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Spectral investigation of alkyl polymethacrylates with halogenated carbazolyl pendant groups

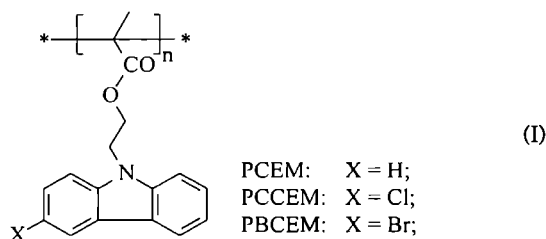
RAPID COMMUNICATION

Summary — Investigations of optical absorption, fluorescence and phosphorescence of alkyl methacrylates with halogenated carbazolyl pendant groups showed that incorporation of bromine and chlorine atoms into a carbazolyl group leads to an essential increase of phosphorescence yield, especially for Br. It was concluded that primarily triplet excitons exist in the polymers prepared.

Key words: triplet exciton, spectral investigation, alkyl methacrylates, carbazolyl pendant groups

Macromolecules exhibiting triplet excitons are very interesting objects, not only due to their pure scientific significance [1, 2], but also 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 photon absorption and/or electric field (with the help of special injection electrodes) applied to thin polymer films [7–9]. In general, there are three ways to design such macromolecules: selection of the monomer units with high singlet→triplet (S→T) conversion, application the classic “effect of heavy atoms” to design and synthesize correspondent monomers, and creation a macromolecule in which the role of elementary units is played by specially designed unconjugated π -electron pairs [10]; in each of such pairs, one causes strong S→T conversion in the other.

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



EXPERIMENTAL

The synthesis of 2-(carbazol-9-yl)ethyl methacrylate (CEM) and its halogenated derivatives was described in our previous papers [7–9, 11].

Polymerization

2-(Carbazol-9-yl)ethyl methacrylate (CEM) 0.5 g was dissolved in toluene (10 mL) with AIBN (1% mole) 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. The reaction was terminated after 48 h by adding THF (15 mL) and the polymer precipitated into a large quantity of methanol. The crude product was dissolved in THF and precipitated into methanol several times to give 0.43 g of poly[2-(carbazol-9-yl)ethyl methacrylate] (PCCEM). Number and weight average molecular weights of all the polymers are given in Table 1.

Table 1. Number and weight average molecular weights of halogenated poly[2-(carbazol-9-yl)ethyl methacrylates]

| Polymer | M_n | M_w | M_w/M_n |
|---------|--------|--------|-----------|
| PCCEM | 15 900 | 40 200 | 2.53 |
| PCCCEM | 12 800 | 65 000 | 5.09 |
| PBCCEM | 14 700 | 33 600 | 2.28 |

Spectral investigations

Experiments were carried out at temperature range of 77 to 300 K. A nitrogen pulse laser with emission wavelength of 337 nm and Hg lamp with a set of optical

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filters were used as a source of luminescence excitation. 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 Kiev T. Shevchenko University.

DISCUSSION OF RESULTS

Absorption spectra of the polymers (*i.e.*, PCEM, PCCEM, and PBCEM) are presented in Fig. 1. In case of PCEM, first two long-wave absorption spectrum bands located at $-29\,000\text{ cm}^{-1}$ (345 nm) and $-30\,000\text{ cm}^{-1}$ (332 nm) are in the same range as those for low-molecular analogs of poly(9-vinylcarbazole) (PVCz) (for example, see [12–14]).

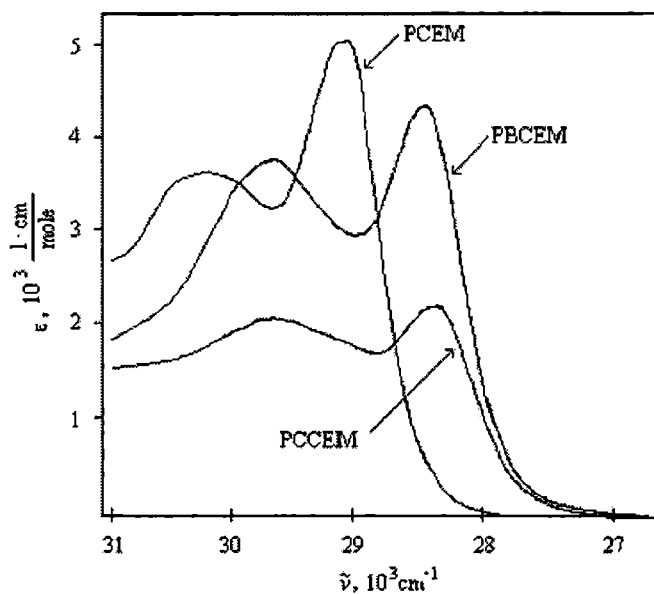


Fig. 1. Absorption spectra (dioxane solution, $c_{\text{PCEM}} = 1,77 \cdot 10^{-4}$ mole/L, $c_{\text{PCCEM}} = 10^{-4}$ mole/L, $c_{\text{PBCEM}} = 1,38 \cdot 10^{-4}$ mole/L)

Fluorescence spectrum of PCEM (Fig. 2) with maxima *ca.* 350, 370 and 380, 390 nm is also typical for low-molecular weight carbazole containing polymers [12–14] and is associated with fast emissions of carbazole π -electron system. At any rate, one can conclude that the nature of absorption and emitting centers are the same for PCEM and carbazole containing macromolecules with only monomer fluorescence manifest (excimer emission is absent); for example, the copolymer of *N*-vinylcarbazole with octhyl methacrylate [15–17] or poly[9-(2,3-epoxypropyl)-carbazole] [18]. The absorption spectra of PCCEM and PBCEM are red-shifted over *ca.* 600 cm^{-1} in comparison with the absorption spectrum of PCEM, but the shape of spectra and vibrational structures are similar (Fig. 1).

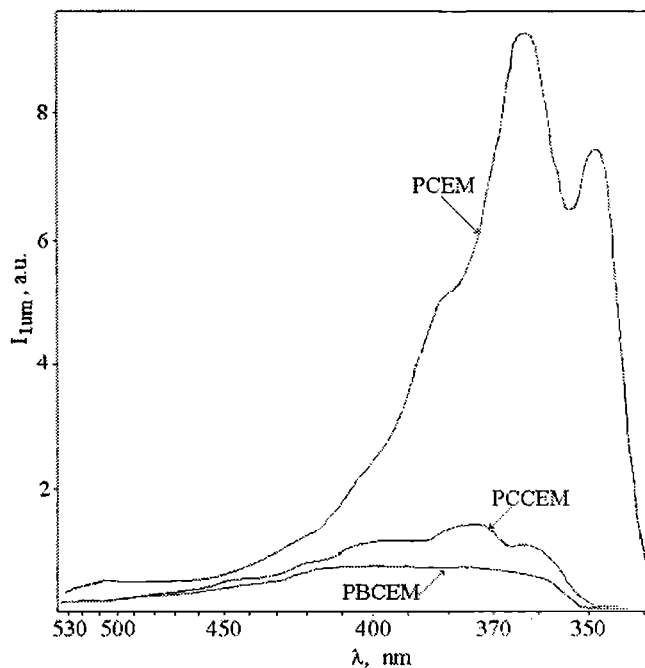


Fig. 2. Luminescence spectra at $T=293\text{ K}$ (dioxane solution, $c_{\text{PCEM}} = 1,77 \cdot 10^{-4}$ mole/L, $c_{\text{PCCEM}} = 10^{-4}$ mole/L, $c_{\text{PBCEM}} = 1,38 \cdot 10^{-4}$ mole/L)

In contrast, dramatic changes can be observed in the luminescence spectra of PBCEM and PCCEM in relation to PCEM. At 293 K, the intensity of PBCEM and PCCEM luminescence is approximately 10 times lower than that of PCEM, and the spectra become practically unstructured and red-shifted relatively to PCEM luminescence (Fig. 2). A different picture is observed at 77 K: additional strong emission of PBCEM and PCCEM appears in the red region of spectra (420–550 nm) (Fig. 3).

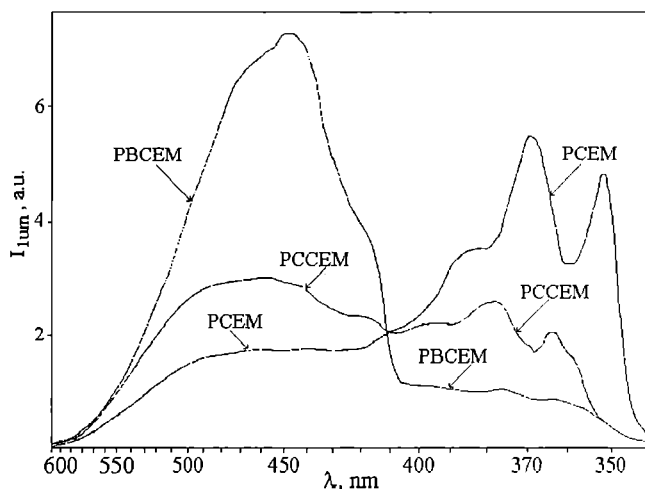


Fig. 3. Luminescence spectra at $T=77\text{ K}$ (dioxane solution, $c_{\text{PCEM}} = 1,77 \cdot 10^{-4}$ mole/L, $c_{\text{PCCEM}} = 10^{-4}$ mole/L, $c_{\text{PBCEM}} = 1,38 \cdot 10^{-4}$ mole/L)

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, 4), the above emissions of PBCEM and PCCEM constitute

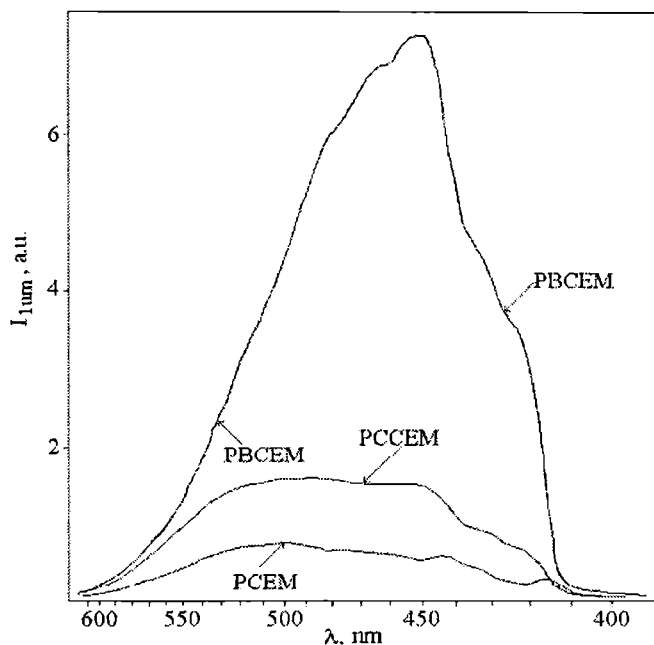


Fig. 4. Phosphorescence spectra at $T=77$ K (dioxane solution, $c_{PCEM} = 1,77 \cdot 10^{-4}$ mole/L, $c_{PCCEM} = 10^{-4}$ mole/L, $c_{PBCEM} = 1,38 \cdot 10^{-4}$ mole/L)

phosphorescence. Thus, incorporation of bromine and chlorine atoms into the carbazoyl group of CEM leads to essential increasing phosphorescence yield, especially for Br. This could be explained by the classic effect of heavy atom influence on probability of $S \rightarrow T$ conversion in a π -electron system. Thus, polymers based on brominated and chlorinated monomers are of our interest because of generating and propagating mainly triplet excitons in such systems.

CONCLUSION

Contrary to absorption spectra that do not show any essential change when passing from pure carbazole-containing macromolecules (PCEM) to macromolecules with Br and Cl substituents in carbazole rings (PCCEM and PBCEM), dramatic changes are detected in luminescence spectra. Spectral investigations prove that high singlet \rightarrow triplet conversion in halogen substituents at carbazole rings of macromolecules investigated takes place. So, mainly triplet excitons can exist in the created

macromolecules. Thus, at 77K primarily delayed emission is observed in luminescence spectra of macromolecules with halogen substituents.

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