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Publication details, including instructions for authors and subscription information:
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Version of record first published: 22 Sep 2010

Mol. Cryst. Liq. Cryst., Vol. 484, pp. 335/[701]–344/[710], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801904732

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Synthesis and Polymerisation of Novel Methacrylates with Carbazolyl and Benzofuranyl Pendant Groups for Photovoltaic Applications

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This article reports properties of photovoltaic devices containing new donor materials – copolymers referred as PCEMB, composed of 2-(carbazol-9-yl)ethyl methacrylate (CEM) and benzofuran-2-carboxylic acid 2-(2-methylacryloyloxy)ethyl ester (MB). Manufactured photovoltaic cells consisted of donor and acceptor (PBT or P3OT) layers sandwiched between ITO covered glass and evaporated aluminum electrode. Performance of the cell was optimized for a copolymer composed of 8% CEM and 92% MB. The efficiency, found equal c.a. $\eta = 0{,}03\%$, was low comparing to other photovoltaic cells reported in the literature. However, following the observed tendencies, it can be supposed that there exists a large reserve for the enhancement of the open circuit voltage through further chemical modifications of the chromophore.

In the case of the PDT containing cells, measured Uoc was substantially lower. This fact may be attributed to difference in carrier mobility between this polymer and PCEMB. Simultaneously, the larger sizes of the MB molecule may favor separation of the charges and leads to enhancement of the corresponding voltage.

Keywords: fill factor; open circuit voltage; photovoltaic cell; short circuit current density

The research was partially supported by the grant number PB-0687/T09/2002/23.
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INTRODUCTION

The conversion of the sun light into the electric power requires generation of both negative and positive charge, their space separation and finally, a driving force pushing these charges trough an external electric circuit. In organic semiconductors, absorption of photons leads to formation of bound electron-hole pairs (excitons) rather than free charges. These excitons can be separated at some number of sites. Next, the separated charges need to travel to respective electrodes, holes to the anode and electrons to the cathode. This separation provides voltage drop between electrodes and can be injected into an external circuit. All these processes are crucial for efficiency of the solar cells.

During the last decade, a whole range of conjugated polymers, copolymers, polymers blends, and fluorescent dye-doped polymers have been reported to issue photovoltaic properties while applied in appropriates structures. Already developed semiconducting and conducting conjugated polymers represents typical advantages like small weight, flexibility, ultra-fast optoelectronic response, nearly continuous tenability of materials energy levels and band-gaps possible to be altered via molecular design and synthesis. They are also versatile materials for processing and device fabrication and low cost on large scale industrial manufacturing [1,2]. Recently, poly(N-vinylcarbazole) (PVK) has attracted attention in applications related to photovoltaic devices and it serves as one of layers either pristine or in or in blends with other materials [3].

In view of design of new materials for photovoltaic devices, we have investigated a group of novel carbazole copolymers, applied as active layer in photovoltaic cells together with poly(3-decylthiophene) (PDT) or poly(3-octylthiophene) (P3OT). The copolymers are composed of 2-(9-carbazolyl) ethyl methacrylate (CEM) and benzofuran-2-carboxylic acid 2-(2-methylacryloyloxy)ethyl ester (MB) (Fig. 1).

MATERIALS

Composition and structure of all synthesised compounds were verified by mean of NMR, IR, GC/MS techniques. ^{1}H-NMR spectra were recorded in $CDCl_3$ on Tesla 80 MHz NMR spectrometer. IR spectra were recorded using BioRad FTS 165 FT-IR spectrophotometer. Mass spectra and purity of all the intermediates were measured using Hewlett-Packard 5971 mass detector. The molecular weight of the reaction was estimated in THF by gel permeation chromatography (GPC) using a Knauer Instrument chromatograph equipped with PL

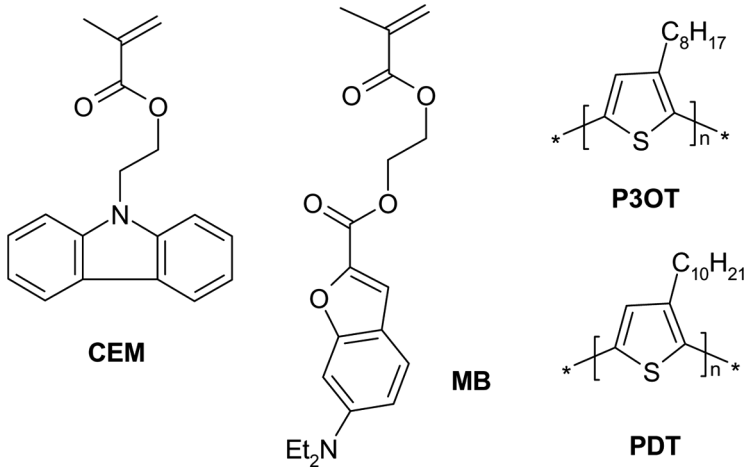

FIGURE 1 2-(9-Carbazolyl) ethyl methacrylate (CEM) and benzofuran-2-carboxylic acid 2-(2-methylacryloyloxy)ethyl ester (MB).

gel 10 μl mixed columns. The calibration curve was obtained using polystyrene standards.

Monomer Synthesis

Both **CEM** (Fig. 2) and **MB** (Fig. 3) were prepared through novel synthetic methods that were recently developed in our laboratory [4,5].

N–(2-hydroxyethyl)carbazole (I): The mixture of **c**arbazole (1.0 g, 0.006 mol) and ethylene carbonate (2.1 g, 0.024 mol) was stirred and irradiated in the microwave reactor NOVA 2004 (Ertec, Poland) for 30 minutes at 150°C. A trace amount of NaOH (0.1 g, 2.5 mmol) was added to the reaction mixture prior to the reaction. After the reaction, the product was precipitated from solvent by water $-C_2H_5OH$ solution and recrystallized from cyclohexane. Yield: 75%, m.p. 69–71°C.

MS = 212 ((M + 1), 5%), 211 (M^+, 30%), 180 (100%), 181 (15%), 152 (18%).

IR (KBr): 3419 (w), 3213 (w), 3048 (w), 2976 (w), 2955 (w), 2937 (w), 2918 (w), 2868 (w), 1687 (m), 1656 (m), 1595 (m), 1485 (s), 1458 (s), 1388 (m), 1364 (s), 1350 (s), 1326 (s), 1245 (m), 751 (s), 720 (s), 559 (w), 491 (m), 423 (m) cm^{-1}.

2–(9–Carbazolyl)ethyl methacrylate (CEM): was prepared in the reaction conducted at ambient temperature: N-(2-hydroxyethyl) carbazole (2.11 g, 10 mmol) was mixed with methacrylic acid (0.9 g,

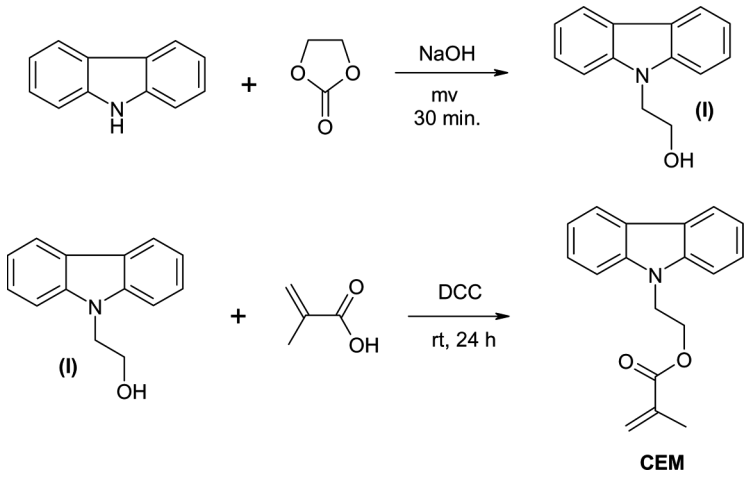

FIGURE 2 Synthesis of 2-(9-carbazolyl) ethyl methacrylate (CEM).

10.5 mmol) and 4-pyrrolidinopyridine (0.2 g, 1.3 mmol) as a catalyst in ethylene dichloride (10 ml). During first 30 minutes of the reaction, an equimolar amount of N,N'-dicyclohexylcarbodiimide (DCC) (1.4 g, 10 mmol) in ethylene dichloride (5 ml) was added. The reaction was

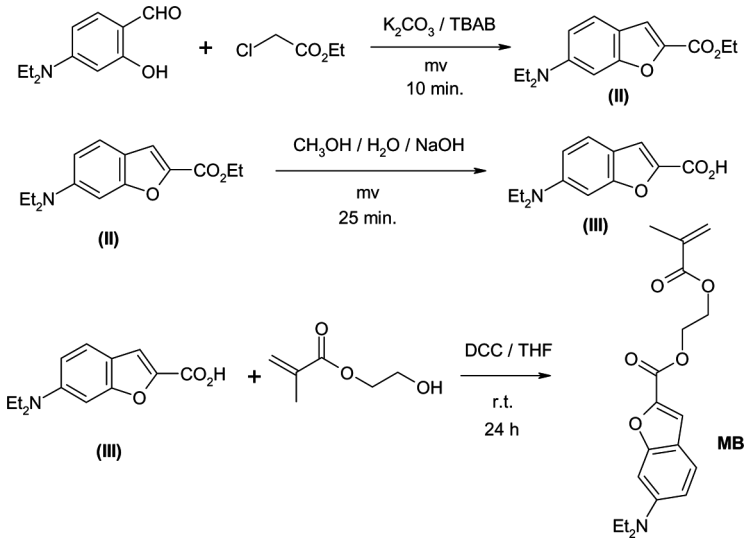

FIGURE 3 The synthesis of and benzofuran-2-carboxylic acid 2-(2-methylacryloyloxy)ethyl ester (MB).

completed after 24 hours to afford CEM conversion higher than 80%. A white solid of the side-product, N,N′-dicyclohexylurea (DCU), was filtered from the solution, and the filtrate was stored and slowly concentrated until white crystals of the desired product precipitated. Then the crude product was recrystallized from ethanol. Yield: 85%.

MS (70 eV): 280 ((M + 1) 7%), 279 (M^+ 34%), 193 (39%), 181 (14%), 180 (100%), 152 (17%).

IR (KBr): 3050 (m), 2978 (m) 2054 (m), 1719(s), 1627 (m), 1596 (m), 1485 (m), 1454 (s), 1358 (m), 1318 (s), 1295 (s), 1171 (s), 1153 (s), 946 (m), 816 (m), 745 (s), 720 (s), 648 (w), 559 (w), 472 (w), 420 (m) cm^{-1}

^1H NMR (80 MHz, $CDCl_3$): 1.79–1.82 (3H, s, CH_2=C−CH_3), 4.53–4.60 (4H, m, CH_2−CH_2), 5.45–5.49 (1H, m, trans C=CH_2), 5.92 (1H, s, cis C=CH_2), 7.13–7.50 (6H, m, aromatic ring), 8.03–8.1 (2H, m, aromatic ring) ppm.

Ethyl 6-diethylamino-2-benzo[b]furancarboxylate (II): Potassium carbonate (2.70 g, 20 mmol), TBAB (0.16 g, 0.50 mmol), and 4-diethylaminosalicylaldehyde (5.0 mmol) were thoroughly mixed and placed in an round-bottom reaction flask. Then chloroacetate ester (10 mmol) was added dropwise The mixture was thoroughly stirred with a spatula for a few seconds and placed in the microwave reactor NOVA 2004 (Ertec, Poland) then irradiated for 10 minutes at 140°C. Upon completion of the reaction, monitored by GC/MS, the mixture was extracted with methylene chloride, and the solvent was then removed. The crude product was purified by column chromatography (cyclohexane/methyl chloride 8 : 2) yielding ethyl 6-diethylamino-2-benzo[b]furancarboxylate as a red oil, yield 80%.

MS (70 eV): 261 (M1, 42), 247 (16), 246 (100), 0218 (23), 190 (10), 116 (6.7%).

IR (KBr): 2973(s), 2931(m), 2899(m), 2872(w), 1716(s), 1626(s), 1578(m), 1556(m), 1509(s), 1398(m), 1372(s), 1357(m), 1303(m), 1270(s),1241(s), 1180(s), 1120(s), 1095(m), 1017(m), 844(w), 795(m), 759(m) cm^{-1};

^1H NMR (80 MHz, $CDCl_3$): 7.49–7.26 (2H, m, aromatic protons), 6.77–6.40 (2H, m aromatic protons), 4.40 (2H, q, CH_2−Me), 3.40 (4H, q, NCH_2Me), 1.40 (3H, t, CH_2−Me), 1.19 (6H, t, Hz, NCH_2Me) ppm.

6-diethylaminobenzo[b]furan-2-carboxylic acid (III): Ethyl 6-diethylamino-2-benzo[b]furancarboxylate was converted into 6-diethylaminobenzo[b]furan-2-carboxylic acid by a hydrolysis reaction in a 0.5 mol NaOH (40 ml) and methanol (40 ml) solution, which was conducted still in the same vessel under microwave irradiation (reactor NOVA 2004, Ertec, Poland) for 25 minutes. Finally, 6-diethylaminobenzo[b]furan-2-carboxylic acid was precipitated

from the solution by the addition of water and hydrochloric acid until pH of the solution reached 2. The crude product was dried and used in the next stage without purification.

Benzofuran-2-carboxylic acid 2-(2-methylacryloyloxy)ethyl ester (MB): A mixture of 6-diethylaminobenzo[b]furan-2-carboxylic acid (0.49 g, 2.1 mmol), 2-hydroxyethyl methacrylate (0.40 g, 3 mmol), 4-pyrrolidinopyridine (0.08 g, 0.5 mmol) as a catalyst in a THF solution was stirred at ambient temperature for 24 hours. During the first 30 min. of the reaction, DCC (0.55 g, 2.7 mmol) in a THF solution was added dropwise. Next, DCU was filtered off from the solution, and the solvent was evaporated under reduced pressure to give crude MB as a heavy oil; yield 70% (Fig. 3).

^{1}H NMR (80 MHz, $CDCl_3$): 7.46–7.22 (2H, m, aromatic protons), 6.70–6.40 (2H, m aromatic protons), 5.92 (1H, s, cis C=CH_2), 5.44–5.49 (1H, m, trans C=CH_2), 4.57–4.62 (4H, m, CH_2-CH_2), 3.40 (4H, q, N$-CH_2$Me), 1.76–1.82 (3H, s, CH_2=C$-CH_3$), 1.19 (6H, t, NCH_2Me) ppm.

Polymerisation

The monomers CEM and MB (total amount 0.5 g) taken in desired molar ratio (see first column of Table 1) were dissolved in toluene (10 ml) and AIBN (1%) was added as initiator. The reaction mixture was flushed with argon for 20 min. and then heated in a water bath at 60°C to initiate polymerisation. After 48 hr the reaction was terminated by adding THF (15 ml) and the polymer precipitated into a large amount of methanol. The product was several times redissolved in THF and reprecipitated into methanol.

The molecular masses of the copolymers were estimated in THF by gel permeation chromatography (GPC) using polystyrene as a standard to give mass and number average masses shown in Table 1.

PDT and P3OT polymers were obtained by courtesy from Prof. Malgorzata Zagorska, Warsaw University of Technology.

TABLE 1 Number and Weight Average Molecular Masses of the Copolymers of MB and CEM

Copolymer	M_n	M_w	P_d
MB (1%) CEM (99%)	$1{,}34 \times 10^4$	$3{,}43 \times 10^4$	2,56
MB (2%) CEM (98%)	$1{,}47 \times 10^4$	$4{,}15 \times 10^4$	2,82
MB (5%) CEM (95%)	$1{,}25 \times 10^4$	$3{,}80 \times 10^4$	3,04
MB (8%) CEM (92%)	$1{,}25 \times 10^4$	$4{,}01 \times 10^4$	3,20

PHOTOCELL PREPARATION

Figure 4 shows the photovoltaic cell architecture. Electron donor (D) and electron acceptor (A) materials were deposited subsequently by spin-coating method from solvents unique for the given polymer to avoid deterioration of deposited layers. Glass substrates were partially coated by indium–tin oxide (ITO). The average thickness of the actives layers was estimated to be about 100 nm. At the end cells were covered with 100 nm thick layer of vacuum evaporated aluminum to ensure good electrical contact.

Both exciton and charge transport in organic materials usually require hopping from chromophore to polymer. In order to meet these specific requirement for efficient photon to charge conversion different device architectures have been developed in the past [1].

Charge separation normally occurs at the interface between D and A polymers. Double layer cell structure benefits from the single charge transport in each layer what provides electrical connectivity to the right electrode and gives tiny probability of carriers mutual recombination.

The difference of work functions of electrodes ΔW_f can cause the bands tilting, which creates a constant electrostatic across the bulk. According to this picture the driving force i.e. V_{oc} is mainly determined by the offset at the D/A junction although the increased built in electric field can help to transport charges through the bulk. The behaviour of photovoltaic cell can be seen in traditional the fourth quadrant of the current-voltage characteristic in [6].

The overall efficiency η of a photovoltaic cell can be calculated by standard formula:

$$\eta = V_{oc}{}^{*}J_{sc}{}^{*}FF/P_{light} \tag{1}$$

where V_{oc} is the open circuit voltage, J_{sc} the short circuit current density in A/m^2, FF is the fill factor and, P_{light} is the incident solar

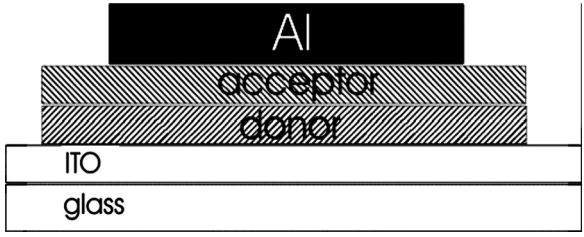

FIGURE 4 Device designs used for cells comprising two components, an electron donor (D) and an electron acceptor material (A).

radiation in μWatt/cm^2. Because of the spectral and intensity dependences the power conversion efficiencies are only meaningful for a given spectral distribution and intensity [6].

RESULTS AND DISCUSSION

Absorption and photoluminescence spectra of four prepared PCEMB copolymers, were measured, because these characteristics play principal role in the photovoltaic response. Samples were prepared in form of free standing few micrometer thick films, obtained from THF solutions at room temperature followed by drying at 40°C in vacuum for 24 h. Alternatively, copolymers were transformed in sub-micrometer thin layers by spin-casting [3].

Both absorption and photoluminescence spectra of all the copolymers are presented in Figure 5.

The photoluminescence maximum was observed at about 430 nm. Current–voltage characteristics of a studied photovoltaic cells in the dark and under illumination (halogen lamp $P_{light} = 1255\,\mu\text{Watt/cm}^2$) are shown in Figure 6. In the dark the devices exhibit a clear current rectification, whereas illuminated, they present a short–circuit current density and an open–circuit voltage. Such behaviors reflect substantial influence of MB content on the output open circuit voltage.

Table 2 presents photovoltaic parameters for double layer photovoltaic cells consisting of ITO/PCEMMB/PDT/Al. The best values of the J_{SC} and V_{OC} parameters for double layer architecture were obtained for the cell number 8, with P3OT and the photovoltaic response for this case is equal to about $\eta = 0{,}03\%$. This value is low compared to the known photovoltaic cells, however following the principal tendencies

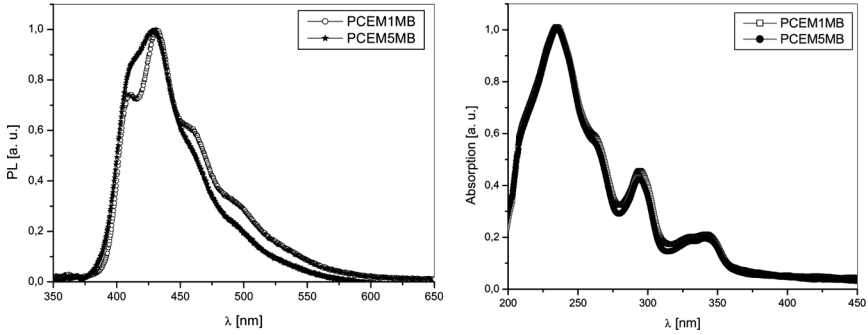

FIGURE 5 Examples of absorption (left) and photoluminescence (right) spectra of copolymer series PCEM × MB.

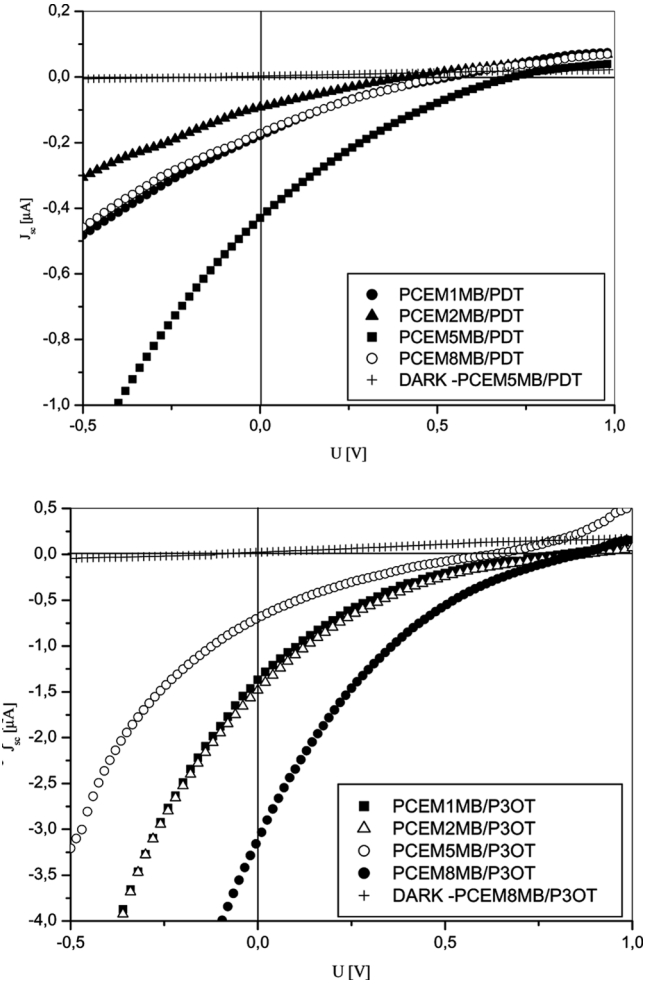

FIGURE 6 J-V Characteristics dark and under illumination of ITO/PCEMMB/Al devices (4th run).

an opportunity appears for the enhancement of the open circuit voltage by further chemical modification of the chromophores.

In the case of the PDT polymers the Uoc is substantially lower and this fact may be related to different carrier mobility for these two types of polymers. Paralelly, the larger sizes of the MB molecule may favor a separation of the charges and leads to enhancement of the corresponding voltage. The similar effects were shown during investigations of

TABLE 2 Photovoltaic Parameters for a Sequence of Layers of ITO/Active Layers/Al Devices

Cell no.	Active layers	J_{sc} [$\mu A/cm^2$]	U_{oc} [mV]	FF
1	PCEM1MB/PDT	0,18	540	0,19
2	PCEM2MB/PDT	0,09	410	0,23
3	PCEM5MB/PDT	0,43	720	0,17
4	PCEM8MB/PDT	0,17	520	0,24
5	PCEM1MB/P3OT	1,36	810	0,16
6	PCEM2MB/P3OT	1,496	840	0,10
7	PCEM5MB/P3OT	0,699	630	0,18
8	PCEM8MB/P3OT	3,120	860	0,15

stilbene chrmophore incorporated into the photopolymer matrices and were manifested in nonlinear optical effects [7].

CONCLUSIONS

Best manufactured in frame of current work photovoltaic cells, cannot compete with leading architectures, already proposed in the extensive literature.

However, the synthesized series of copolymers can serve a starting point for future developing of carbazole-based photovoltaic polymer materials. This direction seems very promising due to well known thermal stability and good charge transport by PVK and its derivatives.

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