

Photo- and Electroluminescent Properties of Polymethacrylates with Carbazolyl and Fluorescent Pendant Groups

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Because polymeric materials have recently found widespread use in light-emitting devices, we decided to exploit a novel group of copolymers as active materials in such devices and managed to obtain polymeric electroluminescent diodes emitting blue light. The electroluminescent devices were fabricated using the copolymers composed of 2-(carbazol-9-yl)-ethyl methacrylate (CEM) and 3-phenyl-7-methacryloyloxyethoxy-1-methyl-1*H*-pyrazolo[3,4-*b*]-quinoline (MEPQ). The concentration of MEPQ in the copolymers was kept at a low level and changed from 0.5, 1, 2, 5 to 8 mol %. The turn-on voltage for light emission was 8 V. It was found that the emission peaks of the electroluminescent devices were blue-shifted by ≈9 nm in comparison to photoluminescence spectra of the copolymers in thin film. Moreover, as the concentration of MEPQ in the copolymers was increased from 0.5 to 8 mol %, the photoluminescence emission peaks shifted slightly to the red from 447 to 455 nm, while the electroluminescence emission peaks moved from 438 to 447 nm. Because MEPQ groups are bound to the polymer backbone, light emission was equally spread on the whole surface.

Introduction

When an organic material is sandwiched between two suitable electrodes and a bias voltage is applied, visible light may be emitted. Such emission produced by the action of an electrical current is called electroluminescence (EL).¹ The generation of light in these systems is a result of the recombination of holes and electrons injected from opposite electrodes. A number of fully conjugated polymers, copolymers, polymer blends, and fluorescent dye doped polymeric materials have been found to exhibit photo- and electroluminescent properties.²

Fabricating a green light-emitting diode (LED), Burroughes et al.² first demonstrated the light emission from poly(*p*-phenylenevinylene) (PPV), which was used in the emitting layer. Since then, a great number of polymers have been reported to have electroluminescence properties and can emit various portions of the visible spectrum.^{3–9}

The reported advantages of using organic materials to manufacture electroluminescent devices are the possibility of preparing thin layers on flexible substrates, excellent film-forming properties, high brightness and efficiency, and the low cost of the fabrication.²

Recently, poly(*N*-vinylcarbazole) (PVK) has attracted attention because of its applications related to organic light-emitting diodes in which the emitting layer is formed by PVK itself or in blends with other materials. Such devices have shown a remarkable increase in luminescence efficiency and relatively facile color tunability^{3–5} as compared to PVK.

Romero et al.⁹ used oligomers and polymers based on carbazole as the material for possible applications in light-emitting devices. They observed an increase of the external quantum efficiency in diodes based on the copolymers with short thiophene segments as compared to PVK.

Because carbazole and its derivatives are one of the main interests in our laboratory, we have investigated carbazole novel copolymers as the emitting layers in the search for new materials for polymer LED's. The copolymers are composed of 2-(9-carbazolyl)ethyl methacrylate (CEM) and 3-phenyl-7-methacryloyloxyethoxy-1-methyl-1*H*-pyrazolo[3,4-*b*]-quinoline (MEPQ) (Scheme 2). As we could show in a preliminary investigation, poly(2-(9-carbazolyl)ethyl methacrylate) (PCEM) exhibited photoluminescence behavior similar to PVK in its solid state.⁹ Recently, electroluminescence properties of

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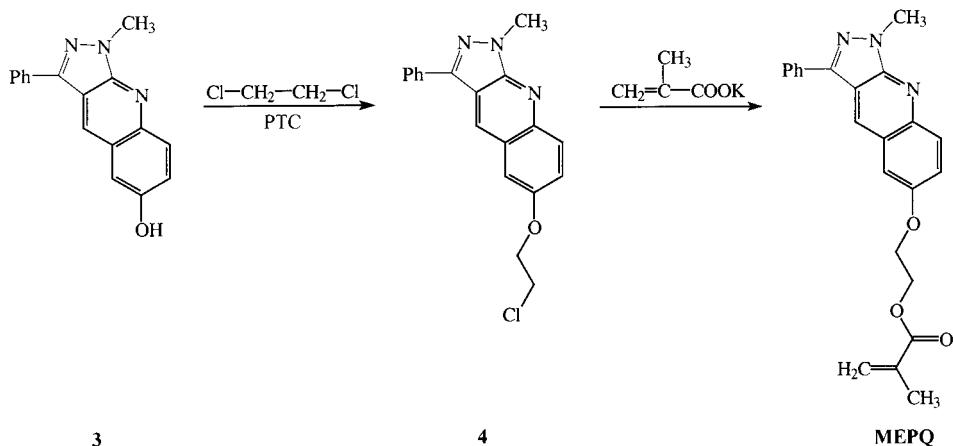
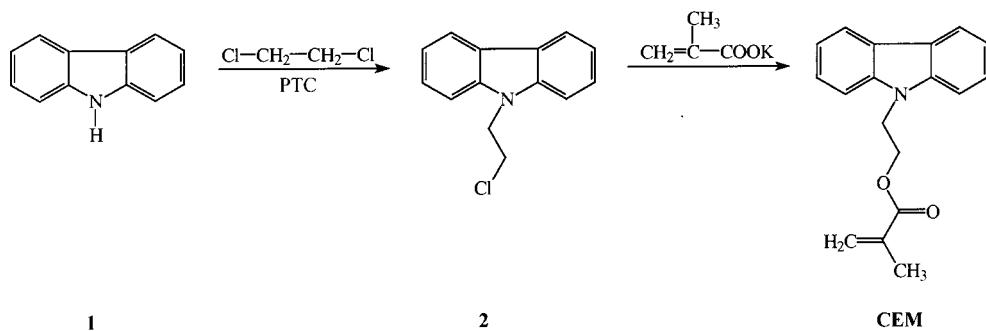
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Scheme 1

PVK and its derivatives^{10,11} and pyrazolo[3,4-*b*]quinoline blends with PVK¹² and copolymers with 2-(9-carbazolyl)-ethyl methacrylate¹³ have been reported. In this paper, we would like to report on the synthesis and polymerization of such monomers, device fabrication, and photo- and electroluminescent properties of the copolymers.

Experimental Section

The structures of all the compounds were verified by means of NMR, IR, GC/MS methods, and elemental analyses. ¹H NMR spectra were recorded in CDCl_3 on a Tesla 80-MHz NMR spectrometer. IR spectra were recorded using a BioRad FTS 165 FT-IR spectrophotometer. Mass spectra and purity of all the intermediates were recorded and verified using a Hewlett-Packard 5890 gas chromatograph coupled with a Hewlett-Packard 5971 mass detector. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer. Melting points, measured on Boetius-PHMK 05 microscope plates, are uncorrected. The progress of the reactions was monitored by thin-layer chromatography (TLC) (Merck Kieselgel 254F; hexane:acetone:bromoform 10:1:2). The molecular weights of the polymers and copolymers were estimated in THF by gel permeation chromatography (GPC) using a Knauer Instrument chromatograph equipped with PL gel 10- μm mixed columns. A calibration curve was obtained by using polystyrene standards.

Solvents and commercially available substrates were purified by conventional methods before use. The PCEM polymer and the copolymers of CEM and MEPQ were prepared accord-

ing to the synthetic route shown in Schemes 1 and 2. Identical experimental procedures were used to prepare all the copolymers, and hence only a representative description is given for the monomer synthesis.

Monomer Synthesis. 9-(2-Chloroethyl)carbazole (**2**). **2** was prepared using a modification of the procedure described by Bogdal and Jaskot.¹⁴ Carbazole (**1**) (2.5 g, 0.015 mol), potassium hydroxide (8.4 g, 0.15 mol), potassium carbonate (20 g, 0.15 mol), and tetrabutylammonium bromide (0.48 g, 0.0015 mol) were stirred in 1,2-dichloroethane (100 mL) at 45 °C for 5 h. The progress of the reaction was monitored by TLC. After being allowed to cool, the mixture was filtered and the residue was washed with 1,2-chloroethane. Then, the organic solutions were combined, washed twice with water (2 × 50 mL), and dried over MgSO_4 . Next, the solvent was evaporated under reduced pressure to give solid material that was recrystallized twice from an ethanol solution to afford 2.5 g of 9-(2-chloroethyl)carbazole (**2**). Yield: 75%. mp 129–130.5 °C.

IR (KBr) ν : 3050 (w), 2960 (w), 2923 (w), 1594 (m), 1487 (s), 1458 (s), 1426 (w), 1381 (w), 1355 (m), 1328 (s), 1296 (w), 1220 (m), 1180 (w), 1159 (w), 1124 (w), 1017 (w), 927 (w), 899 (w), 846 (m), 748 (s), 723 (s), 658 (m) cm^{-1} . MS m/z : 231 (M + 2)⁺, 8.2%, 229 (M⁺, 29%), 180 (100%), 181 (14.5%), 152 (12.7%). ¹H NMR (CDCl_3) δ : 3.83 (t, 2H, J = 7.1 Hz, $-\text{CH}_2\text{Cl}$), 4.62 (t, 2H, J = 7.0 Hz, $=\text{N}-\text{CH}_2-$), 7.14–7.50 (m, 6H, aromatic protons 1–3, 6–8), 8.04–8.13 (m, 2H, aromatic protons 4, 5) ppm.

2-(Carbazol-9-yl)ethyl Methacrylate (**CEM**). **CEM** was prepared according to a modified procedure described by Nakano et al.¹⁵ Thus, methacrylic acid (1.0 g, 0.012 mol) was stirred with potassium hydrogen carbonate (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 DMF solution (70 mL) were added

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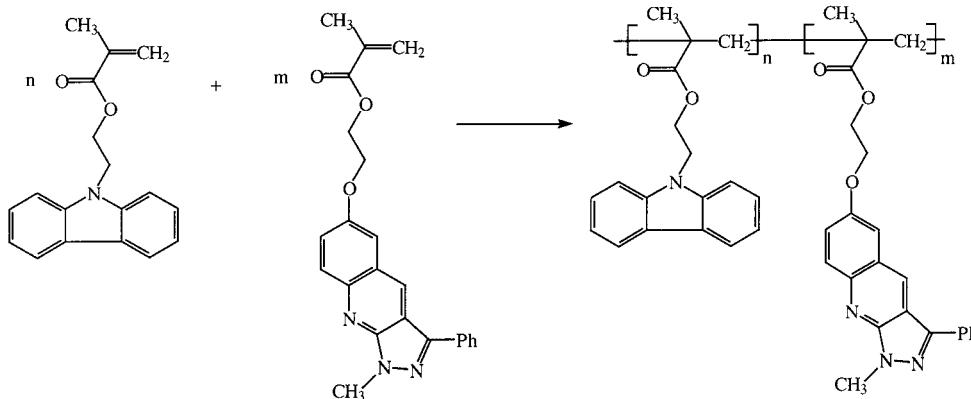
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Scheme 2



to the salt and the mixture was stirred at 100 °C for 24 h. Next, the reaction mixture was allowed to cool, and the solvent was evaporated. The resulting solid material was dissolved in methylene chloride (80 mL) and poured into water (\approx 300 mL). The organic layer was then separated and washed with 5% aqueous solution of sodium hydroxide and finally with water. The organic solution was dried over MgSO_4 and filtered, and the solvent was removed under reduced pressure. The crude product was recrystallized twice from ethanol to afford 2.40 g of 2-(carbazol-9-yl)ethyl methacrylate (**CEM**). Yield 86%. mp 81.5–82.5 °C.

IR (KBr) ν : 3051 (m), 1720 (s), 2978 (m), 1630 (m), 1598 (w), 1489 (w), 1456 (s), 1318 (s), 1172 (s), 1157 (m), 949 (m), 816 (m), 720 (s), 746 (s) cm^{-1} . MS m/z : 280 (($M + 1$)⁺, 6.7%), 279 (M⁺, 33.7%), 193 (38.5%), 181 (14.4%), 180 (100%), 152 (16.8%). ¹H NMR (CDCl_3) δ : 1.79–1.82 (s, 3H, $-\text{CH}_3$), 4.53–4.60 (m, 4H, $-\text{CH}_2-\text{CH}_2-$), 5.45–5.49 (m, 1H, = CH_2 trans), 5.91–5.94 (s, 1H, = CH_2 cis), 7.13–7.50 (m, 6H, aromatic protons 1–3, 6–8), 8.03–8.15 (m, 2H, aromatic protons 4, 5) ppm. Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$ (%): C, 77.4; H, 6.1; N, 5.0. Found (%): C, 77.2; H, 6.0; N, 5.0.

3-Phenyl-7-hydroxy-1-methyl-1H-pyrazolo[3,4-b]quinoline (**3**), the starting material for the synthesis of **MEPQ**, was prepared according to the method given by Danel and Tomaszik and co-workers.^{16,17}

3-Phenyl-7-(2-chloroethoxy)-1-methyl-1H-pyrazolo[3,4-b]quinoline (**4**) and 3-phenyl-7-methacryloyloxyethoxy-1-methyl-1H-pyrazolo[3,4-b]quinoline (**MEPQ**) were obtained by similar procedures as described for 9-(2-chloroethyl)carbazole and 2-(carbazol-9-yl)ethyl methacrylate (**CEM**), respectively.

3-Phenyl-7-(2-chloroethoxy)-1-methyl-1H-pyrazolo[3,4-b]quinoline (**4**). 3-Phenyl-7-hydroxy-1-methyl-1H-pyrazolo[3,4-b]quinoline (**3**) (0.37 g, 0.0013 mol), potassium hydroxide (8.0 g, 0.14 mol), potassium carbonate (8 g, 0.058 mol), tetrabutylammonium bromide (0.15 g, 0.00047 mol), and 1,2-dichloroethane (30 mL) were mixed together to give **4**. Yield: 0.45 g (88%) of **4**. mp 146–8 °C.

IR (KBr) ν : 3046 (w), 2961 (w), 2934 (m), 2877 (w), 1627 (m), 1608 (m), 1487 (m), 1428 (m), 1344 (m), 1223 (s), 1089 (m), 1036 (m), 825 (m), 801 (m), 758 (m) 670 (m), 659 (m), 597 (m) cm^{-1} . MS m/z : 340 (($M + 3$)⁺, 8%), 339 (($M + 2$)⁺, 36%), 338 (($M + 1$)⁺, 23%), 337 (M⁺, 100%), 274 (49%), 246 (28%). ¹H NMR (CDCl_3) δ : 1.88 (3H, s, N– CH_3), 3.82–3.97 (2H, t, CH_2), 4.26–4.43 (2H, t, CH_2), 7.17–7.26 (1H, m, aromatic protons), 7.40–7.67 (4H, m, aromatic protons), 7.99–8.11 (3H, m, aromatic protons), 8.70 (1H, s, aromatic protons) ppm. Calcd for $\text{C}_{19}\text{H}_{19}\text{ClN}_3\text{O}$ (%): C, 67.0; H, 5.6; N, 12.3. Found (%): C, 66.9; H, 5.3; N, 11.8.

3-Phenyl-7-methacryloyloxyethoxy-1-methyl-1H-pyrazolo[3,4-b]quinoline (**MEPQ**). 3-Phenyl-7-(2-chloroethoxy)-1-methyl-1H-pyrazolo[3,4-b]quinoline (**4**) (0.40 g, 0.0012 mol), methacrylic acid (0.16 g, 0.0019 mol), potassium hydrogen carbonate

Table 1. Number and Weight Average Molecular Masses of Copolymers of **MEPQ and **CEM****

copolymer	abbreviation	yield (%)	M_n (10^4)	M_w (10^4)	M_w/M_n
CEM (100%)	PCEM	64	1.12	3.64	3.27
MEPQ (0.5%) CEM (99.5%)	PM05C	56	1.63	5.20	3.18
MEPQ (1%) CEM (99%)	PM1C	60	1.34	3.43	2.56
MEPQ (2%) CEM (98%)	PM2C	57	1.47*	4.15	2.82
MEPQ (5%) CEM (95%)	PM5C	52	1.25	3.80	3.04
MEPQ (8%) CEM (92%)	PM8C	50	1.25	4.01	3.20

(0.18 g, 0.0018 mol), hydroquinone (0.016 g, 0.00015 mol), and DMF (15 mL) were mixed together to give **MEPQ**. Yield 0.39 g (84%). mp 137–8 °C.

IR ν : 3059 (w), 2959 (m), 2933 (m), 1715 (s), 1630 (s), 1608 (s), 1485 (m), 1435 (s), 1401 (m), 1319 (s), 1227 (s), 1183 (s), 1091 (m), 1071 (m), 978 (m), 956 (m), 895 (m), 824 (s), 776 (m), 764 (m), 696 (m), 676 (m), 661 (m), 600 (m) cm^{-1} . MS m/z : 388 (($M + 1$)⁺, 3%), 387 (M⁺, 8%), 113 (100%), 69 (19%), 41 (12%). ¹H NMR (CDCl_3) δ : 1.88 (3H, s, N– CH_3), 1.97 (3H, s, $\text{C}=\text{CH}_3$), 4.29–4.42 (2H, t, CH_2), 4.55–4.69 (2H, t, CH_2), 5.60 (1H, s, $\text{H}-\text{C}=\text{C}-\text{COO}-$ (trans)), 6.18 (1H, s, $\text{H}-\text{C}=\text{C}-\text{COO}-$ (cis)), 7.26 (1H, m, aromatic protons), 7.48–7.57 (4H, m, aromatic protons), 8.00–8.12 (3H, m, aromatic protons), 8.76 (1H, s, aromatic protons) ppm.

Polymerization. Preparation of **PCEM.** 2-(Carbazol-9-yl)-ethyl methacrylate (**CEM**) (0.5 g) was dissolved in toluene (10 mL) with AIBN (1 mol %) added as an 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 precipitated into a large amount of methanol. The crude product was redissolved several times in THF and reprecipitated into methanol to afford 0.43 g of **PCEM**.

Copolymerization of **CEM and **MEPQ**.** The monomers (total amount 0.5 g) taken in the desired molar ratio were dissolved in toluene (10 mL) with AIBN (1 mol %) added as an 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 precipitated into a large amount of methanol. The product was redissolved several times in THF and reprecipitated in methanol.

The molecular weights of the copolymers and polymer as well as abbreviations used in the text are presented in Table 1.

Results and Discussion

Absorption Spectra. Optical absorption spectra were obtained in solution and films by means of a ORIEL MULTISPEC II spectrometer in the range from 270 to 500 nm. The light beams were brought in and out of the sample through the fiber optics. Samples of thin films of the copolymer for absorption measurements

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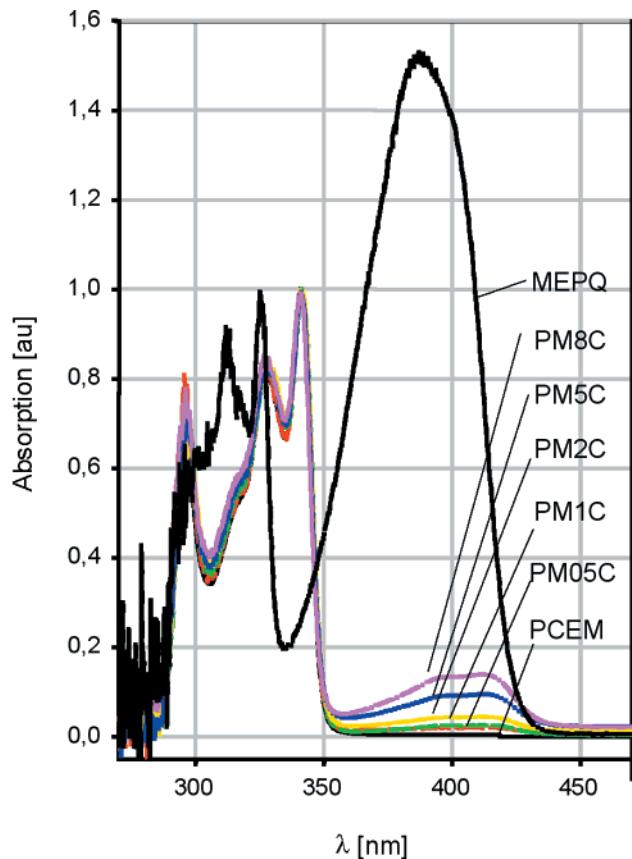


Figure 1. Absorption spectrum of the copolymers and PCEM in solution.

were made employing spin-coating techniques onto quartz using THF as the solvent, whereas in solution the spectral measurements were conducted in a quartz cuvette. To compare the fluorescence properties of polymer solutions, the concentrations of the solutions were adjusted to give the absorbances equal to 1 at a wavelength of 340 nm.

UV-Vis absorption spectra of the copolymers and poly(2-(carbazol-9-yl)ethyl methacrylate) (PCEM) solutions are presented in Figure 1. With regard to pure PCEM, the spectra of the copolymers are quite similar to each other in the spectral range between 270 and 350 nm.

Comparing absorption spectra of the solutions of PCEM and MEPQ and PM05C, PM1C, PM2C, PM5C, and PM8C copolymers, one can observe a clear absorption increase together with the increase of the molar fraction of MEPQ groups in the copolymer in the range from 380 to 440 nm. The absorption is growing linearly with the increase of the MEPQ molar fraction.

When the absorption of the copolymers in solution (Figure 1) and film (Figure 2) were compared, only a slight shift (i.e., 3 nm) of the absorption maxima toward longer waves was observed in the case of the films. The participation of the MEPQ group can be seen in the range from 380 to 440 nm in the solution spectra. For films, the absorbance spectrum structures (Figure 2) are similar; however, a clear displacement, larger with increasing amounts of MEPQ in copolymer, is observed.

Infrared Spectra. Samples of the copolymers were prepared by casting copolymer solutions on KBr plates. Because the concentration of MEPQ in the copolymers

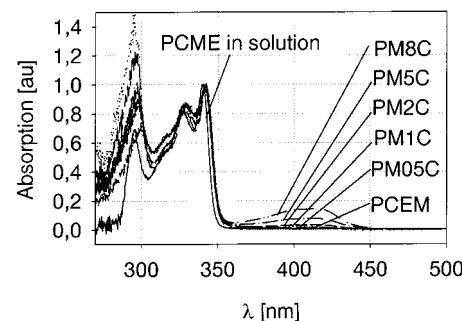


Figure 2. Absorption spectrum of the copolymers and PCEM films in comparison with the solution of PCEM.

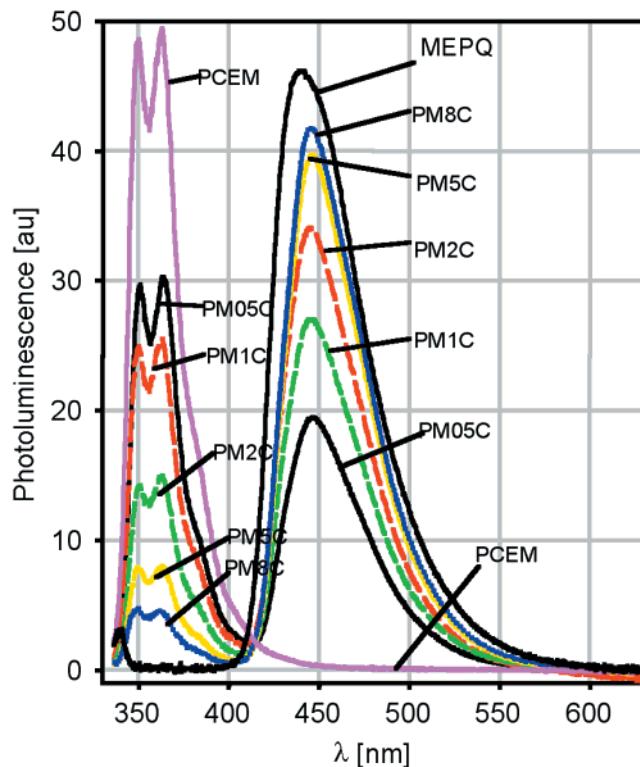


Figure 3. Photoluminescence spectrum of the copolymers and PCEM in solution.

was kept at a low level, the spectra of the copolymers are not so different from the spectra of PCEM in the range between 650 and 4000 cm^{-1} .

Photoluminescence Spectra. Photoluminescent properties were investigated using an ORIEL MULTISPEC II spectrometer with fiber optics. A xenon lamp was used as the source of light. Monochromatic excitation was obtained using a CARL ZEISS JENA monochromator ($\lambda = 340 \text{ nm}$). The photoluminescence spectra were measured for copolymer solutions and films that were a few micrometers thick. The samples of films of the copolymers for photoluminescence measurements were made by spin-coating techniques onto quartz. The films were obtained from THF solutions at room temperature followed by drying at 40 °C in a vacuum for 24 h.

The photoluminescence spectra recorded in solutions and films are presented in Figures 3 and 5, respectively. It can be seen that a profound influence of MEPQ monomer is indicated despite its low content in the copolymers. In solution, photoluminescence spectra of the copolymers can be treated as a sum of the emission

Table 2. PL Intensity of MEPQ and CEM Groups in the Copolymers

molar fraction of the MEPQ group in the copolymer PC _x Q	intensity of the MEPQ group emission in the copolymer (au) ($\lambda_{\text{ex}} = 340$ nm)	intensity of the CEM group emission in the copolymer (au) ($\lambda_{\text{ex}} = 340$ nm)	emission maximum of copolymer in thin films (nm)	photoluminescence intensity of the thin copolymer layer (au)
PCEM		49		
PC05Q	19	30	447.1	1
PC1Q	27	26	447.9	0.847
PC2Q	34	15	449.0	0.721
PC5Q	39	8	452.2	0.692
PC8Q	42	4	455.3	0.673

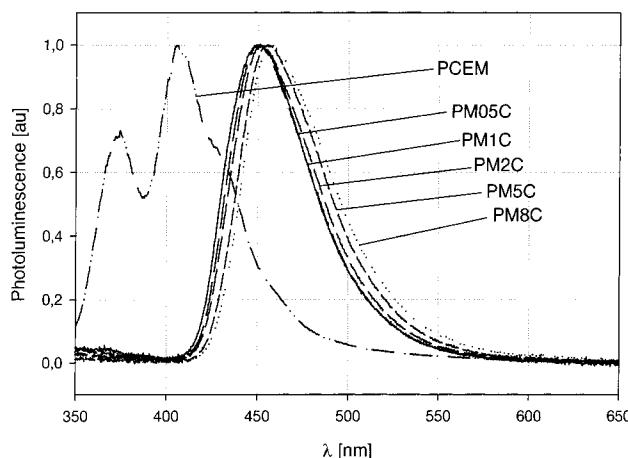


Figure 4. Photoluminescence spectrum of the copolymers and PCEM in film.

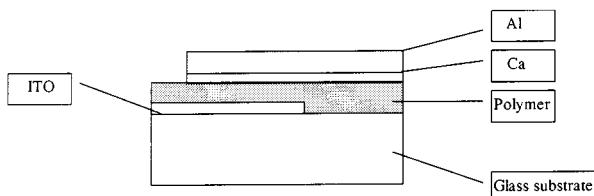


Figure 5. Device structure of ITO/copolymer/Ca/Al.

spectra of PCEM and MEPQ. Higher content of MEPQ in the copolymer causes a clear increase of the emission maximum derived from this group as well as the decrease of this part of the spectrum that originates from PCEM. The intensity of the photoluminescence in the range from 420 to 530 nm is not linear to the participation of MEPQ groups and changes the emission spectra excited at $\lambda = 340$ nm (e.g., excitation of the CEM groups). The maximum emission of light for the MEPQ group in the solution is located at 446 nm. The augmenting of its content in the copolymers results in an increase of the emission peak (Figure 3). The location of the emission maximum for the MEPQ groups does not change. On the other hand, the raise of photoluminescence intensity is not proportional to the MEPQ content in the copolymers. The relationship between the intensity of light and the molar fraction of MEPQ in the copolymers is shown in Table 2. It can be seen that too high a concentration of MEPQ groups in the copolymers leads to growing interaction between them, which results in a decrease of light efficiency. At the same time, the photoluminescence of the CEM group decreases (Figure 3 and Table 2). It might be concluded that in PCEM the excitation energy ($\lambda = 340$ nm) is absorbed by the CEM groups and is then emitted by this group at $\lambda = 350$, 363, and 380 nm. After MEPQ groups are introduced to the copolymers, energy is still

absorbed by the CEM groups, but a part of it is transferred and eventually emitted by the MEPQ groups at $\lambda = 446$ nm.

In thin films, the photoluminescent spectra of PCEM are different from those of the copolymers (Figure 4). For PCEM three maxima at 367, 405, and 427 nm are observed,¹⁸ whereas there is only one emission peak for the copolymers. As the concentration of MEPQ in the copolymers increases, the photoluminescence emission peak is slightly red-shifted from 448 nm for the copolymer MEPQ (0.5%)-CEM (99.5%) to 457 nm for the copolymer MEPQ (8%)-CEM (92%) (Table 2). The influence of the MEPQ group on the photoluminescence spectrum is clearly seen here. Although the CEM group was excited at 340 nm, the entire energy is transferred to the MEPQ group, giving rise to the emission peak around 450 nm. Comparing the intensity of the photoluminescence of each copolymer, the strongest emission is observed by PM05C. The increase of the molar fraction of the MEPQ groups from 0.5% to 8% causes concentration quenching, which leads to a decrease of the photoluminescence by about 30% (Figure 4 and Table 2).

Experiment. Electroluminescent (EL) devices were fabricated using copolymers as the hole-transporting emitter layer. A cell structure of the glass substrate/indium–tin oxide/copolymers/ Ca/Al was employed (Figure 5). Using THF as a solvent, we obtained the films of the copolymers with a thickness of about 100 nm by spin coating onto an indium–tin oxide (ITO) coated glass substrate. Layers of Ca (10 nm) and Al (100 nm) were vacuum-deposited successively at 2×10^{-6} Torr onto the polymer layers. The aluminum electrode was deposited for air protection and electrical contact improvement.

Electroluminescence Spectra. Obtaining electroluminescent diodes emitting blue light made the use of the copolymers described here as active media in polymer light-emitting devices even more interesting and provided more possibilities for their application. In this cell structure, the carrier injection proceeds from the electrodes to the copolymer layer. The mechanism of light emission is based on the injection of electrons and holes by electrodes yielding excitons in the organic layers. The exciton deactivation leads to the emission of one photon. Light is emitted from MEPQ molecules, which act as traps for the charges injected by the electrodes. The situation may be explained with the energy diagram (Figure 6), which was obtained from UPS and UV–Vis experiments. The LUMO level is lower for the MEPQ than for the CEM molecule. Both a hole and electron trapped in the former are waiting

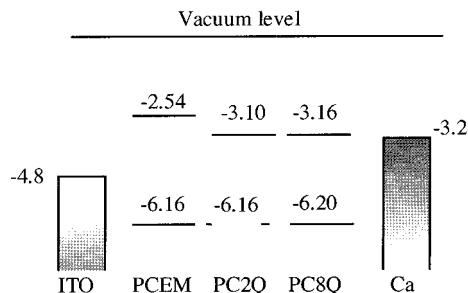


Figure 6. The work functions of ITO and Ca compared with HOMO and LUMO energy levels of the copolymers obtained by means of UPS and UV–Vis.

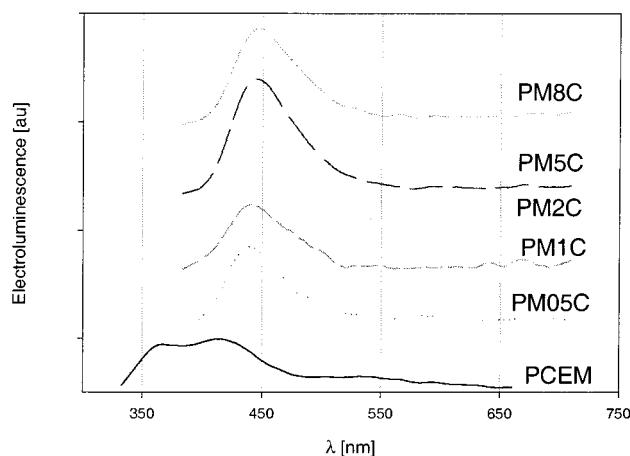


Figure 7. Electroluminescence spectrum of the copolymers under dc forward bias.

for the opposite charge, which after recombination eventually leads to light emission from this molecule. The spectra of electroluminescence are presented in Figure 7. Slight shifts of emission maxima toward longer waves can be observed, which is the result of a higher content of MEPQ in the copolymers (Table 3). These shifts amount to ≈ 6 nm and, in general, they appear only while the concentration of MEPQ in the copolymers is in the range of 0–5%. After the MEPQ molecular fraction exceeds 5% in the copolymers, the change

Table 3. EL Intensity vs Concentration of MEPQ in the Copolymers

molar fraction of the MEPQ group in the copolymer PC _x Q	intensity of electroluminescence maximum (nm)	intensity of electroluminescence (au)
PCEM		0.3
PC05Q	440.2	0.97
PC1Q	441.7	1
PC2Q	442.5	0.94
PC5Q	445.2	0.89
PC8Q	445.8	0.83

becomes marginal. Figure 8 shows the typical current–voltage curve of electroluminescence diodes prepared from the copolymers. It clearly indicates the increase of current at voltages exceeding 3 V, which is caused by the barrier injection of electrons into the polymer layer, but may also be due to the presence of oxygen in the polymers, which generates a disturbance in the function of electroluminescence diodes. The LED starts to emit light at about 7 V and the electroluminescence intensity increases fast (Figure 8). The increase of the MEPQ content in the copolymers also generates the change in the electroluminescence intensity (Table 3). As far as PCEM is concerned, the emission is at about 0.3 au. Raising the MEPQ content in the copolymer leads to the increase of the light intensity 2.5–3 times, and the strongest intensity is received when the content of this group in the copolymers amounts to 1%. A further increase in the amount of the active group in a copolymer does not cause any significant changes in the light emission intensity of the LED based on this copolymer and even results in a slight decrease (Table 3). It was found that relative quantum yields of LEDs that were fabricated on the basis of MEPQ and CEM were more than 3 times higher than those made of PVK. During 150 h of work of our devices the intensity of light dropped to 65% of the initial intensity. The change of voltage does not alter the character of the emission spectrum; only the intensity of the LED emission spectrum is changed.

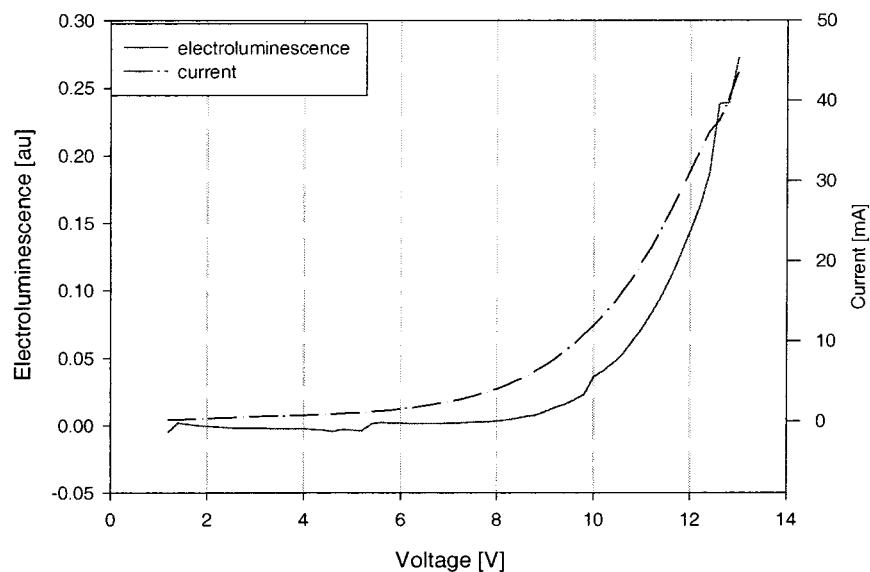


Figure 8. Current–voltage curve of the LED device and the intensity of the electroluminescence–voltage curve of the LED device under dc forward bias for the PC1Q copolymer.

Summation

Our experiments revealed that the application of CEM–MEPQ copolymers as emitting layers in organic LEDs allow blue electroluminescence to be generated. Introducing the MEPQ group in the copolymers causes a change of the emitted color as well as the intensity of emission. In the copolymers, the MEPQ group is the emitting molecule in the electroluminescence process. It has been demonstrated that the intensity of the light can be improved by about three times upon addition of small amounts of such active groups. We found that a 1% molar fraction of MEPQ is sufficient to obtain a saturation of the electroluminescent intensity of the LEDs prepared. Moreover, contrary to blends of polymers and MEPQ¹⁹ that emit light pointwise, light emission was equally spread over the whole surface because MEPQ groups are bound to the copolymer

backbone and their concentration is even throughout the copolymer. The turn-on voltage of the manufactured LEDs for light emission was found at 8 V.

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