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Microwave-assisted synthesis and copolymerization of photo- and electroluminescent methacrylates containing carbazole and coumarin pendant groups

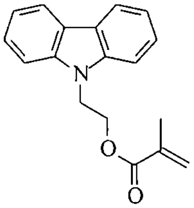
Summary — 2-(9-carbazolyl)ethyl methacrylate (CEM) and 7-(diethylamino)coumarin-3-carboxylic acid 2-(methacryloyloxy)ethyl ester (MK) were synthesized and then copolymerized in molar proportion (99.5:0.5), (99:1), (98:2), and (92:8 mol/mol) to give CEM/MK copolymers. Starting materials for monomers synthesis: *N*-(2-hydroxyethyl)carbazole and 7-(diethyloamino)coumarin-3-carboxylic acid were synthesized under microwave irradiation using novel modified methods. Solutions of the copolymers in THF were examined for their photoluminescence properties, while thin films made of the copolymers for electroluminescence properties.

Key words: carbazole, coumarin, microwave irradiation, photoluminescence, electroluminescence.

Recent advances in the performance of polymer photoluminescent materials confirmed their important role in production of organic opto-electronic devices [1, 2]. An organic electroluminescent device is a light-emitting device similar to semiconductor based light-emitting diodes (LEDs) [3]. The first commercial organic light-emitting diode was introduced in 1983, and it emitted green light [4]. In 1987, Tang and Van Slyke [5] reported light-emitting diodes using multilayer organic thin films, and since then significant progress has been made. In 1996, Pioneer started selling green flat displays (64 x 256 pixel) [2]. An explosive growth of activity followed this event.

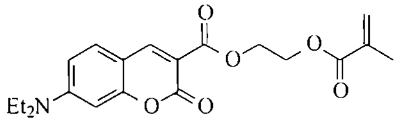
Photo- and electroluminescent polymers have met with considerable interest in applications based on organic opto-electronic devices. Their properties such as high luminescence efficiency and brightness, flexibility, thermal and mechanical stability, excellent film forming possibilities, capability in providing a wide spectral range, application as large, full-color displays and low costs of production [6, 7] may be a source of advantage over traditional inorganic semiconductor materials. Despite these advantages, several problems have been encountered in attaining high efficiency blue emission required in practical polymer applications.

In the series of our research oriented towards the development of polymeric electroluminescent materials [8—13] we wish to present synthesis of copolymers from methacrylic acid 2-(9-carbazolyl)ethyl ester [CEM — formula (I) and 7-(diethylamino)coumarin-3-carboxylic acid 2-(methacryloyloxy)ethyl ester [MK — formula (II)] — copolymers CEM/MK of formula (III).



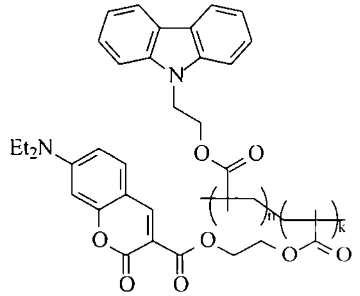
CEM

(I)



MK

(II)



CEM/MK

(III)

Both carbazole and coumarin methacrylates are not very well known, however they exhibit very high quantum yield; lighting efficiency of carbazole methacrylates is higher than that of polyvinylcarbazole [14, 15]. The

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human eye is best accommodated to view green, and worst accommodated to blue light; coumarin methacrylates give blue light and they comprise moieties that carry both electrons and holes. In this paper, we are describing a novel method of monomer synthesis and their polymerization, as well as electroluminescence properties of thin films fabricated of these copolymers.

EXPERIMENTAL

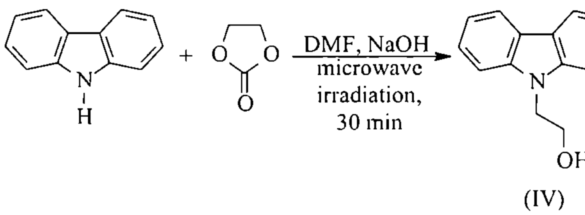
Methods

The structures of all compounds were verified by means of NMR, IR and GC/MS methods. ^{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 recorded and verified using Hewlett-Packard 5971 mass detector. The molecular weights of the reaction products were estimated in THF by gel permeation chromatography (GPC) using a Knauer Instrument chromatograph equipped with PL gel 10 µL mixed columns. A calibration curve was obtained using polystyrene standards.

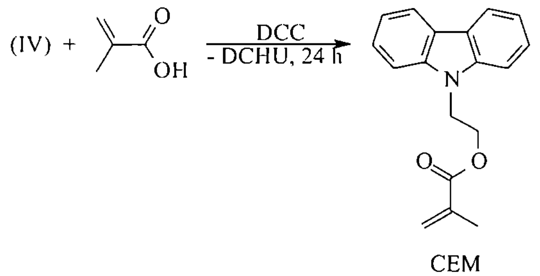
Monomer synthesis

Both CEM and MK were prepared by novel methods that were recently developed in our laboratory [11, 12].

***N*-(2-hydroxyethyl)carbazole** (IV) — synthesized from carbazole (1 g, 0.006 mol) and ethylene carbonate (2.1 g, 0.024 mol) [see eqn. (1a)] by refluxing and stirring in a DMF (10 mL) solution under microwave irradiation in the Plazmatronika (Poland) reactor for 30 minutes. A trace amount of NaOH (0.1 g, 2.5 mmol) was added to the reaction mixture. The resulting product was precipitated from solvent by a water/C_2H_5OH solution and recrystallized from cyclohexane. Yield: 88%, melting point 69—71°C.



(1a)



(1b)

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).

2-(9-carbazolyl)ethyl methacrylate (CEM) — prepared in the reaction [see eqn. (1b)] conducted at ambient temperature: (IV) (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). An equimolar amount of *N,N'*-dicyclohexylcarbodiimide (DCC) (1.4 g, 10 mmol) in ethylene dichloride (5 mL) was added during first 30 minutes of the reaction. The reaction was completed after 24 hours to afford CEM conversion higher than 80%. A white solid of the side-product, *N,N'*-dicyclohexylurea (DCHU), was filtered from the solution, and the filtrate was stored and slowly concentrated until white crystals of the desired product precipitated. Next, the crude product was recrystallized from ethanol. Yield: 86%.

MS: 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).

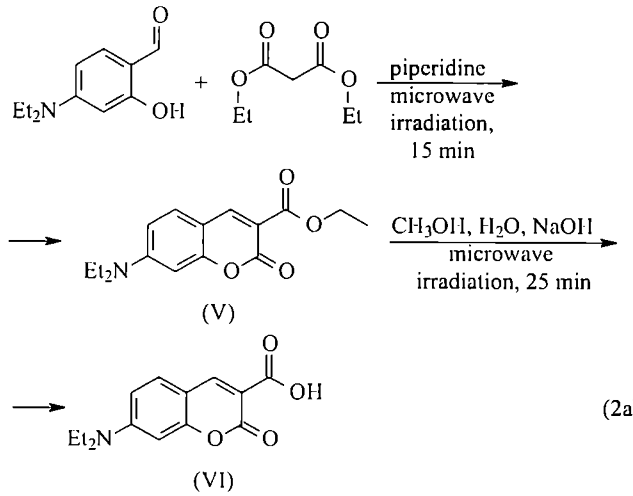
^{1}H NMR: 1.79—1.82 (3H, s, CH_2=C-C$\underline{H}_3$), 4.53—4.60 (4H, m, C$\underline{H}_2$-C$\underline{H}_2$), 5.45—5.49 (1H, m, *trans* C=C$\underline{H}_2$), 5.92 (1H, s, *cis* C=C$\underline{H}_2$), 7.13—7.50 (6H, m, aromatic ring), 8.03—8.1 (2H, m, aromatic ring).

7-(diethylamino)coumarin-3-carboxylic acid (VI) — obtained in the reaction [see eqn. (2a)] of 4-diethylaminosalicylaldehyde (1.9 g, 9 mmol), diethyl malonate (1.69 g, 10.5 mmol) and piperidine (1.4 g, 0.01 mol) as a catalyst by refluxing under microwave irradiation in the Plazmatronika (Poland) reactor for 15 minutes [16]. The mixture was vigorously stirred during the reaction. Next, 7-(diethylamino)coumarin-3-carboxylic acid ethyl ester (V) was converted into (VI) by a hydrolysis reaction in a 0.5 mol NaOH (40 mL) and methanol (40 mL) solution, conducted in the same vessel under microwave irradiation for 25 minutes. Finally, 7-(diethylamino)cumarin-3-carboxylic acid was precipitated from the solution by addition of water and hydrochloric acid until pH of the solution reached 2. The crude product was dried and recrystallized from ethanol. Yield: 90%, melting point: 217—218°C.

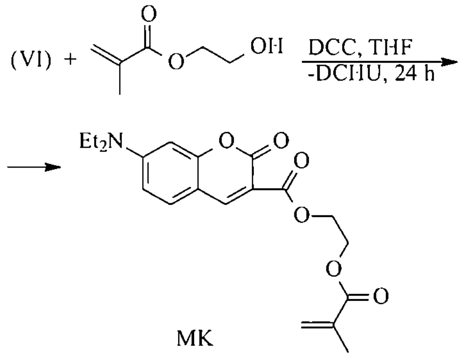
MS: 262 [(M+1), 4%], 261 (M$^+$, 20%), 250 (100%), 206 (11%), 204 (15%), 73 (13%).

IR (KBr): 3072 (w), 2949 (m), 2933 (m), 1746 (s), 1648 (s), 1569 (s), 1512 (m), 1465 (m), 1399 (s), 1344 (m), 1216 (s), 1042 (m), 996 (m), 837 (m), 797 (s), 763 (m), 713 (m), 667 (m), 606 (m), 567 (m), 531 (m), 429 (m).

^{1}H NMR: 7.63—8.48 (6H, m, aromatic ring), 9.69 (1H, s, aromatic ring), 12.25 (1H, s, COO$\underline{H}$).



(2a)



(2b)

7-(diethylamino)coumarin-3-carboxylic acid 2-(methacryloyloxy)ethyl ester (MK) — synthesized as follows [see eqn. (2b)]: a mixture of (VI) (0.7 g, 2.7 mmol), 2-hydroxyethyl methacrylate (0.4 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. DCC (0.55 g, 2.7 mmol) in a THF solution was added dropwise during first 30 min of the reaction. Next, DCHU was filtered off from the solution, and the solvent was evaporated under reduced pressure to give crude MK. Next, the product was recrystallized from ethanol and dried. Yield 88%.

MS: 374 [(M+1) 12%] 373 (M^{+}50%), 359 (22%), 358 (100%), 244 (29%), 200 (10%), 113 (24%), 69 (13%), 41 (12%).

IR: 3123 (w), 2976 (s), 2932 (m), 1760 (s), 1714 (s), 1625 (s), 1586 (s), 1518 (s), 1485 (m), 1424 (m), 1357 (m), 1294 (s), 1220 (s), 1186 (s), 1176 (s), 1101 (s), 1037 (m), 962 (m), 950 (m), 857 (m), 818 (m), 795 (s), 695 (s), 523 (m), 476 (m).

^{1}H NMR: 1.15—1.32 (6H, t, N-CH_2-CH_3), 1.96 (3H, s, CH_2=C—CH_3), 3.41—3.50 (4H, m, N-CH_2), 4.51 (4H, s, O-CH_2-CH_2-O), 5.60 (1H, s, *trans* C=CH_2), 6.16 (1H, s, *cis* C=CH_2), 6.47—6.68 (2H, m, aromatic ring), 7.30—7.41 (1H, m, aromatic ring), 8.40 (1H, s, aromatic ring).

Polymerization

Concentration of MK in the CEM matrix was set to 0.5%, 1%, 2% and 8% mol/mol, and the samples (0.35—0.38 g CEM + MK) placed in measuring test tubes. To the reaction mixture AIBN (1% mol/mol) as an initiator and everytime 7 mL of anhydrous toluene were added and the system was flushed with argon for 10 minutes. Next, the tubes were kept in a dryer at 60°C for 48 hours. Finally, the copolymerization reactions were stopped by dissolving the copolymers in THF solutions, and precipitating from methanol. This purification process was repeated three times. The molecular weights of polymers were estimated in THF by gel permeation chromatography (GPC) by using polystyrene as a standard.

IR: 3852 (w), 3743 (w), 3049 (s), 2954 (s), 2354 (w), 1730 (s), 1652 (w), 1626 (m), 1597 (s), 1558 (w), 1484 (s), 1459 (s), 1351 (s), 1326 (s), 1230 (m), 1215 (s), 1153 (s), 1066 (s), 1020 (m), 1001 (m), 896 (w), 749 (s), 723 (s), 667 (w), 617 (w), 558 (w), 528 (w), 422 (m).

RESULTS AND DISCUSSION

Number and weight average molecular weights of the polymers are shown in Table 1.

Table 1. **The number and weight average molecular weights of the CEM/MK copolymers**

CEM/MK ratio (% mol/mol) in the copolymer	Acronym	M_n	M_w	M_w/M_n
100:0	PCEM	$1.37 \cdot 10^4$	$3.91 \cdot 10^4$	2.85
99.5:0.5	PC05MK	$1.47 \cdot 10^4$	$3.87 \cdot 10^4$	2.63
99:1	PC1MK	$1.53 \cdot 10^4$	$3.68 \cdot 10^4$	2.40
98:2	PC2MK	$1.51 \cdot 10^4$	$4.15 \cdot 10^4$	2.75
92:8	PC8MK	$1.41 \cdot 10^4$	$4.40 \cdot 10^4$	3.10

The application of microwave irradiation during monomer synthesis resulted in substantial reduction of reaction times as compared to conventional methods [17—19]. Moreover, the use of DCC at the monomer synthesis stage allowed to decrease the reaction temperature (from the boiling temperature of used solvent to room temperature). Eventually, application of microwave irradiation followed by DCC resulted in reduced reaction times, an easier to handle synthesis and in attainment of substantial purity of crude products. Polymerization conducted in anhydrous toluene as a solvent is more reliable method than the conventional reaction in dioxane, as confirmed by higher polymerization yield — over 80%, simplification of the process and high purity of resulting copolymers.

Concentration of MK in the copolymers was estimated by comparing absorption spectra of the CEM and MK solutions as well as of their copolymers. We plotted the absorption maxima *vs.* concentration and found that the relation is linear, *i.e.* absorption of the MK group grows linearly with the increase in the MK molar fraction content. Concentration of MK in the copolymers was evaluated by comparing absorption of the copolymer solutions with that of pure monomer solutions. The compositions of copolymers always were identical with the initial compositions of monomers mixture. Moreover, successive copolymer syntheses performed with the same concentration of monomers did not give different results.

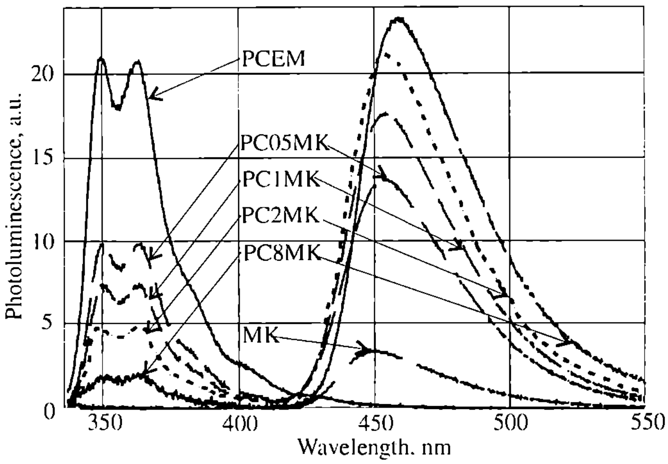


Fig. 1. Photoluminescence spectra of PCEM homopolymer, MK, and CEM/MK copolymers (for symbols see Table 1)

Analysis of the photoluminescence spectra of poly[2-(9-carbazolyl)ethyl methacrylate] (PCEM), MK, and of the CEM/ MK copolymers leads to interesting conclusions (Fig. 1). Thus, the emission band of pure PCEM homopolymer is at about 350 nm, whereas pure MK monomer exhibits an emission band at about 450 nm. After the copolymerization of CEM and MK, the maximum of photoluminescence emission is observed at 460 nm for all the copolymers. As the content of MK in the copolymers is increased, the maximum of photoluminescence emission band shifts slightly towards the red. In addition, it has been found that higher content of MK in the CEM matrix resulted in stronger photoluminescence intensity of. These spectra also confirm that the copolymers are composed only of CEM and MK because their spectra consist of a MK spectrum component and a PCEM spectrum component.

Comparison of PCEM and MK solution absorption spectra with that of the PC05MK PC1MK, PC2MK and PC8MK copolymers (Fig. 2) points to a distinct absorption increase together with the increase of the molar fraction of MK groups in the copolymer over the 410—420 nm range. Absorption increases linearly with increase in the MK molar fraction.

Finally, the electroluminescence spectra of light-emitting diodes made of PCEM homopolymer and the CEM/MK copolymer were compared to show that the maximum emission of the copolymers is actually in the desired blue region (*ca.* 460 nm). In contrast to photoluminescence spectra, the best efficiency for electroluminescence was observed for the PC05MK copolymer (Fig. 3). All these facts confirm usefulness of the CEM/MK copolymers as a substrates for organic opto-electronic devices.

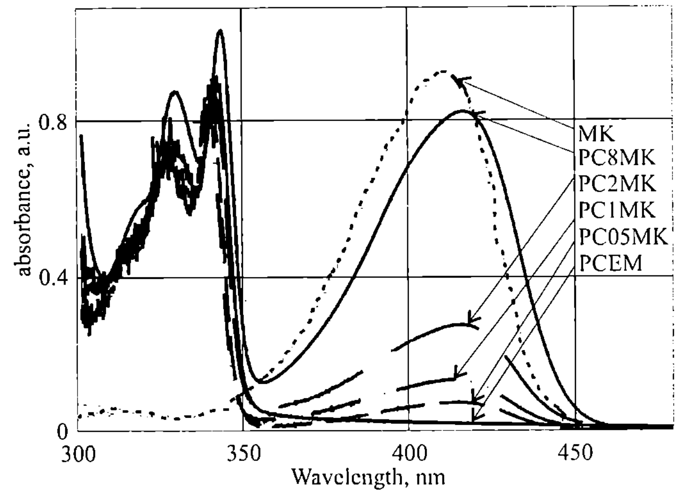


Fig. 2. Absorption spectra of PCEM homopolymer, MK, and CEM/MK copolymers (for symbols see Table 1)

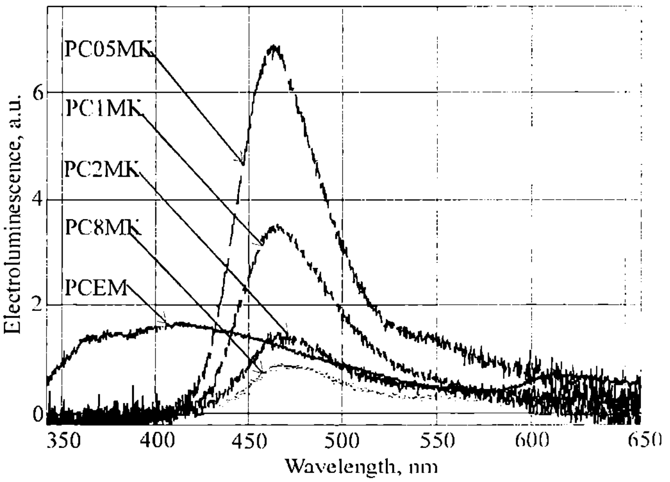


Fig. 3. Electroluminescence spectra of PCEM homopolymer, and CEM/MK copolymers (for symbols see Table 1)

Investigation into the properties, evaluation and optimization of copolymer performance is being continued and will be reported in a subsequent paper.

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