

Fluorescence Decay Curves and Time-Resolved Spectra of Poly(N-Epoxypropylcarbazole), PEPCA, at Room Temperature and at 11 K

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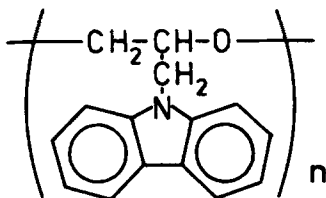
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SUMMARY

Time-resolved fluorescence spectra of solid films of low-molecular-weight poly(N-epoxypropylcarbazole), PEPCA, measured at room temperature and at 11 K are reported. The spectra reveal the presence of two types of emitting centres in the polymer. Below 400 nm, noninteracting carbazolyl side groups emit fluorescence typical of the monomer unit. Above 400 nm, structured emission with peaks at 410, 430, and 460 nm has been observed. Comparison of the detected spectra with that of crystalline N-isopropylcarbazole together with other evidence supports strongly the suggestion that the latter emission is due to intermolecular arrays of the side groups arranged in such a way that their molecular planes are parallel or nearly parallel to each other with antiparallel orientation of the short in-plane molecular axes of the nearest neighbours. The time-resolved spectra and the decay curves show that excitation energy is transferred from monomer side groups to those built in the crystallike arrays and that this transfer becomes less effective at low temperatures.

INTRODUCTION

PEPCA, as a linear polymer with carbazolyl side groups, is a relative of poly(N-vinylcarbazole), PVCA, the most thoroughly studied material among this group of polymers. As seen from the chemical formula of PEPCA, i.e.



its pendant groups are bound to the main chain more loosely than in PVCA and their mutual distance along the chain is also larger. This might lead to an expectation of more simple spectroscopic behaviour in comparison to that of PVCA. However, experimentally, this expectation has not been confirmed.

According to the first spectroscopic reports, due to GAIDELIS et al. (1976, 1980), the absorption spectrum of PEPCA is nearly the same as that of PVCA, which means that individual carbazolyl groups absorb, but the emission spectrum of

thin layers of PEPCA is a rather complicated one consisting of a series of peaks (at 358, 374, 408, 435, 457, and 495 nm) and a broad band around 525 nm. In dilute solutions, they observed only the maxima below 400 nm, in more concentrated solutions, all the maxima observable in the spectrum of layers were present. They ascribed the emission of PEPCA thin films to monomer centra (the short-wavelength part), to phosphorescence and to an intermolecular sandwich excimer with antiparallely oriented short molecular in-plane axes (the broad maximum around 525 nm).

Alternative explanation was suggested by TRCHOVÁ et al. (1981) on the basis of the study of temperature changes in the luminescence spectrum of thin films of PEPCA at temperatures between 103 and 383 K. During the temperature changes, the peaks at 362 and 376 nm changed their height simultaneously as one group, the peaks at 410, 436, and 460 nm as another group and the band around 500 nm behaved like a third separated part of the emission. Irreversible changes of the last mentioned emission above the glass temperature of PEPCA lead them to the conclusion that this emission was due to a product of a photoreaction in the polymer. The short-wavelength emission was the monomer one and the central peaks were suggested to belong to a centrum consisting of two carbazolyl groups arranged sandwichlikely with antiparallely short molecular in-plane axes. Similar arrangement may be expected in the crystals of N-vinylcarbazole in which SANO and MATSUDA (1976) observed the intrinsic emission spectrum consisting of three maxima positioned at the same wavelengths as observed in PEPCA.

The measurement of time-resolved spectra of PEPCA in dilute air-equilibrated solution in benzene (HRSTKA and KLIMOVIC 1981) has revealed only monomer emission with possible small traces of emission above 400 nm at longer time after the excitation. At 360 nm, the decay was monocomponential with lifetime equal to 8,7 ns.

Here, the results of a more detailed study of thin films of PEPCA are presented.

EXPERIMENTAL

Materials

The catalytically prepared PEPCA (kindly donated by prof. Gaidelis) of molecular weight of about 2000 was used. This oligomer was dissolved in benzene and precipitated by methanol. This was done two times.

Polystyrene of M_w 70 000 (Kaučuk, ČSSR) was purified by four similar precipitation procedures. No emission from the polystyrene matrices was observed under the experimental conditions.

N-isopropylcarbazole, NIPCA, (Eastman Kodak, white label) was recrystallized three times from isopropyl alcohol. About 10 mm long white needlelike crystals were obtained.

Solvents

Benzene p.a. and methanol p.a. (both Lachema, ČSSR) and isopropyl alcohol and chloroform (both Baker-Instra-Analyzed)

were used as received.

Preparation of samples

All samples were prepared on optically flat 1 mm thick round sapphire discs. The PEPCA films were cast from a solution in chloroform at room temperature. PEPCA in polystyrene matrix (at the concentration of 5×10^{-4} mole/mole of monomer units of PS) was prepared in the same way. The obtained films were homogeneous and optically clear.

NIPCA crystals were placed on the surface of the sapphire disc and fixed there by a small amount of chloroform. In this way, good contact with the disc was achieved. The samples were opaque due to the presence of some noncrystalline material.

Several hours before the measurement (as well as during the measurement), the samples were kept in vacuum better than 10^{-2} Pa.

Spectrometer

The transient fluorescence measurements were made using a time-correlated single-photon-counting system similar to that of WARE et al. (1971). A gated flashlamp (Applied Photophysics Ltd.) filled with air at 1 atm served as the excitation source. The lamp, operating at 5 kV, yielded pulses of about 3 ns FWHM at a repetition rate of 30 kHz. The excitation line 313 nm was isolated by a narrow-band interference filter (Melles Griot Inc.).

The disc with the sample was placed into the sample holder on the top of the CS-202 optical refrigerator (Air Products and Chemicals Inc.). The emission, viewed at the angle of 145° to the excitation light beam, which entered the sample through the sapphire disc, was focused onto the entrance slit of the H-20 UV grating monochromator (Jobin Yvon) and detected by a RCA 8850 photomultiplier operated at 2.8 kV and cooled to 0°C . The electronic system was assembled of NIM modules from Ortec Inc. and Canberra Inc., the details will be described elsewhere. Data was accumulated and stored in a Canberra Model 3000 pulse-height analyzer and punched on TTY. Further treatment was made using the Hewlett Packard 9830 A calculator.

All the spectra were taken under the same conditions, i.e. 4 nm bandwidth of the monochromator, 1 nm step and the same number (2×10^4) of excitation pulses for each channel, and have not been corrected for the spectral response of the detection system. For each spectrum, the time window was set by the aid of a single channel analyzer. As the zero time, the onset of steep rise of the intensity of the excitation light pulse has been chosen. For the measurement of total spectra, the upper limit of the time window was shifted to 500 ns and the lower limit just before the zero time.

RESULTS AND DISCUSSION

In Fig.1 are plotted the time-resolved spectra of a thin film of PEPCA measured at 295 K. From the time changes of the spectra is clearly seen that the emission is due to two distinct species. The short-wavelength part, the monomer emis-

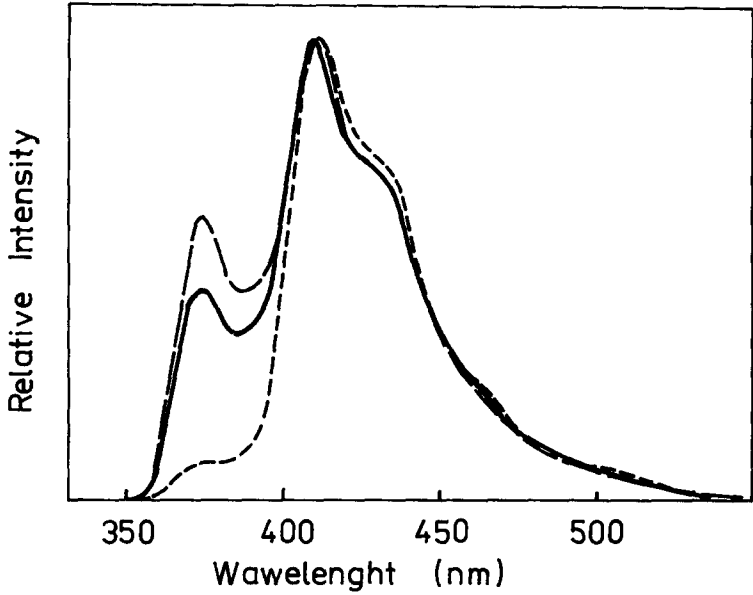


Fig.1. Time-resolved spectra of a PEPCA film at 295 K
 (--- 0 to 1 ns, — 9 to 10 ns, -.- 17 to 19.5 ns)

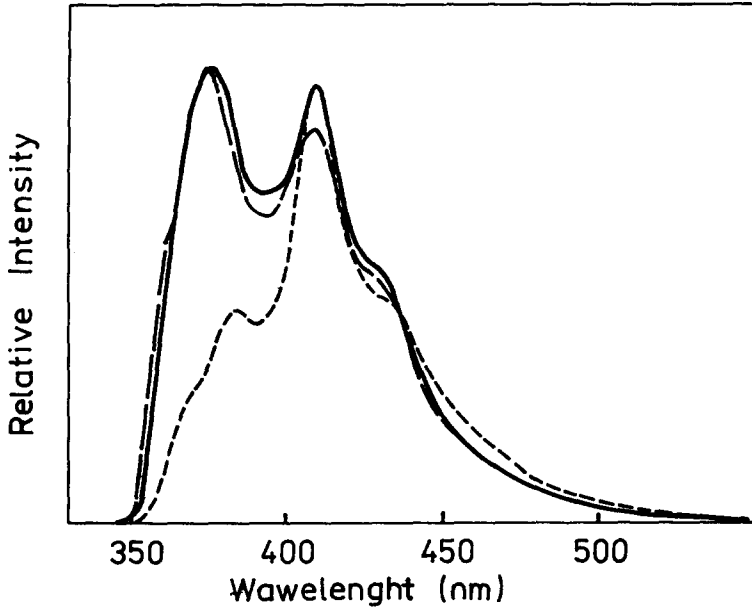


Fig.2. Time-resolved spectra of PEPCA film at 11 K
 (--- 6 to 7 ns, — 9 to 10 ns, -.- 35 to 37.5 ns)

sion, decreases rapidly in respect to the second emission.

The time-resolved spectra of the same sample taken at 11 K are plotted in Fig.2. In this case, the shape of the two parts of the spectrum is almost the same as that of the room temperature spectrum, but the monomer fluorescence decreases much more slowly. As such a large temperature change in the rate constant of radiationless transitions from the excited to the ground state of the monomer seems extremely improbable*, one is lead to suspect the processes of excitation energy transfer from the monomer to the second centrum to be responsible for the observed alteration in the spectral behaviour. Complementary information to this question may be got from the decay curves of the emission of the monomer and of the second centrum. Because of the small overlap of the two parts of the spectra, this information may be obtained easily by proper choose of the wavelengths of measurement of the two decays.

The decay curves of the two emissions (at 370 nm and at 460 nm, resp.) measured at 300 K are plotted in Fig.3 and those taken at 11 K in Fig.4. Semilogarithmic plot has been used in both cases with the time scale of 390 ps per channel. At room temperature, the monomer decay curve follows nearly the shape of the falling part of the excitation pulse and the decay time may be estimated as less than 1 ns. The emission at 460 nm is nonexponential at the beginning but it soon begins to fall exponentially with the decay time of 16 ns (as determined from the slope). This behaviour is typical for an acceptor of excitation energy at high efficiency of the transfer from the donor. At 11 K, the lifetime of excitation is much longer in both the centra. The decay curves are nonexponential throughout the whole interval of detection. This may be explained by a much less effective migration of excitation energy in the polymer at low temperature. The situation may be in general understood within the terms of the Förster model of resonance energy transfer between molecules. According to this model (e.g.FÖRSTER 1948), the excitation energy transfer rate is determined by the mean intermolecular distance, the average orientation factor and the spectral overlap in the system. Rising the temperature, all these variables change in such a way as to enhance the transfer rate.

In order to better understand the nature of the centra responsible for the second emission of PEPCA further experiments were performed. In Fig.5 are plotted the total spectra of a PEPCA film, of PEPCA molecules present at low concentration in polystyrene matrix, and of crystalline NIPCA. The similarity of the spectra of the PEPCA film and of the NIPCA crystals is apparent. Monomer fluorescence in the spectrum of NIPCA crystals is due to the presence of a small amount of the noncrystalline material in the sample. The structure of NIPCA crystals, to the authors' knowledge, has not yet been determined, however, one may expect similarity with the structure of similar materials which is known, e.g. of carbazole

* For comparison, the lifetime of carbazole molecules present at the concentration of 10^{-4} mole/mole of monomer units in a matrix of polystyrene is equal to 11.7 ns at 300 K and to 12.2 ns at 11 K (HRSTKA and KLIMOVIC 1982).

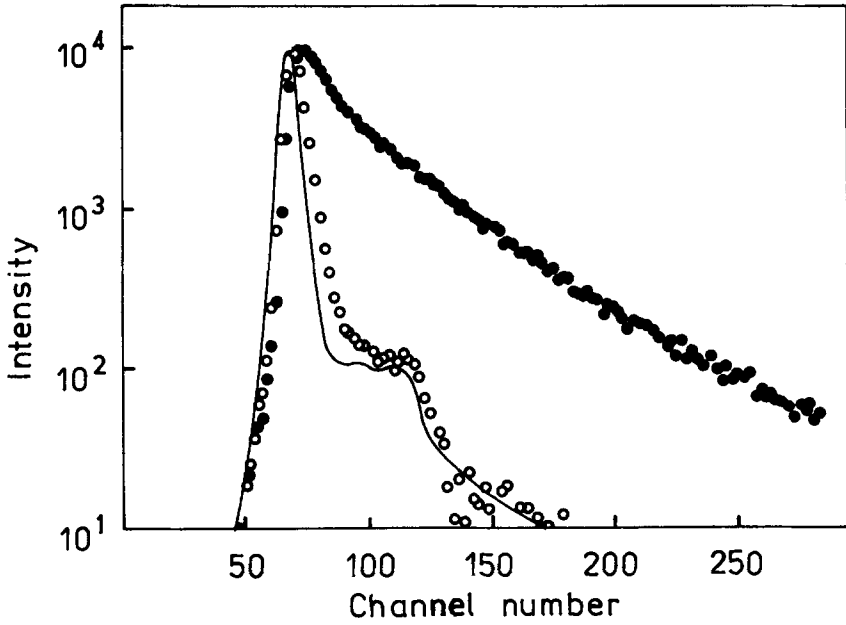


Fig.3. Fluorescence decay curves of PEPCA film at 300 K (— the excitation pulse, ○○○○ emission at 370 nm, ●●● emission at 460 nm)

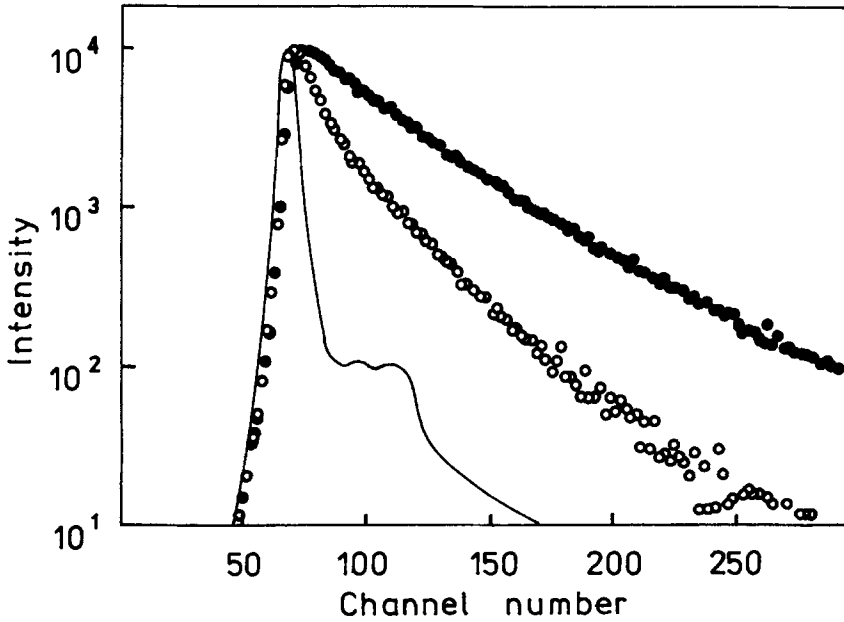


Fig.4. Fluorescence decay curves of PEPCA film at 11 K (— the excitation pulse, ○○○○ emission at 370 nm, ●●● emission at 460 nm)

crystals (LAHIRI 1968) and of dibenzothiophene crystals (SCHAFFRIN and TROTTER 1970, BREE and ZWARICH 1971). In both these cases, pronounced tendency towards the arrangement of neighbouring molecules with the short in-plane molecular axes antiparallel appears, stronger in the latter case. Judging from trials with molecular models, antiparallel sandwich arrangement of carbazolyl groups in PEPCA is easily attainable not only between two different chains but also between sufficiently distant parts of the same chain. Due to the static

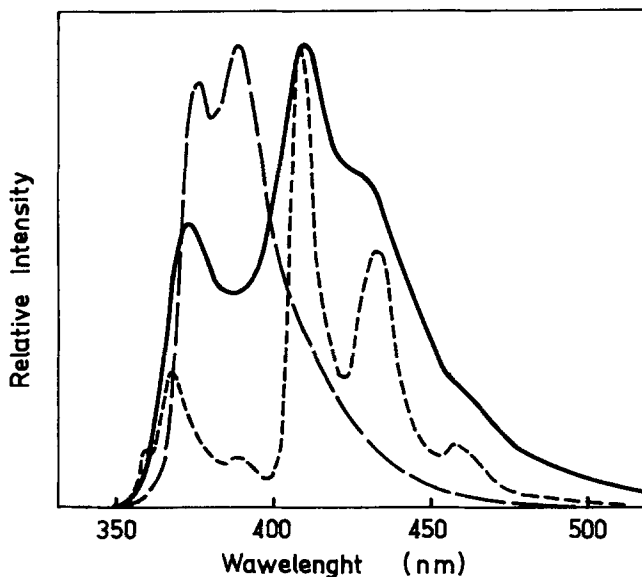


Fig.5. Luminescence spectra; — PEPCA thin film, --- PEPCA in PS (5×10^{-4} mole/mole of monomer units of PS), - - - - crystalline NIPCA

dipole moments of the carbazolyl groups, the sandwichlike arrangement of the neighbours with antiparallel short axes should lead to a gain in the intermolecular interaction energy (compared to the structure of the sandwichlike excimer in PVCA) in the ground state of the side groups and even, as noticed by JOHNSON (1975), in their excited state. This is in line with the observed red shift of the emission.

All the gathered experimental data and the above given arguments as well as the shape of the luminescence spectra of N-vinylcarbazole and of ethylcarbazole crystals (SANO and MATSUDA 1976) seem to support the suggestion that the long-wavelength emission of PEPCA films is due to a physical trap of energy consisting of an array of parallel (or nearly parallel) carbazolyl side groups with antiparallely oriented short molecular in-plane axes. The regularity in the arrangement of the side groups may be responsible for the similarity in luminescence behaviour with the crystals. It should be mentioned here, that all the known facts may be completely explained in a different manner, by assuming the presence of

the same chemical impurity in all the studied materials which might act as an acceptor of the excitation energy and the source of the observed emission. However, it does not look likely that the same impurity might be present in the NVCA and ethylcarbazole of SANO and MATSUDA(1976), in PEPCA from Vilnius and in NIPCA of Eastman Kodak, whilst the similarity in the structural arrangement does look so.

The absence of the emission of PEPCA films above 500 nm, mentioned in the previous papers (GAIDELIS et al.1976,1980, and TRCHOVÁ et al.1981), in the present measurements has been caused without any doubt by careful purification of the materials, excellent vacuum, and low intensity excitation of the samples during the course of the present work.

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