Variety of Photoluminescence Intensity of Fluorescent Whitening Agents Introduced into Polyacrylonitrile Nanofibers

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ABSTRACT: The major objective in this study was the preparation of polyacrylonitrile (PAN) nanofibers composed of 1,4-bis(*o*-cyanostyryl)benzene (ER) and 1-(*o*-cyanostyryl)-4-(*p*-cyanostyryl)benzene (EB), two kinds of fluorescent whitening agents widely used in the textile industry. The scanning electron microscopy images revealed that the diameters of ER/PAN and EB/PAN fibers ranged from 78 to 154 nm. The IR spectra indicated that the peaks of the —CN group blueshift and the generation of a shoulder peak were obviously due to the interaction between ER or EB and PAN. Furthermore, the UV spectra demonstrated that the distributive status of ER or EB tended toward the molecular state in PAN nanofibers. Finally, the most interesting finding in this study was that the photoluminescence intensity of EB/PAN nanofibers increased magnificently, whereas that of ER/PAN nanofibers decreased remarkably. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2382–2386, 2007

Key words: fibers; fluorescence; luminescence

INTRODUCTION

Polymer nanofibers have attracted extensive research attention due to their unique properties, including a high tensile modulus, wonderful heat and electrical conduction, and unique optical and electronic properties.[1] For the preparation of polymer nanofibers, electrospinning is a simple method because the electrostatic surface charging of a polymer solution droplet draws a jet moving at a high speed toward a grounded stationary or rotating collector in a high-voltage direct-current (DC) electric field, by which either oriented or random ultrathin fibers with diameters ranging from the micrometer to nanometer scale are collected. In general, aluminum foil acts as the collector due to its high conductance.[2–4] With electrospinning, many polymer nanofibers have been synthesized and applied successfully for air filtration, optical sensors, drug delivery systems, and so on.[5] Because of the wide utilization of polyacrylonitrile (PAN) and the potential application of nanofibers in textile industry, we herein selected PAN as the polymer matrix to prepare nanofibers by electrospinning.[6] Meanwhile, with optical functionalized groups in the complicated structures, fluorescent whitening agents (FWAs) are available to enhance the white degree and luster in textiles, plastics, doping, washing agents, leathers, and so on, among which distyrylbenzene plays important role because when it is adsorbed to textiles, its strong blue fluorescence eliminates the yellowish cast of white fabrics and whitens the textile eventually.[7,8] For example, 1,4-bis(*o*-cyanostyryl)benzene (ER) and 1-(*o*-cyanostyryl)-4-(*p*-cyanostyryl)benzene (EB) are widely used to whiten the textiles because the UV absorbance of these two FWAs correlate with the position of the —CN group in distyrylbenzene.[9] This fact motivated us to investigate the influence of FWA, after it was introduced into PAN nanofibers, on the photoluminescence (PL) properties of FWA. In this article, we present a study on ER/PAN and EB/PAN nanofibers by IR, UV, and PL spectra. We found that the PL intensity of the EB/PAN nanofibers increased magnificently, whereas that of ER/PAN nanofibers decreased remarkably.

EXPERIMENTAL

Materials

Analytical-grade *N,N*-dimethylformamide (DMF) was purchased from Beijing Chemicals Co., and PAN (average molecular weight = 86,200) was purchased from Jilin Chemical Industry Co. (China). ER (99%) and EB (99%) were purchased from Daqing New Centurial Chemicals Co. (China). All chemicals were used without further purification.
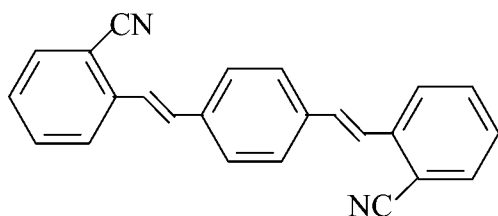
1,4-bis(*o*-cyanostyryl)benzene (**ER**)
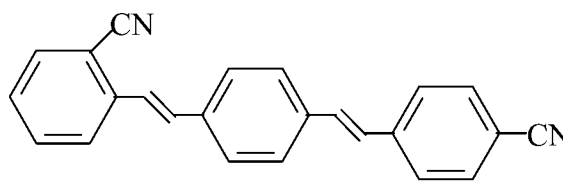
1-(*o*-cyanostyryl)-4-(*p*-cyanostyryl)benzene (**EB**)

Preparation of FWA/PAN nanofibers

PAN (0.4 g) was dissolved in DMF (4.6 g) at room temperature; ER or EB (0.009 g) was added under stirring for 6 h to form a homogeneous solution. This solution was added to a burette, which was then equipped to the electrospinning apparatus (see Scheme 2, shown later).

Characterization of the FWA/PAN nanofibers and related solutions

The morphology of the FWA/PAN nanofibers was observed by scanning electron microscopy (SEM; Shimadzu SSX-550, Japan). The —CN groups in PAN together with ER and EB were detected by IR (Nicolet, Avatar 360 Fourier transform infrared spectrometer). The UV absorbance of ER or EB in DMF solution was determined with a UV spectrometer [Varian, Cary 50 Probe ultraviolet–visible (UV–vis) spectrophotometer]. The UV absorbance of the PAN nanofibers and ER or EB in their solid states along with ER/PAN and EB/PAN nanofibers were detected with a UV spectrometer (Shimadzu, UV-3100 UV–vis–NIR recording spectrophotometer), which was used specifically to detect the UV absorbance of a sample in its solid state. The PL intensities of ER or EB either in DMF or in PAN/DMF solution were determined with a fluorescence spectrometer (FS920, Edinburgh Instruments, UK), in which the liquid sample was excited by the excitation light (380 nm), and the emissive light from the liquid sample was collected by the detector as shown as in Scheme 1(A). As for the determination of the PL intensities of ER/PAN and EB/PAN nanofibers, shown in Scheme 1(B), the liquid sample pool was

replaced by aluminum foil, on which the fibers were collected, whereas the excitation light irradiated the foil at 45° to collect the emissive light from the solid sample. Although reflected light could not be thoroughly prevented, the detected wavelength (λ) was larger than 400 nm rather than the excitation light (380 nm) itself.

RESULTS AND DISCUSSION

SEM observation of FWA/PAN nanofibers

We used a rotary cylinder covered with an aluminum foil to collect the nanofibers in a polymer-solution-filled burette applied with a high-voltage DC (12 kV), between which the distance from the burette tip to the aluminum foil was about 10 cm, as Scheme 2 shows.[2,10,11]

The first concern in this study was the confirmation of the obtained material on the aluminum foil within the nanometer scale; thus, the morphology of these materials was observed by SEM and is illustrated in Figure 1.

The fiber diameters in the SEM images were measured by comparison with the scale bar. As shown in Figure 1, ER/PAN (panel A) and EB/PAN (panel B) exhibited fiber diameter limits within 154 nm; that is, the diameters of ER/PAN fibers ranged from 78 to 119 nm with an average diameter 101.4 nm (±23.4 nm), and the diameters of EB/PAN fibers ranged from 108 to 154 nm with an average value 124.6 nm (±29.4 nm). So, we concluded that the fibers of PAN mixed with FWA were in the nanometer scale and defined them reasonably as nanofibers. Moreover, the SEM images (Fig. 1) show that the FWAs were dissolved in PAN homogeneously because no block of FWA was found in the obtained nanofibers.
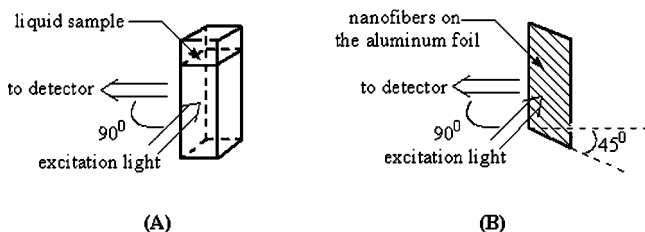
Scheme 1 Determination of PL intensity of the (A) liquid sample and (B) nanofibers.
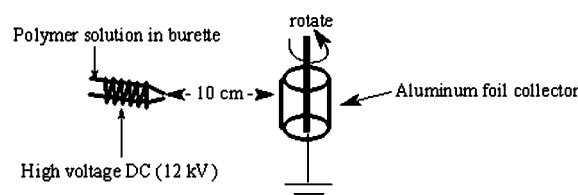
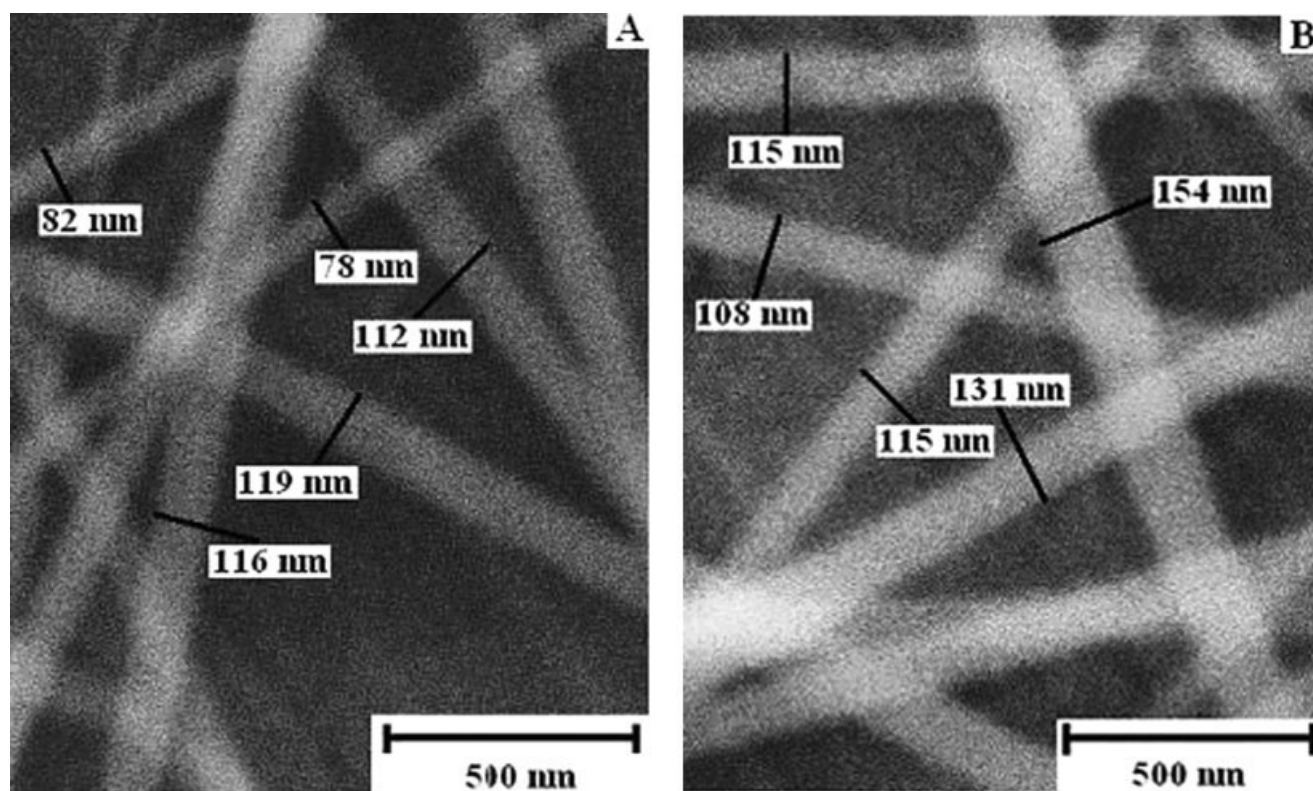**Scheme 2** Preparation apparatus of the nanofibers.

Figure 1 SEM images of (A) ER/PAN and (B) EB/PAN nanofibers.

Characterization of the FWA/PAN nanofibers by IR

To explore the interaction between FWAs and PAN nanofibers, the common group —CN in ER and EB along with PAN were measured by IR spectra, as shown in Figure 2.

As shown by line a in Figure 2 (A,B), the peak of —CN was located at 2245 cm^{-1}, which could be regarded as the IR peak of —CN itself because the —CN attached to the aliphatic chain of PAN. Line b in Figure 2 shows that the peak of —CN in ER and EB redshifted to 2222 cm^{-1} for conjugation with 1,4-distyrylbenzene. We also mixed ER and EB with PAN powder and detected the IR spectra of the mixture, as shown by line c in Figure 2. Two peaks of —CN (2224 and 2244 cm^{-1}) were derived from ER or EB and PAN, respectively, which indicated that the mechanical mixing could not vary the —CN peak position of ER or EB and PAN. Moreover, the similarity of the —CN peak either in the PAN nanofiber or in its powder revealed that the preparation of PAN nanofibers by electrospinning could not change the —CN peak position. As for ER/PAN or EB/PAN nanofibers, as shown by line d in Figure 2, the —CN peak split into two parts, located at 2243 and 2359 cm^{-1}. The former ascribed reasonably to —CN from PAN, and the latter, obviously a blue-shift and generating a shoulder peak (2330 cm^{-1}),

was due to the interaction between ER or EB and PAN. This result indicates that the distributive status of ER and EB was likely to change in the case of electrospinning ER (EB)/PAN nanofibers.

Measurement of FWA in the PAN nanofibers by UV

The Shimadzu UV-3100 UV–vis–NIR recording spectrophotometer was used to detect the UV absorbance of the sample in its solid state. We measured the UV absorbance of the PAN nanofibers, ER and EB in their solid states, and ER (EB)/PAN nanofibers, and the UV absorbance of ER (EB) in DMF solution was determined by the Varian Cary 50 Probe UV–vis spectrophotometer. All the obtained results are collected in Figure 3.

As shown by line a in Figure 3, the UV absorbance of the ER/DMF solution was located at 337 nm, and that of the EB/DMF solution was located at 349 nm. Line b in Figure 3 indicates the absorbance of ER (panel A) and EB (panel B) in their solid states, in which the UV absorbance of ER was located at 428 nm and that of EB was located at 413 nm. Compared with the corresponding UV absorbance, the low peaks of ER (EB) in solution were due to the distribution of ER and EB in the molecular state solvated by DMF. As shown by line c in Figure 3,
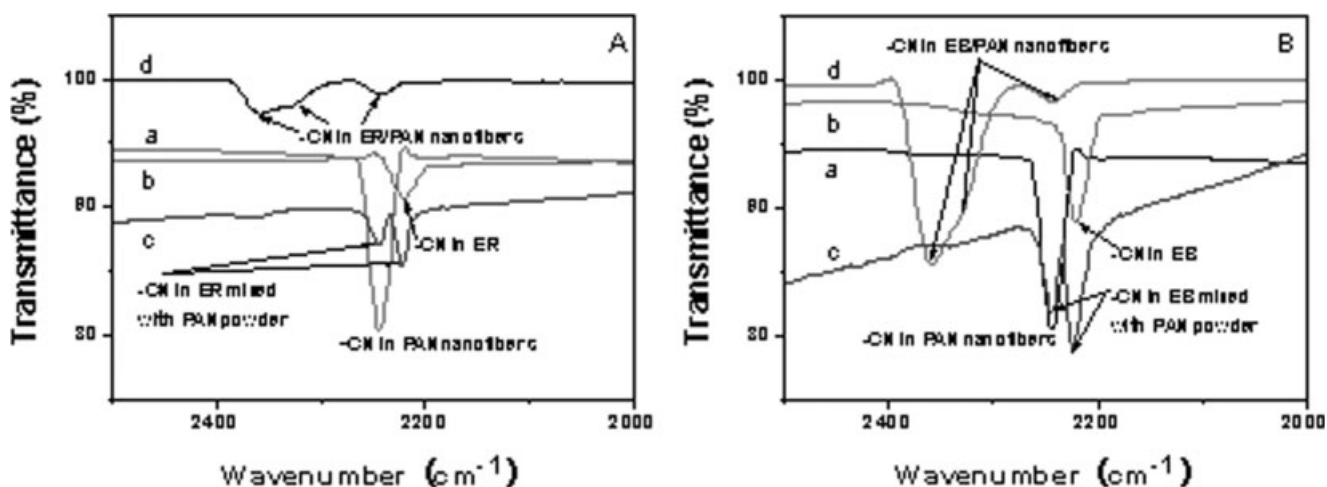
Figure 2 IR spectra correlated to (A) ER and (B) EB: (a) PAN nanofibers, (b) ER (in panel A) and EB (in panel B), (c) ER mixed with PAN powder mechanically (in panel A) and EB mixed with PAN powder mechanically (in panel B), and (d) ER/PAN nanofibers (in panel A) and EB/PAN nanofibers (in panel B).

the absorbances of ER/PAN and EB/PAN nanofibers were located at 407 and 399 nm, respectively. Line d shows the UV absorbance of PAN nanofibers in which no absorptions related to the ER/PAN nanofibers (407 nm) and EB/PAN nanofibers (399 nm) were found. This demonstrated that ER and EB were indeed introduced into the PAN nanofibers. The slight blueshift in the peaks of the ER (EB)/PAN nanofibers revealed that the distributive status of ER (EB) was not congregative as the solid state but tended to disperse in PAN nanofibers. This could be understood by the relationship between the energy level (ΔE) and λ:

$$\Delta E = h\nu = hc/\lambda \qquad (1)$$

in which h is Planck's constant, ν is the frequency, and c is the velocity of light. Equation (1) reveals the inverse proportional relationship between ΔE and λ. The λ values of solid ER and EB were located at 428 and 413 nm, respectively. Although ER and EB were dissolved in DMF and existed in the molecular state, their λ blueshifted to 337 and 349 nm, which demonstrated that ER and EB in DMF solution increased ΔE to the point that ER and EB existed in the molecular state. However, the λ values of the ER/PAN and EB/PAN nanofibers were located at 407 and 399 nm, respectively, blueshift compared with their solid state (ER at 428 nm and EB at 413 nm), indicating that ΔE of ER and EB in the PAN nanofibers increased over their solid state. This fact indicated that ER and EB tended toward their molecular state in the PAN nanofibers, and at least did not accumulate as in their solid state.
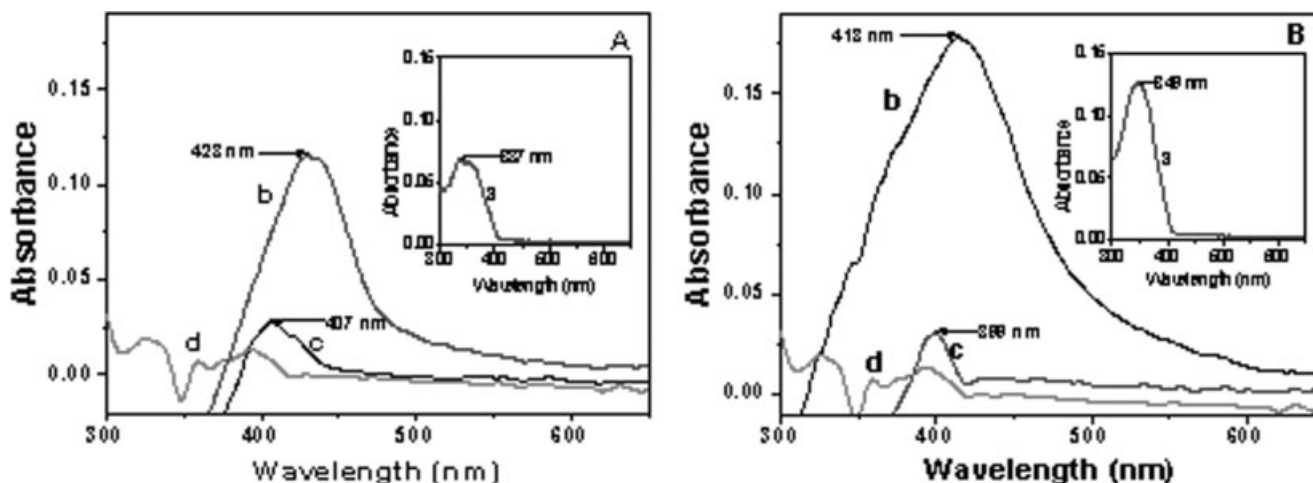

Figure 3 UV spectra related to (A) ER and (B) EB: (a) FWA dissolved in DMF solution ([ER or EB] = 0.963 mM), (b) FWA in the solid state, (c) ER/PAN (panel A) and EB/PAN nanofibers (panel B), and (d) PAN nanofibers.
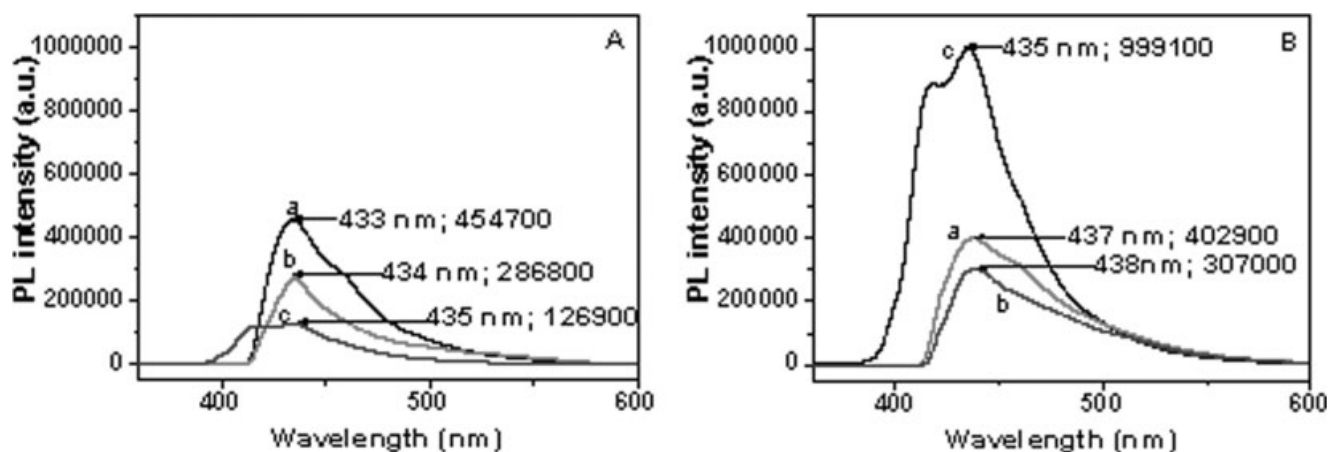
Figure 4 PL spectra related to (A) ER and (B) EB: (a) FWA dissolved in DMF solution, (b) FWA in PAN/DMF solution, and (c) ER/PAN (panel A) and EB/PAN nanofibers (panel B).

Comparison of the PL intensity of FWA/PAN nanofibers

The most important property of FWAs is PL, so the major objective of this study was to detect the PL intensity of FWAs in the PAN nanofibers. Figure 4 outlines the PL spectra of the ER and EB solutions, together with the ER (EB)/PAN nanofibers. The PL spectra of ER and EB dissolved in the PAN/DMF solution is shown in Figure 4 as well.

Line a in panels A and B of Figure 4 indicate that λ and the PL intensity of ER (433 nm, 454,700 a.u.) were quite similar to those of EB (437 nm, 402,900 a.u.) while they were dissolved in DMF. It was necessary to detect the PL intensity of EB and ER dissolved in PAN/DMF solution, which was applied to the electrospin of the FWA/PAN nanofibers. Line b in Figure 4 shows the PL intensity of both EB/PAN/DMF (434 nm, 286,800 a.u.) and ER/PAN/DMF (438 nm, 307,000 a.u.) solution. Dissolving ER or EB in the PAN/DMF solution made the PL intensity decrease remarkably. Interestingly, the PL intensity of the EB/PAN nanofibers [line c in Fig. 4(B)] increased to 999,100 a.u., 2.5 times higher than that of the DMF solution, whereas that of the ER/PAN nanofibers [line c in Fig. 4(A)] decreased to 126,900 a.u., 3.5 times lower than that in DMF solution. This was because of the fact to that one of the two —CN groups in EB attached to the para position of the benzene ring, whereas both —CN groups in ER were located at the ortho positions of the benzene rings; this demonstrated that the electrospinning technology in the preparation of the FWA/PAN nanofibers varied the PL intensity of ER and EB. In addition, a shoulder peak around 415 nm was also found in the ER/PAN nanofibers and EB/PAN nanofibers, which was ascribed to the interaction between ER or EB and the PAN nanofibers as well. The finding of a shoulder peak was in agreement with the IR determination.

CONCLUSIONS

In summary, ER and EB were introduced successfully into the PAN nanofibers by electrospinning. The interesting variety of the PL intensities between the ER/PAN and EB/PAN nanofibers was related to their different structure and the use of electrospinning. This may be useful in the further preparation of nanophotoluminescent fibers.

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