

Synthesis and Spectral Investigation of Alkyl Methacrylates with Halogenated Carbazolyl Pendant Groups for Photonics Applications

D. BOGDAL,¹ V. YASHCHUK,² J. PIELICHOWSKI,¹ T. OGUL'CHANSKY,² M. WARZALA,¹ V. KUDRYA²

¹ Katedra Chemii i Technologii Tworzyw Sztucznych, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland

² Physics Department, Kyiv National Taras Shevchenko University, prosp. Glushkova 6, 03127 Kyiv, Ukraine

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ABSTRACT: The alkyl methacrylates with halogenated carbazolyl pendant groups were prepared, and the analysis of their absorption and emission spectra showed that the polymers containing monohalogenated carbazole rings were capable of exhibiting a high singlet-triplet (S-T) conversion. The reasons that mainly triplet excitons could be observed in such polymers and additional bands appearance in the spectra of the polymers with dihalogenated carbazole rings are discussed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1650–1656, 2002; DOI 10.1002/app.10469

Key words: functionalization of polymers; luminescence; fluorescence; phosphorescence

INTRODUCTION

The macromolecules that exhibit triplet excitons are very interesting objects not only due to their pure scientific significance^{1,2} but to their possible applications in nanoelectronics and photonics.^{3–6} The aim of the present investigation was to prepare and explore macromolecules in which mainly triplet excitons could be generated by photons absorption and/or electric field (with the help of special injection electrodes) applying to thin polymer films.⁷ In general, there are three ways to design such macromolecules: (1) selection of the monomer units with high singlet-triplet (S-T) conversion; (2) application the classical “effect of heavy atoms” to design and synthesis of correspondent monomers; and (3) creation a macromolecule in which the role of elementary units is

played by specially designed unconjugated π -electron pairs;⁸ in each of such pairs, one unit causes strong S-T conversion in another one.

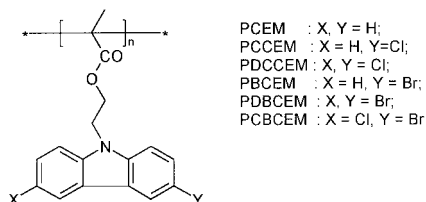
In the present work we have decided to choose the second approach to obtain monomers, i.e., 2-(carbazol-9-yl)ethyl methacrylates (Scheme 1), with heavy halogen substituents at carbazole rings so that the prepared polymers show high singlet-triplet (S-T) conversion.

EXPERIMENTAL

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 CDCl₃ on Tesla 80 MHz NMR spectrometer. IR spectra were recorded using BioRad FTS 165 FTIR spectrophotometer. Mass spectra and purity of all the intermediates were recorded and verified using Hewlett-Packard 5890 gas chromatograph coupled with Hewlett-Packard 5971

Correspondence to: D. Bogdal (pcbogdal@cyf-kr.edu.pl).

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Scheme 1 Halogenated poly[2-(carbazol-9-yl)ethyl methacrylates].

mass detector. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyses. Melting points, measured on a 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 weight of the polymers was estimated in THF by gel permeation chromatography (GPC) using a Knauer Instrument Chromatograph equipped with PL Gel 10-mm mixed columns. A calibration curve was obtained by using polystyrene standards. Solvents and commercially available substrates were purified by conventional methods before use.

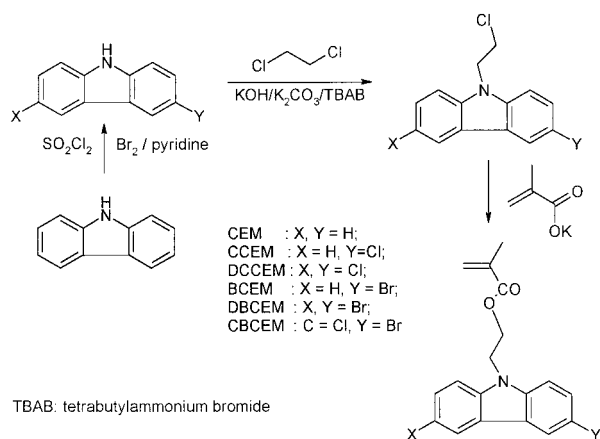
The polymers were prepared according to the synthetic route shown in Schemes 2. Similar experimental procedures were used to prepare all the polymers, and hence, only a representative description is given for the monomer synthesis. 3-Chloro-, 3,6-dichloro-, 3-bromo-, and 3,6-dibromocarbazoles were obtained according to the procedures given in the literature.^{9–12}

Monomer Synthesis

9-(2-Chloroethyl)carbazole was prepared by using a modification of the procedure described by Bogdal et al.⁹ 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 (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-dichloroethane. Then, two organic solutions were combined, washed twice with water (2 × 50 mL), and dried with MgSO₄. Next the solvent was evaporated under the reduced pressure to give solid material that 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.

IR (KBr) $\nu \sim 3050(w)$, 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 (CDCl₃), $\delta = 3.83$ (t, 2H, $J = 7.1$ Hz, —CH₂—Cl), 4.62 (t, 2H, $J = 7.0$ Hz, =N—CH₂—), 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**) was prepared according to the modified procedure described by Nakano et al.¹⁰ 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 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 the water (ca. 300 mL). The organic layer was separated, washed with 5% aqueous solution of sodium hydroxide and then with water. The organic solution was dried over MgSO₄, filtered, and the solvent was removed under the reduced pressure. The crude product was recrystallized twice from ethanol to effort 2.40 g of 2-(carbazol-9-yl)ethyl methacrylate (2a). Yield: 86%; m.p. 81.5–82.5°C, lit. 77–78°C,¹¹ 89°C.¹² IR (KBr) $\nu = 3051(m)$, 1720(s), 2978(m), 1630(m), 1598(w), 1489(w), 1456(s), 1318(s), 1172(s), 1157(m), 949(m), 816(m), 720 (s),



Scheme 2 Synthesis of the 2-(carbazol-9-yl)ethyl methacrylates.

746 (s) cm^{-1} , MS $m/z = 280 ((M+1)^+, 6.7\%), 279 (M^+, 33.7\%), 193 (38.5\%), 181 (14.4\%), 180 (100\%), 152 (16.8\%); ^1\text{H-NMR} (\text{CDCl}_3), \delta = 1.79-1.82$ (s, 3 H, $-\text{CH}_3$), 4.53–4.60 (m, 4 H, $-\text{CH}_2-\text{CH}_2-$), 5.45–5.49 (m, 1 H, $=\text{CH}_2$ *trans*), 5.91–5.94 (s, 1 H, $=\text{CH}_2$ *cis*), 7.13–7.50 (m, 6 H, aromatic protons 1–3, 6–8), 8.03–8.15 (m, 2 H, aromatic protons 4.50) 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.

2-(3-Chlorocarbazol-9-yl)ethyl methacrylate (**CCEM**): m. p. 118–121°C; IR (KBr) $\nu = 3060(\text{w}), 2964(\text{w}), 1719(\text{s}), 1629(\text{m}), 1598(\text{m}), 1455(\text{s}), 1361(\text{m}), 1318(\text{w}), 1294(\text{w}), 1176(\text{s}, \text{b}), 1065(\text{m}), 943(\text{s}), 816(\text{s}), 800(\text{s}), 743(\text{s}), 720(\text{m}), 649(\text{m}), 583(\text{m}), 553(\text{m}), 510(\text{m}), 428(\text{m}), 419(\text{m}); \text{MS } m/z = 316((M+3)^+, 1.7\%), 315((M+2)^+, 10.1\%), 314((M+1)^+, 5.8\%), 313(M^+, 28.6\%), 229(14.2\%), 227(43.6\%), 216(32.4\%), 215(15.1\%), 214(100\%), 152(16.9\%), 151(9.4\%); $^1\text{H-NMR} (\text{CDCl}_3), \delta = 1.80$ (s, 3 H, CH_3), 4.52–4.58 (m, 4 H, CH_2-CH_2), 5.46–5.50 (m, 1 H, $=\text{CH}_2$ *cis*), 5.92 (s, 1 H, $=\text{CH}_2$), 7.25–7.50 (m, 5 H, aromatic protons 1,2,6,7,8), 8.00–8.05 (m, 2 H, aromatic protons 4.5).$

2-(3,6-Dichlorocarbazol-9-yl)ethyl methacrylate (**DCCEM**): m. p. 155–158°C; IR (KBr) $\nu \sim 3061(\text{w}), 2935(\text{w}), 1720(\text{s}), 1631(\text{m}), 1478(\text{s}), 1436(\text{s}), 1361(\text{m}), 1314(\text{s}), 1292(\text{m}), 1218(\text{m}), 1157(\text{s}), 1078(\text{m}), 1058(\text{m}), 943(\text{s}), 855(\text{m}), 797(\text{s}), 680(\text{s}), 644(\text{m}), 566(\text{s}), 510(\text{m}), 480(\text{m}), 419(\text{s}) \text{ cm}^{-1}$, MS $m/z = 352((M+5)^+, 0.8\%), 351((M+4)^+, 4.4\%), 350((M+3)^+, 4.7\%), 349((M+2)^+, 24.2\%), 348((M+1)^+, 7.4\%), 347 (M^+, 37.1\%), 263(37.5\%), 261(57.5\%), 252(10.6\%), 251(9.4\%), 250(63.3\%), 248(100\%), 215(61.2\%), 213(18.5\%), 186(8.3\%), 177(8.2\%), 113(8.3\%); $^1\text{H-NMR} (\text{CDCl}_3), \delta = 1.80$ (s, 3 H, CH_3), 4.56–5.05 (m, 4 H, CH_2-CH_2), 5.46–5.48 (m, 1 H, $=\text{CH}_2$ *cis*), 5.84 (s, 1 H, $=\text{CH}_2$), 7.25–7.43 (m, 4H, aromatic protons 1,2,7,8), 7.96–7.88 (m, 2 H, aromatic protons 4.5)$

2-(3-Bromocarbazol-9-yl)ethyl methacrylate (**BCEM**): yield: 72%; m. p. 123–125°C; IR (KBr) $\nu = 3052(\text{w}), 2985(\text{w}), 2939(\text{w}), 1718(\text{s}), 1630(\text{m}), 1595(\text{m}), 1473(\text{m}), 1454(\text{s}), 1361(\text{m}), 1310(\text{s}), 1298(\text{s}), 1183(\text{s}), 951(\text{m}), 886(\text{m}), 817(\text{m}), 795(\text{s}), 745(\text{s}), 721(\text{m}) \text{ cm}^{-1}$, MS $m/z = 360((M+3)^+, 8.2\%), 359((M+2)^+, 42.1\%), 358((M+1)^+, 10.0\%), 357(M^+, 44.1\%), 274(8.6\%), 273(58.6\%), 272(10.3\%), 271(55.7\%), 261(16.4), 260(100), 259(14.1), 258(98.4\%), 180(10.8\%), 179(58.8\%), 178(30.0\%), 151(14.7\%), 152(18.8\%), 153(11.6\%); $^1\text{H-NMR} (\text{CDCl}_3), \delta = 1.79$ (s, 3 H, $-\text{CH}_3$), 4.52 (s, 4 H, $-\text{CH}_2-\text{CH}_2-$), 5.47–5.51 (m, 1 H, $=\text{CH}_2$ *trans*), 5.91 (s, 1 H, $=\text{CH}_2$ *cis*), 7.25–7.61 (m, 5 H,$

Table I. Number and Weight-Average Molecular Masses of Halogenated Poly[2-(carbazol-9-yl)-ethyl methacrylates]

Polymer	M_n	M_w	M_w/M_n
PCEM	15,900	40,200	2.53
PCCEM	12,800	65,000	5.09
PDCCEM	16,100	55,800	3.64
PBCEM	14,700	33,600	2.28
PDBCEM	10,800	37,900	2.07

aromatic protons 1–2, 6–8), 8.08–8.20 (m, 2 H, aromatic protons 4.5) ppm.

2-(3,6-Dibromocarbazol-9-yl)ethyl methacrylate (**DBCEM**): yield: 76%; m. p. 169–171°C; lit: 170–172°C.¹² IR (KBr) $\nu = 3057(\text{w}), 2934(\text{w}), 1719(\text{s}), 1634(\text{m}), 1559(\text{m}), 1477(\text{s}), 1432(\text{s}), 1360(\text{m}), 1313(\text{m}), 1291(\text{s}), 1218(\text{m}), 1156(\text{s}), 941(\text{m}), 875(\text{m}), 824(\text{m}), 798(\text{s}), 668(\text{w}), 668(\text{w}), 648(\text{m}), 562(\text{w}) \text{ cm}^{-1}$; MS $m/z = 440((M+5)^+, 4.4\%), 439((M+4)^+, 23.5\%), 438((M+3)^+, 8.5\%), 437((M+2)^+, 46.3\%), 436((M+1)^+, 5.2\%), 435(M^+, 24.8\%), 353(36.6\%), 352(12.8\%), 349(38.6\%), 340(50.3\%), 338(100\%), 336(49.8\%), 259(30.7\%), 258(9.9\%), 257(32.8\%), 191(11.4\%), 179(20.0\%), 177(14.1\%), 164(17.8\%), 152(9.3\%), 151(25.5\%), 150(13.7\%); $^1\text{H-NMR} (\text{CDCl}_3), \delta = 1.79$ (s, 3 H, $-\text{CH}_3$), 4.56 (s, 4 H, $-\text{CH}_2-\text{CH}_2-$), 5.46–5.50 (m, 1 H, $=\text{CH}_2$ *trans*), 5.89 (s, 1 H, $=\text{CH}_2$ *cis*), 7.24–7.63 (m, 4 H, aromatic protons 1, 2, 7, 8), 8.12–8.14 (m, 2 H, aromatic protons 4.5) ppm.$

Polymerization

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 several times dissolved in THF and precipitated into methanol to afford 0.43 g of poly[2-(carbazol-9-yl)ethyl methacrylate] (**PCEM**). Number and weight-average molecular masses of all the polymers are given in Table I.

Spectral Investigations

Experiments were carried out at temperature range of 77 to 300 K. A nitrogen pulse laser with

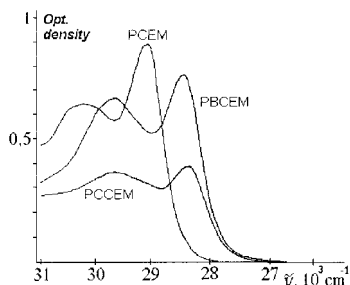


Figure 1 Absorption spectra of **PCEM**, **PCCEM**, and **PBCEM** at 293 K (dioxane solutions, $C_{\text{PCEM}} = 2 \cdot 10^{-4}$ mol/L, $C_{\text{PCCEM}} = 1.8 \cdot 10^{-4}$ mol/L, $C_{\text{PBCEM}} = 1.5 \cdot 10^{-4}$ mol/L).

the wavelength of emission 337 nm and Hg lamp with a set of optical filters were used as a source of luminescence excitation. The absorption spectra were recorded with a Specord UV-Vis spectrophotometer. Luminescence (e.g., fluorescence and phosphorescence) was studied using a spectrometer for steady-state and time-resolved luminescence measurements designed at the Physical Department of Kyiv T. Shevchenko University.

RESULTS AND DISCUSSION

The absorption spectra of the polymers (i.e., **PCEM**, **PCCEM**, and **PBCEM**) are presented in Figure 1. In the case of **PCEM**, first two long-wave absorption spectrum bands located at $\sim 29,000 \text{ cm}^{-1}$ (345 nm) and $\sim 30,000 \text{ cm}^{-1}$ (332 nm) are in the same range as those for low-molecular analogies of poly(9-vinylcarbazole) (**PVCz**) (e.g., see refs. 13–15). The fluorescence spectrum of **PCEM** (Fig. 2) with maxima ~ 350 , 370, and ~ 380 –390 nm is also typical for low-molecular weight carbazole containing polymers,^{2,4,5} and it is associated with fast emission of carbazole π -electron system. At any rate, one can conclude that the nature of absorption and emitting centers is the same for **PCEM** and carbazole containing macromolecules that manifest only monomer fluorescence (excimer emission is absent); for example, the copolymer of N-vinylcarbazole with octyl methacrylate^{16,18,19} or poly[9-(2,3-epoxypropyl)-carbazole].¹⁷ The absorption spectra of **PCCEM** and **PBCEM** are red-shifted over $\sim 600 \text{ cm}^{-1}$ in comparison with the absorption spectrum of **PCEM**, but the shape of spectra and vibrational structures are similar (Fig. 1).

In contrast, in the luminescence spectra of **PBCEM** and **PCCEM** dramatic changes can be observed in relation to **PCEM**. At 293 K, the intensity of **PBCEM** and **PCCEM** luminescence is approximately 10 times lower than the intensity of that of **PCEM**, and the spectra become practically unstructured and red-shifted relatively to **PCEM** luminescence (Fig. 2). At 77 K, another picture is observed: in the red region of spectra (420–550 nm) additional strong emission of **PBCEM** and **PCCEM** appears (Fig. 3). The use of time-resolved spectroscopy system allowed us to obtain phosphorescence spectra of these compounds (Fig. 4). As it follows from the comparison of the steady-state luminescence spectra and phosphorescence spectra of **PBCEM** and **PCCEM** (Figs. 3 and 4), the above emission of **PBCEM** and **PCCEM** is phosphorescence. Thus, incorporation of bromine and chlorine atoms into carbazolyl group of CEM leads to essential increasing phosphorescence yield, especially for Br. It could be explain by classical effect of heavy atom influence on probability of $S \rightarrow T$ conversion in π -electron system. Thus, polymers based on brominated and chlorinated monomers (i.e., **PCCEM**, **PDCCEM**, **PBCEM**, and **PDBCCEM**) are of our interest because of generating and propagating mainly triplet excitons in such systems.

Absorption spectra of the polymers **PDCCEM**, **PDBCCEM**, **PCBCEM** (Fig. 5) in spectral region ν

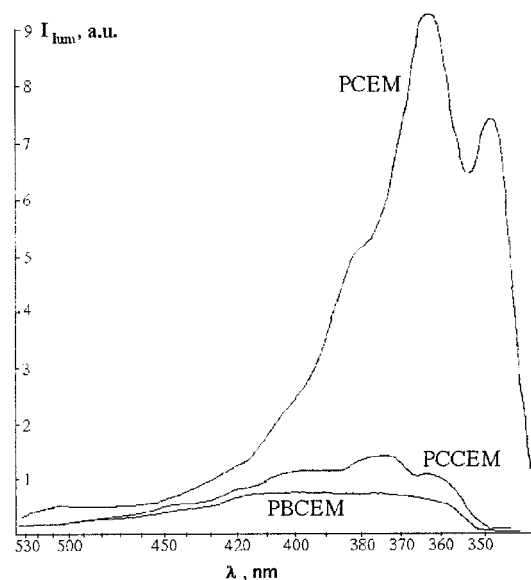


Figure 2 Luminescence spectra of **PCEM**, **PCCEM**, and **PBCEM** at $T = 293 \text{ K}$ (dioxane solutions, $C_{\text{PCEM}} = 2 \cdot 10^{-4}$ mol/L, $C_{\text{PCCEM}} = 1.8 \cdot 10^{-4}$ mol/L, $C_{\text{PBCEM}} = 1.5 \cdot 10^{-4}$ mol/L).

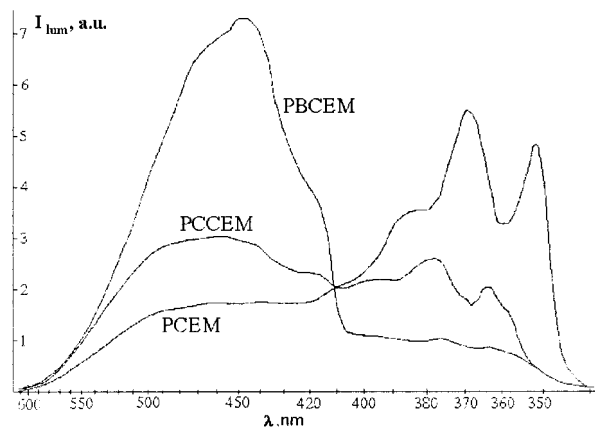


Figure 3 Luminescence spectra of **PCEM**, **PCCEM**, and **PBCEM** at $T = 77$ K (dioxane solutions, $C_{\text{PCEM}} = 2 \cdot 10^{-4}$ mol/L, $C_{\text{PCCEM}} = 1.8 \cdot 10^{-4}$ mol/L, $C_{\text{PBCEM}} = 1.5 \cdot 10^{-4}$ mol/L).

$\geq 27850 \text{ cm}^{-1}$ are similar to that of the polymers investigated earlier (**PCCEM**, **PBCEM**), but for $\nu < 27850 \text{ cm}^{-1}$ the long-wave shoulders appear in the range $27,000\text{--}19,300 \text{ cm}^{-1}$. The existence of bands with $\lambda_{\text{max}1} \approx 29,000 \text{ cm}^{-1}$ and $\lambda_{\text{max}2} \approx 27,850 \text{ cm}^{-1}$ that are similar to absorption bands of **PCEM**, **PBCEM** ($\lambda_{\text{max}1} \sim 29,600 \text{ cm}^{-1}$, $\lambda_{\text{max}2} \approx 28,400 \text{ cm}^{-1}$) testifies that π -electron system of polymers **PDCCEM**, **PDBCEM** does not sufficiently change passing from **PCEM** and **PBCEM** to **PDCCEM** and **PDBCEM**, respectively; however, spectral shift $\sim 600 \text{ cm}^{-1}$ exists. The wide unstructured absorption band ($27,000\text{--}19,300 \text{ cm}^{-1}$) seems to be connected with

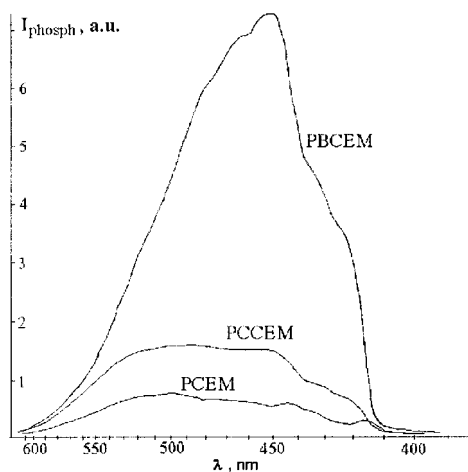


Figure 4 Phosphorescence spectra of **PCEM**, **PCCEM**, and **PBCEM** at $T = 77$ K (dioxane solutions, $C_{\text{PCEM}} = 2 \cdot 10^{-4}$ mol/L, $C_{\text{PCCEM}} = 1.8 \cdot 10^{-4}$ mol/L, $C_{\text{PBCEM}} = 1.5 \cdot 10^{-4}$ mol/L).

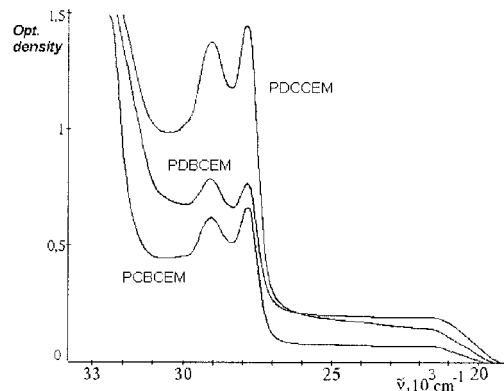


Figure 5 Absorption spectra of **PDBCEM**, **PCBCEM**, **PDCCEM** at $T = 293$ K (dioxane solutions, $C_{\text{PCBCEM}} = 1.4 \cdot 10^{-4}$ mol/L, $C_{\text{PDCCEM}} = 1.6 \cdot 10^{-4}$ mol/L, $C_{\text{PDBCEM}} = 1.2 \cdot 10^{-4}$ mol/L).

the absorption centers of another type. For example, these centers could be associated with the products of oxidation that have been created during the synthesis or storage of polymer powders. It was proved that photooxidation could manifest itself in such a way.^{20,21} On the other hand, Zahdanska et al. reported that changing in optical properties of irradiated solutions and solid films of iodine substituted N-vinylcarbazole-based copolymers was caused by the photochemical separation of halogen atom.²² Additional absorption bands arising in this case were the results of the release of free molecular iodine and its charge transfer complexes with carbazole groups of the copolymers. Hence, luminescence of the polymers (**PDCCEM**, **PDBCEM**) at room temperature

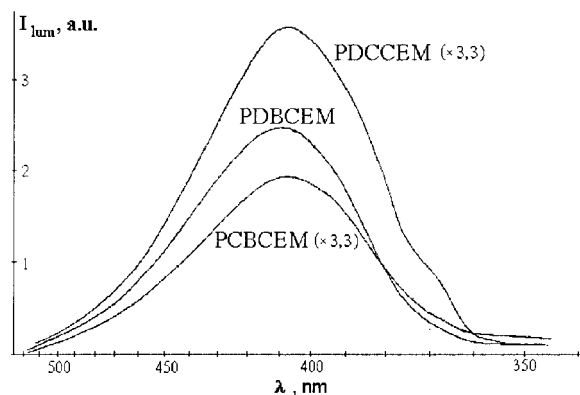


Figure 6 Luminescence spectra of **PDBCEM**, **PCBCEM**, **PDCCEM** at $T = 293$ K (dioxane solutions, $C_{\text{PCBCEM}} = 1.4 \cdot 10^{-4}$ mol/L, $C_{\text{PDCCEM}} = 1.6 \cdot 10^{-4}$ mol/L, $C_{\text{PDBCEM}} = 1.2 \cdot 10^{-4}$ mol/L).

(Fig. 6) is mainly determined by the emission of impurity absorption centers mentioned above.

Comparing luminescence spectra of **PDCCEM**, **PDBCEM**, **PCBCEM** with those of **PCEM**, **PBCEM**, one can observe that **PDCCEM**, **PDBCEM** spectra include both spectrum of inherent emission of the investigated polymers (short-wave range) and spectrum of the emission of non-identified centers (long-wave range). Shape of luminescence bands of the polymers look like the shape of excimer luminescence bands that are well known for carbazole-containing polymers.^{2,4} On the other hand, it is known¹⁷ that excimers do not exist in macromolecules of such a type. Moreover, we did not observe the excimer fluorescence in similar macromolecules but without Cl or Br.^{13,15,20–23} Therefore, we can conclude that the emission of polymers under study is mainly determined by impurity centers. Similar effects can be observed at fluorescence and phosphorescence spectra obtained at $T = 77$ K (Figs. 7 and 8).

SUMMARY

In conclusion, monomers and polymers with halogen substituents at carbazole ring were designed and synthesized. Contrary to absorption spectra that do not show any essential change passing from pure carbazole-containing macromolecules (**PCEM**) to macromolecules with Br and Cl substituents in carbazole rings (**PDCCEM**, **PDBCEM**, **PBCEM**, **PDBCEM**, **PCBCEM**), dramatic changes are detected in luminescence spectra. At 77 K, for the

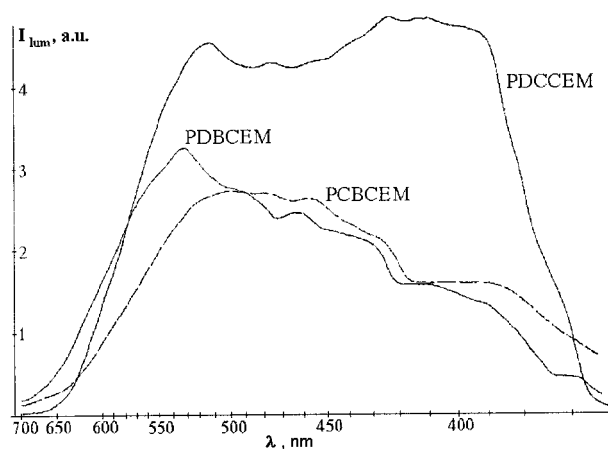


Figure 7 Luminescence spectra of **PDBCEM**, **PCBCEM**, **PDCCEM** at $T = 77$ K (dioxane solutions, $C_{\text{PCBCEM}} = 1.4 \cdot 10^{-4}$ mol/L, $C_{\text{PDCCEM}} = 1.6 \cdot 10^{-4}$ mol/L, $C_{\text{PDBCEM}} = 1.2 \cdot 10^{-4}$ mol/L).

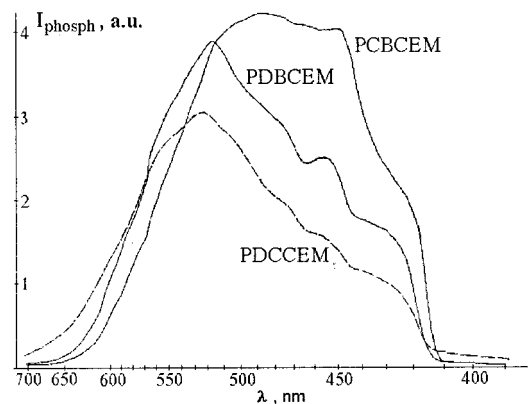


Figure 8 Phosphorescence spectra of **PDBCEM**, **PCBCEM**, **PDCCEM** at $T = 77$ K (dioxane solutions, $C_{\text{PCBCEM}} = 1.4 \cdot 10^{-4}$ mol/L, $C_{\text{PDCCEM}} = 1.6 \cdot 10^{-4}$ mol/L, $C_{\text{PDBCEM}} = 1.2 \cdot 10^{-4}$ mol/L).

polymers with a halogen substituent-delayed emission is mainly observed in luminescence spectra. The spectral results prove that halogen containing carbazole rings exhibit high singlet-triplet (S-T) conversion and mainly triplet excitons can exist in the prepared polymers. The additional bands in absorption and luminescence that appear under passing from a single halogen substituent to double halogen substituents are possibly related to centers created during synthesis and storage of the polymers due to oxidation or separation of halogen atoms followed by charge-transfer complex creation between free halogen atoms and carbazole rings.

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