A) material. These materials were sandwiched between the transparent electrode ITO and aluminum layer. The thickness of the active layers was ~200–250 nm and the active device area was roughly 0.125 cm^2. The films were obtained from THF solutions of polymer blend by spin-casting at room temperature followed by drying at 40 °C in vacuum for 24 h. Their photovoltaic properties were investigated. The characteristics of the current-voltage (*I–V*) were measured both in the dark and under illumination. The tungsten lamp was used for illumination (1320 μW/cm^2). Characteristic properties of the solar cells are open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and the fill factor FF; R_{sh} and R_s apply to a shunt and series resistor, respectively (Table 2).

The percentage content of the BiPy groups in the copolymer slightly changes the photovoltaic cell characteristics. The observed photovoltaic effect in the cells can be explained in terms of the photoinduced interfacial charge transfer between the copolymer and polymer by taking into account the difference between the electronic states of the copolymer and polymer. The best values of the J_{sc} and V_{oc} parameters were obtained for the PCEM8-BiPy:P3OT cell, which provides a basis for further optimization of this architecture.

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