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ScienceDirect
Polymer 48 (2007) 4311–4315
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Using poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] as shell to fabricate the highly fluorescent nanofibers by coaxial electrospinning

Qiang Zhao [a,b], Yi Xin [a], Zonghao Huang [a,*], Sidong Liu [a], Chunhe Yang [c], Yongfang Li [c]

[a] Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, China
[b] Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130024, China
[c] Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 20 October 2006; received in revised form 3 April 2007; accepted 24 April 2007
Available online 3 May 2007

Abstract

Poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is an excellent conjugated polymer and broadly used in the polymer photoelectron devices, but difficult to be electronspun directly. In the present study, the core-shell structured nanofibers were fabricated by coaxial electrospinning MEH-PPV (shell) in chlorobenzene and PVP (core) in 1,2-dichloroethane. MEH-PPV was soluble in the above two solvents, which prevented the precipitation of MEH-PPV and enhanced the adhering action between the two polymers in coaxial electrospinning process. We anticipate that these uniform core/shell PVP/MEH-PPV nanofibers with highly fluorescent property will have potential applications in the fabrication of polymer nano-photoelectron devices.

Keywords: Electrospinning; MEH-PPV; Core-shell

1. Introduction

Electrospinning is a method of producing continuous ultrafine fibers with diameters ranging from a few nanometers to microns, which has attracted much attention in the past decade [1–8]. Recently, the electrospun fibers with core-shell structure using the coaxial electrospinning were reported by several groups [9–12], which causes wide interest since this method not only can improve relative properties of fibers such as strength etc., but also provides a new possible route to prepare the nanofibers of polymers that are difficult to be electrospun directly.

As a kind of poly(phenylene vinylene) (PPV) [13] derivative, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) [14] is easy to be dissolved in common organic solvents different from PPV obviously, but difficult to be electrospun as 1-D nanofibers directly. Because MEH-PPV possesses excellent multifunctional photoelectron properties, such as photoluminescence (PL), electroluminescence (EL), photovoltage (PV) and good solubility, it has been one of the most important and useful materials in electronic polymer area. Therefore, the preparation of uniform MEH-PPV nanofibers by electrospinning have been studied recently [12,15,16].

Xia and coworkers have demonstrated that MEH-PPV nanofibers were fabricated by coaxial electrospinning MEH-PPV (core) in chloroform and PVP (shell) in water and ethanol mixture, followed by extraction of PVP [12]. The resulting fibers exhibited a ribbon-like structure with wrinkled surface due to the extraction process. Here, we report the PVP (core)/MEH-PPV (shell) nanofibers by coaxial electrospinning MEH-PPV in chlorobenzene and PVP in 1,2-dichloroethane. Compared with other MEH-PPV based nanofibers, these PVP (core)/MEH-PPV (shell) nanofibers possess good morphology and outstanding fluorescent property. Therefore they can be directly used as the MEH-PPV nanofibers and should have good potential applications for fabrications of the polymer nano-photoelectron devices.

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* Corresponding author. Tel.: +86 431 5099206; fax: +86 431 5098768.
E-mail address: huangzh295@nenu.edu.cn (Z. Huang).

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doi:10.1016/j.polymer.2007.04.068

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP, $M_w = 1{,}300{,}000$) was supplied by Acros Corp. (New Jersey, USA), 1,2-dichloroethane and chlorobenzene by Beijing Beihua Fine Chemicals Corp. (China), MEH-PPV has been synthesized according to the published procedure with modifications [17]. All reagents were of analytical grade and used with further purification.

2.2. Electrospinning process

Our electrospinning setup is shown in Fig. 1a. It is essentially the same as that of a conventional electrospinning setup, except for the introduction of an inner needle as shown in Fig. 1b. We have attempted to prepare PVP (core)/MEH-PPV (shell) fibers with the solutions that have been used by Xia and coworkers [12], but failed because MEH-PPV immediately precipitated when the MEH-PPV solution in chloroform met the PVP solution in the water/ethanol near the nozzles. The core-shell structured nanofibers fabricated by coaxial electrospinning two kinds of polymers in the same solvent have been reported by Zhang et al. [11]. Considering chlorobenzene and 1,2-dichloroethane are miscible and are good solvents for MEH-PPV and PVP, respectively, we selected them as the solvents for MEH-PPV and PVP in order to prevent the precipitation of MEH-PPV and enhance the adhering action between the shell and core.

To a dry round-bottom flask were added MEH-PPV (0.5098 g), chlorobenzene (25 ml), stirred under ultrasonic vibrations, then a N_2 atmosphere was established, the solution was heated to reflux for 3 h. After allowing the solution to cool to ambient temperature, the centrifugal machine was used to remove the undissolved MEH-PPV. We adjusted the concentration to be 17.61 mg/ml. To a dry conical flask added PVP (0.8000 g) and 1,2-dichloroethane (10 ml), stirred until the PVP dissolved completely (80.00 mg/ml). The PVP solution was added to the center syringe and the MEH-PPV solution was added to the outer one connected to the metal needles.

The two solutions were fed into the needles by two syringe pumps. The feed rate for the PVP solution was set at 0.5 ml h^{-1}, and the feed rate for the MEH-PPV solution was varied in the range of 0.5–0.8 ml h^{-1}. The metal needle was connected to a high-voltage DC generator, and a piece of aluminum foil was placed 18–25 cm from the tip of the needle to collect the nanofibers. The spinning voltage was set at 15 kV. PVP droplet sustained at the edge of the nozzles, formed the Taylor cone, and then was pulled by the electric field. As mutual charge repulsion on the drop surface overcomes surface tension, a PVP jet is ejected with MEH-PPV adhered to the surface. After evaporation of the solvents, the core-shell structured nanofibers were present.

2.3. Characterization of as-spun fibers

The resulting nanofibers were characterized by SEM (S-570, Hitachi Corp., Japan), TEM (H600, Hitachi Corp., Japan), FTIR (Magna560, Nicolet Corp., USA), fluorescence microscope (BX51, Olympus Corp., Japan) and Eclipse fluorescence spectrophotometer (Varian Corp., USA).

3. Results and discussion

The pure PVP fibers are not fluorescent, but the electrospun PVP/MEH-PPV fibers show an orange-red color (Fig. 2a), the same as the fluorescent color of pure MEH-PPV film. It can be affirmed that the MEH-PPV was coated on the surface of the PVP fibers. The TEM image of PVP/MEH-PPV fibers in Fig. 2c clearly shows a core-shell structure relative to PVP fibers (Fig. 2b). The core is thick and composed of PVP (about 470 nm), and the outer shell is composed of MEH-PPV (about 70–140 nm). It was reported that the sharp boundaries of the core-shell structure formed due to the characteristic time of bending instability during electrospinning was much shorter than that of diffusion spreading [9,10]. However, the core/shell boundaries in our PVP/MEH-PPV fibers are unclear. We consider that the evaporation and diffusion of the solvents could

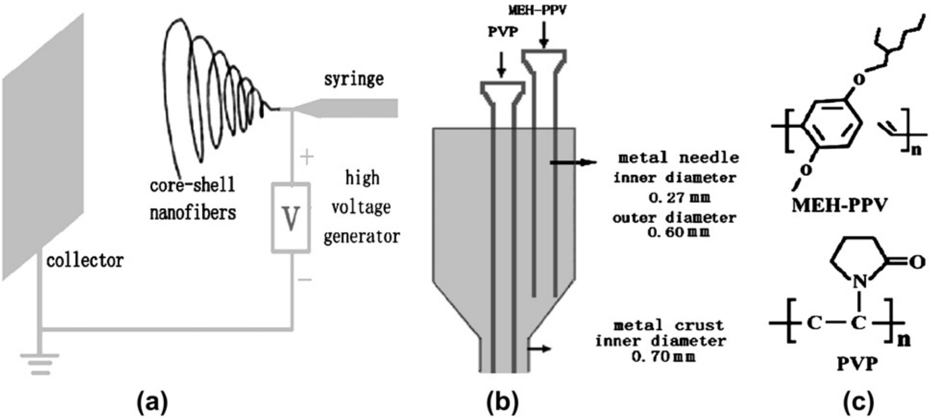

Fig. 1. (a) Schematic of the electrospinning setup, (b) the coaxial spinneret and (c) the molecular structures of MEH-PPV and PVP.

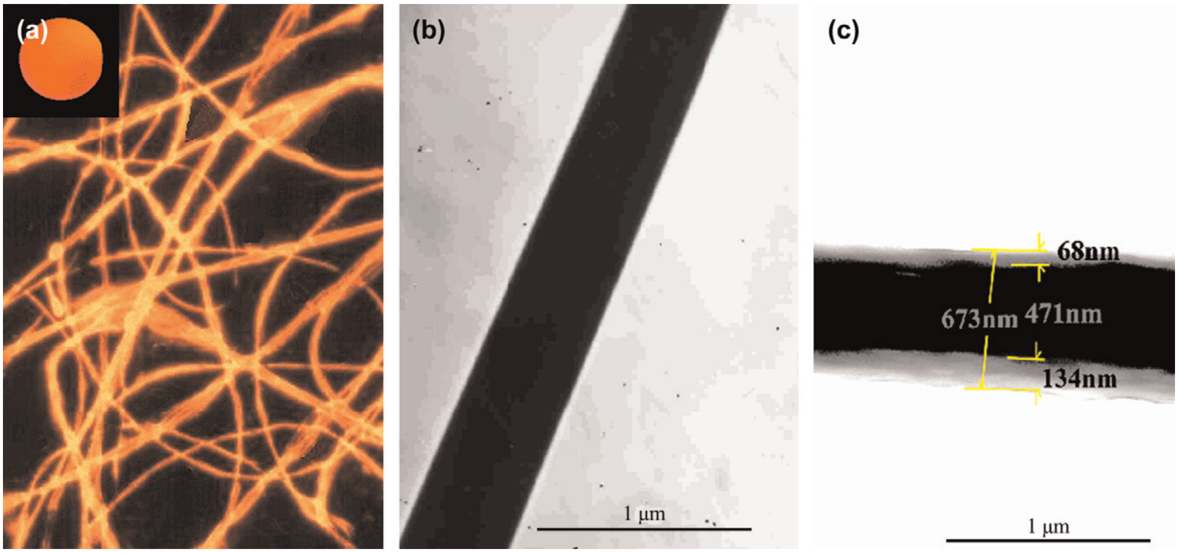

Fig. 2. (a) The fluorescence microscope image of PVP/MEH-PPV fibers (inset is the spin cast MEH-PPV film), (b) TEM image of PVP fiber and (c) TEM image of the PVP/MEH-PPV fiber.

drive the two polymers to mix together to some extent on the interface of the core and shell in the electrospinning, the shell could be the pure MEH-PPV.

As shown in Fig. 3, the FTIR spectroscopy of the bulk MEH-PPV, the core-shell fibers and the PVP fibers was performed. The triplet peaks (Fig. 3b) at 1548 cm^{-1} with two shoulders at 1511 cm^{-1} and 1646 cm^{-1} are characteristic of the MEH-PPV. The 1511 cm^{-1} and 1548 cm^{-1} correspond to the symmetric stretch of the phenyl group, and the one at 1646 cm^{-1}corresponds to the C=C stretch of the vinylene group. The peak at 1038 cm^{-1} is the C–O–C stretch and the peak at 1280 cm^{-1} is attributed to the Ar–O–R group. The peak at 1670 cm^{-1} is the C=O stretch, which is characteristic of the PVP (Fig. 3c). The peak at 2360 cm^{-1} can be attributed to CO_2, and the band at 3500 cm^{-1} is due to water.

To further study the properties of the core/shell PVP/MEH-PPV fibers, we also performed the photoluminescence (PL) spectra. An excitation spectrum with a $\lambda_{\max}$ of 583 nm was obtained for MEH-PPV film (Fig. 4). Subsequently, emission spectra were obtained with exciting light of 583 nm that produced an emission maximum of 635 nm (Fig. 5). In a similar manner, excitation and strong emission spectra were taken for the PVP/MEH-PPV fibers. Compared with the MEH-PPV film, the excitation and emission spectrum of PVP/MEH-PPV fibers exhibit a notable blue shift. This phenomenon may be mainly caused by the nano-effect of the thin MEH-PPV shell in the surface of the fiber. Another possible reason is that the PVP diffused in MEH-PPV shell may serve as a nanospacer preventing the aggregation, which might prevent π–π stacking to some extent during

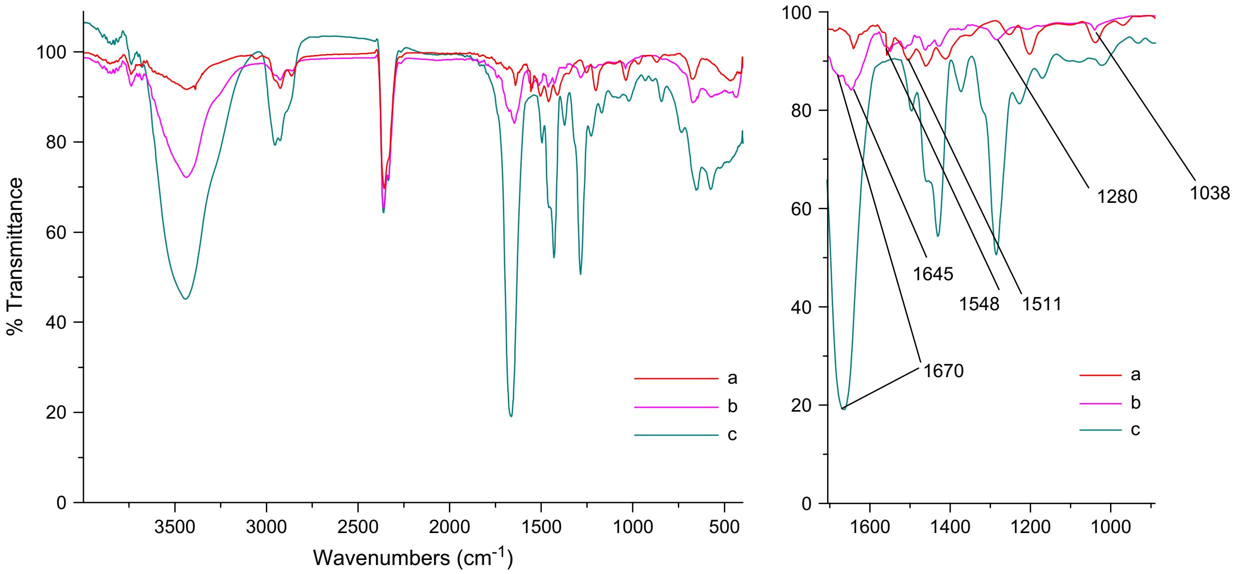

Fig. 3. FTIR spectra of (a) MEH-PPV film, (b) the as-spun fibers and (c) the PVP fibers ; the right part is the enlarged spectra in the range 1700–900 cm^{-1}.

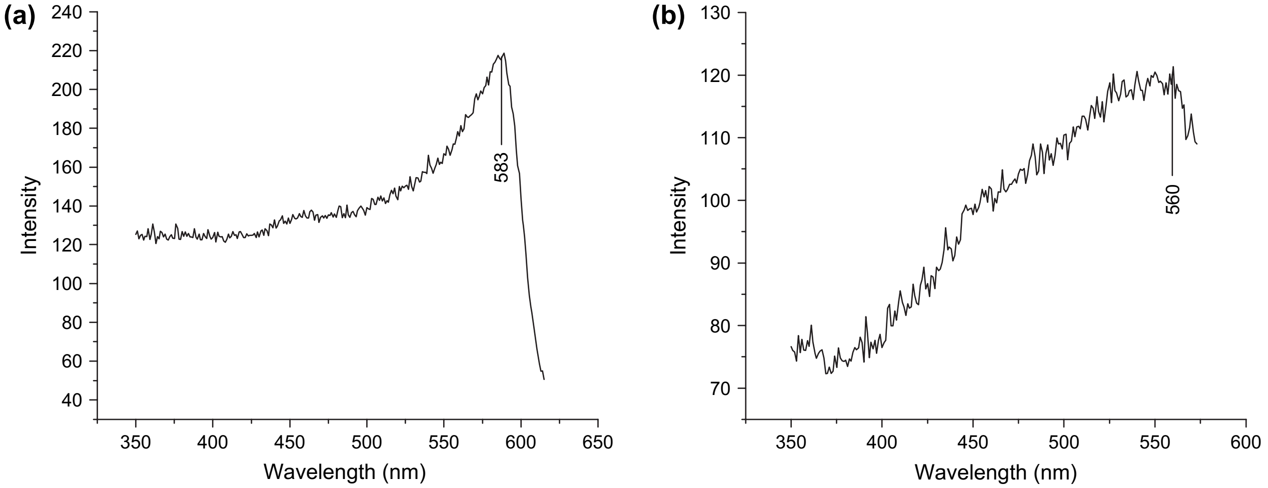

Fig. 4. Excitation spectrum of (a) the MEH-PPV film, (b) the as-spun PVP/MEH-PPV fibers.

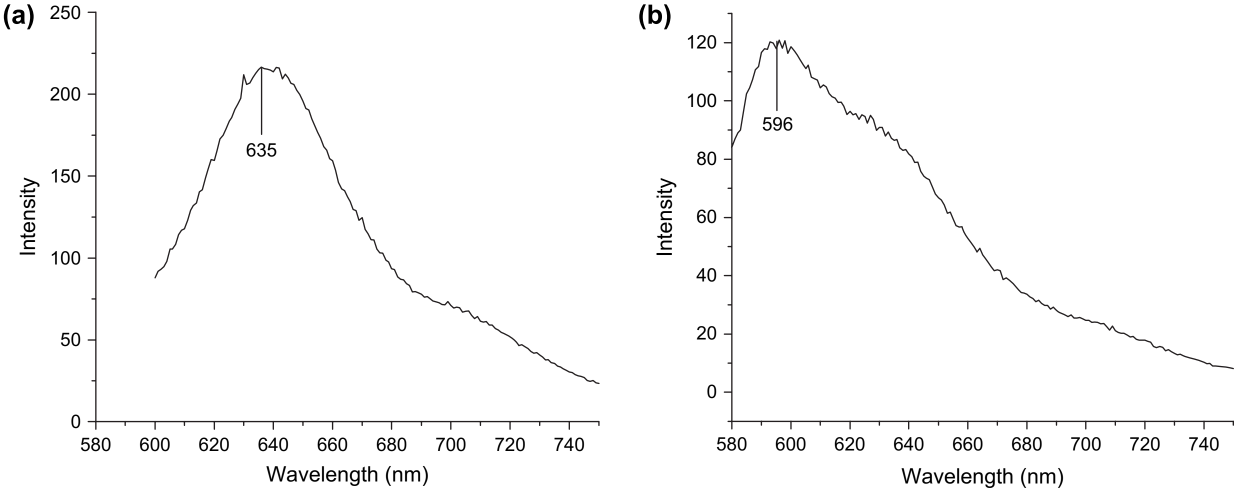

Fig. 5. Emission spectrum of (a) the MEH-PPV film, (b) the as-spun PVP/MEH-PPV fibers.

electrospinning. In addition, the weak shoulder peak of about 630 nm (Fig. 5b) may be from the thick part of the MEH-PPV shell.

4. Conclusions

In conclusion, we have demonstrated the fabrication of the PVP (core)/MEH-PPV (shell) nanofibers by coaxial electrospinning MEH-PPV in chlorobenzene and PVP in 1,2-dichloroethane. The PVP (core)/MEH-PPV (shell) fibers show a blue shift in PL spectra relative to MEH-PPV film, which is mainly attributed to the nano-effect of the thin MEH-PPV shell in the surface of the fiber. In comparison with other MEH-PPV composite fibers reported recently [15], the core-shell structured PVP/MEH-PPV fibers are uniform with less leaflike morphology. It also shows an excellent fluorescent property due to the shell composed of the fluorescent polymer (MEH-PPV), therefore this kind of core-shell constructed nanofibers can be directly used as the nanofibers of MEH-PPV and to fabricate the polymer nano-photoelectron devices.

Acknowledgements

This work was supported by National Nature Science Foundation of China (Grant no. 20474008), and Foundation of Key Laboratory of Organic Solids Institute of Chemistry, Chinese Academy of Sciences.

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