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Short communication

# Preparation of poly(ε-caprolactone)/poly(trimethylene carbonate) blend nanofibers by electrospinning

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ABSTRACT

Poly(ε-caprolactone) (PCL)/poly(trimethylene carbonate) (PTMC) blend nanofibers have been prepared for the first time using an electrospinning process. The mixed dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF) (75/25, v/v) was found to be the most suitable solvent for electrospinning. Various blends of PCL/PTMC solutions were investigated for the formation of nano-scale fibers and it was found that the average diameter of the fibers was reduced and the morphology became finer when PTMC content was increased. FT-IR and DSC analysis indicated that the molecular interactions between PCL and PTMC were weak and they were phase-separated in the fibers. Due to the biocompatible properties of PCL and PTMC, the spun nanofibers developed here could have applications in the biomedical field.



## 1. Introduction

Recently, electrospinning has aroused much interest as an attractive technique for producing polymer fibers with diameter ranging from several micrometers to nanometer dimensions (Ignatova, Manolova, & Rashkov, 2007). Due to the unique properties of electrospun fibers, such as large surface area to volume ratio, small pore size and superior performance of mechanical properties, they have been considered as possible candidates for many applications such as separation filters (Aussawasathien, Teerawattananon, & Vongachariya, 2008), carbonaceous materials (Ji & Zhang, 2009), biosensors (Patel, Li, Yuan, & Wei, 2006) and biomedical devices including tissue engineering scaffolds (Mo, Xu, Kotaki, & Ramakrishna, 2004), wound dressing materials (Powell, Supp, & Boyce, 2008), and drug delivery platforms for delivering various bioactive agents (Kim, Lee, & Park, 2007; Luu, Kim, Hsiao, Chu, & Hadjiargyrou, 2003; Maretschek, Greiner, & Kissel, 2008; Suwantong, Opanasopit, Ruktanonchai, & Supaphol, 2007; Xu et al., 2009a; Zeng et al., 2005).

Electrospinning also provides a promising and direct way to produce novel functional biomaterials. By selecting a combination of components and adjusting the ratio of the constituents, physical and biological properties of the result electrospun fibers, such as hydrophilicity, mechanical modulus and strength, biodegradability, biocompatibility, and specific cell interactions can be tailored with the desired effects (Liang, Hsiao, & Chu, 2007). Numerous studies have been devoted to the study of electrospinning blend polymers, especially those composed of biocompatible and biodegradable materials. Chen, Mo, and Qing (2007) and Xu, Chen, Wang, and Jing (2009b) prepared electrospun collagen/chitosan and chitosan/PLA blend fibers, respectively, to mimic the native extracellular matrix for tissue engineering. Yang, Li, and Nie (2007) utilized gelatin/PVA electrospun nanofibers as a drug controlled release vehicle, and recently, electrospun fiber mats from gelatin/PLLA blends has been investigated for potential application for wound dressings (Gu, Wang, Ren, & Zhang, 2009).

Poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) (structures see in Fig. 1) are two aliphatic polyesters. They are both biodegradable and biocompatible but have different biodegradation rates and different biomedical applications. PCL is a semi-crystalline polymer and has been widely used in tissue engineering scaffolding, that being due to the properties including: nonimmunogenicity, slow biodegradability and good drug permeability (Luong-Van et al., 2006). PTMC is an amorphous biomaterial which holds elastic properties at ambient temperature. It exhibits good mechanical resistance and high chemical and thermal stability. *In vivo* biocompatibility and toxicity assays revealed that PTMC blend had no influence on heart, liver, and kidney tissues (Qin et al., 2006). The synthetic copolymer of the two, P(εCL-TMC), has been investigated as biopolymer to be used for surgery and nerve guide repairs because of its high biocompatibility and the advantage of controllable both the mechanical property and the degradation rates (Fabre et al., 2001; Jia, Liu, Song, & Shen, 2005).

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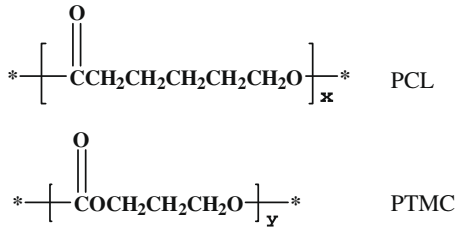


**Fig. 1.** Chemical structures of PCL and PTMC.

In addition, the electrospinning of neat PCL or PTMC has also been studied as biomaterials, respectively (Kenawya, Abdel-Hay, El-Newehy, & Wnek, 2009; Luong-Van et al., 2006; Song et al., 2008). Hitherto, the more promising electrospinning of PCL/PTMC complex has not as yet been reported.

The aim of this paper is to study electrospinning of PCL and PTMC blends in order to gain more details relating to the development of novel functional biomaterials. A very convenient method by using a single syringe was introduced for the preparation of blend fibers and the morphology and properties of the resultant fibers were subsequently characterized.

## 2. Experimental

### 2.1. Materials

PCL (Mw ~ 100,000) and PTMC (Mw ~ 100,000) were provided by Minghe Functional Polymer Co., Ltd. (Qingdao, China). Dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals and reagents were of analytical quality and used without further purification.

### 2.2. Electrospinning

Different blend ratios of PCL and PTMC (9:1, 7:3 and 5:5, w/w) were dissolved in a mixture of DCM/DMF (75:25, v/v) to prepare the electrospinning solutions at a concentration of 8 wt.%. Prior to electrospinning, the mixtures were stirred for 2 h and then degassed with a ultrasonator (59 Hz, 350 w, Shanghai Jinghong Instrument Co., Ltd. Shanghai, China) for 30 min to obtain the homogeneous co-dissolved spinning dopes. They were then carefully placed into a 5 mL syringe which included a metallic needle with an internal diameter of 0.5 mm. Electrospinning was carried out under a fixed electric field of 14 kV/18 cm. The feeding rate of the solutions was controlled at 0.8 mL/h by means of a single syringe pump (Cole-Parmer®, USA). All experiments were carried out at room temperature and a relative humidity of 40%. The resulting fibers were further dried for 24 h at ambient temperature in a vacuum drying oven (320 Pa, Shanghai Laboratory Instrument Work Co. Ltd., Shanghai, China) to remove the residual organic solvent and moisture.

### 2.3. Characterization of electrospun fibers

#### 2.3.1. Morphology

The surface morphology of electrospun fibers was assessed using a JSM-5600LV scanning electron microscope (Japan ElectronOptics Laboratory Co. Ltd.). Prior to the examination, the samples were gold sputter-coated under argon atmosphere to render them electrically conductive and pictures were taken at an excitation voltage of 10 kV.

#### 2.3.2. FT-IR spectroscopy

The molecular interactions of the blend electrospun fibers were assayed on a Fourier-transform infrared (FT-IR) spectrometer (Nicolet-Nexus 670, Nicolet Instrument Corporation, Madison, USA). The test sample was dissolved in chloroform and the solution was laid on a KBr disk. FT-IR spectrum of the samples was recorded after removal of chloroform by evaporation.

#### 2.3.3. Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analyses were carried out using an MDSC 2910 differential scanning calorimeter (TA Instruments Co., USA). Test samples were heated from −60 to 250 °C at a heating rate of 10 °C/min. The nitrogen gas flow rate was set as 40 mL/min.

## 3. Results and discussion

### 3.1. Morphology

One of the most important qualities related with electrospinning is the fiber morphology (Huang, Zhang, Kotaki, & Ramakrishna, 2003). From our initial experiments, it was found that without PTMC or the content of PTMC more than 50%, continuous fiber-structures could not be formed; while when the ratios of PCL and PTMC in the range of 9:1–5:5, nano-scale fibers could be obtained successfully. So, the ratios of 9:1, 7:3 and 5:5 were selected as the typical to be further investigated in this study. The surface morphologies of the electrospun fibers were demonstrated in Fig. 2. It can be observed that they possess common features of being round-shaped, randomly arrayed and highly porous. PCL and PTMC were well blended in the fibers. It should be noted that the fiber morphology was significantly affected by PCL/PTMC blend ratios. The 9/1 blend fibers exhibited some stump-like structures (in white circles, Fig. 2a), thus reflecting the fragility of the polymer fibers at this blending ratio. When the content of PTMC was raised to 30% (PCL/PTMC 7:3), fewer stump-like structures were noted and the fibers appeared more continuous and smoother (Fig. 2b). The most consistent fiber morphology was obtained when PCL and PTMC were equally blended (PCL/PTMC 5:5) (Fig. 2c). Moreover, it was demonstrated in Fig. 3 that with PCL/PTMC blend ratios of 9:1, 7:3 and 5:5, the diameter of the resultant fibers was 302 ± 109, 266 ± 101 and 203 ± 77 nm, respectively. Fiber diameter and diameter distribution were seen to decrease with the increasing content of PTMC. These results could be related to the overall property of the polymer solution. That included viscosity, surface tension and conductivity. Increasing the content of PTMC could assist in achieving thinner and more uniform nanofibers in this study, probably due to the increased suitability of the polymer solution used for electrospinning.

Selecting an appropriate solvent system is crucial for successful electrospinning (Chen et al., 2007). DCM is a good solvent for both PCL and PTMC, but is not appropriate for electrospinning, as when DCM alone was used as the solvent, the resultant fibers exhibit larger diameters and with many beads. However it is known that DMF is a good electrospinning solvent due to its high dielectric constant (Fong, 2007). Here, DMF was added into the solution of PCL/PTMC in DCM to improve the fiber formation. During this study, several mixtures with different DCM/DMF ratios were explored as the solvents for preparing of the spin dopes. The solvent mixture with the DCM/DMF ratio of 75/25 was identified as the optimal system based upon the morphology of the nanofibers and the stability of the electrospinning. Similar observations have also been reported by Liao, Zhang, Gao, Zhu, and Fong (2008) who used a mixture of chloroform/DMF as the electrospinning solvent for PLGA.

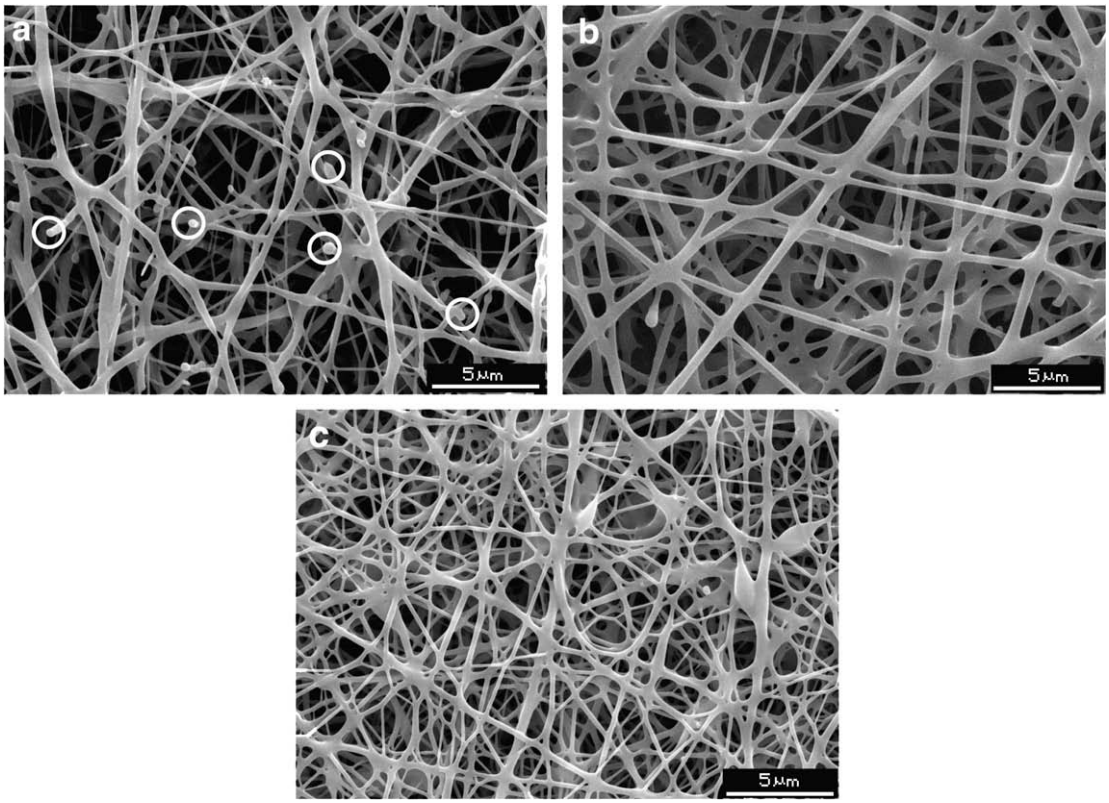


**Fig. 2.** SEM morphologies of electrospun PCL/PTMC fibers with various PCL/PTMC blend ratios: (a) PCL/PTMC 9:1; (b) PCL/PTMC 7:3; (c) PCL/PTMC 5:5.

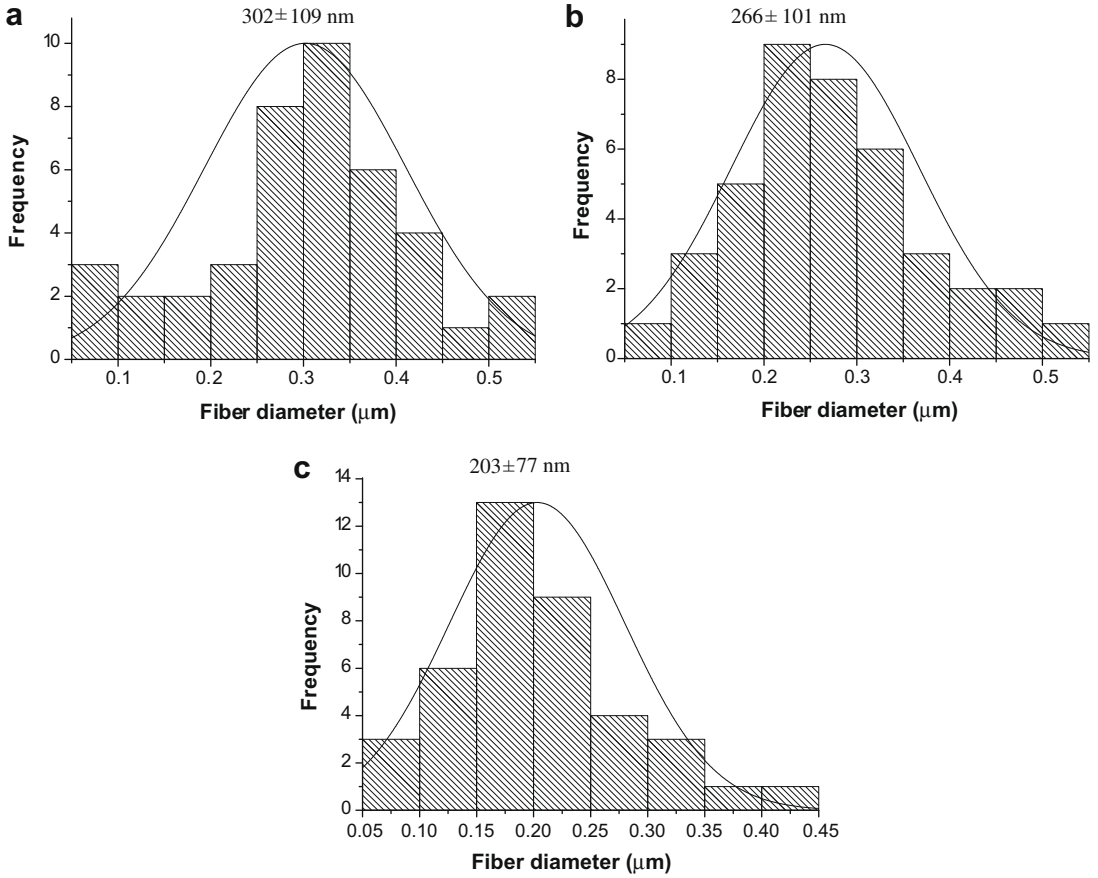


**Fig. 3.** Diameter distributions of electrospun PCL/PTMC fibers with various PCL/PTMC blend ratios: (a) PCL/PTMC 9:1; (b) PCL/PTMC 7:3; (c) PCL/PTMC 5:5.

### 3.2. FT-IR analysis

The FT-IR spectra of PCL, PTMC and electrospun PCL/PTMC fibers are shown in Fig. 4. The spectrum of PCL and PTMC were similar (Fig. 4a and b) this being due to the similarity of chemical structures of the two principle component. The peaks located at 2945, 2865, and 1725 $cm^{-1}$ of PCL (Fig. 4a) and 2971, 2909, and 1744 $cm^{-1}$ of PTMC (Fig. 4b) were assigned to the stretching vibration of $-CH_2-$ and vibration of $-C{=}O$ bonds, respectively; while in the blend materials these peaks were found in the neutralized regions of 2952, 2874, and 1735 $cm^{-1}$ (Fig. 4c–e). Moreover, it could be observed that with the increasing content of PTMC, the relative strength of peaks1295, 1244 and 1191 $cm^{-1}$ which belongs to PCL decreased and peaks became broaden. Almost no changes in the positions of these peaks were noted. This may be explained as the molecular interaction between PCL and PTMC are weak, because there are no chemical active groups (such as $-OH$ and $-NH_2$) exist in the structure of either PCL or PTMC that would create a hydrogen bond forming environment.

### 3.3. DSC analysis

Fig. 5 shows the DSC thermograms of pure PCL, PTMC and PCL/PTMC nanofibers. The glass transition temperature (*Tg*) for PTMC was observed at −12 °C, which is higher than that of other reported values such as −15 or −17 °C (Albertsson & Sjoling, 1992; Wang, Dong, & Qiu, 1998). This would be due to the *Tg* of PTMC homopolymers being dependent on molecular weight. For example, PTMC with a molecular weight of 47,000 gives a *Tg* value of −17 °C, which is higher than that of PTMC with molecular weight of 6000, −36 °C (Albertsson & Sjoling, 1992). The *Tg* of PCL was reported to be −60 °C (Jia et al., 2005) but it was not detected in the present experiment. It is well known that PTMC is an amorphous polymer, while PCL is a semi-crystallized polymer. As expected, the melting point (*Tm*) of PCL was shown as 67 °C, and that of

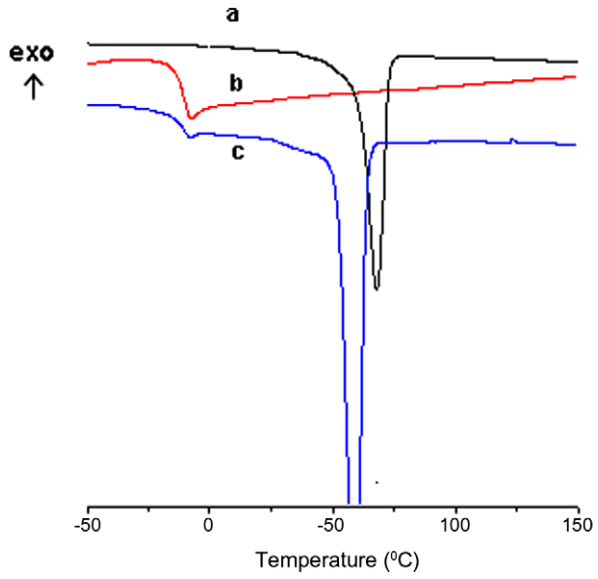


**Fig. 5.** Differential scanning calorimeter (DSC) thermograms of: (a) PCL, (b) PTMC, (c) electrospun PCL/PTMC fibers (PCL: PTMC 5:5).

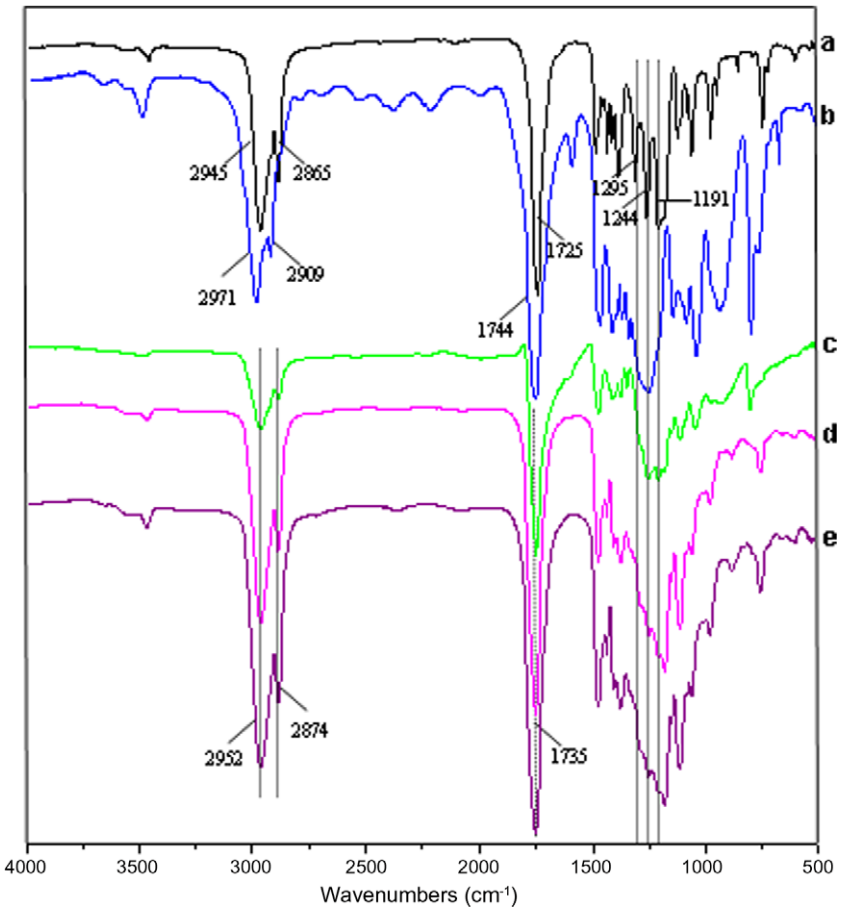


**Fig. 4.** The FT-IR spectra of: (a) PCL, (b) PTMC, (c) PCL/PTMC 9:1, (d) PCL/PTMC 7:3, (e) PCL/PTMC 5:5.

PTMC was not detected. When PCL and PTMC were electrospun into blend fibers, *Tg* of PTMC was not changed (−12.2 °C), while the *Tm* of PCL was decreased from 67 to 59 °C. These results suggested that PCL and PTMC existed in a phase-separated way in the fibers. The same results have also been observed for the diblock copolymer of P(CL-TMC) (Luyten, Bogels, Alberda van Ekenstein, & ten Brinke, 1997). The significant decrease of *Tm* for PCL might be due to: (i) the presence of PTMC affecting the thermo-property of PCL; (ii) the chain orientations of the polymer were changed during electrospinning.

## 4. Conclusions

In this study, a facile method for the preparation of PCL/PTMC blend fibers was demonstrated. The mixed DCM/DMF (75/25, v/v) was found as an appropriate solvent for electrospinning of the PCL–PTMC complex. With the increasing content of PTMC, the fiber diameter decreased and the fiber morphology became finer. According to FT-IR and DSC results, it was found that the interaction between PCL and PTMC was weak and they were presented as phase-separated in the fibers. The data showed here are of significant importance for the design of novel, nanostructured and functional fiberous biomaterials. The prepared material is potential candidate for biomedical applications and its biological behavior is the subject of a forthcoming publication.

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## References

Albertsson, A.-C., & Sjoling, M. (1992). Homopolymerization of 1, 8-dioxon-2-one to high molecular weight poly(trimethylene carbonate). *Journal of Macromolecular Science Part A: Pure Applied Chemistry, 29*, 43–54.

Aussawasathien, D., Teerawattananon, C., & Vongachariya, A. (2008). Separation of micron to sub-micron particles from water: Electrospun nylon-6 nanofibrous membranes as pre-filters. *Journal of Membrane Science, 315*, 11–19.

Chen, Z. G., Mo, X. M., & Qing, F. L. (2007). Electrospinning of collagen–chitosan complex. *Materials Letters, 61*, 3490–3494.

Fabre, T., Schappacher, M., Bareille, R., Dupty, B., Soum, A., Bertrand-Barat, J., et al. (2001). Study of a (trimethylene carbonate-co-ε-caprolactone) polymer – Part 2: In vitro cytocompatibility analysis and in vivo ED1 cell response of a new nerve guide. *Biomaterials, 22*, 2951–2958.

Fong, H. (2007). Electrospun polymer, ceramic, carbon/graphite nanofibers and their applications. In H. S. Nalwa (Ed.), *Polymeric nanostructures and their applications* (pp. 451–474). Stevenson Ranch, California: American Scientific Publishers.

Gu, S. Y., Wang, Z. M., Ren, J., & Zhang, C. Y. (2009). Electrospinning of gelatin and gelatin/poly(L-lactide) blend and its characteristics for wound dressing. *Materials Science and Engineering C*. doi:10.1016/j.msec.2009.02.01.

Huang, Z. M., Zhang, Y. Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology, 63*, 2223–2253.

Ignatova, M., Manolova, N., & Rashkov, I. (2007). Electrospinning of poly(vinyl pyrrolidone)-iodine complex and poly(ethylene oxide)/poly(vinyl pyrrolidone)-iodine complex – A prospective route to antimicrobial wound dressing materials. *European Polymer Journal, 43*, 1609–1623.

Ji, L. W., & Zhang, X. W. (2009). Generation of activated carbon nanofibers from electrospun polyacrylonitrile-zinc chloride composites for use as anodes in lithium-ion batteries. *Electrochemistry Communications, 11*(3), 684–687.

Jia, Y. T., Liu, Z. M., Song, M. S., & Shen, X. Y. (2005). Characterization and development of biodegradable polymers from trimethylene carbonate and ε-caprolactone (in Chinese, with English abstract). *Journal of Liaodong University, 12*(2), 32–34.

Kenawya, E.-R., Abdel-Hay, F. I., El-Newehy, M. H., & Wnek, G. E. (2009). Processing of polymer nanofibers through electrospinning as drug delivery systems. *Materials Chemistry and Physics, 113*, 296–302.

Kim, T. G., Lee, D. S., & Park, T. G. (2007). Controlled protein release from electrospun biodegradable fiber mesh composed of poly(ε-caprolactone) and poly(ethylene oxide). *International Journal of Pharmaceutics, 338*, 276–283.

Liang, D. H., Hsiao, B. S., & Chu, B. (2007). Functional electrospun nanofibrous scaffolds for biomedical applications. *Advanced Drug Delivery Reviews, 59*, 1392–1412.

Liao, Y. L., Zhang, L. F., Gao, Y., Zhu, Z. T., & Fong, H. (2008). Preparation, characterization, and encapsulation/release studies of a composite nanofiber mat electrospun from an emulsion containing poly(lactic-co-glycolic acid). *Polymer, 49*, 5294–5299.

Luong-Van, E., Grondahl, L., Chua, K. N., Leong, K. W., Nurcombe, V., & Cool, S. M. (2006). Controlled release of heparin from poly(ε-caprolactone) electrospun fibers. *Biomaterials, 27*, 2042–2050.

Luu, Y. K., Kim, K., Hsiao, B. S., Chu, B., & Hadjiargyrou, M. (2003). Development of a nanostructured DNA delivery scaffold via electrospinning of PLGA and PLA-PEG block copolymers. *Journal of Controlled Release, 89*, 341–353.

Luyten, M. C., Bogels, E. J. F., Alberda van Ekenstein, G. O. R., & ten Brinke, G. (1997). Morphology in binary blends of poly(vinyl methyl ether) and ε-caprolactone-trimethylene carbonate diblock copolymer. *Polymer, 38*(3), 509–519.

Maretschek, S., Greiner, A., & Kissel, T. (2008). Electrospun biodegradable nanofiber nonwovens for controlled release of proteins. *Journal of Controlled Release, 127*, 180–187.

Mo, X. M., Xu, C. Y., Kotaki, M., & Ramakrishna, S. (2004). Electrospun P(LLA-CL) nanofiber: A biomimetic extracellular matrix for smooth muscle cell and endothelial cell proliferation. *Biomaterials, 25*, 1883–1890.

Patel, A. C., Li, S. X., Yuan, J. M., & Wei, Y. (2006). In situ encapsulation of horseradish peroxidase in electrospun porous silica fibers for potential biosensor applications. *Nano Letter, 6*(5), 1042–1046.

Powell, H. M., Supp, D. M., & Boyce, S. T. (2008). Influence of electrospun collagen on wound contraction of engineered skin substitutes. *Biomaterials, 29*, 834–843.

Qin, Y. Y., Yuan, M. L., Li, L., Guo, S. Y., Yuan, M. W., Li, W., et al. (2006). Use of polylactic acid/polytrimethylene carbonate blends membrane to prevent postoperative adhesions. *Journal of Biomedical Materials Research Part B: Applied Biomaterials, 79*(2), 312–319.

Song, Y., Yang, F., Jansen, J. A., Kamphuis, M. M. J., Zhang, Z., Poot, A. A., et al. (2008). Poly(trimethylene carbonate) porous tubular structures made by electrospinning. *Journal of Controlled Release, 132*(3), e79–e80.

Suwantong, O., Opanasopit, P., Ruktanonchai, U., & Supaphol, P. (2007). Electrospun cellulose acetate fiber mats containing curcumin and release characteristic of the herbal substance. *Polymer, 48*, 7546–7557.

Wang, H., Dong, J. H., & Qiu, K. Y. (1998). Synthesis and characterization of ABA-type block copolymer of poly(trimethylene carbonate) with poly(ethylene glycol): Bioerodible copolymer. *Journal of Polymer Science. Part A: Polymer Chemistry, 36*, 695–702.

Xu, X. L., Chen, X. S., Wang, Z., & Jing, X. B. (2009b). Ultrafine PEG-PLA fibers loaded with both paclitaxel and doxorubicin hydrochloride and their in vitro cytotoxicity. *European Journal of Pharmaceutics and Biopharmaceutics, 72*(1), 18–25.

Xu, J., Zhang, J. H., Gao, W. Q., Liang, H. W., Wang, H. Y., & Li, J. F. (2009a). Preparation of chitosan/PLA blend micro/nanofibers by electrospin-ning. *Materials Letters, 63*, 658–660.

Yang, D. Z., Li, Y. N., & Nie, J. (2007). Preparation of gelatin/PVA nanofibers and their potential application in controlled release of drugs. *Carbohydrate Polymers, 69*, 538–543.

Zeng, J., Aigner, A., Czubayko, F., Kissel, T., Wendorff, J. H., & Greiner, A. (2005). Poly(vinyl alcohol) nanofibers by electrospinning as a protein delivery system and the retardation of enzyme release by additional polymer coatings. *Biomacromolecules, 6*, 1484–1488.