PHOTOPHYSICAL PROPERTIES OF A QUINOLINE DERIVATIVE IN POLYMER MATRICES

C. Rogge, S. R. Ahmad

Department of Environmental and Ordnance Systems
Royal Military College of Science Cranfield University
Shrivenham, Swindon, Wiltshire, SN6 8LA UK

The photophysical properties of a quinoline derivative were studied to evaluate its use as a marker for the optical identification and subsequent automatic sorting of polymers. The steady state fluorescence spectra and fluorescence lifetimes of the derivative in additive-free PVC and commercial-grade HDPE are reported. The fluorescence properties of the dye in PVC, which contained an optical brightener and a light stabiliser, and in methanol and cyclohexane were also studied. The results show that the steady state fluorescence characteristics of the dye, attributed to an excited state intramolecular proton transfer (ESIPT) process, are nearly independent of the environment. The emission peak wavelength was found to vary between 514 nm (in methanol) and 521 nm (in PVC). The results of fluorescence lifetime measurements strongly indicate that hydrogen bonding leads to non-radiative deactivation of the excited dye molecules. The fluorescence lifetime of the dye in cyclohexane, PVC and HDPE ranges from approximately 3.7 ns to 4.2 ns, but in methanol is reduced to a value beyond the time resolution limits of the setup employed. A strong decrease in the fluorescence quantum yield of the dye in this solvent is also observed.

1. Introduction

Fluorescent dyes have been used as tracers in many applications. They also have potential as marker materials for the automatic and rapid identification and separation of plastic waste by providing characteristic fluorescence "fingerprints"[1,2].

Dependent on the application, various requirements may be placed on the properties of such marker substances. Light stability, toxicity and migration of the marker in the polymer are of concern in addition to heat stability and a high fluorescence quantum yield. Moreover, the tracers should not produce any discolouration of marked articles, as appearance is critical in many applications. This could be achieved by the use of compounds that absorb exclusively or primarily in the ultraviolet. A distinctive emission, which should be nearly independent of the environment of the marker, is needed in order to provide a reliable basis for an optical identification.

Some quinoline derivatives with excited state intramolecular proton transfer (ESIPT) characteristics exhibit UV absorption and a large Stokes shift, and may therefore be suitable as marker materials for optical identification of substances.

In contrast to intermolecular excited state proton transfer, that generally occurs in protic solvents [3,4], IPT can be almost independent of the environment. For example, 10-hydroxybenzo[h]quinoline shows a relatively solvent-independent ESIPT and emission characteristics[5]. The results and analysis of spectroscopic studies on a quinoline derivative, not investigated hitherto, are presented in this paper.

2. Materials and methods

The quinoline derivative materials were obtained from Riedel-de Haën, (Germany). The company provided the information that the large Stokes shift of the compound is due to an excited state intramolecular proton transfer in a functional group of the molecule as shown in Fig. 1. However, the exact structure of the dye, which was used as received, was not disclosed, and the dye and the additives were added to the samples by weight. Spectroscopic grade methanol and cyclohexane were used as solvents. The quinoline derivative showed good solubility in methanol but was practically insoluble in cyclohexane. Comparative measurements were thus carried out on methanol solutions with dye concentrations between 50 ppb and 1 ppm.
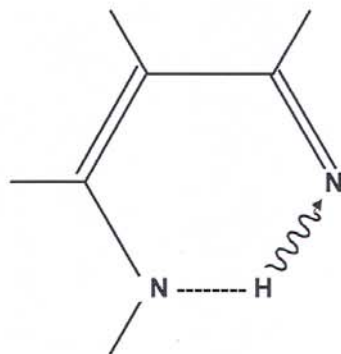

Fig. 1. Excited-state proton transfer scheme in quinoline derivatives.

Additive-free polyvinylchloride (PVC, 1.4 g/cm^3) was obtained in powder form from Hydro Polymers, UK. The commercial-grade HDPE samples were supplied by Pira International, UK. The optical brightener Uvitex OB and the light stabiliser Tunisian 328 were obtained from Ciba Geigy UK. The PVC samples of approximately 0.5-mm thick plaques were produced by solution casting from stabiliser-free tetrahydrofuran. Various PVC samples were produced by dissolving and mixing the additives and the appropriate amount of a concentrate film containing 1000 ppm of the dye with the virgin PVC powder. Resulting dye concentrations in the PVC samples ranged from 200 ppb to 125 ppm. Tinuvin 328 was used at a concentration of 500 ppm and Uvitex OB at 10 ppm and 50 ppm. For a comparison with results in PVC matrices, commercial-grade HDPE samples containing 10 ppm of the dye were also tested. The latter were produced by Pira International (UK), by extrusion moulding of a mixture of pure HDPE and a previously moulded 1000 ppm concentrate.

Measurements of the steady state excitation and emission spectra were carried out using a commercial spectrofluorometer (SPEX FluoroMax^{TM}), equipped with an ozone-free Xenon lamp and operated in signal-over-reference mode. A Schott GG 420 edge filter was used for the suppression of the second order of the excitation wavelength, where necessary. The fluorescence decay kinetics measurements were carried out using a pulsed laser set-up as shown in Fig. 2.

The excitation source was an excimer laser-pumped dye laser (model: Lambda Physik FL 2002). The excimer laser was operated at the 308 nm using Xe-Cl gas and the dye laser operated with di-methyle quinoline (DMQ) provided a peak output at 360 nm. After passage through a SPEX 1404 double monochromator, the fluorescence signal was detected by a photomultiplier (model: Hamamatsu -H 5773 – 01). The output from the photomultiplier was fed into a Hewlett Packard 54111-D digitising oscilloscope, which was triggered by a signal from a photodiode receiving a fraction of the exciting laser power.
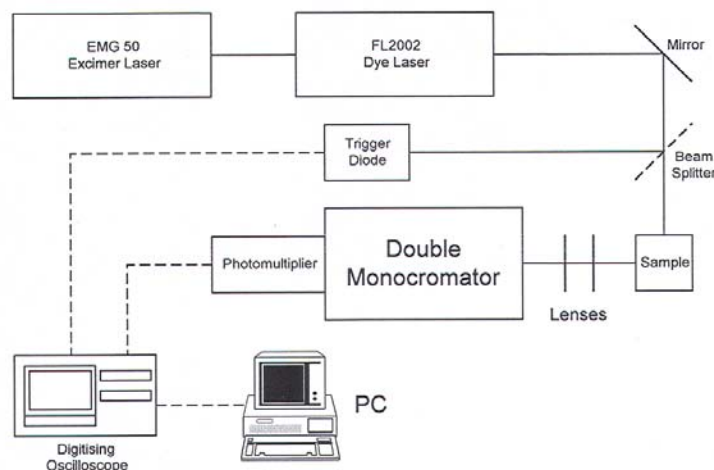
Fig. 2. Experimental arrangement for the fluorescence decay time measurements.

The short fluorescence lifetime of the quinoline dye made the evaluation of its fluorescence decay kinetics by means of re-convolution necessary [6,7]. For this, the laser pulse scattered by the sample itself, and the fluorescence pulse were detected and transferred from the HP 54111 D to a PC. The convolution of the excitation pulse and the assumed decay curve was fitted to the measured fluorescence decay curve by varying the parameters, employing a Simplex algorithm. The accuracy of the results was verified by measuring values for the fluorescence lifetimes of anthracene and 1,4-bis[2-(5-phenyloxazolyl)]benzene in cyclohexane (4.0 ns ± 0.1 ns and 1.1 ns ± 0.1 ns, respectively) and comparing with those quoted in the literature (3.99 ns ± 0.03 ns and 1.10 ns ± 0.02 ns, respectively) [8].

3. Results and analysis

Figs. 3 and 4 show the steady state excitation and emission spectra respectively, of the quinoline derivative in different matrices. The wavelength positions of the main peaks in the excitation and emission spectra in the four environments, viz. methanol, cyclohexane, commercial-grade HDPE and additive-free PVC, are summarised in Table 1.

The two bands in the emission spectra of the dye are better resolved in HDPE and cyclohexane than in PVC and methanol. This indicates the presence of dipole-dipole interactions between solute and solvent in PVC and methanol, both of which have an inherent dipole moment, and also hydrogen bonding interactions in methanol. In contrast, only induced dipole interactions take place in the non-polar environments HDPE and cyclohexane.
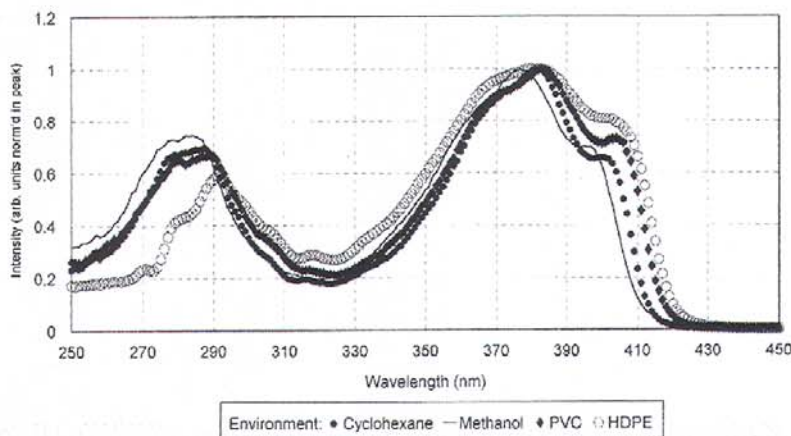
Fig. 3. Steady-state excitation spectra of the quinoline derivative in different matrices.
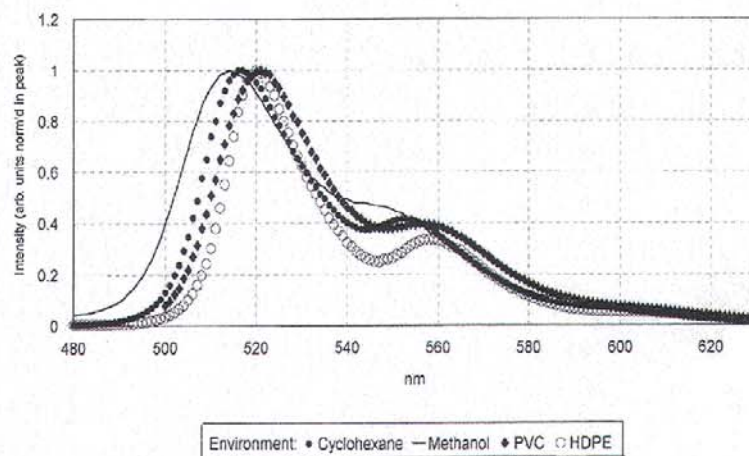
Fig. 4. Steady-state emission spectra of the quinoline derivative in different matrices.

The peak positions in the emission spectra show a hypsochromic shift, which increases with increasing solvent polarity. The same effect was observed for 10-hydroxybenzo[h]quinoline and can be explained by the decrease in the dipole moment of the quinoline dye upon excitation. The reduced dipole moment leads to a lesser degree of solvation and hydrogen bonding interactions with the solvent in the excited state than in the ground state. The energy gap between the two states therefore increases with increasing solvent polarity. The hydrogen bonding and solvation interactions were obviously larger than polarisation effects, which lead to a red shift [9], resulting in net hypsochromic shifts in the excitation and emission spectra in solution. The steady state fluorescence characteristics in PVC and methanol were found to be independent of the dye concentration within the range of present measurements.

The fluorescence decay kinetics of the dye were found to be mono-exponential in all samples studied within the time resolution limitations set by the duration of the excitation pulse (10 ns) and the response time of the photomultiplier (0.65 ns). The fluorescence lifetime of the quinoline derivative in cyclohexane (3.7 ns ± 0.1 ns) was not very different from that in PVC (4.0 ns ± 0.1 ns) and HDPE (4.2 ns ± 0.2 ns). However, it was found to be much shorter in methanol and considered to be beyond the resolution limit of the system (1 ns) for any meaningful result. Fig. 5 shows the laser pulse, the fluorescence pulse and the fitted decay curve of a measurement on a PVC sample as an example and the weighted residuals for this measurement are shown in Fig. 6. The laser pulse and the fluorescence pulse for the measurement in the methanol environment are also included in Fig. 7 for comparison. The temporal and spectral characterestics of the fluorescence of the dye in different matrices are given in table below.

Table 1. Spectral and temporal characteristics of quinoline derivatives in different matrices.

Matrix	Wavelength of the excitation peak (nm)	FWHM (cm^{-1})	Wavelength of emi-ssion peak (nm)	FWHM (cm^{-1})	Decay time (ns)
None (as powder)	380, (4o4), **432**	1580	532,573,620	1340	2.36 ± 0.18
Methanol	(360), 377, 396	1270	**514**, (547)	1170	0.20 ± 0.02
Cyclohexane	(363), **381**, 400	1250	**517**, 553	1260	3.17 ± 0.13
PVC	(364), **383**, 404	1360	**521**, (556)	1210	3.98 ± 0.13
HDPE	(366), **381**, (402)	1370	**520**, 559, (604)	1340	4.16 ± 0,21

(Main peaks are in bold, the data in brackets are from poorly defined spectra)
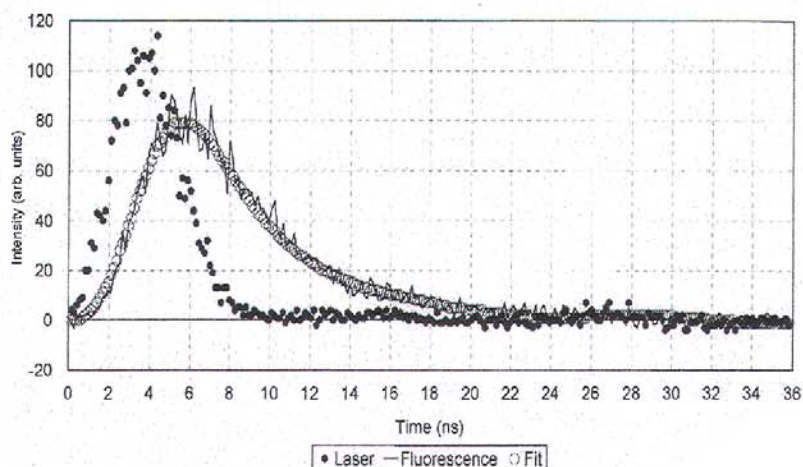

Fig. 5. Temporal histories of laser and the fluorescence signals of the dye in PVC.
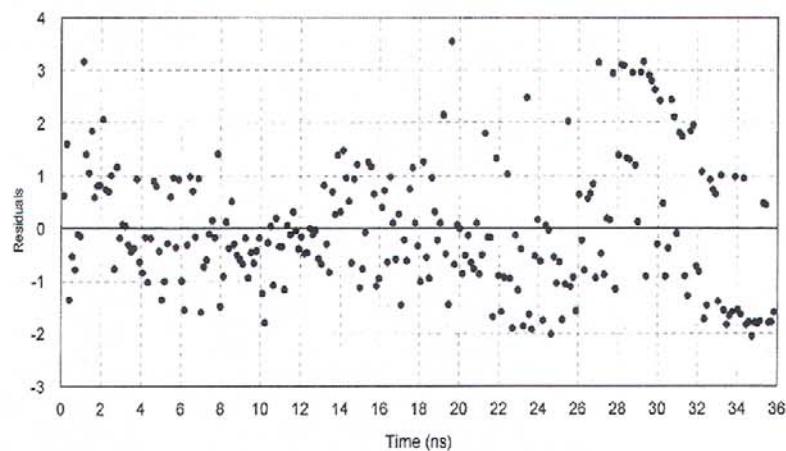
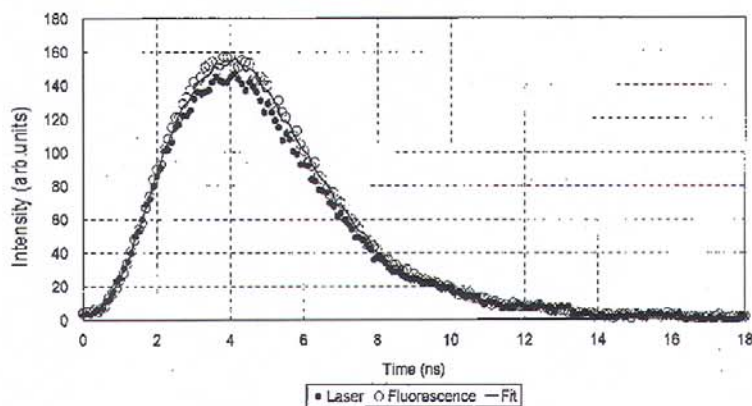Fig. 6. Weighted residuals for the above measurements.

Fig. 7. Temporal histories of laser and fluorescence signals of the dye in methanol.

4. Discussion

The difference in the fluorescence lifetime of the dye is attributed to the presence of the methanol hydroxy groups. The stretching vibrations of the groups can provide non-radiative pathways to the ground state by coupling to the ring breathing modes of the dye molecules, as in the case of 10-hydroxybenzo[h]quinoline [10]. This effect can combine with hydrogen bonding between dye and solvent, with aromatic compounds acting as weak hydrogen bond acceptors [9]. However, other studies on 10-hydroxybenzo[h]-quinoline, designated as 4-hydroxy-5-azaphenanthrene, showed a shorter fluorescence lifetime in cyclohexane than in methanol, despite the apparent presence of non-radiative pathways due to O-H stretches [11].

Nonetheless, for the quinoline dye studied the presence of O-H stretches in methanol is likely to be the explanation for the shortening of the fluorescence lifetime of the dye. The presence of non-radiative pathways in the fluorescence decay is strongly supported by the fact that the emission from

a methanol solution containing 500 ppb of the dye was much lower than that from a comparatively very small concentration of dyes in cyclohexane solution.

Although the fluorescence lifetimes in the two polymers are equal within the standard deviation, a slightly longer lifetime in HDPE in comparison to that in PVC is consistent with the degree of dipole-dipole interactions in each of the polymers, that is apparent from the steady state emission (vide supra). An increased non-radiative decay rate due to the presence of C-Cl stretches in PVC is unlikely, because the C-Cl vibration has an energy of only approximately 800 cm^{-1}, in comparison to about 3000 cm^{-1} for O-H and C-H vibrations.

The fluorescence lifetime in cyclohexane is shorter than that in the the polymer environments. This is attributed to the rigidity of the polymer matrices as observed for other dyes in polymer systems [12, 13], this rigidity reduces the degree of non-radiative relaxation processes and thus increases the fluorescence lifetime.

The studies of the additive-containing PVC-samples showed, that the presence of the optical brightener Uvitex OB and the UV stabiliser Tinuvin 328 had no appreciable effect on the steady state emission of the dye or its fluorescence lifetime as shown in Fig. 8. The offset at the short wavelength limit in the curve for the PVC sample containing 50 ppm dye and 50 ppm optical brightener is caused by the emission from the brightener. The measured emission decay time of this system was 4.0 ns.
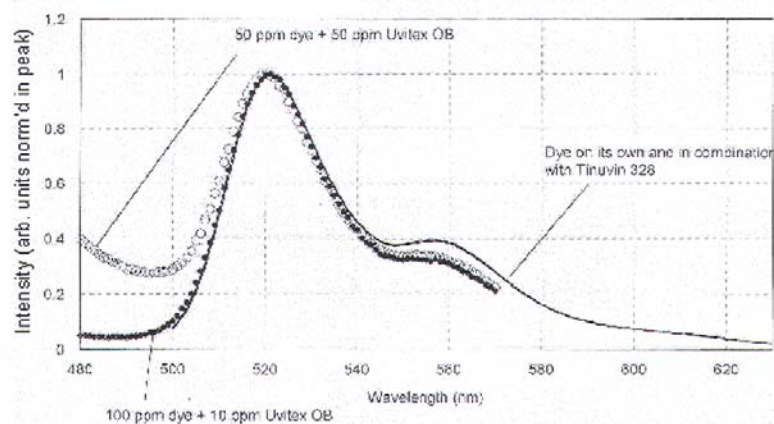

Fig. 8. Steady state emission spectra of the dye with optical brighteners in PVC.

5. Conclusions

The very small shifts in the steady state spectral characteristics of the quinoline dye in the various samples indicate that the ESIPT process occurs nearly undisturbed by the environment, and the shifts are even smaller than those observed by Martinez et al. [5] for 10-hydroxybenzo[h]quinoline. However, the results for the methanol samples strongly indicate that hydrogen bonding severly increases the rate of non-radiative deactivation processes.

The insensitivity of the quinoline emission to the polymer environments studied provides a reliable basis for using it as a tracer in polymers for an automatic identification. The strong emission observed in all samples would allow a dye concentration in the region of a few ppm to be used. Considering the emission characteristics of the dye in methanol, further studies on the suitability of the dye as a marker in hydrogen bonding polymers are needed.

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