The Influence of Polystyrene and Polyvinylpyrrolidone Nanofiber on the Intensity of Photoluminescence of Fluorescent Whitening Agents

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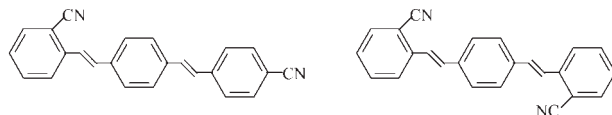
ABSTRACT: 1-(o-Cyanostyryl)-4-(p-cyanostyryl) benzene (EB) and 1,4-bis(o-cyanostyryl) benzene (ER) were two fluorescent whitening agents (FWAs) widely used in textile industry. The major subject in this work was to investigate whether EB and ER could be introduced into polystyrene (PS) and polyvinylpyrrolidone (PVP) nanofiber by electrospinning. Another aim of this work was to detect the intensity of photoluminescence (IPL) of EB and ER in the nanofiber of PS and PVP. The scanning electron microscope (SEM) revealed that the diameter of the obtained nanofiber ranged from 74 to 366 nm. The ultraviolet (UV) spectra demonstrated that EB and ER existed in PS and PVP nanofiber. In addition, the concentrations of EB and ER in PS and PVP nanofiber were calculated according to the determination of UV spectra. Moreover, the IPLs of EB and ER in PS nanofiber increased magnificently, especially EB in PS nanofiber. On the contrary, the IPLs of these two FWAs in PVP nanofiber decreased remarkably. This information might be useful in the application for textile industry. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1696–1700, 2008

Key words: fluorescent whitening agent; nanofiber; photoluminescence; polystyrene; polyvinylpyrrolidone

INTRODUCTION

Fluorescent whitening agents (FWAs) were widely used in textile industry because they were able to enhance the white degree. FWAs were a series of distyrylbenzene, in which some functional groups adjusted the ultraviolet (UV) absorbance of the parent structure. For example, 1-(o-cyanostyryl)-4-(p-cyanostyryl) benzene (EB) and 1,4-bis(o-cyanostyryl) benzene (ER) containing two cyano groups made the UV absorbance at ~430 nm, and eliminated the yellowish cast when absorbed to fiber.[1–5]

1-(o-cyanostyryl)-4-(p-cyanostyryl) benzene (**EB**)   1,4-bis(o-cyanostyryl) benzene (**ER**)

Electrospinning played an important role in preparing polymer fiber. Owing to the charge on the surface of a polymer solution in high voltage direct current (DC) electric field, a droplet of the polymer solution drew a jet moving towards a stationary or rotating collector, on which the diameter of obtained fiber reached to nanoscale in this case.[6–9] It would be an interesting topic to introduce FWAs into polymer nanofiber directly in the process of electrospinning.[10–16] We have succeeded in introducing EB and ER into poly(acrylonitrile) (PAN) nanofiber, and found that the intensity of photoluminescence (IPL) of EB in PAN nanofiber increased magnificently, whereas IPL of ER in the same nanofiber decreased remarkably.[17] This result motivated us to investigate whether the aforementioned phenomenon could be observed in another polymer nanofiber.[18–24] Presented here was the study on the variety of IPL of EB and ER in polystyrene (PS) and polyvinylpyrrolidone (PVP) nanofiber. The reason why PS and PVP were selected to be polymer matrix was due to the former contained benzene rings, and the later involved aliphatic rings. Thus, it could compare the influence of the benzene ring in polymer on the IPL of EB and ER.

EXPERIMENTAL

Materials

1-(o-Cyanostyryl)-4-(p-cyanostyryl) benzene (EB, 99%) and 1,4-bis(o-cyanostyryl) benzene (ER, 99%) were purchased from Daqing New Centurial Chemicals Co., China. PS (M_w = 280,000) and PVP (M_w = 1,300,000) were from Jilin Chemical Industry Co., China. N,N-dimethylformamide (DMF) was of analytical grade, and all the chemicals were used without further purification.

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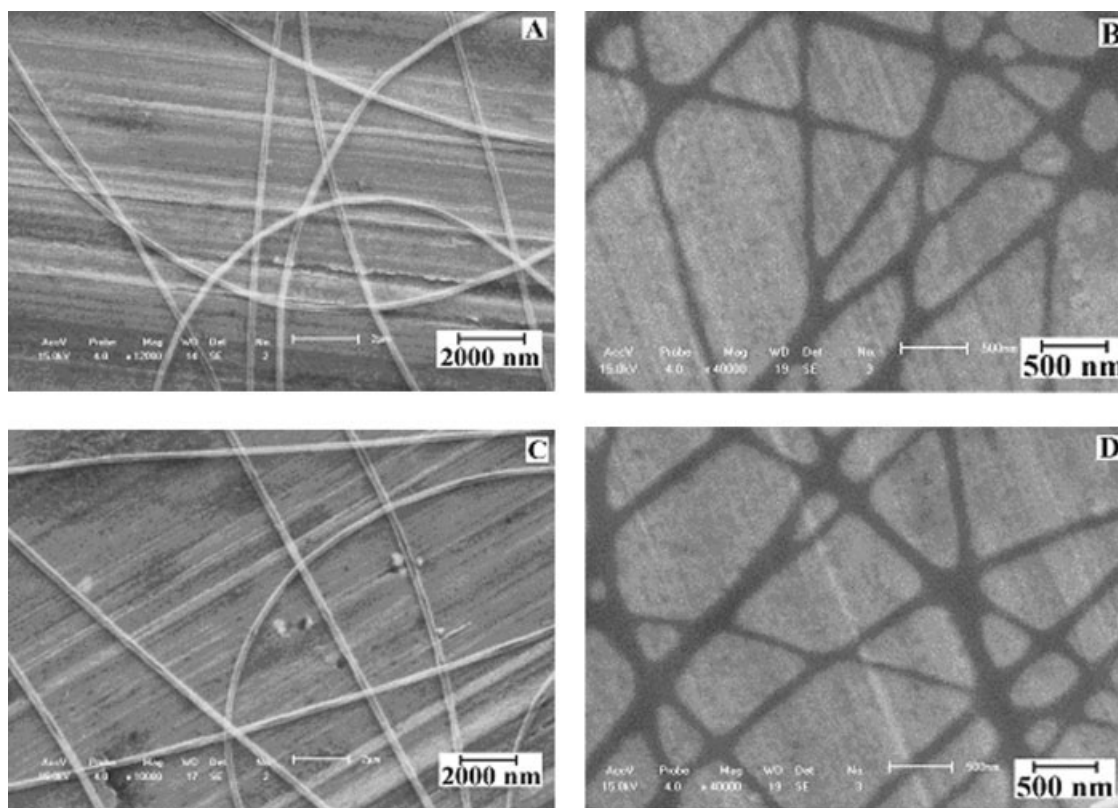
Figure 1 SEM images of EB/PS nanofiber (A), EB/PVP nanofiber (B), ER/PS nanofiber (C) and ER/PVP nanofiber (D).

Preparation of FWAs/polymer nanofiber

EB or ER (1.897 mg) and polymer matrix (PS or PVP, 105.4 mg) were added to 1.0 mL DMF in turn to form a homogeneous solution. Then the solution was added to a plastic syringe that the needle of the syringe was connected with a 10 kV DC positive voltage (the high-voltage power was purchased from Gamma High Voltage Supply, USA, ES 30-0.1P), and a piece of aluminum foil was applied to collect the nanofiber. The distance between the tip of the needle and the surface of the foil was about 15 cm.[17] After the power was switched on, the nanofiber was collected on the foil at ambient temperature. The majority of solvent volatilized in the air during electrospinning, and the obtained samples were preserved in vacuum desiccator for several days before characterization.[6,9,25]

The characterization of samples

The UV absorbances of the obtained nanofiber containing EB or ER were measured by SHIMADZU, UV-3100 UV–vis-NIR RECORDING Spectrophotometer (Japan), which was applied to detect UV absorbance of a solid sample. The UV absorbances of liquid samples were measured by VARIAN, CARY 50 Probe UV-visible Spectrophotometer (USA).

The IPL of liquid samples were carried out by FS920, Edinburgh Instruments (UK). In the process of detecting the IPL of samples, the excitation light was perpendicular to the emission light that could be received by the detector. As for the determination of the IPL of FWAs/PS (or PVP) nanofiber, the liquid sample pool was replaced by the FWAs/PS (or PVP) nanofiber with 45° to the excitation light. The detector in the photoluminescence (PL) spectrometer could receive the emission light reflected by FWAs/PS (or PVP) nanofiber.[17]

RESULTS AND DISCUSSION

The morphology of FWAs/PS (or PVP) nanofiber

The morphology of the obtained nanofiber could be observed by scanning electron microscope (SEM, Shimadzu SSX-550, Japan) as shown as in Figure 1.

Figure 1 revealed that the diameter of these fiber ranged from 74 to 366 nm compared with the scale bar.

The UV spectra of the FWAs/PS (or PVP) nanofiber

Figure 2 illustrated that the UV absorbance of PS in its solid state located at 268 nm with a shoulder peak at 328 nm (line a), and PVP had no remarkable absorbance around this wavelength (line b). The UV
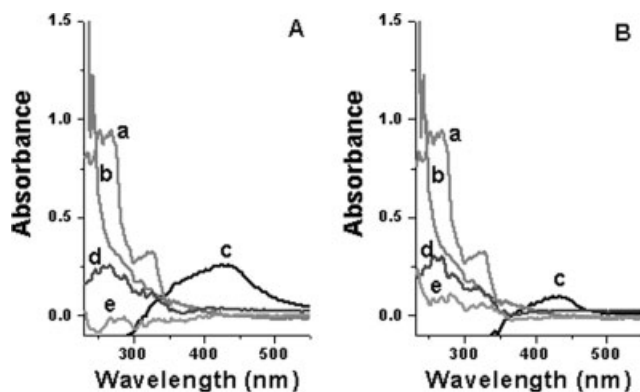
Figure 2 The *in situ* UV spectra of PS nanofiber (line a), PVP nanofiber (line b), EB (line c in panel A), ER (line c in panel B), EB/PS nanofiber (line d in panel A), EB/PVP nanofiber (line e in panel A), ER/PS nanofiber (line d in panel B) and ER/PVP nanofiber (line e in panel B).

absorbance of EB and ER in their solid states located at 433 nm (line c in Fig. 2). The absorbance peaks of EB and ER should appear in the UV spectra of PS and PVP nanofiber if EB and ER were introduced into these nanofiber. Unfortunately, characteristic peaks of EB and ER (433 nm) have not been observed in FWAs/PS (or PVP) nanofiber (line d and e in Fig. 2). This meant that EB and ER did not adhere to the surface of PS and PVP nanofiber. Therefore, the *in situ* UV measurement was not suitable for elucidating the existence of EB and ER in these nanofiber.

When PS and PVP were dissolved in DMF, Figure 3 indicated that there were no UV absorbance (line a in Fig. 3), whereas the UV absorbance of EB and ER located at $\sim$ 350 nm when dissolved in DMF (line b in panel A and B of Fig. 3). As can be seen from Figure 3, when EB and ER were dissolved in PS/DMF and PVP/DMF solution, respectively, the UV absorbance of EB and ER still located at around 350 nm, demonstrating that PS and PVP did not influence the UV absorbance of EB and ER in DMF solution.

To prove that EB and ER were introduced into the polymer nanofiber, EB/PS (or PVP) and ER/PS (or PVP) nanofiber were redissolved in DMF, respectively. As shown as line e and f in Figure 3(A), the absorbance of EB could be observed as a shoulder plateau near 315 nm (line e) and a single peak at 329 nm (line f), demonstrating that EB was dispersed homogeneously in polymer nanofiber. This was in agreement with our previous report.[17] The remarkable blue-shift of EB could be ascribed to the preparation of EB/PS (or PVP) nanofiber by electrospinning, which could be understood by the relationship between the energy level, ΔE, and the absorbance of wavelength, λ, as eq. (1),

$$\Delta E = (hc)/\lambda \tag{1}$$

in which h stood for Planck constant and c for light velocity. Equation (1) revealed the inverse proportional relationship between ΔE and λ. After EB/PS (or PVP) nanofiber was dissolved in DMF, the wavelength of EB (315 or 329 nm) was lower than that of EB dissolved in PS (or PVP)/DMF solution directly (350 nm). This fact implicated that ΔE of EB in PS (or PVP) nanofiber was larger than that of EB in PS (or PVP)/DMF solution. It could be understood that high voltage during electrospinning resulted in the interaction between EB and PS (or PVP) nanofiber, even the solvation from DMF could not separate EB from PS (or PVP). The aforementioned phenomenon was also found in the case of ER/PS (or PVP) nanofiber. The UV absorbance of ER dissolved either in DMF or in PS (or PVP)/DMF solution was around 350 nm (line b, c, and d in panel B of Fig. 3), and the absorbance of ER was also blue-shift to around 320 nm when ER/PS (or PVP) nanofiber was dissolved in DMF (line e and f in panel B of Fig. 3). Therefore, it could be concluded that EB and ER were introduced into PS (or PVP) nanofiber.

Moreover, we have measured the absorbance of EB and ER under various concentrations when they were dissolved in polymer/DMF solution. A perfect proportional relationship between the absorbance and the concentration indicated that Lambert–Beer law was available for determining the concentration of EB and ER. Thus, the content of EB and ER in PS
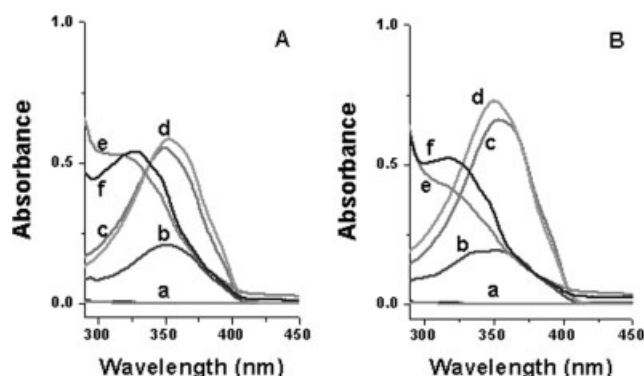
Figure 3 The UV spectra of the related materials dissolved in DMF. PS and PVP (line a), EB (line b in panel A) and ER (line b in panel B) with the concentration of 3.07 × 10^{-3} mg/mL DMF, EB (line c in panel A) and ER (line c in panel B) dissolved in PS/DMF solution with the concentration of EB (or ER)/PS = 7.59 × 10^{-3} mg/0.42 mg/mL DMF, EB (line d in panel A) and ER (line d in panel B) dissolved in PVP/DMF solution with the concentration of EB (or ER)/PVP = 7.59 × 10^{-3} mg/0.42 mg/mL DMF, EB/PS nanofiber (line e in panel A, 1.04 mg EB/PS nanofiber per mL DMF) and ER/PS nanofiber (line e in panel B, 0.91 mg ER/PS nanofiber per mL DMF) dissolving in DMF. EB/PVP nanofiber (line f in panel A, 1.09 mg EB/PVP nanofiber per mL DMF) and ER/PVP nanofiber (line f in panel B, 1.02 mg ER/PVP nanofiber per mL DMF) dissolving in DMF.
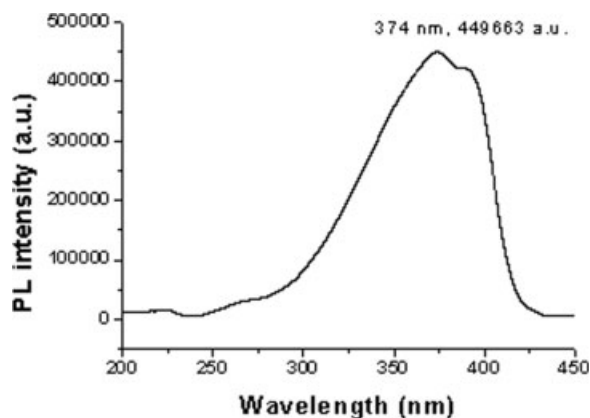
Figure 4 The excitation spectrum of EB/PS nanofiber.

(or PVP) nanofiber could be quantified by UV measurement on the basis of eq. (2),

$$A_1/C_1 = A_2/C_2 \qquad (2)$$

where A_1 and C_1 referred to the absorbance and the concentration of EB (or ER) in PS (or PVP)/DMF solution, respectively, and A_2, C_2 referred to the corresponding items of EB (or ER)/PS (or PVP) nanofiber dissolved in DMF solution. Concretely, as shown as line c in Figure 3(A), the value of the absorbance of EB in PS/DMF solution was 0.55 while the concentration of EB in the solution was 7.59×10^{-3} mg per mL DMF. As shown as line e in Figure 3(A), the absorbance value of EB/PS nanofiber dissolved in DMF solution was 0.53, so the concentration of EB/PS nanofiber dissolved in DMF solution was 7.31×10^{-3} mg per mL DMF. This result indicated that 96.3% of EB (7.31×10^{-3} mg/7.59×10^{-3} mg) was introduced into PS nanofiber. In addition, when this calculation method was performed in other nanofiber, 92.2% of EB was introduced into PVP nanofiber, together with 65.2% and 71.3% of ER were introduced into PS and PVP nanofiber, respectively.

The IPL of FWAs/PS (or PVP) nanofiber

The excitation spectra of all samples were firstly performed. Figure 4 represented an excitation spectrum of EB/PS nanofiber. It was found that the maximum IPL located at 374 nm. Thus, the determination of emission spectra of the obtained samples was performed at this wavelength.

The IPL of PS and PVP nanofiber have not been found (data not shown). As can be seen in Figure 5, either the wavelength or IPL of EB (line a, 437 nm, 26,410 au) was quite similar to those of ER (line b, 433 nm, 27,100 a. u.). But the IPL of EB dissolved in PS/DMF increased to 82,830 a.u. [line c in Fig. 5(A)], which was higher than that of ER dissolved in this solution [line d in Fig. 5(A), 63,600 a.u.]. Moreover,

the IPL of either EB or ER in PS/DMF solution were much higher than that just dissolved in DMF. On the contrary, as shown as line c and d in Figure 5(B), the IPL of either EB or ER dissolved in PVP/DMF solution (26,100 a.u. and 29,920 a.u., respectively) was lower than that dissolved in PS/DMF solution, but similar to that just dissolved in DMF. This fact revealed that the influence of PVP, on the IPL of FWAs was not as distinct as PS.

On the basis of the proportional relationship between the IPL and the concentration of FWAs, the theoretic value of IPL of FWAs in polymer nanofiber should be the IPL of FWAs in the solution before electrospinning multiplied by the percentage of FWAs in polymer nanofiber. For example, the theoretic value of the IPL of EB/PS nanofiber could be calculated as the IPL of EB in PS/DMF solution (82,830 a.u.) multiplied by 96.3% and equaled to 79,765 a.u. The factual value, however, was 865,300 a.u., about 10-fold larger than that of EB dissolved in the solution before electrospinning. All the varieties of the IPL of other FWAs in polymer nanofiber were listed in Table I.

Table I listed such an interesting result that the IPL of either EB or ER increased after introduced into PS, especially in PS nanofiber. However, the IPL of two FWAs in PVP decreased remarkably. This fact motivated us to apply the concept of exciplex for explaining the increase of IPL of FWAs after introduced into PS nanofiber.

Hammond and Wamser have utilized the concept of exciplex to explain the PL phenomenon in the molecular system involving benzene rings.[26] In particular, Claire has pointed out a trigonometric model in poly(N-vinylcarbazole), that was, parallel carbazole rings in this polymer could form exciplex, which
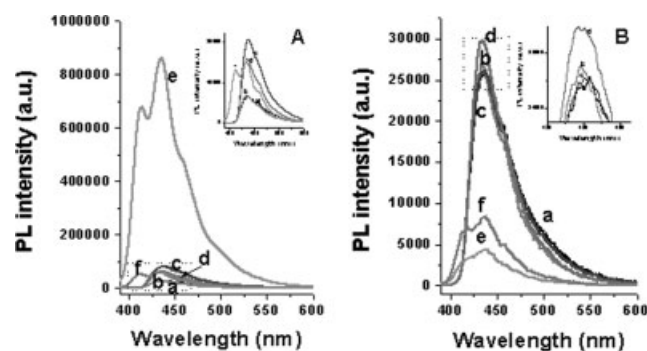
Figure 5 The PL spectra of the nanofiber composed of FWAs and related materials. EB (line a) and ER (line b) dissolved in DMF, EB dissolved in PS/DMF (line c in panel A) and PVP/DMF (line c in panel B), ER dissolved in PS/DMF (line d in panel A) and PVP/DMF (line d in panel B), EB/PS nanofiber (line e in panel A) and EB/PVP nanofiber (line e in panel B), ER/PS nanofiber (line f in panel A) and ER/PVP nanofiber (line f in panel B). The dashed rectangles were shown as the inset for clarity.

TABLE I
The IPL of FWAs Dissolved in DMF Solution, Polymer/DMF Solution and in Polymer Nanofibre

FWA	The IPL dissolved in DMF (a.u.)	The IPL dissolved in polymer/DMF (a.u.)	Percentage of FWA in polymer nanofibre (%)	The theoretic value of the IPL in polymer nanofibre (a.u.)	The factual value of the IPL in polymer nanofibre (a.u.)	Ratio between factual and theoretic value
EB	26,410	82,830 [in PS, line c in Fig. 5(A)]	96.3	79,765	865,300 [in PS, line e in Fig. 5(A)]	10.8
		26,100 [in PVP, line c in Figure 5 (B)]	92.2	24,064	4,410 [in PVP, line e in Fig. 5(B)]	0.2
ER	27,100	63,600 [in PS, line d in Fig. 5(A)]	65.2	41,467	60,830 [in PS, line f in Fig. 5(A)]	1.5
		29,920 [in PVP, line d in Fig. 5(B)]	71.3	21,333	8,566 [in PVP, line f in Fig. 5(B)]	0.4

made many electrons on the ground-state transmit to excited-state more easily.[27] Although we could not confirm the real existence status of EB and ER in PS nanofiber, the increase of IPL of EB and ER in PS nanofiber implicated the formation of exciplex between EB or ER and the benzene rings in PS nanofiber. Because the aliphatic ring in PVP could not be the moiety to form exciplex with FWAs, the IPL of FWAs did not increase in PVP nanofiber. Because of the *ortho* effect, the *o*-CN substituted phenyl moiety in ER could not be in plane of the remaining part of the molecule. This might weaken the formation of exciplex between ER and PS, and would be the topic of our further research work.

CONCLUSION

To sum up, EB and ER were introduced into PS (or PVP) nanofiber by electrospinning. The IPL of the obtained nanofiber involving EB and ER demonstrated that PVP nanofiber decreased the IPL of FWAs, whereas, PS nanofiber increased the IPL of EB because of the formation of exciplex between PS and FWAs. This might provide useful information for the preparation of PL nanofiber and application in textile industry.

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