

Short Communication

Some remarks on donor properties of polystyrene

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The integral overlap I is one of the factors which governs the value of the electronic excitation energy resonance transfer parameters [1]:

$$I = \int F(\nu)\epsilon(\nu)\nu^{-4} d\nu$$

where $F(\nu)$ is the spectral distribution of the donor fluorescence normalized so that $\int F(\nu) d\nu = 1$, $\epsilon(\nu)$ is the molar extinction coefficient of the acceptor and ν is the wavenumber.

The values of the transfer parameters for a large number of donor-acceptor systems are given by Berlman [2].

For polystyrene (PSt) the situation is especially complicated and a detailed analysis is essential.

As Ghigginio *et al.* [3] have shown the pulse excited luminescence spectrum evolves with time. The luminescence spectrum has a maximum at about 290 nm in the early stages and a maximum at about 340 nm in the later stages. The evolution of the spectrum is the result of migration of the excitation energy of the singlet state from the originally excited styrene (St) molecules to excimer sites (in the macromolecule) followed by excimer luminescence. Thus the electronic properties of molecules immediately after their excitation, characterized by the spectrum of the earliest stage of luminescence, govern the migration.

To calculate the integral overlap for energy migration in PSt, a normalized luminescence spectrum of the earliest luminescence stage should be used. However, it is difficult to determine the energy distribution in a luminescence spectrum of originally excited St molecules (in the macromolecule) because, even when apparatus with a good time resolution (time gate, 3 ns) is used, excimer luminescence is partially observed, deforming the original spectrum [3].

A solution of this complexity is proposed by using St copolymers with non-luminescent monomers, such as methyl methacrylate (MMA). For steady state excitation of the St-MMA copolymer with an St content of less than 30% a short wavelength luminescence spectrum, similar to the early stage PSt luminescence spectrum [3], is obtained with a maximum at about 290 nm. This band is the result of emission from excited states of St

molecules which are chemically bonded in the macromolecule but which do not interact with other molecules of the same kind. The band is of the so-called "monomer" or molecular luminescence of PSt. The PSt excimer luminescence band increases with an increase in the St concentration in the copolymer as a result of trapping of the excitation energy in excimer sites [4, 5] and has the shape shown in Fig. 1, curve F, for the homopolymer.

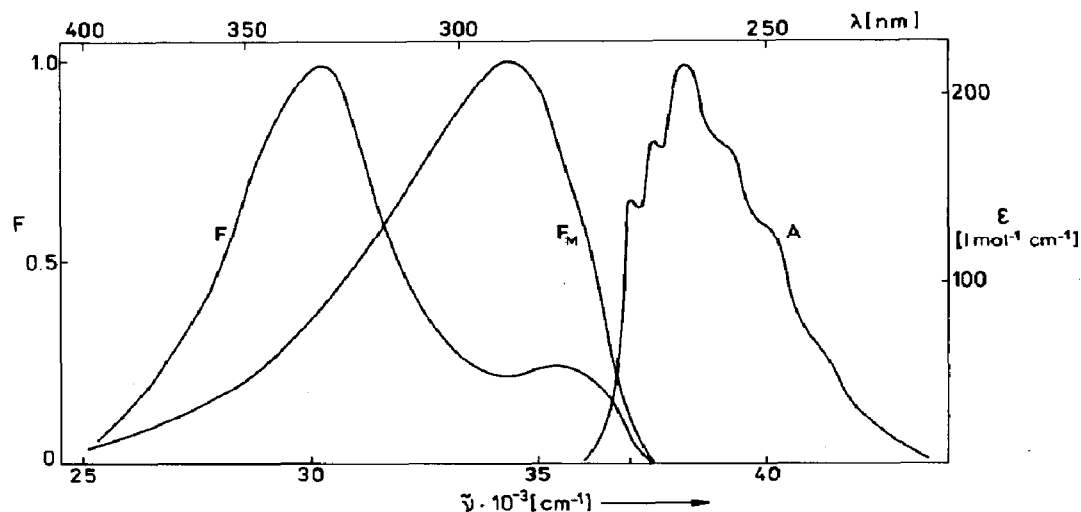


Fig. 1. Fluorescence spectra (curve F_M , St-MMA copolymer (27.8% St) in 1,4-dioxane ($[St \text{ monomer}] = 3 \text{ g l}^{-1}$); curve F, PSt homopolymer in cyclohexane ($[St \text{ monomer}] = 3 \text{ g l}^{-1}$)) and the PSt and St-MMA absorption spectrum (curve A).

It is obvious that the integral overlap values will be different for the spectral distribution of the copolymer and the homopolymer (Fig. 1, curves F_M and F).

The transfer parameter values according to Berlman (for PSt in cyclohexane) and those calculated for the St-MMA copolymer (in 1,4-dioxane solution) are given in Table 1. The c_0 and R_0 values were formally obtained from Berlman's values after the new integral overlap values and the higher

TABLE 1
Energy transfer parameters

Donor-acceptor	$I (\times 10^{-15} \text{ cm}^6 \text{ mol}^{-1})$	$c_0 (\text{mol l}^{-1})$	$R_0 (\text{Å})$
<i>PSt-PSt</i>			
Homopolymer	0.00030 ^a	13.228 ^a	3.23 ^a
Copolymer	0.00250	2.88	5.78
<i>PSt-St</i>			
Homopolymer	0.04206 ^a	1.118 ^a	7.37 ^a
Copolymer	0.17405	0.35	11.74

^a After Berlman [2].

quantum yield value Q_m of the PSt "monomer" compared with the quantum yield value Q_{PSt} of the homopolymer had been taken into account ($Q_m \approx 4Q_{PSt}$ [6]).

Also for the PSt-St system the transfer parameters are different from those given in the table [2]. For PSt solutions with different luminescent additives the existing transfer parameter values should be revised. In particular, when the acceptor concentration is considerable (e.g. plastic scintillators) and the transfer is fast, the excimer traps an insignificant amount of energy. In such a situation the transfer process is characterized by the PSt molecular ("monomer") fluorescence spectrum.

It can be assumed that the revision of the transfer parameter values will allow us to eliminate the discrepancies in the theoretical and the experimental values of the excitation energy transfer yield in PSt scintillating solutions, indicated in refs. 6 and 7.

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- 1 Th. Förster, *Discuss. Faraday Soc.*, 27 (1959) 7.
- 2 I. B. Berlman, *Energy Transfer Parameters of Aromatic Compounds*, Academic Press, New York, 1973.
- 3 K. P. Ghiggino, R. D. Wright and D. Phillips, *J. Polym. Sci., Polym. Phys. Edn.*, 16 (1978) 1499.
- 4 C. David, M. Lampereur and G. Geuskens, *Eur. Polym. J.*, 9 (1973) 1315.
- 5 L. Alexandru and A. C. Somersall, *J. Polym. Sci., Polym. Chem. Edn.*, 15 (1977) 2013.
- 6 Z. Polacki, *J. Polym. Sci., Polym. Phys. Edn.*, in the press.
- 7 T. P. Belikova and M. D. Galanin, *Izv. Akad. Nauk S.S.S.R., Ser. Fiz.*, 22 (1958) 48; *Bull. Acad. Sci. U.S.S.R., Phys. Ser.*, 22 (1958) 46.