

Fluorescence probe for microenvironments: effect of solvent vapour on the properties of vapour-swollen polymers

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The effect of solvent vapour on the properties of vapour-swollen vinyl chloride–vinyl acetate (83/17) copolymer has been studied by a fluorescence probe, a *p*-*N,N*-dialkylaminobenzylidenemalononitrile derivative (1). Results show that the fluorescence quantum yield (Φ_f) of 1 in vinyl chloride–vinyl acetate (83/17) matrix decreases by a factor of ≈ 10 , an indication of the increase in free volume or in polymer chain mobility, upon vapour swelling. The variations of Φ_f observed in various swollen matrices, which correlate only with the density of the swelling solvent, indicate that there is a profound vapour effect on the properties of swollen polymer. A density effect on the mobility of polymer chains in swollen polymer is proposed.

Keywords Fluorescence probe; swollen polymers; solvent effect; vinyl chloride–vinylacetate copolymer; solvent vapour; fluorescence quantum yield

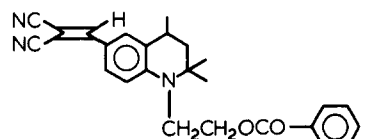
INTRODUCTION

Relaxation behaviour of polymer chains both in solution and in bulk polymer has been the subject of intensive investigation for years^{1,2}. Among various techniques, photophysical and photochemical probes have been very attractive in these studies because polymer chain motion of a wide range of time scales ranging from milliseconds to nanoseconds can be studied using probes of various time scales^{3–5}. Very little work has been reported on the relaxation behaviour of various solvent-swollen polymers.

In an earlier report, it has been shown that, when a dye-in-polymer film is solvent-coated under fast drying conditions, thermodynamically less stable dye aggregates can be formed during the film formation⁶. In a subsequent investigation⁷, the conversion (or recrystallization) of these kinetically formed aggregates to thermodynamically more stable aggregates was studied by exposing various solvent-coated films to solvent vapours and it was established that thermodynamic factors, such as solvent–dye and solvent–polymer interactions, control the initiation but not the completion of the recrystallization process. For compatible solvents, the completion of this vapour-induced dye recrystallization process is related to the activation barrier imposed by the swollen polymer chain towards the dye migration (or diffusion). This observation prompted this examination of the effect of solvent vapour on the properties of swollen polymer matrices.

In a study⁸ on the photochemistry of *p*-*N,N*-dialkylaminobenzylidenemalononitriles, it has been shown that the S_1 state of this class of compound is a charge-transfer π, π^* state which undergoes predominantly radiationless decay via molecular relaxation. The rate of this molecular relaxation process is free-volume-dependent and can conveniently be studied by the

fluorescence quantum yield (Φ_f). The validity of using the *p*-*N,N*-dialkylaminobenzylidenemalononitrile chromophore as a probe to study the flexibility of its surrounding environment has been discussed in an earlier report where the Φ_f of *p*-*N,N*-dialkylaminobenzylidenemalononitrile derivative, 1, was studied⁹ in a variety of alcoholic solvents and it was established that Φ_f of 1 increases as the solvent viscosity increases (or as the mobility of the surrounding molecules decreases). Because of the high-sensitivity of the Φ_f of 1 towards a microenvironment, it has been used recently as a probe to study the local flexibility of polymer chains in poly(alkyl methacrylate) and poly(alkyl acrylate) polymers¹⁰.



Here, preliminary results are reported for the use of 1 as a fluorescence probe to study the effect of solvent vapour on the properties of swollen vinyl chloride–vinyl acetate (83/17) matrices. Φ_f of 1 decreases rapidly and reaches an equilibrated value upon vapour swelling. The Φ_f values in various swollen matrices, however, vary suggesting that there is a vapour effect on the properties of swollen polymer. This result is discussed in terms of a vapour effect on the mobility of the polymer chain in the swollen polymer.

EXPERIMENTAL

Materials

Compound 1 was obtained from Eastman and was purified as described previously⁸. Solvents were used as

received and they were obtained from the following sources: methylene chloride, chloroform, ethyl acetate, tetrahydrofuran, methyl ethyl ketone and acetone were analysed reagent from Baker; 1,1,2-trichloroethane was technical grade from Baker; 1,1-dichloroethane was from Aldrich; 1,2-dichloroethane was spectroanalysed grade from Fisher; and 3-pentanone was technical grade from Eastman. Vinyl chloride–vinyl acetate (83/17) copolymer was purchased from Scientific Polymer Products Inc.

Preparation of dye-in-polymer films

Dye-in-polymer films for fluorescence quantum yield measurement were prepared by casting a dye–polymer solution, consists of 20 mg of **1** and 2.5 g of vinyl chloride–vinyl acetate (83/17) copolymer in 50 ml of methylene chloride, onto pre-cleaned 5 × 5 cm glass substrates (Corning 7059) as described previously¹⁰. Films for the vapour effect study were prepared by casting the same dye–polymer solution onto the inside wall of a quartz fluorescence cell. The films were air-dried at room temperature for 16 h and then vacuum-dried at 50°C for 48 h. The thickness of these films are in the range of 0.2–0.5 μm as estimated from their optical densities.

General technique

Absorption spectra were recorded with a Cary 17 spectrophotometer. Fluorescence emission and fluorescence excitation spectra were obtained using a Perkin-Elmer MPF-44A spectrofluorimeter, which was equipped with a differential corrected spectra unit (DCSU-2). The methodology for recording corrected fluorescence spectra, both in solution and in polymer film, has been described previously^{8,10}.

The solvent vapour effect was studied by monitoring the fluorescence emission intensity (I_f) at the emission maximum (λ_f) on the DCSU-2 as a function of time before and after the introduction of the solvent vapour (obtained by putting 1–2 drops of solvent into the fluorescence cell).^{*} Typical traces are shown in *Figure 1*. Controlled experiments indicated that solvent vapours produced no solvatochromic shift on the fluorescence emission other than reducing the fluorescence intensity.

RESULTS AND DISCUSSION

Electronic spectroscopy of **1** in organic solvents

The absorption and fluorescence spectral data of **1** in the organic solvents used in the present work are shown in *Table 1*. In good agreement with previous results, **1** exhibits an intense absorption band at $\lambda_{\max} \approx 450$ nm with a molar extinction coefficient of $5\text{--}6 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ and a weak fluorescence emission band at $\lambda_f \approx 490$ nm; λ_f of **1** shifts systematically to the red as the solvent dielectric constant increases¹².

The results in *Table 1* also show that the fluorescence quantum yield (Φ_f) of **1** is constant ($2 \pm 0.4 \times 10^{-3}$) within experimental error in all the solvents studied except in 1,1,2-trichloroethane. The Φ_f of **1** has been studied previously in a large variety of solvents of different viscosities and of different polarities and it has been

* Great care has to be exercised in introducing the solvent, especially those highly compatible ones (e.g. methylene chloride) as excess amounts of solvent tends to wash the swollen film away from the monitoring area. With a proper amount of solvent (1–2 drops) the results are reproducible ($\pm 2.5\%$).

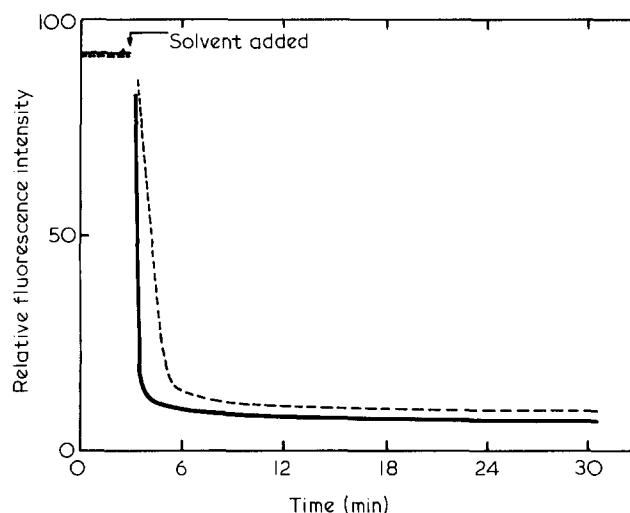


Figure 1 Plot of fluorescence intensity of **1** in vinyl chloride–vinyl acetate (83/17) copolymer as a function of vapour exposure time. —, Ethyl acetate; ---, 1,1,2-Trichloroethane

established that Φ_f of **1** is insensitive to solvent polarity and is only sensitive to solvent viscosity in high viscosity solvents (e.g. $\eta > 1 \text{ mN s m}^{-2}$). Details have been discussed previously⁹. The essentially constant Φ_f of **1** in the solvent shown in *Table 1* is in good agreement with earlier results. The slightly higher Φ_f value in 1,1,2-trichloroethane is attributable to its high viscosity ($\eta = 1.2 \text{ mN s m}^{-2}$).

Electronic spectroscopy of **1** in vinyl chloride–vinyl acetate (83/17) copolymer

Compound **1** exhibits strong monomer absorption with λ_{\max} at 454 nm and a weak monomer fluorescence emission with λ_f at 490 nm at dye concentrations $< 10^{-3} \text{ M}$ in vinyl chloride–vinyl acetate (83/17) copolymer. The Φ_f of **1** in vinyl chloride–vinyl acetate (83/17) copolymer is 4.5×10^{-3} . It has been reported previously¹⁰ that the Φ_f values of **1** in poly(vinyl acetate), poly(methyl methacrylate) and poly(methyl acrylate) are 0.011, 0.012 and 0.013, respectively, and that their similarity is attributed to the similarity of the location of **1** in these polymers (around the polymer backbone). The Φ_f of **1** in vinyl chloride–vinyl acetate (83/17) copolymer is, therefore, 2.5 less than predicted based on the expectation that **1** would locate around the backbone in this polymer also. The low Φ_f value is not due to any heavy atom effect because such an effect is not observed in chlorinated solvents. At the present, there is no satisfactory explanation for this discrepancy.

Effect of solvent vapour on Φ_f of **1**

Upon exposure of dye-in-polymer films to solvent vapour, the fluorescence emission intensity (I_f) of **1** at λ_f (490 nm) decreases rapidly and reaches a constant value. Typical traces are shown in *Figure 1*. The rate of the decrease in I_f and the time required to achieve the equilibrated state are dependent on the solvent–polymer compatibility and the properties of the solvent. The kinetic aspects concerning the diffusion of solvent vapour into a polymer film is beyond the scope of the present work. As control experiments show that solvent vapours cause no solvatochromic shift on the fluorescence emission of **1**, these results thus indicate that the decrease in I_f corresponds to the decrease in Φ_f . The results in *Table*

Table 1 Absorption and fluorescence spectral data of 1 in organic solvents

Solvent	ϵ^a	η^b (mN s m ⁻³)	λ_{\max}^c (nm)	$\log \epsilon^d$ (cm ⁻¹ M ⁻¹)	λ_F^e (nm)	$\Phi_f \times 10^3^f$
Chloroform	4.7	0.542	449.4	4.76	487.5	2.1
1,2,3-Trichloroethane	—	1.2 (20°C)	449.4	4.75	487	2.8
Ethyl acetate ^g	6.02	0.441	442.3	4.77	481.5	1.8
Tetrahydrofuran ^g	7.32	0.55 (20°C)	447.7	4.79	485	2.0
Methylene chloride ^g	8.9	0.449 (15°C)	450	—	489	1.7
1,1-Dichloroethane	10.0	0.505	446	4.70	^h	^h
1,2-Dichloroethane	10.4	0.80	448.5	4.70	489	2.2
3-Pentanone	17	0.49 (15°C)	445.6	4.71	489	2.3
Methyl ethyl ketone	18.5	0.423 (15°C)	445.9	4.75	491.5	2.2
Acetone ^g	20.7	0.316	447.6	—	494	1.5

^a Dielectric constant, data taken from refs. 20 and 21^b Viscosity at 25°C or at specified temperature, data taken from refs. 20 and 21^c Absorption maximum, accuracy $\sim \pm 0.2$ nm^d Molar absorption coefficient^e Fluorescence emission maximum, accuracy $\sim \pm 1$ nm^f Fluorescence quantum yield, estimated error $\sim \pm 20\%$ ^g Data taken from ref. 11^h Fluorescence emission could not be measured in this solvent due to the presence of fluorescent impurity

Table 2 Effect of swelling solvent on the fluorescence quantum yield of 1 in vapour swollen vinyl chloride–vinyl acetate (83/17) copolymer

Solvent	b.p. ^a (°C)	δ^b (cal ^{1/2} cm ^{-3/2})	ρ^c (g cm ⁻³)	$\Phi_f \times 10^3^d$
Chloroform	61.7	9.2	1.48	0.470
1,1,2-Trichloroethane	113.8	10.2	1.44	0.448
Ethyl acetate	77.1	9.1	0.90	0.372
Tetrahydrofuran	66	9.5	0.889	0.375
Methylene chloride	40	9.7	1.33	0.401
1,1-Dichloroethane	57.3	9.8	1.176	0.398
1,2-Dichloroethane	83.5	9.8	1.235	0.414
3-Pentanone	101.7	8.9	0.814	0.364
Methyl ethyl ketone	79.6	9.3	0.805	0.363
Acetone	56.2	9.8	0.79	0.377

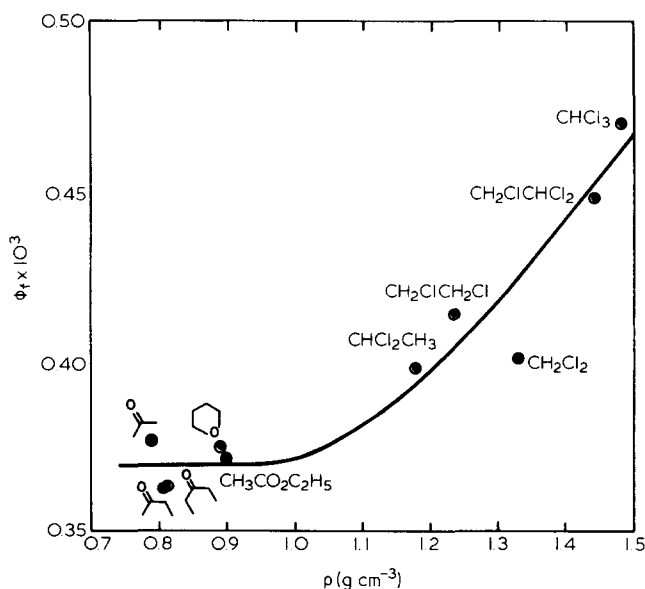
^a Boiling point, data taken from refs. 20 and 21^b Solubility parameter, data taken from ref. 22^c Density at 20°C, data taken from refs. 20 and 21^d Fluorescence quantum yield, better than $\pm 3\%$, average of three determinations

2 indicate that Φ_f of 1 in the polymer decrease from 4.5×10^{-3} to 0.36×10^{-3} – 0.47×10^{-3} when the polymer film is vapour swollen. The Φ_f values in swollen polymers are actually smaller than those in organic solvents; this is at least in part attributed to the low Φ_f of the polymer film itself. As only the relative effect of the vapour is important in the present work, the low Φ_f values should have no adverse effect on the interpretation here.

As the extent of the solvent–polymer interaction is expected to relate to their solubility parameters, correlation of these parameters with the Φ_f of 1 was attempted but was unsuccessful. Nor was there correlation between the viscosity and the volatility of the solvent. Although very little information is available in the literature regarding the relaxation behaviour of swollen polymers, much has been reported for the related process of diffusion of solvent (or small) molecules in polymer matrices^{12–18}. Generally, the diffusion coefficient of small molecules in a polymer matrix increases as the solvent concentration increases^{15,16}. At low solvent concentration (e.g. 2% volume fraction), Duda and Vrentas¹⁷ established that thermodynamic interaction

between solvent molecules and the polymer chain has very little influence on the diffusion coefficient; the size and the shape of the diffusant are the controlling factors of the diffusion processes. An estimation of the volume fraction of solvent in some of these vapour-swollen films, by measuring the increase in weight or in thickness, indicates that the volume fraction of solvent should be $< 10\%$. According to Chalykh and Vasenin¹⁶, the vapour-swollen polymer system in the present work can be considered as a low solvent concentration solvent–polymer binary system, the absence of a correlation between the Φ_f of 1 and the solubility parameter, the boiling point and the viscosity of the solvent is thus rational.

When Φ_f of 1 is plotted as a function of the density of the swelling solvent (Figure 2), there is a good correlation. Φ_f of 1 is solvent-density independent in the low density solvents regime ($\rho \lesssim 1$ g cm⁻³) and increases as solvent density increases in the high-density solvent regime ($\rho \gtrsim 1$ g cm⁻³). It is unlikely that the observed effect is produced by solvent molecules due to the solvation of 1 in

Figure 2 Plot of Φ_f of 1 as a function of the density of the swelling solvent

the swollen polymer because (1) no solvatochromic shift on λ_f of **1** is observed in the swollen film; (2) a limiting Φ_f value similar to that in organic solvent should have been observed if **1** is solvated by solvent molecules; (3) analogous density effect is not observed in the organic solvent. Thus, the observed vapour effect is attributed to a property of swollen polymer.

From the radiative decay rate constant ($\sim 3 \times 10^8 \text{ s}^{-1}$)⁸ and the Φ_f value, the lifetime of the S_1 state of **1** in swollen polymer can be calculated to be < 10 ps. Because of the relatively slow diffusion of solvent molecules in polymers, solvent molecules are practically stationary during the lifetime of the S_1 state of **1**. Consequently, despite the volume expansion in swollen polymer, the 'voids' seen by **1** are actually decreased due to the occupancy of these voids by solvent molecules. Therefore, if Φ_f of **1** is free-volume-dependent, an increase in Φ_f should occur upon vapour swelling. However, the opposite is observed to occur which indicates that **1** probes some very fast motions of the polymer chain in swollen polymer. The variation of Φ_f of **1** in swollen polymer is a consequence of the different polymer chain mobility produced by solvent molecules of various densities. The nature of this density effect remains to be investigated.

CONCLUSIONS

The fluorescence quantum yield of **1** has been used as a probe to study the effect of solvent vapour on the properties of swollen polymers. Results suggest that Φ_f of **1** is influenced by the mobility of the polymer chain in swollen polymer and that the mobility of the polymer chain is correlated with the density of the swelling solvent. Although it is difficult to establish any direct relation between the relaxation of segment in swollen polymer and that in solution, Zager and Freed¹⁹ have recently shown a very similar solvent-density effect in their study of the e.p.r. relaxation of PD-Tempone (an e.p.r. probe) in toluene- d_8 . Their results were theorized and were explained by an expanded volume theory, which is analogous to the mobility control process(es) described in

the text. It is hoped that the present work will stimulate more research in this area.

Finally, the present work also demonstrates the sensitivity of Φ_f of **1** towards the admission of solvent vapour into polymer, it is thus anticipated that, with a proper experimental design, Φ_f of **1** can be used as a probe to study the kinetic aspect (e.g. adsorption, permeability, etc.) of solvent-polymer binary systems.

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