The fluorescence of polybenzoxazole dispersed in poly(ether ether ketone)

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Blends of poly(*p*-phenylenebenzo[1,2-*d*:5,4-*d'*]bisoxazole) (PBO) dispersed in poly(ether ether ketone) (PEEK) have been prepared by casting and coagulating methanesulfonic acid (MSA) solutions containing different fractions of each polymer. At PBO fractions greater than about 1%, the fluorescence spectra resemble that of 'bulk' PBO coagulates; but at lower PBO concentrations, the spectra show a sharper, blue-shifted peak, close to the 0–0 peak of dilute PBO/MSA. This emission most likely originates from PBO chains that have been isolated in a photophysical sense. This result, along with the solvent shift seen in a model compound, suggests that the deprotonation minimally perturbs the emission spectrum of PBO relative to the changes caused by aggregation.

(Keywords: fluorescence; polybenzoxazole; poly(ether ether ketone))

INTRODUCTION

Poly(*p*-phenylenebenzo[1,2-*d*:5,4-*d'*]bisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBZT) show significant spectral differences between the dilute solution and coagulated solid phases[1–3]. For both polymers, the absorbance and emission spectra are broadened and red-shifted upon coagulation. In a PBZT–bipyridyl copolymer in polyphosphoric acid, Wei-Berk and Berry have ascribed a similar shift seen upon the addition of water as mainly due to deprotonation of the copolymer[4]. However, there is some ambiguity in resolving the effects of deprotonation by water, and the subsequent tendency of the deprotonated rods to phase-separate, particularly if the protonated rods exist as aggregates[5].

This issue could be clarified in a system where the deprotonated macromolecules are molecularly dispersed in a non-acidic medium, i.e. a molecular composite[6]. Wang *et al.* have studied the luminescence of a 60% PBZT/40% nylon-6,6 film, and concluded that the PBZT existed in an aggregated state[1]. Here, we extend this approach by studying the photoluminescence of PBO/poly(ether ether ketone) (PEEK) blends prepared with varying PBO concentrations, and comparing these results with luminescence spectra of a model compound in acidic and non-acidic media.

EXPERIMENTAL

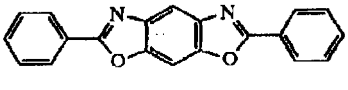
PBO in polyphosphoric acid was prepared by standard methods[7]. The polymer was isolated from the polymerization medium by water coagulation followed by exhaustive rinsing to remove traces of solvent. The resulting coagulate was dried, and yielded an intrinsic viscosity of 25 dl g^{-1}, measured in a solution of methanesulfonic acid (MSA) saturated with methanesulfonic anhydride (MSAA), and 0.1 M sodium methanesulfonate[8]. The dehydrating action of MSAA serves to limit the effect of any water contamination[9], and does not appear to affect the state or solubility of PBO[10]. MSA was purchased from Fluka Chemika, and the MSAA was obtained by distillation of a mixture of MSA and P_2O_5 (refs. 8, 9).

Commercial-grade PEEK (Victrex 380G, $M_w \simeq 36\,000$) was obtained from ICI. Nylon-6,6 was obtained from Scientific Polymer Products Inc. Both polymers were dried at ca. 120°C for ca. 24 h before dissolution.

Casting solutions were prepared by co-dissolving the appropriate polymers in the MSA/MSAA with mild stirring at ambient temperature over several days. All solutions were prepared with a total polymer content of ca. 4 wt%. In all cases this gave visually transparent, homogeneous solutions, with no appearance of liquid crystallinity, in agreement with the phase diagrams shown for PBZT/PEEK ternary solutions in MSA[11].

Free-standing films were prepared by spreading the casting solution over a glass slide, and immersing the slide in boiling water, to effect rapid coagulation. The films were dried in vacuum at 100°C for ca. 12 h. This produced free-standing films ca. 0.2 to 0.5 mm thick. For PEEK-based films, this produced yellow to white (depending on the PBO content) opaque films. D.s.c. analysis[12] indicated that the crystallinity content of the PEEK was ca. 15%.

The model compound (MC), whose structure is shown below, was prepared by the reaction of diaminoresorcinol dihydrochloride and benzoic acid[13]:



MODEL COMPOUND (MC)

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Solutions of PBO and MC used for emission spectra were prepared with maximum optical densities between 0.15 and 0.25 in the absorbance band of interest. The reversible nature of the dissolution of MC in MSA was shown by dissolving it in MSA and precipitating it out by addition of water. The crystals obtained were dried and dissolved in chloroform, and the spectral properties of this solution were found to be indistinguishable from those of the compound before MSA dissolution.

Fluorescence spectra were obtained on a Spex Fluorolog spectrometer, equipped with 0.22 m double monochromators, typically run at 1 nm bandpass. Solution spectra were run at right angles, while film spectra were run in the front face mode. Spectra are uncorrected for instrumental emission response, which would somewhat alter the shape of the coagulate emission band. Absorbance spectra were obtained on a Shimadzu UV-3101 PC.

RESULTS AND DISCUSSION

Model compound

Figure 1 shows absorbance spectra of MC in MSA and chloroform, while *Figure 2* shows the emission spectra in these solvents. The absorbance and fluorescence spectra in chloroform agree with those previously reported[13]. Extinction coefficients were similar in both solvents. While we did not measure luminescence yields, the integral emission intensity in MSA was about half that in chloroform, indicating a luminescence yield in MSA of roughly 0.3[13].

For MC in 'organic' solvents, the high extinction coefficients in the near-u.v. indicate a transition to a π,π^* excited state[14]. The small Stokes loss and mirror symmetry between the absorption (excitation) and emission spectra indicate that the emissive state is the same as the near-u.v. absorbing state. This, along with the high fluorescence yield and short lifetime[13], indicates that the lowest excited state is predominantly π,π^* in character[15].

The spectral perturbations seen in MSA relative to the 'organic' solvent are typical for aromatic hydrocarbons possessing a site for specific solvent interactions[16], and include a red shift for both absorption and emission spectra, broadening of the vibronic bands and an increase in the Stokes loss. The relatively small magnitude of these protonation effects is also characteristic of aromatic azines possessing a π,π^* lowest excited state[17,18]. The loss of vibronic structure and red shift in the absorbance spectrum in MSA are qualitatively similar to that reported for a model of PBZT[2].

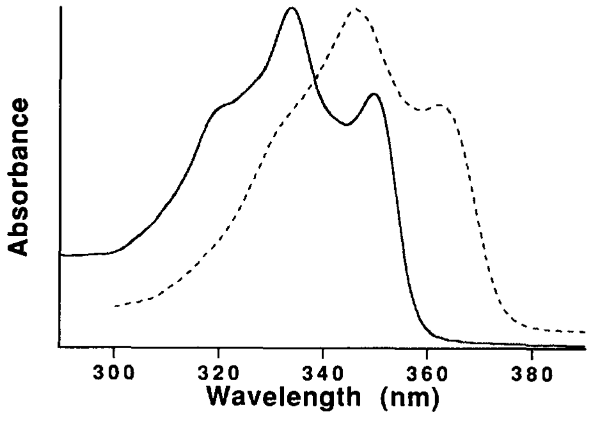

Figure 1 Normalized absorbance spectra of ca. 5×10^{-6} M MC in chloroform (-----) and MSA (——)

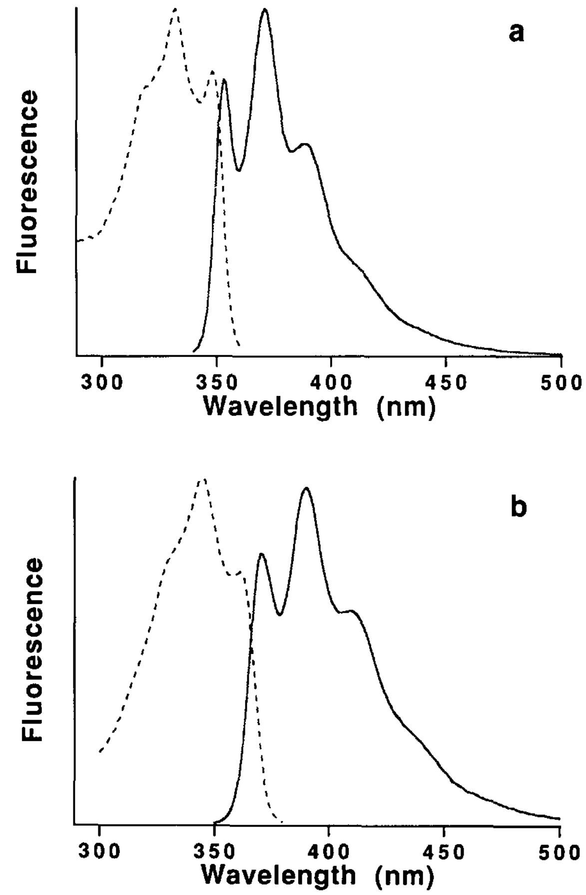

Figure 2 (a) Fluorescence of MC in chloroform: (-----) excitation (emission 375 nm) and (——) emission (excited at 334 nm). (b) Fluorescence of MC in MSA: (-----) excitation (emission 390 nm) and (——) emission (excited at 345 nm)

PBO

Figure 3 shows the emission spectra of a 1.6 ppm PBO in MSA solution and PBO coagulate. While the solution spectra are indicative of a single emissive species, the coagulate emission is significantly excitation-dependent, indicating disorder in the solid, and depends on the details of the coagulation and drying process. In any case, the coagulate emission spectra are invariably broadened and red-shifted from the dilute solution spectra.

PBO/PEEK

Figure 4 shows the emission spectra of a series of PBO/PEEK films. All spectra were excited at 350 nm, which is sufficiently energetic to excite PBO coagulate, dilute protonated PBO in solution and PEEK. PEEK does intrinsically fluoresce (*vide infra*), but the intensity is so low that it does not significantly contribute to these spectra.

Down to ca. 5 wt% PBO, the emission is similar to that of solid PBO. However, at ca. 1 wt% PBO there appears a new, sharper peak at 419 nm, whose relative intensity becomes quite pronounced at 0.1 wt%. We ascribe this peak to deprotonated PBO, which is sufficiently isolated to fluoresce like an unaggregated rod. Assuming that the 419 nm peak corresponds to the 0–0 transition, this is blue-shifted ca. 400 cm^{-1} from the corresponding PBO emission in MSA. As stated above

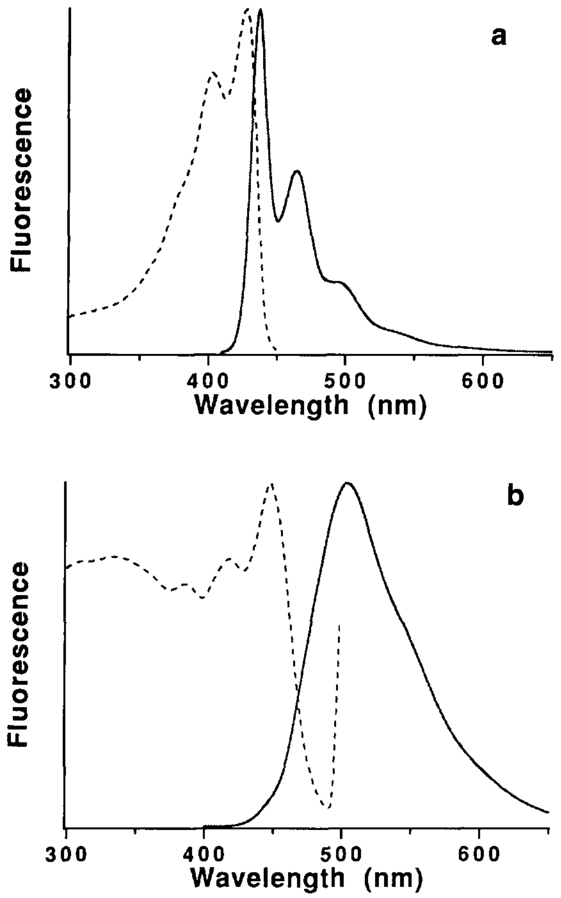

Figure 3 (a) Fluorescence of 1.6 ppm PBO in MSA: (-----) excitation (emission 464 nm) and (——) emission (excited at 402 nm). (b) Fluorescence of PBO coagulate: (-----) excitation (emission 512 nm) and (——) emission (excited at 350 nm)

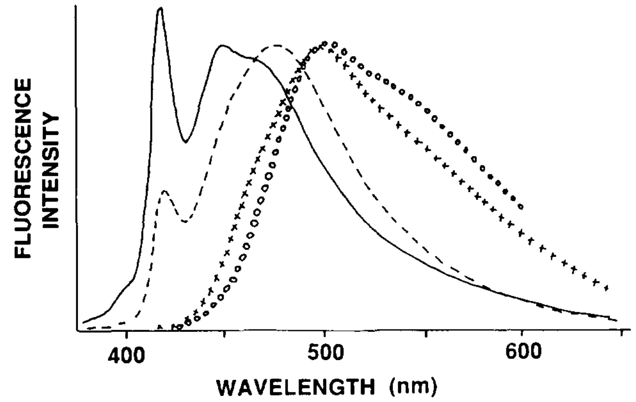

Figure 4 Emission of PBO/PEEK films excited at 350 nm: (ooooo) 33 wt% PBO; (xxxxx) wt% PBO; (-----) 1 wt% PBO; (——) 0.1 wt% PBO

for the model monomer, this relatively minor deprotonation effect is typical for aromatic azines possessing a π,π^* lowest excited singlet state. Indeed, the small blue shift could be rationalized in terms of 'bulk' solvent effects[19], without recourse to specific solvent–PBO interactions.

Figure 4 also shows that the PBO aggregate emission is somewhat concentration-dependent, shifting to shorter wavelength and becoming more structured at lower PBO contents. To clarify this behaviour, we prepared a PBO/PEEK film very dilute in PBO (0.02 wt%), whose emission spectrum is shown in *Figure 5*. At this low PBO concentration, PEEK fluorescence contributes significantly to the total emission. Roughly correcting the total spectrum for the PEEK contribution reveals a discrete band at 450 nm, intermediate in energy between the 'isolated' rod (419 nm) and aggregate (ca. 500 nm) bands. This suggests the existence of a species in an incomplete state of aggregation, either lacking a sufficient number of neighbouring rods, or with interchain angles and/or distances perturbed relative to a true aggregate.

The concentration-dependent appearance of emission from deaggregated PBO in PEEK raises the issue of the mechanism of rod isolation in the coagulate. From another perspective, the unusual observation could be the persistence of aggregate formation even at 'trace' PBO levels in the coagulate. Furukawa and Berry have inferred the presence of solution aggregates of a PBZT copolymer in rather dilute MSA solutions containing added salts[5]. Analogous PBO aggregates could be present in the MSA casting solutions, where they would be expected to be in equilibrium with isolated PBO molecules. If we assume that coagulation occurs rapidly, it could 'freeze' the solution aggregate–rod equilibrium into the solid blend. Hence, the isolated rod/aggregate population ratio in a coagulate could reflect a similar population ratio existing in the MSA solution. Note that the concentrations of our more PBO dilute solutions were similar to Furukawa and Berry's, and while we did not add salt as such, the dissolved PEEK would give the solutions a reasonable ionic strength.

A more prosaic mechanism for PBO rod isolation in PEEK assumes that PBO is unaggregated in the casting solution, and that at low PBO concentrations coagulation occurs before the rods can completely aggregate. It is also possible that PBO may be truly miscible in PEEK, at the trace concentrations where isolated rod emission is seen. While rod-like polymers show strong tendencies to aggregate in polymeric matrices[6,11], we are not aware of studies at such low rod concentrations. Some support for this miscibility hypothesis is provided in *Figure 6*, showing the emission of films of 0.1% PBO in PEEK and nylon-6,6. No isolated rod emission is seen in the polyamide, which could be less compatible with PBO than the highly aromatic PEEK. This is not conclusive, as the two matrices could also substantially differ in their MSA solution properties, coagulation rates[11] and photophysical properties. Chen and Kyu have noted the appearance of an 'entrapped single phase' in a blend of

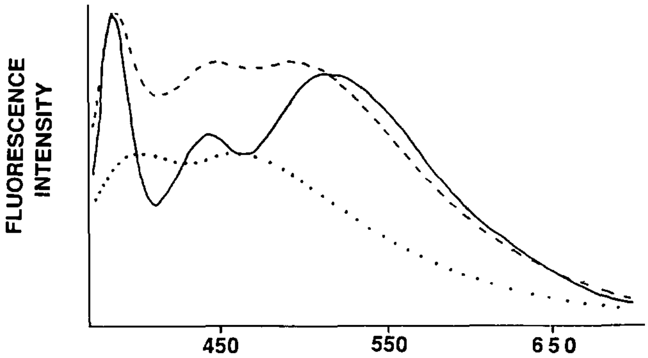

Figure 5 Emission of films excited at 350 nm: (·····) PEEK; (-----) 0.02 wt% PBO/PEEK; (——) PBO/PEEK–PEEK

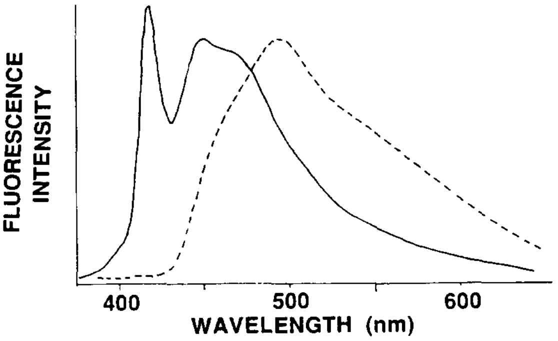

Figure 6 Emission of 0.1 wt% PBO film excited at 350 nm: (-----) in nylon-6,6; (——) in PEEK

amorphous nylon and PBO prepared from MSA solutions[20], though their nylon had aromatic moieties, and their methods might not be as sensitive to PBO aggregation on the molecular level.

CONCLUSIONS

When dispersed in PEEK at sufficiently low concentrations, PBO shows an emission at ca. 420 nm, which most likely originates from 'isolated' rods. This spectral assignment is consistent with the solvent effects seen in a model compound. The proximity of this emission to that seen in dilute solutions of PBO in MSA is also consistent with previous studies of protonation effects on the excited states of aromatic azines, which indicate only minor spectral perturbations when the lowest excited states are mainly π,π^* in nature[17,18]. We then ascribe the red shifts seen in PBO coagulates to aggregation effects.

The 'isolation' of PBO macromolecules is a phenomenological description, and does not imply that the 419 nm emitting species are homogeneously dispersed in the PEEK matrix. It is not clear to what extent the interchain interactions in the solid need to be disrupted to 'turn off' the concentration effects that lead to aggregate emission, since the structural origins of this emission (and excitation) are not clear. Analogies to excimer emission[21,22] seem apparent, but the red shift seen in the aggregate excitation spectra indicates that, to some extent, the interaction giving rise to the aggregate emission originates in the ground electronic state. Rationalization of the aggregate emission spectrum is further complicated by its multicomponent nature.

However, puzzling out the excited-state properties of PBO coagulates is the first step in using PBO's intrinsic photophysics as a fundamental and applied structural probe.

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