

PHOTOBHAVIOR OF PYRENE END-LABELLED POLY(ETHYLENE OXIDE) IN METHANOL-WATER MIXTURES

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Summary

The photobehavior of pyrene end-labelled poly(ethylene oxide) and methyl 4-(3-pyrenyl)-butyrate was studied in methanol, water and methanol-water mixtures. It was found that the solvent dependence of the pyrene lifetime in the polymer is different from that of the unbonded molecule. The results are discussed in terms of specific solvation effects on the chromophore in the polymer and it is emphasized that these effects must be taken into account when the photobehavior of an unbonded molecule is taken as a model for that of an isolated chromophore in a polymer.

1. Introduction

The cyclization dynamics of polymer chain ends is of current interest. Most of the studies in this area have been carried out employing fluorescent [1, 2] or phosphorescent [3] groups attached to the ends of the polymer. In an interesting study in which the effects of the solvent on end-to-end cyclization of poly(ethylene oxide) (PEO) were probed by intramolecular pyrene excimer formation, Cheung *et al.* [4] observed that in ten non-protic solvents the average rate constant $\langle k_1 \rangle$ for end-to-end cyclization was inversely proportional to the solvent viscosity, as expected for a diffusion-controlled process. Nevertheless, in protic solvents (methanol and water), the rate of intramolecular excimer formation was substantially greater than one would expect on the basis of solvent viscosity alone. The values of $\langle k_1 \rangle$ were obtained by assuming that pyrene lifetimes in the absence of excimer formation in the polymer were equal to those measured for a small pyrene-containing model compound (methyl 4-(3-pyrenyl)-butyrate (MPB)), and the anomalous results obtained in methanol and water were explained by assuming that in these solvents the pyrene chromophores are not uniformly distributed outside and inside the polymer coil. In order to test this hypothesis and to evaluate further the differences in behavior of a chromophore

isolated in a polymer and in a model compound in different solvents and solvent mixtures, we have undertaken a study of the photobehavior of a pyrene group incorporated into the small molecule MPB, and into the end of a PEO chain under conditions such that excimer formation is minimized.

2. Experimental details

The pyrene end-labelled poly(ethylene oxide) (PEOPy) was obtained by esterification of a PEO sample (Unilever, Research Laboratories, Welwyn, U.K.; nominal molecular weight, 2×10^4) with 4-(3-pyrenyl)-butyric acid (PBA; Koch-Light). The esterification was performed by following the procedure of Cuniberti and Perico [5], but employing a very small [PBA]/[PEO] stoichiometric ratio in order to obtain single labelling of the chain ends. The degree of substitution of the polymer sample was determined by UV spectroscopy. The absorption spectra of dilute tetrahydrofuran (THF) solutions of the polymer were the same as those for PBA and MPB. For the peak at 330 nm the extinction coefficient was equal to $3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for both PBA and MPB. This value was employed for the end group analysis of the polymer. The number of pyrene groups per chain so obtained was 0.4.

Viscosity measurements were carried out at 25 °C with a Desreux and Bischoff dilution viscometer [6]. Intrinsic viscosities $[\eta]$ were determined by extrapolation to zero concentration of the reduced viscosity *vs.* concentration plot.

Equilibrium dialysis experiments were carried out in a dialyzer with a total volume of about 15 cm³. The semipermeable cellophane membrane was conditioned in each solvent mixture before being used. The dialytic equilibrium was obtained in about 6 h. The refractive index increments of the polymer solutions were measured at 25 °C using a Brice-Phoenix differential refractometer. The preferential adsorption coefficient λ^* was determined by using the relation

$$\lambda^* = \left(\frac{dn}{dc} \right)_\mu - \frac{(dn/dc)_k}{dn/dk}$$

where $(dn/dc)_k$ is the polymer refractive index increment in the solvent mixture, dn/dk is the variation in the refractive index of the solvent mixture as a function of the volumetric composition and $(dn/dc)_\mu$ is the polymer solution refractive index increment after equilibrium dialysis has been established.

Fluorescence spectra were recorded using an LS5 Perkin-Elmer luminescence spectrometer. Lifetime measurements were performed employing a Nitronite nitrogen laser light source coupled to a Tektronix 7633 oscilloscope. Measurements were taken at 20 °C in air-free (nitrogen purged) solutions.

3. Results and discussion

The emission spectra of dilute aqueous solutions of PEOPy consist of the monomer band alone (see Fig. 1). This indicates that only unimolecular processes take place under our experimental conditions. The measured lifetimes in methanol, water and several methanol-water mixtures are shown in Fig. 2. The lifetimes measured in methanol (236 ns and 225 ns for MPB and PEOPy respectively) were similar and in good agreement with the value

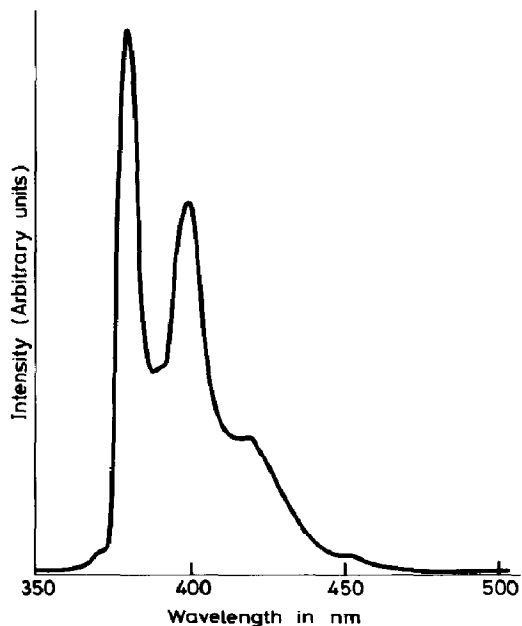


Fig. 1. Fluorescence spectrum of PEOPy in water ($[PEOPy] = 0.01$ wt.%; excitation wavelength, 337 nm; nitrogen purged).

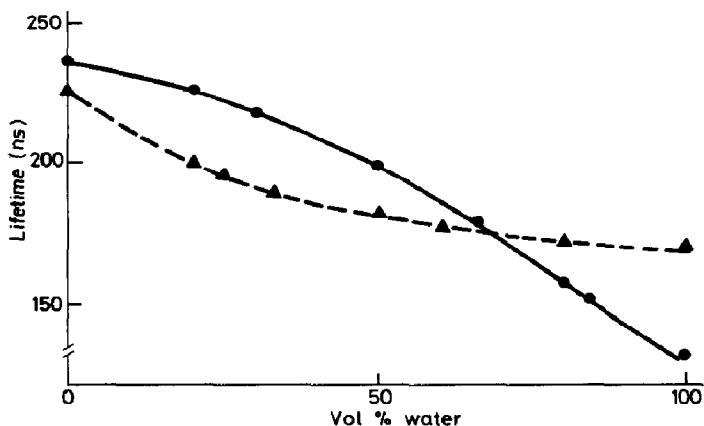


Fig. 2. Solvent dependence of pyrene lifetimes in MPB (—) and PEOPy (---) in methanol-water mixtures (emission wavelength, 400 nm).

reported by Cheung *et al.* [4] for MPB (233 ns). In contrast, the value obtained for PEOPy in water (170 ns) is longer than that measured for MPB (133 ns) and considerably different from the value assumed by Cheung *et al.* [4] (200 ns). The differences observed in water can be explained by considering that the hydrophobic end group containing the pyrene moiety in the PEOPy is not completely exposed to the solvent (water) but is imbedded in the polymer coil, rendering its microenvironment less polar [4, 7] and leading to a longer lifetime (the lifetimes for the model compound in 1,4-dioxane and ethyl acetate are 196 ns and 202 ns respectively). It is interesting to note that the slightly shorter lifetime of the polymer in methanol can be explained by a similar argument, since in this solvent the lifetime of the model compound is longer than in solvents similar to PEO [4].

In the solvent mixtures, besides the effect of the polymer chain on the chromophore microenvironment, the effect of specific solvation around the chromophore resulting from preferential adsorption of the components in the binary solvent has to be considered. Figure 3 shows the results obtained

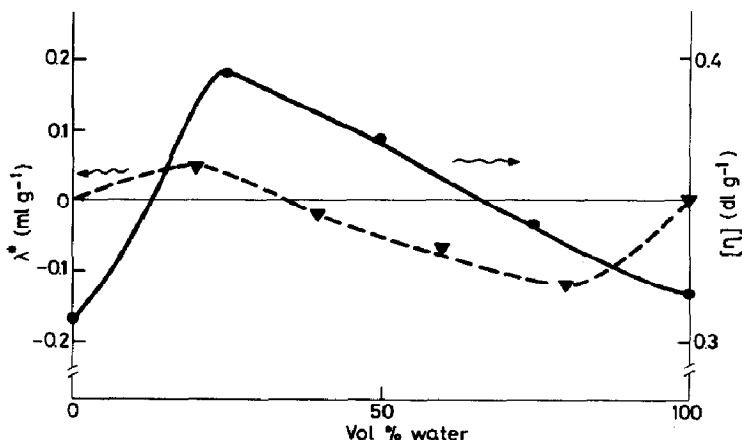


Fig. 3. Plot of the preferential adsorption coefficient λ^* (---) and the intrinsic viscosity $[\eta]$ (—) vs. the solvent composition in the methanol-water mixtures.

in the equilibrium dialysis/differential refractometry experiments and the viscosimetric behavior of the polymer in the solvents considered. The λ^* indicate that water is preferentially adsorbed in methanol-rich mixtures up to about 38 vol.% water where the inversion point occurs ($\lambda^* = 0$). After this composition methanol is preferentially adsorbed. Preferential adsorption, which seems to be a general phenomenon when a polymer is dissolved in a binary solvent [8], is explained in terms of specific interactions in the ternary systems [9]. The viscosimetric behavior is such that $[\eta]$ increases when water is preferentially adsorbed and then decreases, this being a co-solvent effect which frequently accompanies preferential adsorption in solvent mixtures.

The data in Fig. 2 show that the solvent dependence of pyrene lifetimes in PEOPy is different from that of MPB. These results can be explained,

at least qualitatively, in terms of a combination of the effects introduced by the polymer chain and the specific solvation on the chromophore micro-environment. In the methanol-rich mixtures, the lower values for PEOPy reflect the preferential adsorption of water. From the increase in $[\eta]$ in this zone, it can be ruled out that the shortening of the lifetime is due to an effect of the solvent on the polymer conformation which favors excimer formation in the small number of double-labelled chains (estimated as about 5%; see Section 2). However, the results obtained in the water-rich mixtures can be explained in terms of "pyrene adsorption" onto the polymer chain and/or preferential adsorption of methanol from the solvent mixture.

The data obtained in this work and the analysis of the solvent effects emphasize the shortcomings of using a small molecule as a model for an isolated chromophore in a polymer.

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