Notes

Intramolecular Charge-Transfer Fluorescence of 1-Phenyl-4-(4-cyano-1-naphthylmethylene)-piperidine in Binary Mixtures of α,ω-Diacetylpoly(ethylene glycols) 1000 and 3000. Preferential Solvation in the Solid State

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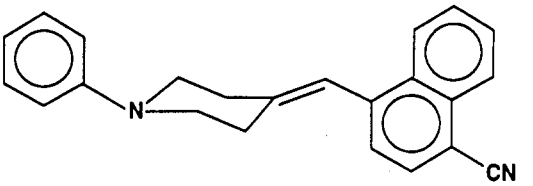
Introduction

1-Phenyl-4-(4-cyano-1-naphthylmethylene)piperidine, hereafter dubbed Fluoroprobe, displays strong intramolecular charge-transfer (CT) fluorescence from a highly dipolar excited state $[D^{\bullet+}A^{\bullet-}]^*$ (dipole moment of 25 ± 2 D) populated by rapid photoinduced charge separation after excitation ($\nu_{exc} > 27\ 397\ cm^{-1}$; Chart I).[1,2] In mobile, low molecular weight solvents the fluorescence maximum of Fluoroprobe was observed to be extremely sensitive to changes of the molecular environment; i.e., with increasing solvent polarity and/or polarizability a substantial bathochromic shift is found due to stabilization of the dipolar excited state $[D^{\bullet+}A^{\bullet-}]^*$ (for example, *n*-hexane, ν_{CT} 24 631 cm^{-1}; acetonitrile, ν_{CT} 14 409 cm^{-1}). In comparison with the absorption solvatochromism of the E_T probe,[3,4] the fluorescence solvatochromism of Fluoroprobe is twice as large![2] Recently, we have started investigations to employ the strong medium sensitivity of the emissive behavior of Fluoroprobe for the characterization of organic solid matrices. When used to monitor the progress of the polymerization of methyl methacrylate (MMA) to amorphous poly(methyl methacrylate) (PMMA)[5] or to study morphology changes concomitant with molecular weight in α,ω-diacetylpoly(ethylene glycols) (PEGAC's),[6] temperature-dependent continuous and time-resolved (nanosecond time scale) fluorescence measurements showed that relaxation of the dipolar excited state $[D^{\bullet+}A^{-}]^*$ of Fluoroprobe on the photophysical time scale is markedly influenced by changes in the mobility of the matrix sites, which accommodate the probe molecule. With decreasing mobility fluorescence takes place from non-relaxed excited states, leading to a hypsochromic shift of the fluorescence maximum. Since the probe molecule will be dissolved in either the amorphous or interlamellar regions of the solid matrices,[7] we were prompted to investigate the emissive behavior of Fluoroprobe in solid, binary mixtures of PEGAC's based on the following reasoning. It is well documented that low molecular weight PEGAC's (M_w < 6000) form fully extended lamellar crystals, with the chain end groups occupying the surface layers of the lamellar crystals.[8] If, in the case of solid, binary mixtures of PEGAC's, complete segregation of the components occurs, different matrix sites will be available for the accommodation of the probe molecule; in principle, two distinct fluorescence maxima for Fluoroprobe may be observed (PEGAC 1000, ν_{CT} 16 892 cm^{-1}; PEGAC 3000, ν_{CT} 17 762 cm^{-1}).[6] However, if homogeneous crystals are formed in which the chain end groups of the PEGAC's occupy the surface layers of the lamellar crystals, the interlamellar regions will be modified systematically within the series and preferential solvation of the probe molecule in the solid state may be discernible. In this paper we present evidence that within the series of binary mixtures of PEGAC's 1000 and 3000, preferential solvation of Fluoroprobe occurs due to the modification of the matrix sites which accommodate the probe molecule. The emissive behavior of Fluoroprobe, as a function of the binary mixture composition, can be described by an equation as derived by Langhals for the analysis of binary solvent mixtures with optical probe molecules.[4,9]

Chart I
Fluoroprobe



Results and Discussion

The PEGAC's were synthesized from the corresponding poly(ethylene glycols) (PEG's) and characterized by IR, NMR, and size-exclusion chromatography (SEC), respectively.[6] Binary mixtures of PEGAC's 1000 and 3000 were prepared by mixing the polymers, followed by two subsequent melting and crystallization cycles. The homogeneity of the bulk binary mixtures was assessed with differential scanning calorimetry (DSC, heating and cooling rate 10 $K \cdot min^{-1}$). In the DSC curves a single melting transition is observed with a peak position intermediate between those found for the starting materials PEGAC's 1000 and 3000, respectively. These results indicate that in the bulk the solid, binary mixtures are homogeneous.

For the continuous fluorescence measurements dilute solutions of Fluoroprobe (concentration < 1 mM) in the blends were used. The maximum of the CT fluorescence band was measured with a Spex Fluorolog 2 spectrophotometer equipped with a RCA c31034 detector in front-face geometry at ambient temperature (ν_{exc} 32 258 cm^{-1}); the spectra were corrected for the detector response. Note that the fluorescence maxima of Fluoroprobe in the PEGAC 1000 and 3000 matrices, respectively, are markedly different (PEGAC 1000, ν_{CT} 16 892 cm^{-1}; PEGAC 3000, ν_{CT} 17 762 cm^{-1}).[6] For all solid, binary mixtures only one characteristic broad CT emission band was observed; the width and shape of the band remained virtually unaffected

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Table I
Composition of the Solid, Binary Mixtures, i.e., Bulk (X_{1000}) and Local Mole Fraction (X^L_{1000}), R, and Continuous Fluorescence Maxima ν_{CT}, $\nu_{CT(1)}$, and $\nu_{CT} - \nu_{CT(1)}$ (Cf. Text)

X_{1000}	X^L_{1000}[a]	R[b]	ν_{CT}[c]	$\nu_{CT(1)}$[c,d]	$\nu_{CT} - \nu_{CT(1)}$
1.00	1.00	1.00	16 892[e]	16 892	0
0.67	0.90	1.34	16 978	17 179	-201
0.50	0.87	1.60	17 007	17 327	-320
0.33	0.83	2.51	17 036	17 475	-439
0.14	0.80	5.71	17 065	17 640	-575
0.09	0.63	7.00	17 212	17 684	-472
0.05	0.46	9.20	17 361	17 719	-358
0.00	0.00		17 762[e]	17 762	0

[a] Cf. eq 5. [b] Cf. eq 6. [c] In cm^{-1}. [d] Cf. eq 1. [e] ν_{CT1000} and ν_{CT3000}, respectively.[6]

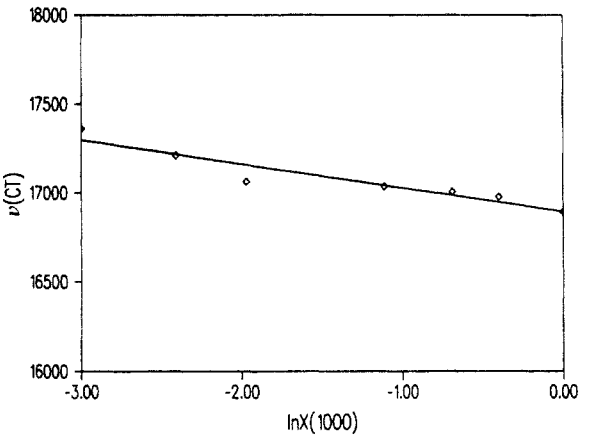

Figure 1. Linear relation between ν_{CT} of Fluoroprobe and ln X_{1000} of the solid, binary mixtures (cf. text).

over the entire range of binary mixtures (fwhm 1875 cm^{-1}; red edge of the CT emission band). While, as a function of the composition of the binary mixture, the CT band of Fluoroprobe shifts, it is evident (see Table I) that ν_{CT} deviates from a linear interpolation between the fluorescence maxima found in the pure components (eq 1); $\nu_{CT} \neq \nu_{CT(1)}$). In contrast, the bathochromic shift of the fluorescence maximum ν_{CT} of Fluoroprobe toward the value found for PEGAC 1000 is much more pronounced than predicted by eq 1, upon addition of a small mole fraction of PEGAC 1000 (X_{1000}) to PEGAC 3000 (Table I)

$$\nu_{CT(1)} = X_{1000}(\nu_{CT1000}) + X_{3000}(\nu_{CT3000}) \quad (1)$$

with $X_{1000} + X_{3000} = 1$.

This indicates that preferential solvation of Fluoroprobe occurs in the solid, binary mixtures. The change of the fluorescence maximum of Fluoroprobe concomitant with the binary mixture composition can be rather well described by eq 2 with B and C being parameters with the

$$\nu_{CT} = B \ln X_{1000} + C \quad (2)$$

dimension cm^{-1} ($B = -0.14 \times 10^3$ cm^{-1} and $C = 16\,894$ cm^{-1}, and correlation coefficient $r = -0.954$; Figure 1).

Intriguingly, eq 2 resembles the general relation (eq 3) derived by Langhals for the evaluation of either absorption

$$\nu_{CT} = E_D \ln (X/X^* + 1) + \nu^0_{CT} \quad (3)$$

or fluorescence solvatochromism of probe molecules in binary solvent mixtures containing a polar and an apolar component, which, under the assumption $X \gg X^*$ in the case of preferential solvation, transforms into eq 4.[4] In

$$\nu_{CT} = E_D \ln X + (\nu^0_{CT} - E_D \ln X^*) \quad (4)$$

the case of the Langhals equation X is the concentration of the more polar component in the binary solvent mixture, ν^0_{CT} is the absorption or fluorescence energy of the probe molecule in the pure, less polar component, and the parameters E_D and X^*, respectively, represent an energy with the dimensions cm^{-1}, which is a measure of the sensitivity of ν_{CT} toward changes in concentration X, and the critical concentration X above which ν_{CT} is affected by interactions between the components of the binary solvent mixture.[4,8,9] Obviously, for the solid binary mixtures of PEGAC's 1000 and 3000, different factors may be responsible for the observation that the emissive behavior of Fluoroprobe can be described by a Langhals-type equation (cf. eqs 2 and 4) rather than in the case of binary solvent mixtures consisting of a polar and apolar solvent.[4,9] In a previous paper we have reported that the position of the fluorescence maximum of Fluoroprobe, when dissolved in solid α,ω-diacetylpoly(ethylene glycol) matrices, depends on the morphology of the matrix which changes concomitantly with its molecular weight.[6] Continuous and time-resolved (nanosecond time scale) fluorescence measurements indicated that relaxation of the dipolar excited state $[D^{\bullet+}A^-]^*$ of Fluoroprobe on the photophysical time scale becomes impaired with increasing molecular weight of the matrix leading to the onset of fluorescence from nonrelaxed dipolar excited states $[D^{\bullet+}A^-]^*$; i.e., a hypsochromic shift of the fluorescence maximum concomitant with an increase in molecular weight was found. Since it is well established that molecular relaxation phenomena of solid polymers occur on a time scale much longer than the time window (ca. 30–60 ns) of the time-resolved fluorescence measurements,[6,10] we concluded that relaxation of the dipolar excited state $[D^{\bullet+}A^-]^*$ of Fluoroprobe on the photophysical time scale takes place via rotational motions of the probe molecule and functional groups, such as end groups, present in the matrix sites which accommodate the probe molecule. Therefore, we anticipate that the change of the fluorescence maximum of Fluoroprobe as a function of binary mixture composition, in combination with the observed deviation from a linear interpolation between the fluorescence maxima found in the pure components (cf. eq 1), signals the occurrence of preferential solvation of the probe molecule in the solid state due to a specific modification of the matrix sites. From a graphical evaluation of Figure 1 both E_D and X^* for the solid, binary mixtures can be obtained; i.e., $E_D = -0.14 \times 10^3$ cm^{-1} and $X^* = 1.6 \times 10^{-3}$ $mol \cdot L^{-1}$ (cf. eq 2 and 4). The analysis indicates that the assumption $X \gg X^*$ is valid for all the solid, binary mixtures. Additional support is obtained from a survey of a plot of ln $(X_{1000}/X^*_{1000} + 1)$ versus ν_{CT}, which gives $E_D = -0.14 \times 10^3$ cm^{-1} and $\nu^0_{CT} = 17\,764$ cm^{-1} with a correlation coefficient $r = -0.988$ (Figure 2).

The value of E_D is in excellent agreement with that derived from a graphical evaluation according to eqs 2 and 4, respectively. The value obtained for ν^0_{CT} (17 764 cm^{-1}) is within experimental accuracy equal to ν_{CT} (17 762 cm^{-1}) of Fluoroprobe dissolved in pure PEGAC 3000. The deviations from the linear behavior given by eq 1 and the negative E_D value found upon application of eq 4 thus imply that the local mole fraction (X^L_{1000}) of PEGAC 1000 in the matrix sites, which accommodate Fluoroprobe, is larger than the stoichiometric concentration, thus leading to preferential solvation. It appears interesting to see whether a quantitative measure for the degree of enrichment of the sites at which Fluoroprobe resides can be obtained. Equation 5 directly derived from eq 1 has been employed to calculate the effective local mole fraction

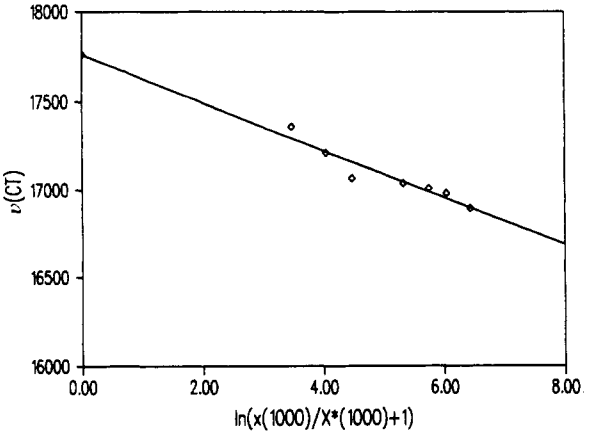

Figure 2. Linear relation between ln $(X_{1000}/X^*_{1000} + 1)$ and ν_{CT} of Fluoroprobe in the solid, binary mixtures (cf. text).

$$X^L_{1000} = (\nu_{CT} - \nu_{CT3000})/(\nu_{CT1000} - \nu_{CT3000}) \quad (5)$$

(X^L_{1000}) of PEGAC 1000 "seen" by the fluorescent probe molecule. A measure of the extent of enrichment of PEGAC 1000 at these sites, i.e., of the "preferential solvation", is then given by the ratio R $(=X^L_{1000}/X_{1000})$, which can be assessed from eq 6. Values of $R > 1$ indicate

$$R = X^L_{1000}/X_{1000} \; (=\nu_{CT} - \nu_{CT3000})/(\nu_{CT(1)} - \nu_{CT3000}) \quad (6)$$

that Fluoroprobe is preferentially solvated by the PEGAC 1000 component (Table I). Very significant enrichment factors up to $R = \sim 10$ are indeed calculated at low stoichiometric X_{1000} values!

Conclusions

In summary, the results of the continuous fluorescence measurements of Fluoroprobe, dissolved in a series of solid, binary mixtures, indicate that preferential solvation occurs in the solid state presumably via selective modification of the matrix sites due to segregation of the PEGAC 1000 molecules toward the interlamellar regions.

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Registry No. PEGAC (SRU), 27252-83-1; Fluoroprobe, 91759-52-3.