polymer communications

Annealing effects on the intrinsic fluorescence of PBO/amorphous nylon blends

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The photo-fluorescence of a solution-cast film containing a 30/70 blend of poly(*p*-phenylene benzobisoxazole) (PBO)/amorphous nylon shows a substantial decrease in fluorescence yield, and a blue-shifted spectrum upon annealing at around 220°C, corresponding to the transition from an entrapped single phase to a multiphase system. This indicates a substantial dependence of PBO fluorescence on its domain structure in this blend.

(Keywords: PBO; amorphous nylon; fluorescence)

The fate of the electronic excited states of main-chain chromophoric polymers is of substantial interest for both its fundamental and applied significance. In particular, the origins of non-radiative decay processes in conjugated polymers have been subject to recent scrutiny[1,2]. Here, we utilize a system of poly(*p*-phenylene benzobisoxazole) (PBO)/amorphous nylon (AN), shown by Chen and Kyu[3] to form an 'entrapped single phase' blend when solution cast with thermally induced phase separation, to study the effect of aggregation state on the fluorescence spectrum and efficiency of PBO.

The AN used was SELAR^R (Du Pont registered trademark) PV 3426, made by the condensation polymerization of hexamethylene diamine with isophthalic and terphthalic acids. PBO was obtained in fibre form. Casting solutions were prepared by mixing solutions of each polymer dissolved in methanesulfonic acid (MSA), saturated with methanesulfonic anhydride with 0.1 M sodium methanesulfonate. Films were prepared by spreading the casting solution on a glass slide and coagulating either in water, or in isopropanol followed by water. Films were dried either in a 70°C vacuum oven, or by gently heating with a heat gun. Annealing was done either on a hot stage or by rigorous heating to around 220°C with hot air, and could be followed by visualizing the fluorescence using a 365 nm black light (*vide infra*). Both dried and annealed films showed no changes in fluorescence after overnight storage at 21°C and 50% humidity. Fluorescence spectra were obtained on a Spex Fluorolog instrument, at ~2 nm bandpass, while u.v.–vis. spectra were obtained on a Shimadzu UV-3101PC.

Figure 1 shows the absorbance spectra of a 30/70 PBO/AN film, ~150 nm thick, before and after annealing. Both show peaks at ~403 and 429 nm, similar to both neat PBO films prepared by a soluble coordination complexation process[4], and dilute PBO/MSA solution[5]. The similarity of the spectra indicates that annealing has not significantly changed either the nature of the absorbing chromophores or their numbers, i.e. the integral extinction coefficient, hence the natural fluorescence lifetime, of the PBO chromophores in the film is not affected by annealing.

However, annealing has a dramatic effect on the visual fluorescence of the film, changing from a bright orange in the dried material to a dull green after annealing. *Figure 2* shows the fluorescence of the dried and annealed film, both excited near the excitation maximum. The dried film shows a relatively intense emission, peaking at ~560 nm, while annealing decreases the fluorescence intensity, shifting the maximum to ~500 nm with a discernible shoulder at ~550 nm, similar to bulk PBO coagulates. The intensity normalized excitation spectra are quite similar, and essentially independent of emission wavelength. Qualitatively, these annealing effects are similar in films with relative PBO concentrations from 1 to 30%, and appear independent of film thickness, casting solution polymer content (from 0.05 to 3%), and details of the casting and coagulation processes. Also, similar spectral changes have been observed upon annealing a 0.1% PBO/poly(ether ether ketone) film[6].

The fluorescence of the dried film, corresponding to an entrapped single phase[3], does not originate from isolated PBO rods, as these have been shown to emit at ~420 nm. The fluorescence changes then correspond to the growth of the PBO domains, rather than an isolated rod–aggregate transition. It is not obvious whether the fluorescence of the PBO aggregates depends solely on the size of the domain, or on a size-related structural change in the PBO domain.

For this film, the relative quantum yield of the annealed film is equivalent to the relative integral fluorescence intensity (I_{ann}/I_{dried}), since the absorbance spectra indicate no substantial changes in the film's absorptivity or optical properties. Integrating the film intensities over the emission bands (in energy space) gives a relative annealed film yield of 0.40 ± 0.05. Since the natural lifetime of the sample is not changed by annealing, the decreased yield would appear to reflect a greater rate of non-radiative decay in the annealed sample. The mechanism for enhanced non-radiative decay in the annealed sample could reflect changes in the vibrational deactivation of the fluorophore's excited state[1,2], or possibly more efficient excited energy transfer[7] to sites possessing lower fluorescence yields.

The photophysical mechanisms for the effects of annealing on the fluorescence of these PBO/AN blends

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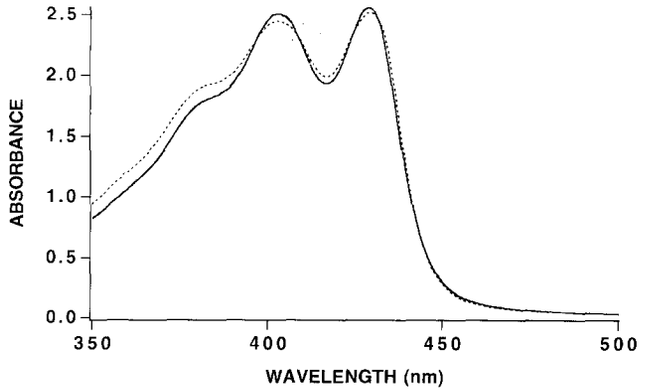

Figure 1 Absorbance spectra of 30/70 PBO/AN film: —, dried; – – –, annealed

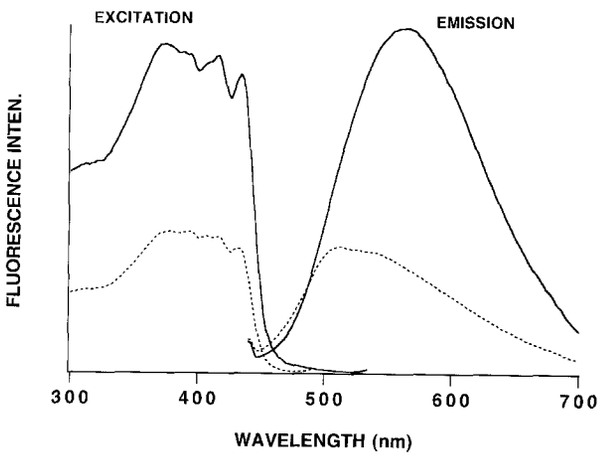

Figure 2 Fluorescence spectra of 30/70 PBO/AN film: —, dried; – – –, annealed. Both emission spectra were excited at 430 nm, and excitation spectra were run at respective emission maxima

are not clear to us. We may obviously rule out any protonation changes[1]. There appears to be some similarity with the spectral changes observed on gel-orienting a conducting polymer/polyethylene blend, particularly the apparent fluorescence blue shift[8], and it is conceivable that annealing increases the order of the PBO domains. In any case, we are continuing our investigations of this system in order to better understand the effects of PBO domain size and structure on its fluorescence spectra and efficiencies.

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