

# Preparation and characterization of electrospun poly(2,5-dicyclohexylphenylene-1,4-ethynylene) (C<sub>24</sub>H<sub>30</sub>)<sub>n</sub>/poly(ethylene oxide) (PEO) hybrid nanofibers

John A. Ajao · Adurafimihan Abiona ·  
Samuel Chigome · Jean Bosco Kana Kana ·  
Malik Maaza

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**Abstract** We report the preparation of poly(2,5-dicyclohexylphenylene-1,4-ethynylene) (PDE)/poly(ethylene oxide) (PEO) hybrid nanofibers by electrospinning technique. The hybrid nanofibers were characterized by a host of characterization techniques such as X-ray diffraction, Fourier transform infrared spectroscopy, atomic force microscopy, optical and scanning electron microscopy. The results showed a successful preparation of PDE/PEO composite nanofibers. The diameter of the hybrid nanofibers ranges between 500 and 1000 nm. The results showed that this kind of hybrid nanofibers could be a possible candidate in color display devices.

## Introduction

Composite polymer nanofibers are promising candidates for the next generation of light-emitting diodes (LEDs) and flat panel displays [1–3]. For example, Wang et al. [1] have successfully prepared copper-doped zinc sulphide/poly(vinyl

alcohol) (PVA) composite nanofibers by electrospinning technique which can be described as the application of external electrical forces to produce polymeric nanofibers of diameters in the order of 100 to 800 nm. They reported marked changes in the fluorescent properties of the doped material compared to the undoped samples. In a recent study [4], high-quality composite polymer nanofibers with uniform morphology have been prepared by electrospinning technology from polymer P as excellent fluorescence chemosensor for the detection of electron-deficient nitroaromatic explosive. The polymer P, which was obtained through a Sonogashira cross-coupling polymerization, showed high affinity and excellent fluorescence quenching property toward electro-deficient compound DNT in solution. In the same vein, fluorescent polyimide (PI) web has been prepared by electrospinning from a polyamic acid (PAA) solution in *N,N*-dimethylacetamide mixed with one hemicyanine dye, DHEASPI-C1 by Qin et al. [5]. Similarly, in various recent studies on single light emitters [2, 6, 7], the fluorescent composite nanofibers were produced via the route of electrospinning. Furthermore, it has been shown that optical sensors utilize the fluorescence quenching of the sensing material against targeted chemical molecules [7]. It has been reported that electrospun composite nanofibers made from these fluorescent polymers had an average fiber diameter of 300–1000 nm [8]. Also, Zhu et al. [9] in their study of the fluorescence properties of conjugated polymers reported the fabrication of composite hybrid poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV)/polyethylene oxide (PEO) nanofibers by the technique of electrospinning. They showed that the microscopic studies of a single MEH-PPV/PEO electrospun nanofiber indicated that the fluorescence spectra of the nanofiber did not depict any polarization dependence. Furthermore, in their study of

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J. A. Ajao (✉) · A. Abiona  
Materials and Electronics Division, Centre for Energy Research  
and Development, Obafemi Awolowo University, Ile-Ife, Osun  
State, Nigeria  
e-mail: johnajao2000@yahoo.com; jajao@cerd.gov.ng

J. A. Ajao · A. Abiona · S. Chigome · J. B. Kana Kana ·  
M. Maaza  
Nanosciences and Nanotechnology Laboratories, Materials  
Research Group, iThemba LABS, P.O. Box 722, Somerset West  
7129, South Africa

S. Chigome  
Department of Chemistry, Rhodes University, P.O. Box 94,  
Grahamstown 6140, South Africa

organic light-emitting diode (OLED), Yan et al. [10] used the electrospinning technology to fabricate PEO/tris (8-quinolinolato) aluminum (Alq<sub>3</sub>) fluorescent hybrid fibers with smooth surface and uniform morphology with diameter in the 800–850 nm range. More works have equally been reported on electrospun OLED and composite polymers [11–14]. However, to the best of our knowledge, no work has reported the synthesis and characterization of poly(2,5-dicyclohexylphenylene-1,4-ethynylene) (PDE)/PEO fluorescent hybrid polymer nanofibers via the route of electrospinning. Hence, the interests of the present work on the preparation and characterization of this hybrid polymer. The ease of solubility in chloroform and electrospinning of PEO has made it a suitable precursor candidate in the synthesis of PDE/PEO hybrid polymer. In this work, PDE/PEO fluorescent hybrid nanofibers were synthesized by electrospinning of PDE/PEO solution. The resulting nanofibers were characterized by a host of spectroscopic and microscopic techniques.

## Experimental

### Materials

PDE was supplied by Aldrich and used without further purification. Poly(ethylene oxide) (PEO), with an average molecular weight of  $3 \times 10^5$  (g/mol), was equally obtained from Sigma-Aldrich and used without further purification while chloroform was used as solvent.

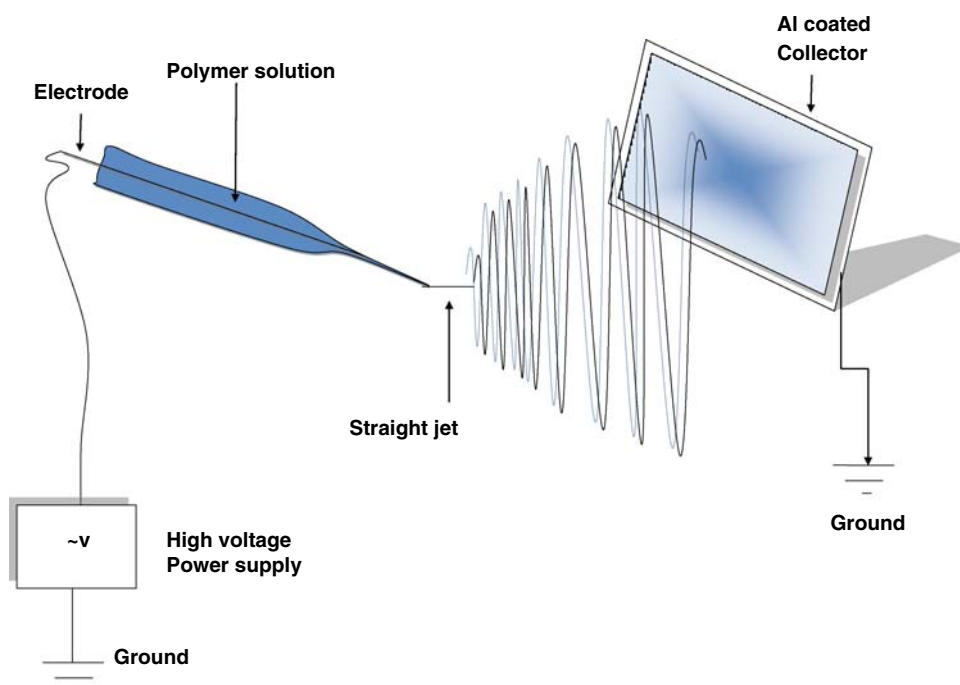
### Preparation of PDE/PEO solutions

Two different solutions of 0.025 g of PDE in 15.0 g of chloroform were prepared with vigorous stirring for about 45 min. Then, 0.15 and 0.2 g of PEO was added into the solution to obtain two different weight ratios of PDE/PEO (1:6 and 1:8). The two different solutions were then stirred for about 48 h to ensure complete dissolution of PEO.

### Electrospinning setup

Electrospinning was carried out using the set-up as shown in Fig. 1. The polymer solutions were loaded into a glass Pasteur pipette. The electric field was provided by a dual polarity high-voltage power supply (HVPS) that can generate DC voltages up to 25 kV. The pipette was clamped to a tripod stand located in front of a grounded target. The positive (anode) terminal of the variable high-voltage transformer was attached to the copper wire inserted into the polymer solution in the pipette for electricity to be conducted through the solution. A stationary grounded aluminium mesh target was placed at a distance of 15 cm opposite and perpendicular to the tip of the pipette into which the fibers were deposited. The capillary was tilted approximately  $10^\circ$  from the horizontal to maintain a droplet of solution at the tip of the pipette [15]. The whole set-up was enclosed in order to minimize the effect of air currents on the trajectory of the electrospun jet. The solutions were electrospun with a critical voltage of 15 kV onto the target made up of  $8 \times 8$  cm aluminium mesh. On the

**Fig. 1** Simple schematic drawing of single-nozzle electrospinning setup used in this work



grounded aluminium mesh were equally mounted various other substrates such as glass, glass on which one side was coated with a thin film of fluorine doped tin oxide (FTO) and silicon wafers for the collection of the nanofibers for characterization. Higher voltages (say >15 kV in our case) led to instability of the polymer jets as it caused a chaotic oscillation of the electrospinning jet as the charged polymer melt transversed the electric field potential. Detailed investigations of this phenomenon have been reported by Deitzel et al. [16]. In fact, a stronger electric field will lead to greater stretching of the solution due to the greater coulombic forces in the jet, thereby leading to the reduction in the diameter of the fibers. Deitzel et al. [16] also found that there is a greater tendency for beads formation at higher electric fields.

### Characterization

Ultraviolet–visible (UV–Vis) spectra were recorded on a Varian 500 UV–Vis/NIR spectrophotometer in the 190–1100 nm range. Fourier transform infrared (FTIR) spectra were obtained using a Perkin Elmer Pragon 1000PC FTIR spectrometer. The supermolecular structure which describes the configuration of the macromolecules in the hybrid nanofibers was characterized by wide-angle X-ray diffraction (WAXD). The X-ray diffraction (XRD) patterns of the

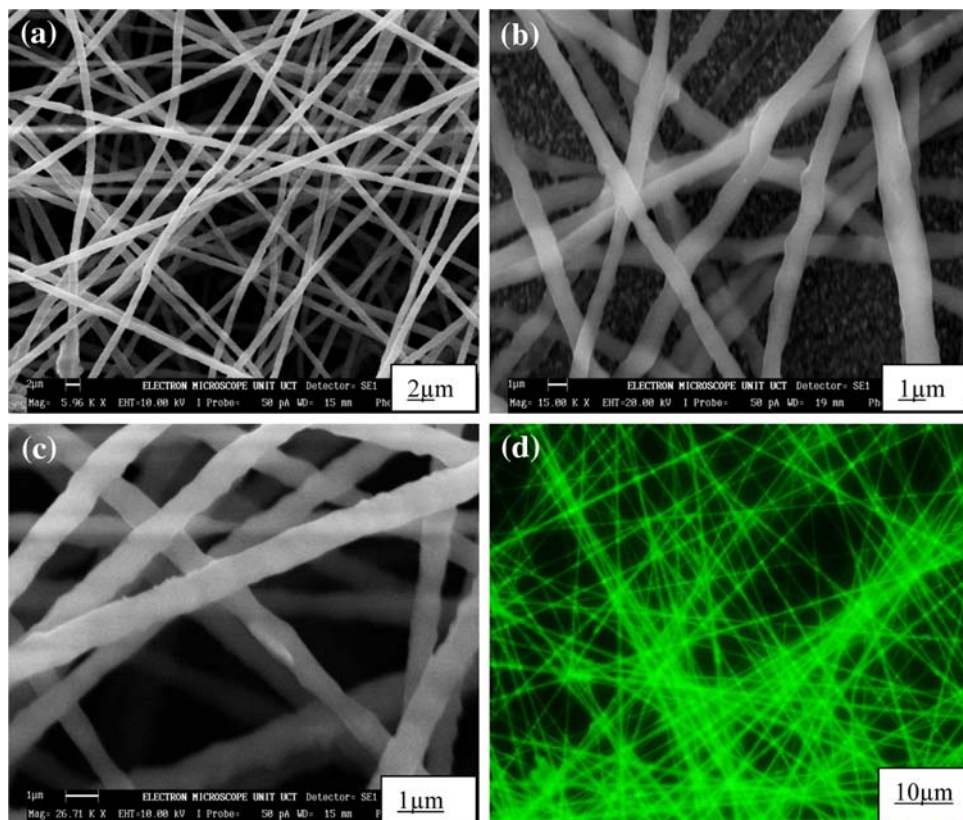
samples were obtained on a Bruker AXS D8 Advance diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Optical microscopy was performed on the electrospun fibers using a polarized optical compound microscope Nikon Eclipsen 90i/80i. For higher magnifications and detailed morphology of the fibers, samples were mounted onto scanning electron microscope (SEM) plates; sputter coated with carbon and examined using a Leo-StereoScan 440 scanning electron microscope. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope III Digital Instrument in tapping mode in air with etched Si probe.

## Results and discussion

### Scanning electron microscopy

Figure 2 shows the scanning electron micrographs of pure PEO fibers (Fig. 2a) and the PDE/PEO hybrid fibers with their weight ratio in experiment solutions of 1:6 (Fig. 2b) and 1:8 (Fig. 2c), respectively. In all the samples, the fibres are randomly oriented and there exist many curvatures along the axis of fibers, which might be attributed to the asynchronous deposition of different parts of the electrospun fiber because of its own instabilities, such as whipping or non-axisymmetric instability [17]. It should be noted

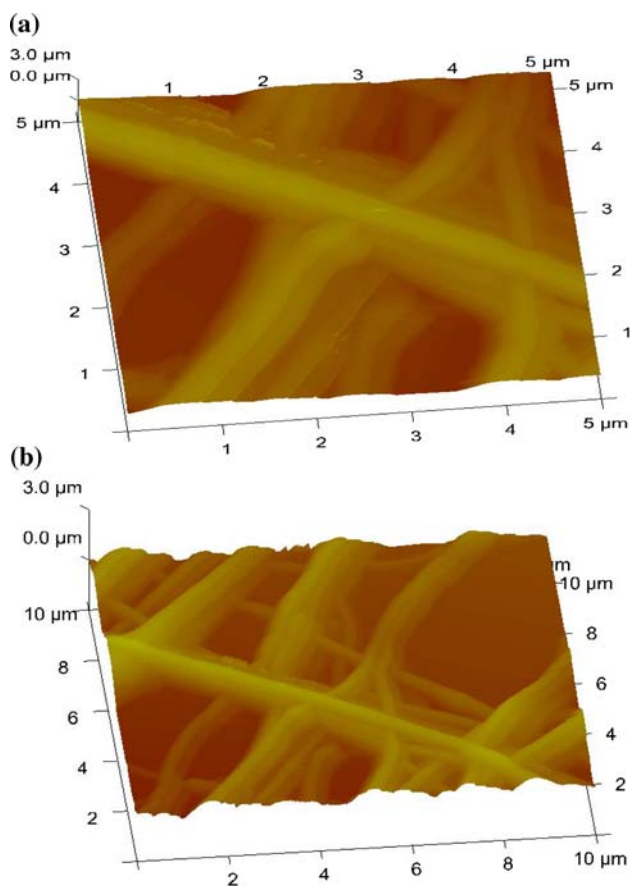
**Fig. 2** SEM images of pure PEO fibers (a) and PDE/PEO hybrid fibers with their weight ratios of 1:6 (b), 1:8 (c) and the green fluorescence image (optical) of the PDE/PEO hybrid fibers (d)



that the fibers in their overall morphology are bead- and junction-free. Beads are caused by failure to completely overcome the surface tension brought about by the solvent. Pure PEO fibers exhibit a rough surface with diameter ranging between 200 and 500 nm (Fig. 2a), whereas the PDE/PEO hybrid nanofibers have a regular, cylindrical morphology and on average have a larger and more uniform diameter (Fig. 2c). Their diameter ranges between 500 and 1000 nm. The addition of the PDE has enhanced the formation of smoother fibers with larger diameters due to the formation of PDE/PEO composite nanofibers. In the fluorescence microscope image of Fig. 2d, the hybrid nanofibers with green fluorescence can be seen indicating the possible photoluminescent properties of the PDE.

#### Atomic force microscopy measurements

Figure 3 shows the three-dimensional (3D) atomic force microscope (AFM) images of the hybrid nanofibers with two different weight ratios of PDE/PEO. It could be observed that the average fiber diameter (AFD) of the solution with weight ratio 1:6 is larger than that of 1:8. For



**Fig. 3** AFM images of PDE/PEO hybrid nanofibers for weight ratios of 1:6 (a) and 1:8 (b)

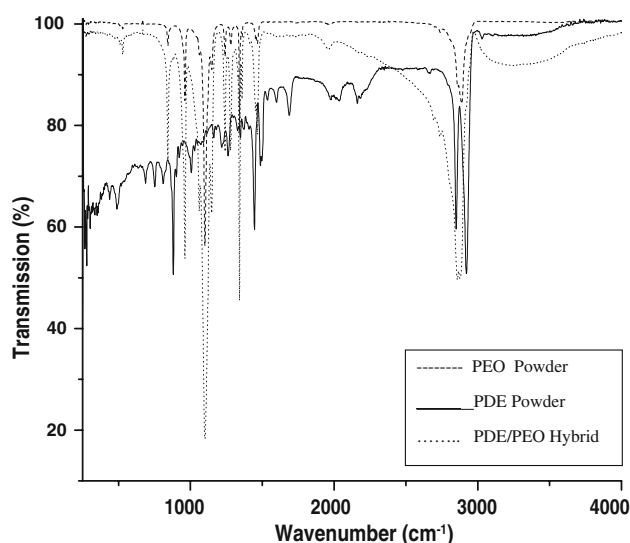
the solution with weight ratio 1:6, the average fiber diameter is about 800 nm while for 1:8 weight ratio, it is about 650 nm. Hence, the power-law relationship of

$$\text{AFD} = (\text{Concentration})^3$$

was obeyed, indicating that solution concentration plays an important role in determining the fiber diameter [15]. It can be seen from the AFM images that the hybrid fibers have uniform surfaces with cylindrical structure with diameters in the range of 500 to 1000 nm as was observed in the scanning electron micrographs. In fact, an accurate measurement of the electrospun fiber diameter with AFM requires a rather precise procedure. The fibers appear larger than their actual diameter because of AFM tip geometry [18]. As suggested by Demir et al. [15], for a precise measurement, two fibers crossing each other on the surface were chosen. The upper horizontal tangent of the lower fiber was taken as reference, and the vertical distance above this reference was considered to be the exact diameter of the upper nanofiber. The AFM was also used to characterize the roughness of the fibers. As reported by Demir et al. [15], the roughness value is the arithmetic average of the deviations of height from the central horizontal plane given in terms of millivolts of measured current. The options of plane fit and flatten filters available in the Nanoscope software were employed to subtract the contribution from the cylindrical curvature of the electrospun nanofibers. Since the roughness measured by the AFM depends on the size of the area selected, in this report, the area used varied between 50 and 150  $\mu\text{m}^2$ .

#### FTIR analysis

The molecular interactions between the PDE and PEO hybrid nanofibers were determined from the FTIR spectra obtained from the pure PEO, pure PDE and PDE/PEO fibers as shown in Fig. 4. It is known that PEO is one of such polymers with hydrophilic oxygen atom and hydrophobic ethylene group aligned alternatively. The FTIR spectrum of PEO powder (Fig. 4) shows a strong band near  $2900\text{ cm}^{-1}$  attributed to the symmetric and asymmetric C–H stretching modes. The bands at about  $1456$  and  $1350\text{ cm}^{-1}$  are attributed to the vibrations of  $-\text{CH}_2-$  group and the bands at about  $1102$  and  $962\text{ cm}^{-1}$  are assigned to the asymmetric stretching vibration of the C–O group [19]. Furthermore, in the FTIR spectrum of pure PEO, the intensity of the vibration bands of  $-\text{CH}_2-$  group is close to that of C–O group, which indicates as reported by Sui et al. [19] that the weight of extended oxygen atom is small and the PEO molecule exhibits a zigzag configuration. Interestingly, there was no significant shift in these peaks in the PDE/PEO hybrid nanofibers. However, the vibration bands of C–O group become sharp and intense, and the intensity

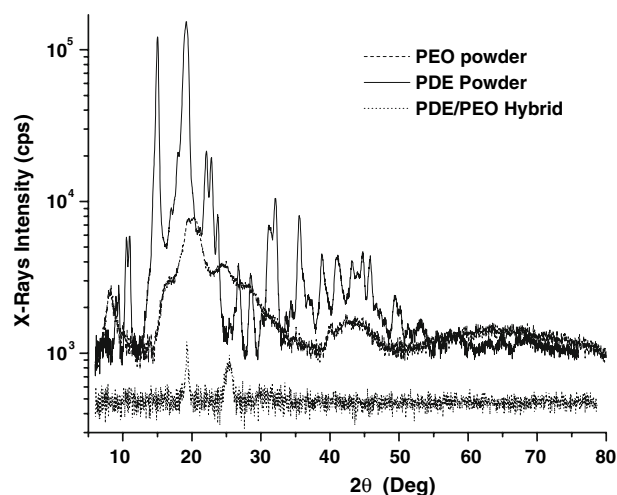


**Fig. 4** FTIR spectra of pure PEO, pure PDE and PEO/PDE hybrid fibers

of C–O group vibration band gets even stronger than that of  $-\text{CH}_2-$  group (Fig. 4). It could then be safely concluded that the oxygen atom of the C–O group was interacting with the PDE molecule. The chemical interactions between PDE and PEO molecules can affect the chemical environment of PEO by providing a polar environment to make the oxygen atoms of the backbone of PEO molecules to stretch out. Similar observations have been reported in the study of PEO/tris (8-quinolinolato) aluminium fluorescent hybrid nanofibers [10]. From the spectrum of pure PDE powder (Fig. 4), the strong absorption bands at 2950 and  $875\text{ cm}^{-1}$  could be associated with the vibrations of the  $-\text{CH}_3-$  group.

#### X-ray diffraction

XRD studies were performed on the pure PEO, pure PDE and PDE/PEO fibers as shown in Fig. 5. From the figure, for pure PEO the diffraction peaks at  $2\theta = 19.35$  and  $22.55^\circ$  correspond to the PEO crystalline phase. This is in agreement with the report of Yan et al. [10]. From the peaks corresponding to the pure PDE (Fig. 5), it can be seen that the PDE is essentially crystalline while the PEO is semi crystalline. In the resulting PDE/PEO hybrid nanofibers (Fig. 5), the diffraction peaks of PDE at  $10.50$ ,  $19.35$  and  $25.05^\circ$  could be seen which suggests the presence of PDE/PEO composite nanofibers, hence could be responsible for the luminescence of the material. The identification of these peaks could equally be attributed to the change in the crystalline phase of the PDE in the hybrid nanofibers due to the molecular interactions between the PDE molecules and the oxygen atoms on the PEO chain.



**Fig. 5** XRD patterns of pure PEO, pure PDE and PEO/PDE hybrid fibers

#### Conclusion

A simple and versatile technique of electrospinning was used to prepare PDE/PEO hybrid nanofibers with diameter ranging between 500 and 1000 nm as observed in the SEM and AFM. The FTIR spectrum shows no significant shift in vibration bands of C–O and  $-\text{CH}_2-$  groups in the PDE/PEO hybrid nanofibers. However, the vibration bands of C–O group become sharp and intense, and the intensity of C–O group vibration band gets even stronger than that of  $-\text{CH}_2-$  group, suggesting an interaction between the oxygen atom of the C–O group and the PDE molecule. XRD measurement showed that the PDE is essentially crystalline while the PEO is semi crystalline. In the resulting PDE/PEO hybrid nanofibers, the diffraction peaks of PDE at  $10.50$ ,  $19.35$  and  $25.05^\circ$  suggest the presence of PDE/PEO composite nanofibers which could be responsible for the luminescence of the material.

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#### References

1. Wang H, Lu X, Zhao Y, Wang C (2006) Mater Lett 60:2480
2. Tomczak N, Gu S, Han M, Hulst NF, Vancso GJ (2006) Eur Polym J 42:2205
3. Lu XF, Li LL, Zhang WJ, Wang C (2005) Nanotechnology 16:2233
4. Long Y, Chen H, Yang Y, Wang H, Yang Y, Li N, Li K, Pei J, Liu F (2009) Macromolecules 42:6501

5. Qin C, Wang J, Cheng S, Wang X, Dai L, Chen G (2009) *Mater Lett* 63:1239
6. Camposeo A, Benedetto FD, Stabile R, Cingolani R, Pisignano D (2007) *Appl Phys Lett* 90:143115-1
7. Moran-Mirabal JM, Slinker JD, DeFranco JA, Verbridge SS, Ilic R, Flores-Torres S, Abrun H, Malliaras GG, Craighead HG (2007) *Nanoletters* 7(2):458
8. Lee SH, Ku BC, Wang X, Samuelson LA, Kumar J (2002) *Mater Res Soc Symp Proc* 708:BB10.45.1
9. Zhu Z, Zhang L, Smith S, Fong H, Sun Y, Gosztola D (2009) *Synth Met* 159:1454
10. Yan E, Wang C, Huang Z, Xin Y, Tong Y (2007) *Mater Sci Eng A* 464:59
11. Xin Y, Huang Z, Chen J, Wang C, Tong Y, Liu S (2008) *Mater Lett* 62:991
12. Tang CW, VanSlyke SA (1987) *Appl Phys Lett* 51:913
13. VanSlyke SA, Chen CH, Tang CW (1996) *Appl Phys Lett* 69:2160
14. Frenot A, Chronakis IS (2003) *Curr Opin Colloid Interface Sci* 8:64
15. Demir MM, Yilgor I, Yilgor E, Erman B (2002) *Polymer* 43:3303
16. Deitzel JM, Kleinmeyer J, Harris D, Tan NCB (2001) *Polymer* 42:261
17. Liu CK, Sun RJ, Lai K, Sun CQ, Wang YW (2008) *Mater Lett* 62:4467
18. Srinivasan G, Reneker DH (1995) *Polym Int* 36:195
19. Sui X, Shao C, Liu Y (2007) *Polymer* 48:1459