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Short Communication

Phosphorescence emission of PMMA matrices

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Some 15 years ago, plastics were introduced into ultra-violet spectroscopy as solid matrices [1 - 3]. Compared to other solvents, which form rigid matrices (glasses) at low temperatures only, plastics offer the advantage that they allow the investigation of phosphorescence emission at a greater range of temperatures, even well above room temperature. Other unescapable conditions, which guarantee widespread application, *e.g.* easy sample preparation, optical clarity and transparency are also fullfilled.

Despite the fact that many luminescence studies using poly(methyl methacrylate) (PMMA) matrices are reported, there still exist contradictory statements on the spectroscopic behaviour of pure PMMA matrices. U.v. transparency until well above 30,000 cm^{-1} is stated [4]. Earlier studies, which claim the absence of any phosphorescence [5] are contradicted by later work [6]. There, a phosphorescence, which is interpreted as being due to monomeric methyl methacrylate (energy of the triplet state 25,000 cm^{-1}) is reported.

Although a weak emission of the solvent may be tolerable in the case of strongly emitting solutes, the matrix luminescence is particularly objectionable in the study of solutes with a low quantum yield of phosphorescence, as is done nowadays very often by means of phase-sensitive detection or single photon counting. This communication therefore will deal with the emission properties of PMMA matrices.

Experimental

To remove the inhibitor, methyl methacrylate (MMA) as supplied by Merck was washed with aqueous sodium hydroxide. Purification was achieved by repeated distillation over phosphorus pentoxide and by passing it through a column of silica.

Samples were prepared by thermally polymerizing the solutions of purified monomer and solute under study without addition of any chemical initiator (temperature applied was 60 °C for 72 h followed by 6 h at 100 °C).

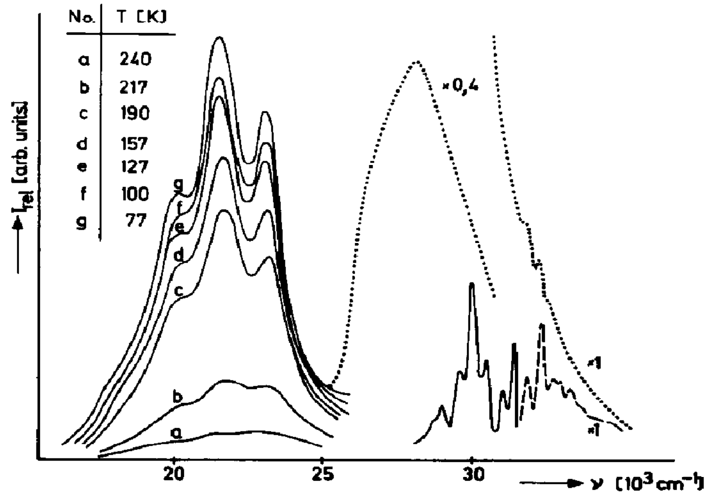


Fig. 1. Phosphorescence (—— curves a - g) and fluorescence spectra (——) of a naphthalene containing PMMA sample at various temperatures. For comparison the uncorrected excitation spectra are shown: .... $\tilde{\nu}_{obs}$ = 21,300 cm^{-1} ≙ phosphorescence of PMMA; ---- $\tilde{\nu}_{obs}$ = 27,500 cm^{-1} ≙ fluorescence of naphthalene.

This *in situ* polymerization guarantees a homogeneous distribution of the solute molecules [7].

The apparatus used to record the emission spectra is described elsewhere [8]. Lifetime measurements were made by a phase shift technique (phase fluorimetry). To reduce the disturbing effects of straylight or fluorescence a newly developed "electrical" phosphoroscope was applied [9].

Results and Discussion

In Fig. 1, the spectral distribution of the blue PMMA-phosphorescence is displayed for various temperatures (curves a - f, $\tilde{\nu}_{ex}$ = 32,600 cm^{-1}). The phosphorescence decay time was determined to be 2 ms throughout the temperature range $77 < T < 240$ K. In the uncorrected excitation spectrum ($\tilde{\nu}_{obs}$ = 21,400 cm^{-1}) a strong peak shows up at around 28,200 cm^{-1}, which corresponds to a very weak transition found in the u.v. absorption spectrum.

The decrease in signal at higher energy is due to the decrease in intensity of the excitation light. Nevertheless, one sees two shoulders which can be assigned by comparison with the fluorescence excitation spectrum (taken under identical conditions) of naphthalene as belonging to the first two vibronic transitions of this solute (concentration 1.28 mg $C_{10}H_8$ in 10 ml MMA). From this one can conclude that the phosphorescence emission of the solute is completely covered by the emission of the matrix.

The latter statement is also proved by Fig. 2 where the emission spectra of a PMMA sample with various concentrations of solute (naphthalene) are recorded. By visual inspection one concludes that the matrix emission is about as intense as the fluorescence of naphthalene in case b. Since the

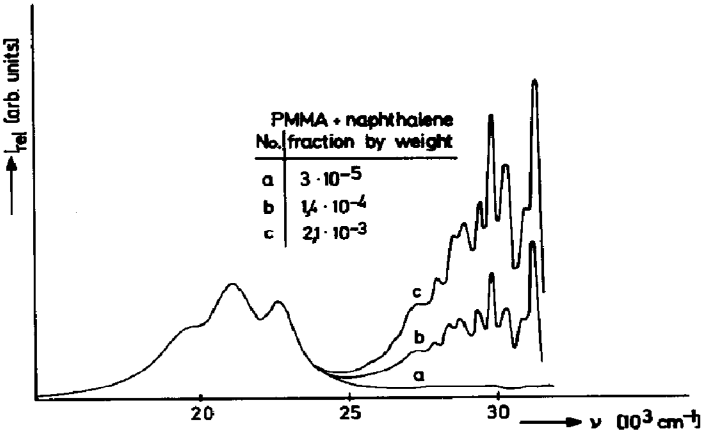
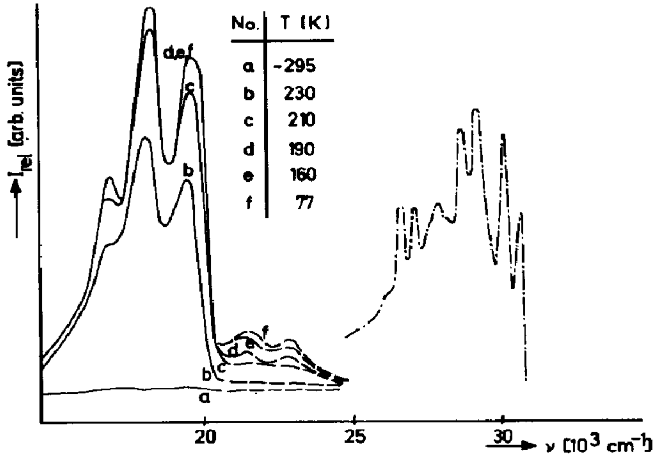


Fig. 2. Emission spectra of PMMA matrices holding various amounts of naphthalene ($T = 77$ K, $\tilde{\nu}_{ex} = 32{,}600$ cm^{-1}).



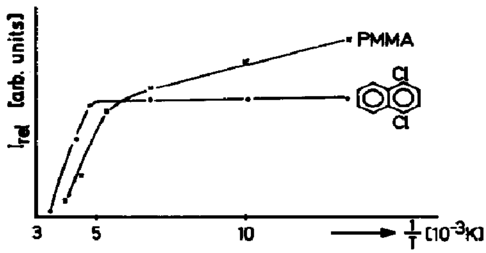


Fig. 3. Emission spectra of a sample (2 mg 1,4-dichloronaphthalene in 10 ml MMA) at various temperatures, phosphorescence of PMMA (– – – –), phosphorescence (———) and fluorescence (–·–·) of solute ($\tilde{\nu}_{ex} = 32{,}600$ cm^{-1}).

Fig. 4. Plot of relative intensity of phosphorescence *vs.* $1/T$.

ratio of quantum yields $\Phi_f(S_1 \rightarrow S_0)/\Phi_p(T_1 \rightarrow S_0)$ is approximately 10 for naphthalene its phosphorescence emission must be negligible in comparison to the matrix phosphorescence.

To prove whether the emission observed could be due to a remainder of monomeric methyl methacrylate, we polymerized some samples by addition of α,α-azo diisobutyronitrile as initiator. Despite a variation of initiator concentration by nearly three orders of magnitude ($3 \times 10^{-4} < c_I < 10^{-1}$ *M*), spectral distribution and relative intensity of the phosphorescence emission remained unchanged. We therefore believe that the observed emission is not caused by monomeric MMA, whose phosphorescence decay time was determined to be 1.5 s [6].

Since most plastic matrices are used to study the temperature dependence of solute emissions, it is important to know how the ratio of emission intensities of solvent and solute respectively, vary with temperature. To this end, Fig. 3 shows the emission of a sample prepared of 2 mg 1,4-dichloronaphthalene dissolved in 10 ml MMA. The phosphorescence spectrum of this solute is shifted to a longer wavelength, its quantum yield $\Phi_p(T_1 \rightarrow S_0) = 0.25$ is much higher than in the case of naphthalene itself [10]. Therefore the contributions of solvent and solute can easily be distinguished.

Figure 4 demonstrates that the variation in phosphorescence intensity with temperature is very similar for solvent and solute, *i.e.* there is no temperature interval where the solute emission would outweigh the solvent emission.

Because of the similarity in the variation of the phosphorescence intensity with temperature one could suppose that both emissions are determined by a diffusion controlled quenching process. Such a mechanism is reported to play a major role in the temperature dependence of the phosphorescence of organic molecules [11] for which reason, great efforts are made to remove even trace impurities of O_2 [12]. In the case of the PMMA and 1,4-dichloronaphthalene emissions shown in Fig. 3, such a quenching process could account for the temperature behaviour, since all samples were prepared without any precautions to prevent oxygen from diffusing into the plastic. Before polymerization the solutions were neither degassed nor saturated with nitrogen. As a consequence and in contrast to ref. [1], where the samples were prepared oxygen-free, the emission of our samples did not change anymore over several months of storage.

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