Intramolecular Charge-Transfer Fluorescence of 1-Phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine as a Morphology Probe in α,ω-Diacetylpoly(ethylene glycol) Matrices

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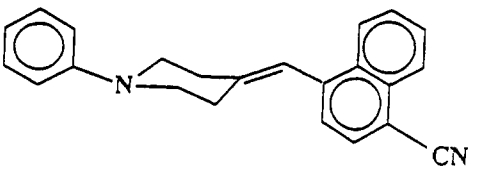
ABSTRACT: Continuous and time-resolved fluorescence measurements of 1-phenyl-4-[(4-cyano-1-naphthyl)-methylene]piperidine (Fluoroprobe) dissolved in α,ω-diacetylpoly(ethylene glycols) (PEGAC's) show that its fluorescence maximum is a sensitive probe of the microenvironment. Morphology changes of the PEGAC's concomitant with increasing molecular weight lead to the onset of fluorescence prior to full relaxation of the surrounding matrix sites.

Introduction

1-Phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine, hereafter dubbed Fluoroprobe, displays strong intramolecular charge-transfer fluorescence (Chart I).[1,2] Ultraviolet excitation ($\lambda < 365$ nm) of Fluoroprobe produces a dipolar excited state $[D^{\bullet+}A^{\bullet-}]^*$ for which a dipole moment of 25 (±2) D was estimated. Evidently, complete photoinduced intramolecular electron transfer from the dialkylanilino one-electron donor (D) moiety to the 1-vinyl-4-cyanonaphthyl one-electron acceptor (A) takes place across the interconnecting saturated framework that separates the D and A groups. When dissolved in mobile, low molecular weight solvents, Fluoroprobe is known to respond sharply to changes in solvent polarity and polarizability. Thus, while its emission maximum is located near the blue edge of the visible region in a saturated hydrocarbon solvent like *n*-hexane (406 nm), it shifts to the red edge (694 nm) in the polar solvent acetonitrile.[2] However, when it was used to monitor the progress of polymerization of methyl methacrylate to poly(methyl methacrylate), a hypsochromic shift of ca. 100 nm was observed.[3] Although this may be interpreted to indicate a decrease of medium polarity, it should be stipulated that also a decrease in medium mobility of the surrounding matrix sites may allow fluorescence to occur from nonrelaxed dipolar excited states $[D^{\bullet+}A^{\bullet-}]^*$.[4,5] This leads to the schematical representation of the fluorescence behavior of Fluoroprobe presented in Figure 1. To discriminate between polarity and mobility contributions, we compared the effect of increasing molecular weight on the fluorescence maxima of Fluoroprobe in a series of α,ω-diacetylpoly(ethylene glycols) (PEGAC's) with that of binary solvent mixtures of ethyl acetate and diethylene glycol dimethyl ether (diglyme) containing increasing mole fractions of the latter.[6] These mixtures provide reasonable models for the PEGAC's; i.e., the molar fraction of diglyme mimics the number of repeating units $(-(OCH_2CH_2)-)$. As anticipated, a bathochromic shift occurs with increasing mole fraction of the more polar solvent (diglyme) in the binary solvent mixtures. However, an opposite trend was found for the PEGAC's. Despite the fact that the dipole moment of poly(ethylene glycols) is known to increase monotonously with the number of repeating units,[7] the maximum of the broad charge-transfer emission band of Fluoroprobe undergoes a hypsochromic shift with increasing molecular weight of the matrix (Figure 2). This remarkable phenomenon was tentatively explained by invoking the onset of fluorescence from nonrelaxed dipolar excited states $[D^{\bullet+}A^{\bullet-}]^*$,[6] when the effective mobility of the matrix drops below a certain threshold (cf. also refs 4 and 5). Here we report the results of continuous and time-resolved fluorescence measurements, which show that the emissive behavior of Fluoroprobe is a sensitive probe for changes in the microenvironment. The observed hypsochromic shift of the fluorescence maximum of Fluoroprobe concomitant with increasing molecular weight of the PEGAC matrices at 293 K can be attributed unambiguously to the onset of fluorescence from nonrelaxed dipolar excited states $[D^{\bullet+}A^{\bullet-}]^*$ due to a decrease of mobility of the surrounding matrix sites on the photophysical time scale.

Chart I
1-Phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine (Fluoroprobe)



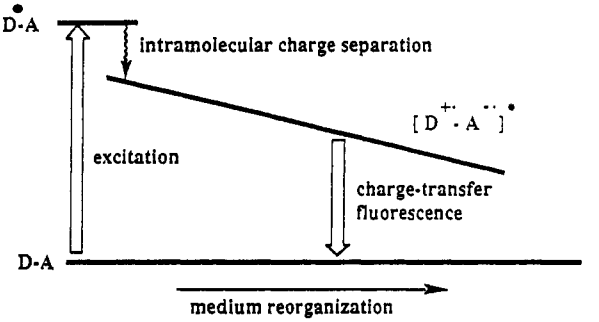


Figure 1. Schematical representation of the fluorescence behavior of Fluoroprobe as a function of dynamic medium reorganization following photoinduced intramolecular charge separation.

Experimental Section

Synthesis and Characterization of the PEGAC's. The α,ω-diacetylpoly(ethylene glycols) (PEGAC's) were prepared by

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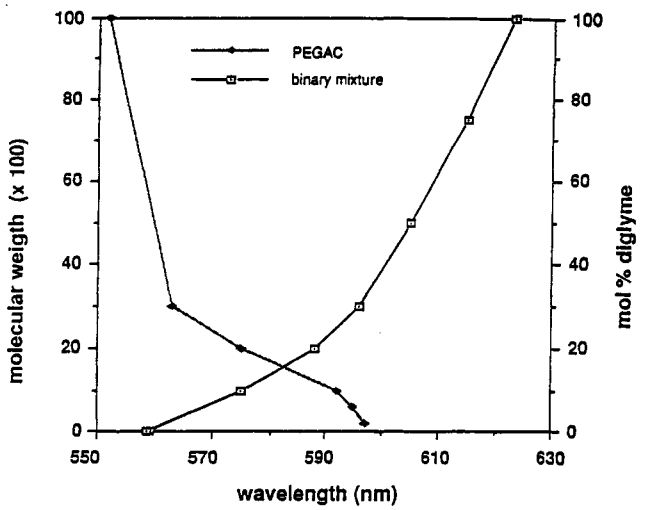
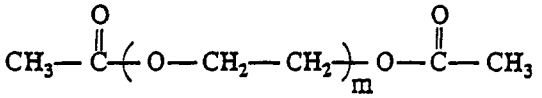


Figure 2. Comparison of the continuous fluorescence maximum of Fluoroprobe in PEGAC's and related binary solvent mixtures at 293 K (cf. text and the Experimental Section). No quantitative relation between the left and right vertical scales is implied.

Chart II
α,ω-Diacetylpoly(ethylene glycols) (PEGAC's)



treatment of dichloromethane solutions of the corresponding poly(ethylene glycols) (molecular weights 200, 600, 1000, 2000, 3000, and 10 000, respectively) with excess acetyl chloride for 1 h at room temperature under a nitrogen atmosphere (Chart II). After evaporation of the solvent and excess acetyl chloride under reduced pressure, the crude PEGAC's were purified by column chromatography (aluminum oxide 70–230-mesh ASTM, eluent dichloromethane). Both IR and ^{1}H NMR spectroscopy showed that the conversion of the hydroxyl end groups was quantitative. Size-exclusion chromatography (0.2 M sodium dihydrogen phosphate/0.0045 M disodium hydrogen phosphate pH = 5.0, 0.8 mL/min flow rate, TSK 2000 PW column, room temperature) revealed no differences in the dispersity of the molecular weight distribution of the samples before and after end-group modification. Thermal properties of the PEGAC's were determined with differential scanning calorimetry (Mettler DSC 30) using the following temperature program: 123 K – 10 K min^{-1} → 423 K – 10 K min^{-1} → 123 K – 10 K min^{-1} → 423 K. The glass transition temperature (T_g) and/or melting temperatures (T_m) were derived from the second heating ramp.

Continuous and Time-Resolved Fluorescence Spectroscopy. Continuous fluorescence spectra were measured on a Spex Fluorolog II spectrophotometer equipped with a RCA-c31034 detector; the spectra were corrected for the detector response. Solid solutions of the PEGAC's, containing Fluoroprobe (concentration <1 mM) were measured in front-face geometry at 293 K (λ_{exc} 310 nm). Continuous fluorescence spectra at 343 K of the liquid samples were measured in a right-angle geometry (λ_{exc} 310 nm). Time-resolved fluorescence spectra were obtained by using light pulses from an excimer laser (XeCl, λ_{exc} 308 nm, fwhm ca. 10 ns) for excitation and observing the emission via a spectrograph with an electronically gated (gate width 5 ns) intensified diode-array detector.

The system (EG&G OMA-III) allows the observation time window to be delayed incrementally with respect to the excitation pulse. The time-resolved fluorescence spectra were not corrected for the detector response. For both the continuous and time-resolved fluorescence measurements the reported fluorescence wavelengths correspond to the maximum of the charge-transfer emission band.

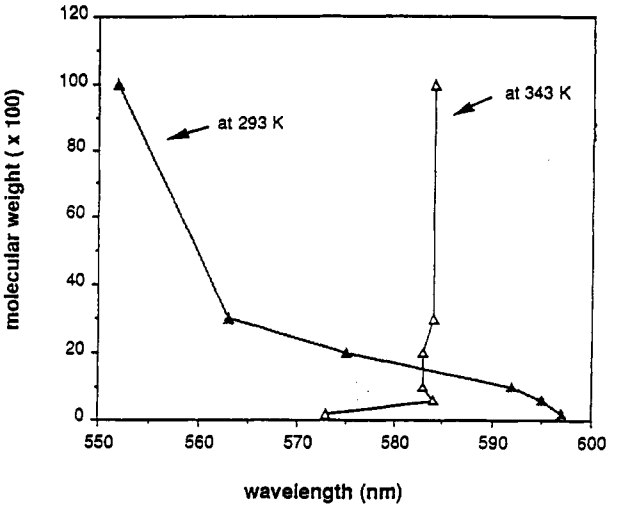


Figure 3. Comparison of the continuous fluorescence maximum of Fluoroprobe in PEGAC's at 293 and 343 K, respectively (cf. text and the Experimental Section).

Results and Discussion

Continuous Fluorescence Measurements at 343 K. In Figure 3 the fluorescence maxima of Fluoroprobe dissolved in PEGAC's of different molecular weight (cf. the Experimental Section) at 293 and 343 K, respectively, are compared. The results show that, at the latter temperature, which is well above the melting temperature of the PEGAC's, the fluorescence maximum of Fluoroprobe is independent of the molecular weight within experimental accuracy (λ_{fluor} ca. 583 nm). Only for PEGAC 200 was a slightly shorter wavelength (λ_{fluor} 573 nm) observed. This may indicate a modest decrease of effective polarity as expected upon decrease of the number of repeating units. However, for the PEGAC 200, evaporation of material occurred during the continuous fluorescence measurement at 343 K. Consequently, the determined fluorescence maximum is not representative, and we refrain from further discussion. The bathochromic shift of the fluorescence maximum in going from 293 to 343 K for PEGAC's with a molecular weight larger than 1000, which are solids at 293 K, is the anticipated behavior; with increasing temperature, relaxation pathways leading to a stabilization of the dipolar excited state [D$^{\bullet+}$A$^{\bullet-}$]* will become available on the photophysical time scale.[3] In contrast, for PEGAC's with molecular weights smaller than 1000, which are liquid or a waxy solid at 293 K, a hypsochromic shift of the fluorescence maximum is observed upon increasing temperature. Apparently for these samples, solvation of the dipolar excited state [D$^{\bullet+}$A$^{\bullet-}$]* of Fluoroprobe becomes impaired by the thermal motions of the liquid matrix at the elevated temperature. In fact similar pronounced thermochromic shifts have been observed for the absorption bands of dye molecules dissolved in several polar and nonpolar solvents.[8] In conclusion, the continuous fluorescence results obtained at 343 K support the assumption that the hypsochromic shift of the fluorescence maximum concomitant with an increase in molecular weight of the PEGAC matrices at 293 K is due to the onset of fluorescence from nonrelaxed dipolar excited states [D$^{\bullet+}$A$^{\bullet-}$]* of Fluoroprobe after excitation and the intramolecular charge transfer.[6] Presumably, even in the solid regime, morphology changes of the PEGAC matrices affect the relaxation of the dipolar excited state [D$^{\bullet+}$A$^{\bullet-}$]* of Fluoroprobe.

Time-Resolved Fluorescence Measurements at 293 K. To gain more detailed insight in the molecular dynamics of Fluoroprobe after excitation and its depen-

Table I
Initial and Final Fluorescence Maximum of Fluoroprobe in PEGAC's at 293 K As Determined by Time-Resolved Fluorescence Spectroscopy with 5-ns Resolution[a]

PEGAC, mol wt	λ(initial), nm	λ(final), nm	Δλ,[b] nm
600	578.0	586.5	8.5
1000	571.5	581.0	9.5
2000	551.5	566.0	14.5
3000	536.5	557.0	20.5
10000	501.0	554.5	53.5

[a] Cf. the Experimental Section. [b] $\Delta\lambda = \lambda(\text{final}) - \lambda(\text{initial})$.

dence on the molecular weight of the PEGAC matrices at 293 K, time-resolved fluorescence spectra were recorded for the PEGAC's with molecular weights in the range of 600–10 000. In Table I the initial fluorescence maximum (λ(initial)) of Fluoroprobe, determined within 5 ns after the onset of fluorescence, and the final fluorescence maximum (λ(final)), reached after 30–60 ns, both detected with a time window of 5 ns for the gate of the optical multichannel analyzer are compared. In agreement with the continuous measurements, a considerable hypsochromic shift is found with increasing molecular weight for λ(final) within the series. Note, however, that an analogous behavior is already discernable for λ(initial) within the series. This indicates that even primary relaxation processes, which occur on a subnanosecond time scale, after excitation of Fluoroprobe in these solid solutions are already markedly influenced by the matrix. The bathochromic shift Δλ between λ(initial) and λ(final) displays a pronounced increase, which increases in value concomitantly with the molecular weight of the PEGAC matrices; a linear correlation (r 0.9996) is found between Δλ and the PEGAC molecular weight within the series.

Although 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 and,[3,9] therefore, cannot be related to the increase of Δλ, the time-resolved data suggest that, on the photophysical time scale, relaxation of the dipolar excited state $[D^{\bullet+}A^{\bullet-}]^*$ of Fluoroprobe mainly occurs via rotational motions of the probe molecule and functionalities, such as end groups, of the surrounding matrix. Under the assumption that Fluoroprobe will be dissolved either in the amorphous regions of the matrices or in the interlamellar layers between crystals,[10] we anticipate that the hypsochromic shift of the fluorescence maximum of Fluoroprobe with increasing molecular weight in the series of PEGAC matrices reflects the occurrence of morphology changes. For poly(ethylene glycols) and end-group-modified derivatives, it is documented that the morphology changes as a function of molecular weight (M_w 200 and 600, liquid at 293 K; $1000 \leq M_w < 3000$, extended chain lamellar crystals; $M_w \geq 3000$, variously folded lamellar crystals).[11-13] Differential scanning calorimetry revealed that PEGAC 200 consists of amorphous material (T_g 199 K), while PEGAC 600 and 1000 consist of both amorphous and crystalline material (PEGAC 600, T_g 199 K and T_m 287.6 K; PEGAC 1000, T_g 207 K and T_m 306.4 K). The higher molecular weight PEGAC's are all crystalline (PEGAC 2000, T_m 325.1 K; PEGAC 3000, T_m 324.7 K and 329.0 K; PEGAC 10 000, T_m 329.0 K, respectively; cf. the Experimental Section).

The detection of two melting peaks in the case of PEGAC 3000 is indicative of the presence of both extended and folded lamellar crystals in the solid state.[14] Therefore, we conclude that, with increasing molecular weight of the PEGAC matrices, relaxation of the dipolar excited state $[D^{\bullet+}A^{\bullet-}]^*$ of Fluoroprobe at 293 K will be impaired due to morphology changes of the surrounding matrix, thus, leading to the onset of fluorescence from nonrelaxed dipolar excited states $[D^{\bullet+}A^{\bullet-}]^*$.[6]

Conclusion

Continuous and time-resolved fluorescence studies of Fluoroprobe dissolved in PEGAC matrices reveal that fluorescence occurs prior to full relaxation of the surrounding matrix sites. The position of the fluorescence maximum at 293 K depends on the morphology of the matrix, which changes concomitantly with its molecular weight. The high sensitivity of the emissive behavior of Fluoroprobe toward its microenvironment holds a promise for future applications in the characterization of crosslinkable, surface-bound, and reinforced polymers and polymer blends. Experiments are in progress, and the results will be reported in due course.

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