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Synthesis of Polymethacrylates with Carbazole and Benzofuran Pendant Groups for Photovoltaic Applications

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Summary: The article focuses on the photovoltaic devices made from copolymers of 2-(carbazol-9-yl)ethyl methacrylate (CEM) with benzofuran-2-carboxylic acid 2-(methacryloyloxy)ethyl 6-(diethylamino)benzo[*b*]furan-2-carboxylate (MB) and poly(3-decylthiophene) (PDT) or poly(3-octylthiophene) (P3OT). Photovoltaic cell structure consisted of ITO/active materials/Al. The photophysics of such photoactive devices is based on the photo-induced charge transfer from donor-type semiconducting conjugated polymers to the acceptor-type polymers. The monomer synthesis and polymerization as well as the device fabrication are presented. The copolymers can be spin-coated from a solution at room temperature without subsequent processing and heat treatment. The photovoltaic properties of the devices are shown.

Keywords: benzofuran; carbazole; methacrylates; photovoltaic properties

Introduction

A number of fully conjugated polymers, copolymers, polymers blends, and fluorescent dye-doped polymer systems have been found to exhibit photovoltaic properties. In the general context of organic photovoltaics, the polymer materials combine the photoelectric properties of semiconductors with the large-scale and low-cost technology of polymer materials. The semiconducting and conducting conjugated polymers developed in recent years possess some inherent advantages, including low weight, flexible shape, ultra-fast optoelectronic response, nearly continuous tunability of energy levels of materials and band-gaps via molecular design and synthesis, versatile materials processing and device fabrication schemes, and low cost of large-scale industrial manufacture.[1,2] Recently, poly(*N*-vinylcarbazole) (PVK) has attracted attention in applications related to photovoltaic devices in which the layer is formed by PVK itself or by blending with other materials.[3]

Since carbazole derivatives rank among the main subjects in our laboratories, we have investigated, in the search for materials for photovoltaic devices, a group of novel carbazole copolymers which were used as active layers in photovoltaic cells together with poly(3-decylthiophene) (**PDT**) or poly(3-octylthiophene) (**P3OT**). The copolymers are composed of 2-(carbazol-9-yl)ethyl methacrylate (**CEM**) and 2-(methacryloyloxy)ethyl 6-(diethylamino)benzo[*b*]furan-2-carboxylate (**MB**) (Figure 1).

Experimental Part

Monomer Synthesis

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

9-(2-hydroxyethyl)carbazole (HEC): a mixture of carbazole (1.0 g, 0.006 mol) and ethylene carbonate (2.1 g, 0.024 mol) was stirred and irradiated in a microwave reactor Nova 2004 (Ertec, Poland) at 150 °C

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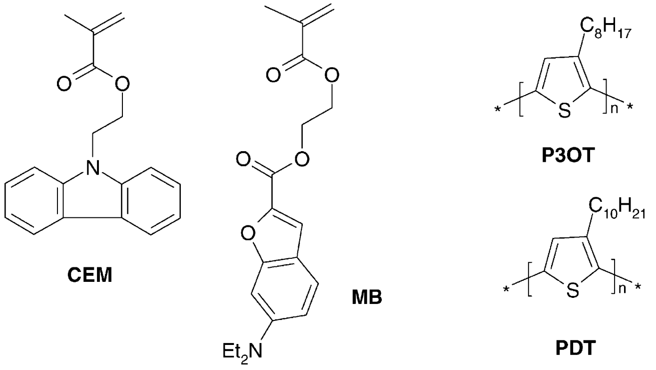

Figure 1.
2-(Carbazol-9-yl)ethyl methacrylate (**CEM**) and 2-(methacryloyloxy)ethyl 6-(diethylamino)benzo[*b*]furan-2-carboxylate (**MB**), poly(3-octylthiophene) (P3OT) and poly(3-decylthiophene) (PDT).

for 30 min. A small amount of NaOH (0.1 g, 2.5 mmol) was added to the reaction mixture prior to the reaction. The product was precipitated from the solvent with aqueous C_2H_5OH and recrystallized from cyclohexane. Yield: 75%, m.p. 69–71 °C.

2-(Carbazol-9-yl)ethyl methacrylate (CEM) was prepared by the reaction conducted at ambient temperature: 9-(2–hydroxyethyl)-carbazole (2.11 g, 10 mmol) was mixed with methacrylic acid (0.9 g, 10.5 mmol) and 4–pyrrolidinopyridine (0.2 g, 1.3 mmol) as a catalyst in ethylene dichloride (10 ml). During first 30 min 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 complete after 24 h affording CEM conversion higher than 80%. The by-product, *N,N′*-dicyclohexylurea (DCU), was filtered off from the solution, 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%.

Ethyl 6-(diethylamino)benzo[b]furan-2-carboxylate (EMB): to a mixture of potassium carbonate (2.70 g, 20 mmol), tetrabutylamonium bromide (TBAB) (0.16 g, 0.50 mmol) and 4-(diethylamino)salicylaldehyde (5.0 mmol), ethyl chloroacetate

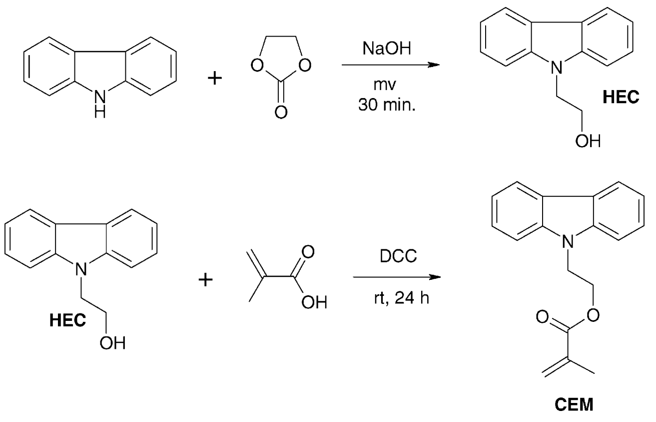

Figure 2.
Synthesis of 2-(carbazol-9-yl)ethyl methacrylate (CEM)

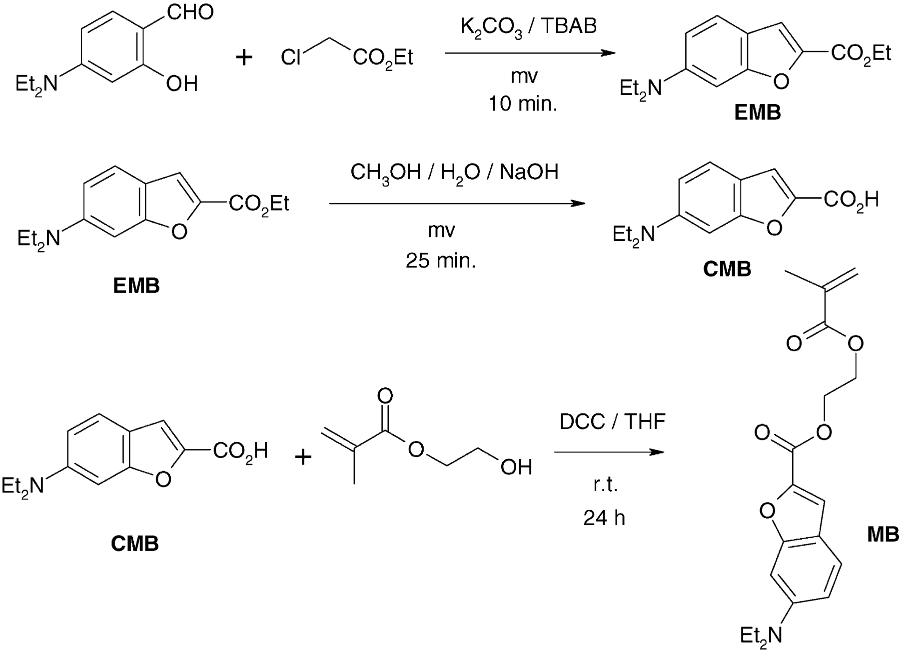

Figure 3.
The synthesis of **CMB** and 2-(methacryloyloxy)ethyl 6-(diethylamino)benzo[*b*]furan-2-carboxylate (**MB**).

ester (10 mmol) was added dropwise. The mixture was placed in a microwave reactor Nova 2004 (Ertec, Poland) and irradiated at 140 °C for 10 min. 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/methylene chloride 8:2) giving ethyl 6-(diethylamino)-benzo[*b*]furan-2-carboxylate as a red oil, yield 80%.

6-(Diethylamino)benzo[b]furan-2-carboxylic acid (CMB): Ethyl 6-(diethylamino)-2-benzo[*b*]furan-2-carboxylate was converted to 6-(diethylamino)benzo[*b*]furan-2-carboxylic acid by hydrolysis with a 0.5 mol NaOH (40 ml) in methanol (40 ml) solution, conducted in the same vessel under microwave radiation for 25 min. Finally, 6-(diethylamino)benzo[*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 step without purification.

2-(2-Methacryloyloxy)ethyl 6-(diethylamino)benzo[b]furan-2-carboxylate (MB): a mixture of 6-(diethylamino)benzo[*b*]furan-2-carboxylic acid (0.49 g, 2.1 mmol), 2-hydroxyethyl methacrylate (0.40 mg, 3 mmol), 4–pyrrolidinopyridine (0.08 g, 0.5 mmol) as a catalyst in a THF solution was stirred at ambient temperature for 24 h. During the first 30 min. of the reaction, DCC (0.55 g, 2.7 mmol) in a THF solution was added dropwise. Then, 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% (Figure 3).

Polymerization

The monomers CEM and MB (total 0.5 g) in the desired molar ratio 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 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 product was

Table 1.
Number- and weight- average molecular weight of copolymers of MB and CEM.

Copolymer (mol%) composition	Code	M_n	M_w	M_w/M_n
MB (1%) **CEM** (99%)	PCEM1MB	1.34×10^4	3.43×10^4	2.56
MB (2%) **CEM** (98%)	PCEM2MB	1.47×10^4	4.15×10^4	2.82
MB (5%) **CEM** (95%)	PCEM5MB	1.25×10^4	3.80×10^4	3.04
MB (8%) **CEM** (92%)	PCEM8MB	1.25×10^4	4.01×10^4	3.20

redissolved in THF several times and reprecipitated into methanol (Table 1).

Results and Discussion

Four prepared copolymers containing MB and CEM units (Table 1) together with PDT and P3OT units were the subject of preliminary investigations carried out in order to compare their photovoltaic properties. The photovoltaic cell structure consisted of an ITO/active layer of polymer blend/Al. The photovoltaic properties were measured for the polymer films (active layers) that were about 100 nm in thickness. The films were obtained from THF solutions at room temperature followed by drying at 40 °C in vacuum for 24 h. The copolymers allow the solar cell fabrication by spin-casting the layer from solution at room temperature [3] (Figure 4).

Using the I(V)characteristics for polymer films (Figure 4), we determined the parameters of solar cells which are presented in Table 2. The parameters are open circuit voltage (U_{oc}), short circuit current (I_{sc}), fill factor FF.

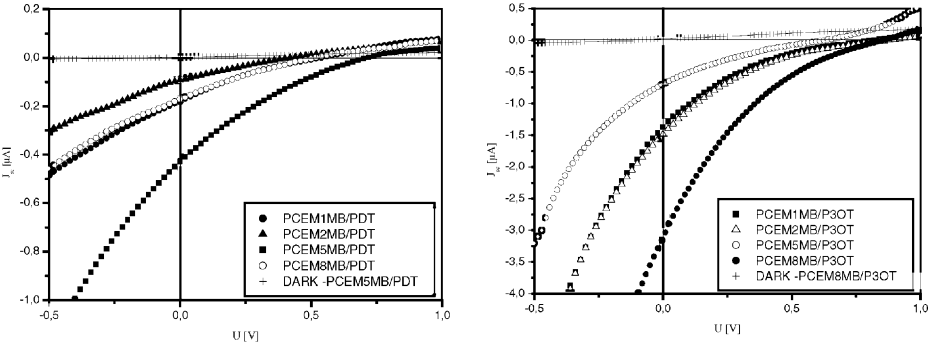

Figure 4.
Characteristics I(V): dark and under illumination of ITO/active layers/Al devices.

Table 2.
Photovoltaic parameters for ITO/active layers/Al devices.

Cell No	Active layers (50:50 weight ratio)	I_{sc} [nA/cm^2]	U_{oc} [mV]	FF
1	PCEM1MB/PDT	178.4	540	0.19
2	PCEM2MB/PDT	92	410	0.23
3	PCEM5MB/PDT	429.6	720	0.17
4	PCEM8MB/PDT	171.2	520	0.24
5	PCEM1MB/P3OT	1360	810	0.16
6	PCEM2MB/P3OT	1496	840	0.10
7	PCEM5MB/P3OT	699	630	0.18
8	PCEM8MB/P3OT	3120	860	0.15

Conclusions

The content of the MB group in the copolymer slightly changes the photovoltaic cell characteristics. The best values of the I_{sc} and U_{oc} parameters were obtained for the ITO/PCEM8MB/P3OT/Al cell which provides a basis for further optimization of this architecture. Further optimization of this structure may lead to its industrial applications.

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