PROMPT AND DELAYED EXCIMER FLUORESCENCE OF NAPHTHALENE IN POLY(METHYL METHACRYLATE) MATRIX

BOGUMIŁA POLACKA

Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk (Poland)

Summary

The concentration change of prompt and delayed fluorescence spectra of naphthalene in poly(methyl methacrylate) (PMMA) was investigated at 293 and 77 K. For high concentrations, delayed and prompt excimer fluorescence were observed. It is suggested that molecular pairs of naphthalene are responsible for the excimer fluorescence in the PMMA matrix.

The ratio ϕ_E/ϕ_M of the excimer fluorescence yield to the molecular fluorescence yield was determined and was found to be considerably larger for the delayed than for the prompt fluorescence. The difference is explained by excitation energy transfer in the triplet state.

1. Introduction

Excimer prompt fluorescence (EPF) for molecules of pyrene [1], 2,1-naphthyl-5-phenyloxazole [2], 2-methylnaphthalene [3], 2,5-diphenyloxazole [4] and perylene [5] has been detected in a polymer matrix. The absorption and excitation prompt fluorescence (PF) spectra observed at high concentrations of perylene [5] and pyrene [6, 7] in a polymer matrix are not characteristic of the crystal phase. Therefore, it can be concluded that no microcrystals are formed [5 - 7].

P-type delayed fluorescence (DF) was first identified for naphthalene in poly(methyl methacrylate) (PMMA) by Czarnecki [8]. The phenomenon was attributed to triplet–triplet annihilation. Excimer delayed fluorescence (EDF) in a polystyrene matrix was only found for 1,2-benzanthracene (1,2-BA) [9]. However, for 1,2-BA in polystyrene EPF was not observed. It has been assumed that the formation of molecular pairs is responsible for the EDF of 1,2-BA in a polymer matrix [9].

The fluorescence spectrum of naphthalene in the crystal phase is monomer like [10]. Excimer fluorescence of naphthalene is observed only in compressed crystals, where defects are formed in the naphthalene crystal lattice [10].

In liquid solution, the EPF was observed only for high concentrations of naphthalene [11].

In this paper, we investigate both the EDF and the EPF of naphthalene in a PMMA matrix. It is interesting that for naphthalene in PMMA the relative intensity of excimer emission to monomer emission is considerably larger at 77 K than at 293 K. For other molecules in a polymer matrix the excimer (relative to the monomer) emission is slightly smaller at 77 K than at 293 K [5, 7]. Thus, we can compare the relative excimer-to-monomer fluorescence yields for the DF and the PF at both 293 K and 77 K.

2. Experimental details

The naphthalene-doped PMMA samples were obtained by thermal polymerization of naphthalene solutions in methyl methacrylate.

Naphthalene was refined by sublimation. Methyl methacrylate was distilled under reduced pressure. The solutions were polymerized in stoppered tubes at temperatures below 60 °C. The naphthalene-doped PMMA samples of appropriate dimensions and shapes were obtained by cutting and polishing. The samples were stored and investigated in the presence of air.

The prompt fluorescence PF and DF spectra were measured on a Perkin–Elmer MPF-2A spectrophotometer. A chopper was used to observe the DF. Naphthalene was excited at 296 nm. Each recorded spectrum was corrected for the spectral response of the spectrophotometer and normalized to the amount of light absorbed. For naphthalene, owing to the small spectral overlap between absorption and fluorescence, re-absorption was found to be negligible. Different equipment sensitivities were employed for measurements of the DF and the PF.

3. Results and discussion

The concentration change of the PF spectrum at 293 K and the DF and the PF spectra at 77 K are shown in Figs. 1, 2 and 3 respectively. Fluorescence spectra at 293 K (Fig. 1) are the pure PF spectra since the DF is undetectable. The lack of DF at 293 K is presumably caused by oxygen quenching. The relative intensities at all concentrations are normalized for a fixed wavenumber $\tilde{\nu}_n$ which is chosen between the region of self-absorption of monomer emission and the region of excimer emission [12]. The aim of this procedure is to equate the total molecular quantum yield of monomer fluorescence to some arbitrary value ϕ_M independent of concentration C. The value $\phi_M = \int_M \phi_{\tilde{\nu}} \, d\tilde{\nu}$ is evaluated from the pure monomer emission spectrum at the lowest concentration (0.05 M). The excimer emission spectrum is obtained by subtraction of the monomer spectrum from the total spectrum at high concentration.

The quantum yield ϕ_E of excimer fluorescence is expressed in the same units as ϕ_M. The value $\phi_E = \int_E \phi_{\tilde{\nu}} \, d\tilde{\nu}$ is evaluated from the excimer emission spectrum at $C = 2.2$ M (Figs. 1, 2 and 3).
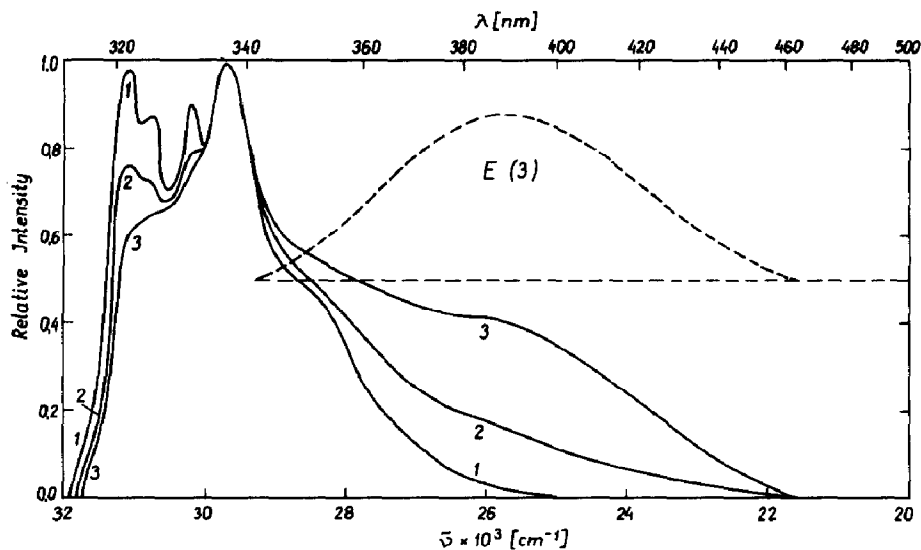
Fig. 1. Normalized prompt fluorescence spectra at 293 K of naphthalene in PMMA at the following concentrations: curve 1, 0.05 M; curve 2, 1.1 M; curve 3, 2.2 M. E(3) is the excimer band (2.2 M).
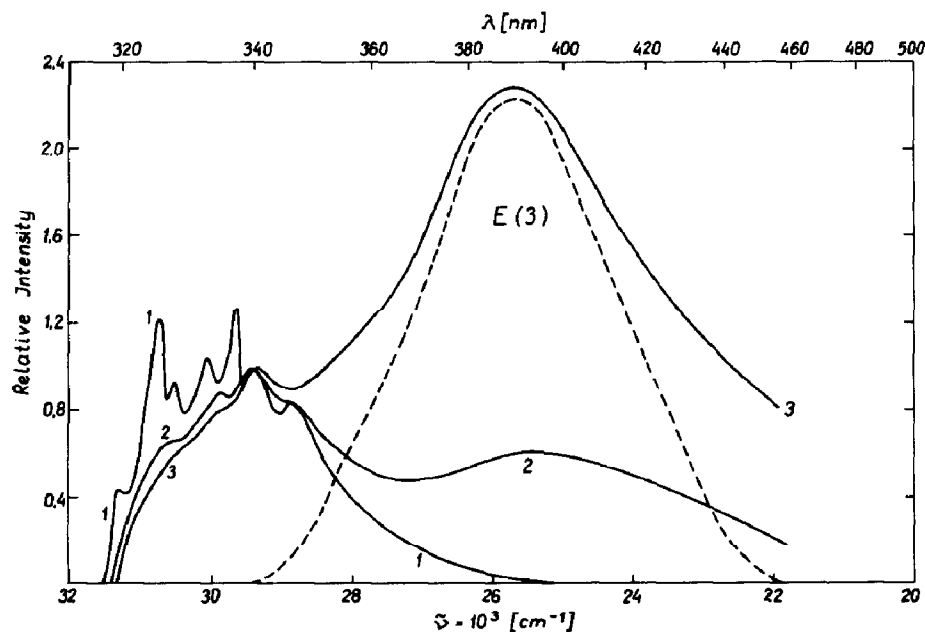

Fig. 2. Normalized delayed fluorescence spectra at 77 K of naphthalene in PMMA at the following concentrations: curve 1, 0.05 M; curve 2, 1.1 M; curve 3, 2.2 M. E(3) is the excimer band (2.2 M).

The phosphorescence spectrum overlaps the long-wavelength region of the fluorescence spectrum (Figs. 2 and 3). Thus the long-wavelength portion of the excimer spectrum is drawn to mirror the short-wavelength region.
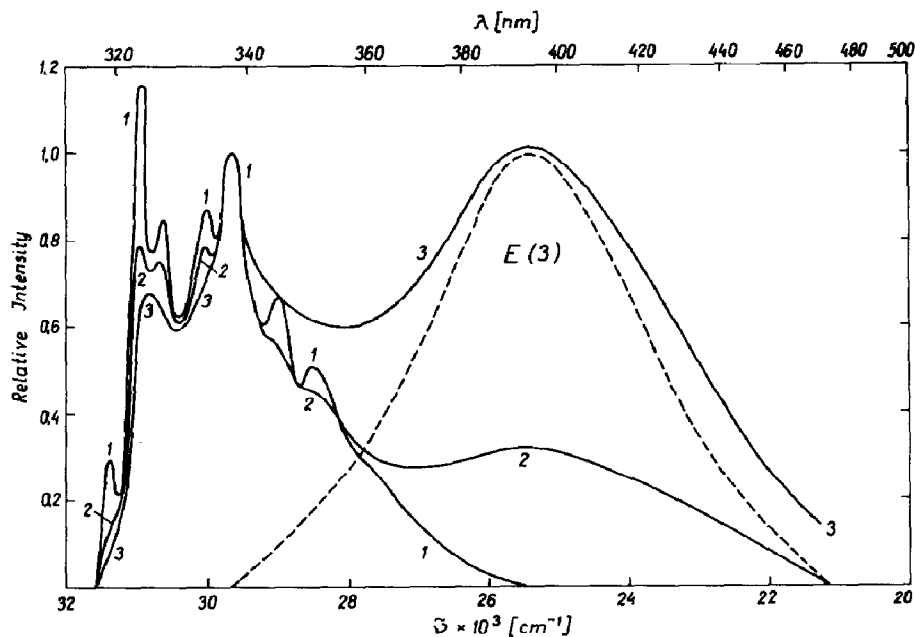
Fig. 3. Normalized total prompt plus delayed fluorescence spectra at 77 K of naphthalene in PMMA at the following concentrations: curve 1, 0.05 M; curve 2, 1.1 M; curve 3, 2.2 M. E(3) is the excimer band (2.2 M).

The 77 K fluorescence spectra measured without the chopper (Fig. 3) can be interpreted as a sum of the delayed and the prompt fluorescence spectra ((D + P)F).

The spectrum of naphthalene microcrystals was also measured. The naphthalene microcrystals were obtained by evaporation of a naphthalene-saturated solution of toluene. The molecular spectrum of naphthalene microcrystals was observed.

For $C = 2.2$ M naphthalene in PMMA the obtained values of the excimer fluorescence yield relative to that of the monomer for the PF at 293 K, the DF at 77 K and the (D+P)F at 77 K are $(\phi_E/\phi_M)_P \approx 0.6$, $(\phi_E/\phi_M)_D \approx 2.7$ and $(\phi_E/\phi_M)_{D+P} \approx 1.7$ respectively. $(\phi_E/\phi_M)_D$ is considerably larger than $(\phi_E/\phi_M)_P$. A similar relation, $(\phi_E/\phi_M)_D > (\phi_E/\phi_M)_P$, has been found to apply to the liquid solution [13], but the mechanism was different.

In liquid solution, after excitation to the singlet state the initially excited species are monomers ($^1M^*$) and then excimers ($^1D^*$) are formed. After triplet–triplet annihilation in liquid solution, initially the $^1D^*$ as well as the neighbouring pairs of singlet monomers ($^1M^*$:^1M) are produced [14]. Thus in liquid solution $(\phi_E/\phi_M)_D$ is always larger than $(\phi_E/\phi_M)_P$.

Since the spectrum of naphthalene microcrystals is monomer like we assume that in a polymer matrix the EDF and EPF originate from the presence of molecular pairs.

It is supposed that the statistical molecular pairs ($2M_P$) can be formed during the preparation of naphthalene-doped PMMA matrices. The number

of molecular pairs increases with the concentration of naphthalene in PMMA. The intermolecular separation in the molecular pair may be suitable for excimer formation. After the excitation of naphthalene to the first singlet state, the molecular pairs can attain the excimer conformation and EPF can be observed. This takes place according to the following scheme:

$$h\nu_A + 2M_P \rightarrow {}^1M_P + {}^1M_P{}^* \rightarrow {}^1D^* \rightarrow 2M_P + h\nu_{EPF}$$
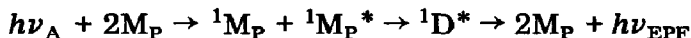
where $h\nu_A$ is a quantum of absorbed energy and $h\nu_{EPF}$ is a quantum of emitted energy.

The triplets of naphthalene are formed by intersystem crossing. Since EDF is observed, it can be assumed that both molecules in the molecular pair are transferred to the triplet state and the next process may be

$${}^3M_P{}^* + {}^3M_P{}^* \rightarrow {}^1D^* \rightarrow 2M_P + h\nu_{EDF}$$
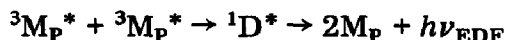
In general, the mechanism of excimer formation in liquid solutions is diffusion controlled. Another type of energy migration which may lead to excimer formation is successive resonance energy transfer. Since in polymeric media the material diffusion is negligible, the excimer formation depends on the diffusion of excitation energy (an exciton diffusion) to sites with the excimer configuration. The molecular pairs can act as traps for the migrating excitation energy. Energy transfer in the singlet state can be described by the Förster mechanism.

The ${}^3M^*$ energy migration process may occur by electron exchange interaction over distances of up to 15 Å [15]. In randomly distributed molecules of naphthalene the average nearest-neighbour separation is about 10 Å for $C = 1$ M. A certain number of molecular pairs can be excited directly but it is supposed that exciton diffusion is more important. The transition of both molecules in the molecular pair to triplet state, necessary for EDF emission, can be obtained by diffusion of the singlet exciton as well as the triplet exciton. Moreover, the triplet excitons have a relatively larger migratory range because of their large lifetimes.

In addition, triplet naphthalene—polymer (P) interaction is also possible [16] according to the following scheme:

$${}^3N^* + P \rightarrow N + {}^3P^*$$

and

$${}^3P^* + P \rightarrow P + {}^3P^*$$
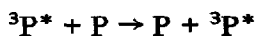
The contribution of polymer triplets to the triplet energy transfer increases the chance of excitation of the molecular pair to the triplet state.

Energy trapping in the molecular pair is more probable for the triplet state than energy trapping in the singlet state. Thus for naphthalene in PMMA $(\phi_E/\phi_M)_D$ is larger than $(\phi_E/\phi_M)_P$. The lack of any EPF for 1,2-BA in polystyrene is also explained by the relatively small migratory singlet range [9].

We can assume that for naphthalene the oxygen quenching is larger for excimer fluorescence than for molecular fluorescence. Besides, oxygen

quenching is larger at 293 K than at 77 K. Therefore, the larger value of ϕ_E/ϕ_M for the PF at 77 K than at 293 K may result from the difference of naphthalene fluorescence quenching by oxygen.

Acknowledgment

References

1 G. Oster, N. Geacintow and A. U. Khan, *Nature (London), 196* (1962) 1089.
2 B. Polacka and H. Szymkowiak, *Acta Phys. Pol., 36* (1969) 1017; *Z. Naturforsch., Teil A, 26* (1971) 171.
3 Z. Polacki, B. Polacka and H. Szymkowiak, *Zesz. Nauk. Politech. Gdańskiej, 67* (1971) 8 (in Polish).
4 B. Polacka, *Int. Conf. on Luminescence, Academy of Sciences U.S.S.R., Leningrad, 1972*, p. 235.
5 J. A. Ferreira and G. Porter, *J. Chem. Soc., Faraday Trans. II, 73* (1977) 340.
6 B. Polacka and I. Weyna, *Bull. Acad. Pol. Sci. Ser. Sci. Math. Astron. Phys., 26* (1978) 935.
7 P. Avis and G. Porter, *J. Chem. Soc., Faraday Trans II, 70* (1974) 1057.
8 S. Czarnecki, *Bull. Acad. Pol. Sci. Cl. 3, 9* (1961) 561.
9 R. D. Burkhart, *Chem. Phys., 46* (1980) 11.
10 P. F. Jones and M. Nicol, *J. Chem. Phys., 43* (1965) 3759.
11 B. K. Selinger, *Aust. J. Chem., 19* (1966) 825.
12 J. B. Birks, *Photophysics of Aromatic Molecules,* Wiley-Interscience, New York, 1970, p. 100.
13 C. A. Parker, *Photoluminescence of Solutions,* Elsevier, Amsterdam, 1968 (Russian version, p. 349).
14 K. R. Naqui, H. van Willigen and D. A. Capitanio, *Chem. Phys. Lett., 57* (1978) 197.
15 K. R. Naqui, *Chem. Phys. Lett., 1* (1968) 561.
16 A. N. Jassim, J. R. MacCallum and R. T. Moran, *Eur. Polym. J., 19* (1983) 909.