Electrospun Nanofibers of Block Copolymer of Trimethylene Carbonate and ε-Caprolactone

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ABSTRACT: The electrospinning behavior of a block copolymer of trimethylene carbonate (TMC) and ε-caprolactone dissolved in *N*,*N*-dimethylformamide (DMF) and methylene chloride (MC) was studied. The effects of the blended solvent volume ratio, concentration, voltage, and tip–collector distance (TCD) on the morphology of the electrospun fibers were investigated by scanning electron microscopy. The results indicated that the diameter of the electrospun fibers decreased with a decreasing molar ratio of MC to DMF, but beads formed gradually. With a decreasing concentration of the solution, the fiber diameter decreased; at the same time, beads also appeared and changed from spindlelike to spherical. A higher voltage and larger TCD favored the formation of smaller diameter electrospun fibers. The results of differential scanning calorimetry and X-ray diffraction showed that the crystallinity and melting point of the electrospun fibers decreased when increasing the TMC content in the copolymer. Compared with the corresponding films, the crystallinity and melting point of the electrospun fibers were obviously increased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1462–1470, 2006

Key words: block copolymer; electrospinning; nanofiber; crystallinity; ε-caprolactone; trimethylene carbonate

INTRODUCTION

Liner aliphatic polymers based on ε-caprolactone (ε-CL) and trimethylene carbonate (TMC) are receiving more and more attention because of their nontoxicity, biocompatibility, permeability, and biodegradability.[1–4] The main studies and applications of the copolymers are found in such areas as biodegradable sutures, artificial skin, biodegradable prostheses, drug delivery applications, and nerve guides.[4–6] Considerable efforts to develop scaffolds for tissue engineering have been recently attempted using biodegradable and biocompatible polymers such as poly(DL-lactide-*co*-glycolide), poly(L-lactide-*co*-glycolide), or poly(ε-CL) (PCL).[7–10] Principally, the scaffold should be designed by mimicking the structure and biological function of native extracellular matrix (ECM) proteins, which provide mechanical support and regulate cell activities. The polymer morphology, such as the crystallinity and melting point, plays an especially important role in the degradation process.[11,12] Many researchers have investigated the effect of the morphology on the degradation process.[13,14] As we know, electrospinning represents an attractive approach for polymer biomaterials in medical areas because electrospun nonwoven mats have high porosity and surface area.[15] These particularities in the morphology are architecturally similar to the collagen structure of the ECM. Therefore, they can be used as scaffolds for tissue engineering.[16] Moreover, they can be used for immobilized enzymes and catalyst systems, wound dressing articles, artificial blood vessels, materials for the prevention of postoperative induced adhesions, and so forth.[17] The electrospinning method can especially make the morphology of polymers change. The morphology of electrospun fibers depends on various parameters such as the solution concentration of the polymer; the electric potential at the tip and the tip–collector distance (TCD); ambient parameters including temperature, humidity, and air viscosity in the electrospinning chamber; and so forth.[15]

Electrospinning is a process in which a polymer can produce nanofibers using electrostatically driven jets of polymer solution or polymer melt. A schematic description of electrospinning is shown in Figure 1. A polymer solution is charged via a connection to a high voltage power supply and suspended from a small needle. Because of its charge, a thin jet of this solution is ejected from the tip of the needle and drawn toward a grounded target. As the jet travels toward the collector, the solvent evaporates, depositing a nonwoven nanofiber mat on the target.

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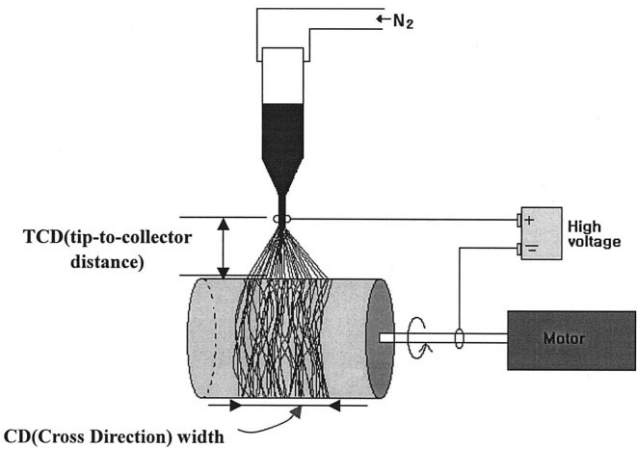


Figure 1 A schematic of the electrospinning process.

Encouraged by our success in the preparation of the block copolymer of TMC to ε-CL,[18] the present paper studies the electrospinning behavior of the block copolymer of TMC and ε-CL dissolved in both *N*,*N*-dimethylformamide (DMF) and methylene chloride (MC). The effects of various processing parameters in electrospinning on the morphology of the block copolymer fibers were investigated. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) techniques were used to characterize the structure and morphology of the fibers. Moreover, the melting point and crystallinity of the fibers were compared with those of the corresponding films.

EXPERIMENTAL

Materials and instruments

Block copolymer of TMC and ε-CL was synthesized according to the literature.[18] MC and DMF were used as received.

An Amray 3000 SEM microscope was employed to take the SEM photographs, using an accelerating voltage of 20 kV. DSC measurements were carried out on a thermal analysis instrument (DSC2010, TA Instruments, Ltd., New Castle, U.K.) covering a 30–100°C temperature range in a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The crystallinity measurements were carried out at room temperature with a Philips diffractometer, with a Geiger counter, connected to a computer. The diffraction scans were collected at 2θ 5–40°.

Preparation of block copolymer fibers

The solution of the block copolymer with different molar ratios and blended solvent of MC/DMF (molar ratio = 50/50) was prepared at room temperature with vigorous stirring. The concentrations of the block copolymer solution ranged from 20 to 28 wt %. The solution was placed in a syringe. Then, the syringe was clamped to a ring stand, which was above a grounded tubular layer. The tubular layer was covered by a piece of aluminum foil. The power supply was connected to the metal syringe tip. The droplet instantly disintegrated into fibers, which were drawn to the tubular layer. The voltage ranged from 5 to 20 kV. The TCD ranged from 5 to 20 cm.

RESULTS AND DISCUSSION

Effect of different electrospinning parameters on morphology of fibers

MC is an excellent solvent for the block copolymer of ε-CL and TMC. However, the solution cannot form fibers in electrospinning process. Although DMF is a nonsolvent for the block copolymer, empirically it has been found to be helpful in the formation of electrospun fibers. Figure 2 shows SEM images of the block copolymer fibers with solvent molar ratios of MC/DMF from 90/10 to 50/50. The diameter of the electrospun fibers decreased with increasing the content of DMF, and the average diameter changed from 1500 to 200 nm when decreasing the molar ratio of MC/DMF [see Fig. 3(a)]. The beads were found at molar ratios of 60/40 and 50/50. Figure 4 shows SEM images of the block copolymer fibers with different solution concentrations. When the concentration was lower (20 wt %), spherical beads were found. When increasing the concentration of the solution, the shape of the beads changed from spherical to spindlelike. As the concentration was further increased (at 26 and 28 wt %), the beads disappeared. However, the diameter of the fibers increased gradually [Fig. 3(b)]. All results indicated that the DMF solvent favored the formation of electrospun fibers with molar ratios of 90/10 to 70/30 (MC/DMF) without beads, and higher concentration of the block copolymer favored the formation of fibers without beads.

Apart from the effect of the factors discussed above, the voltage is another effective factor for electrospun fibers [Figs. 3(c), 5]. The average diameter of the electrospun fibers was decreased with increased voltage. The polymer solution was held by its surface tension in the form of a droplet at the end of the capillary tube. As the voltage was increased, a charge was induced on the fluid surface and the droplet was distorted. Above a critical voltage, a single jet was ejected from the apex of a conical meniscus. Beyond the conical base immediately at the end of capillary tube, the jet continued to thin. In other words, the electrostatic

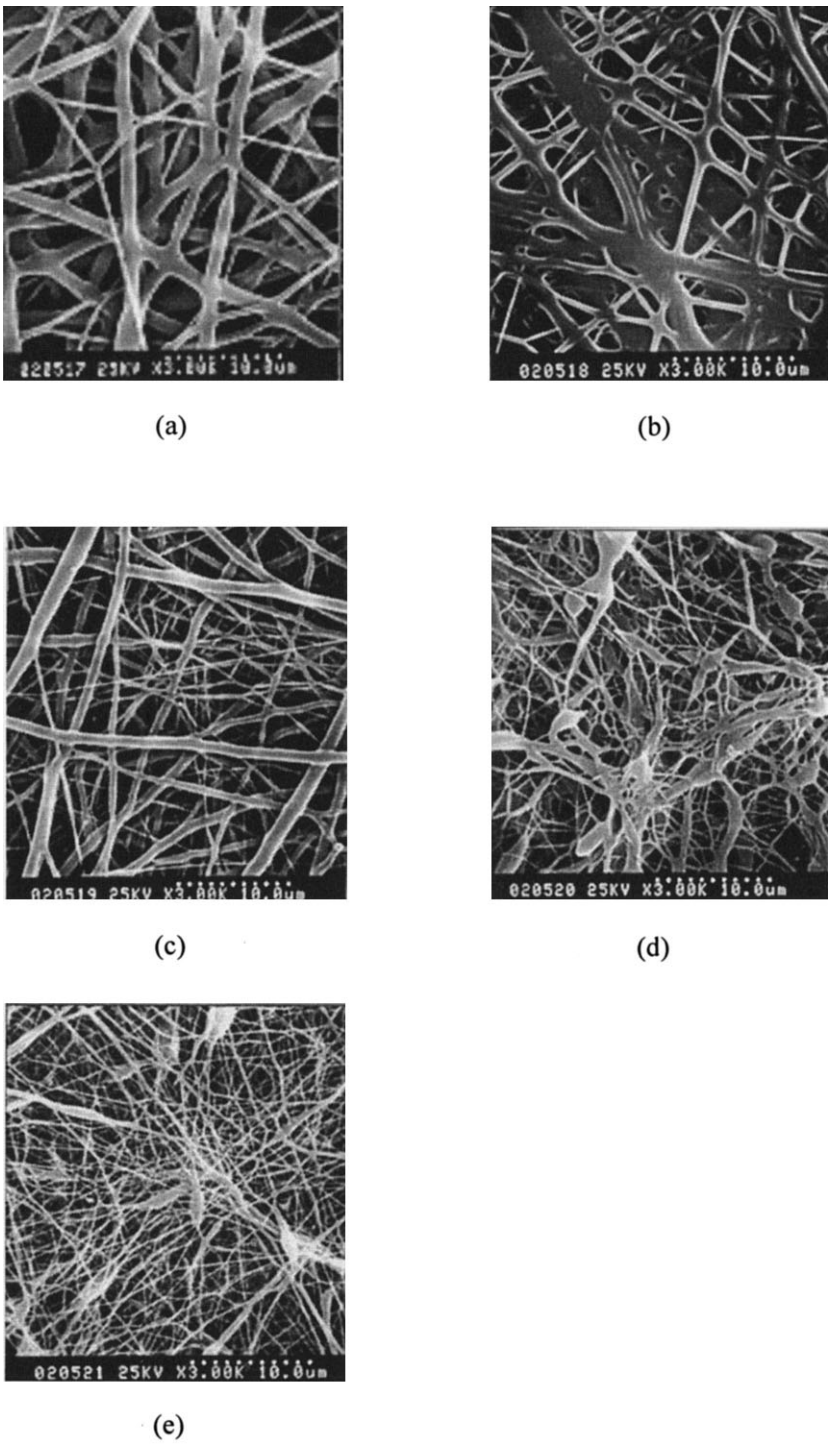


Figure 2 SEM photos of the electrospun fibers as a function of the volume ratio of MC/DMF: (a) 90/10, (b) 80/20, (c) 70/30, (d) 60/40, and (e) 50/50).

force was gradually increased with increasing voltage and the split ability of the droplet was reinforced. Figures 6 and 3(d) show SEM photographs and the average diameter of the electrospun fibers as a function of the TCD in the range of 5–20 cm, respectively. It was obvious that the fiber diameters decreased from 2000 to 220 nm with increasing TCD. This confirmed that the droplet was split into a cone, and then the diameter of the fibers became smaller during the electrospinning process.

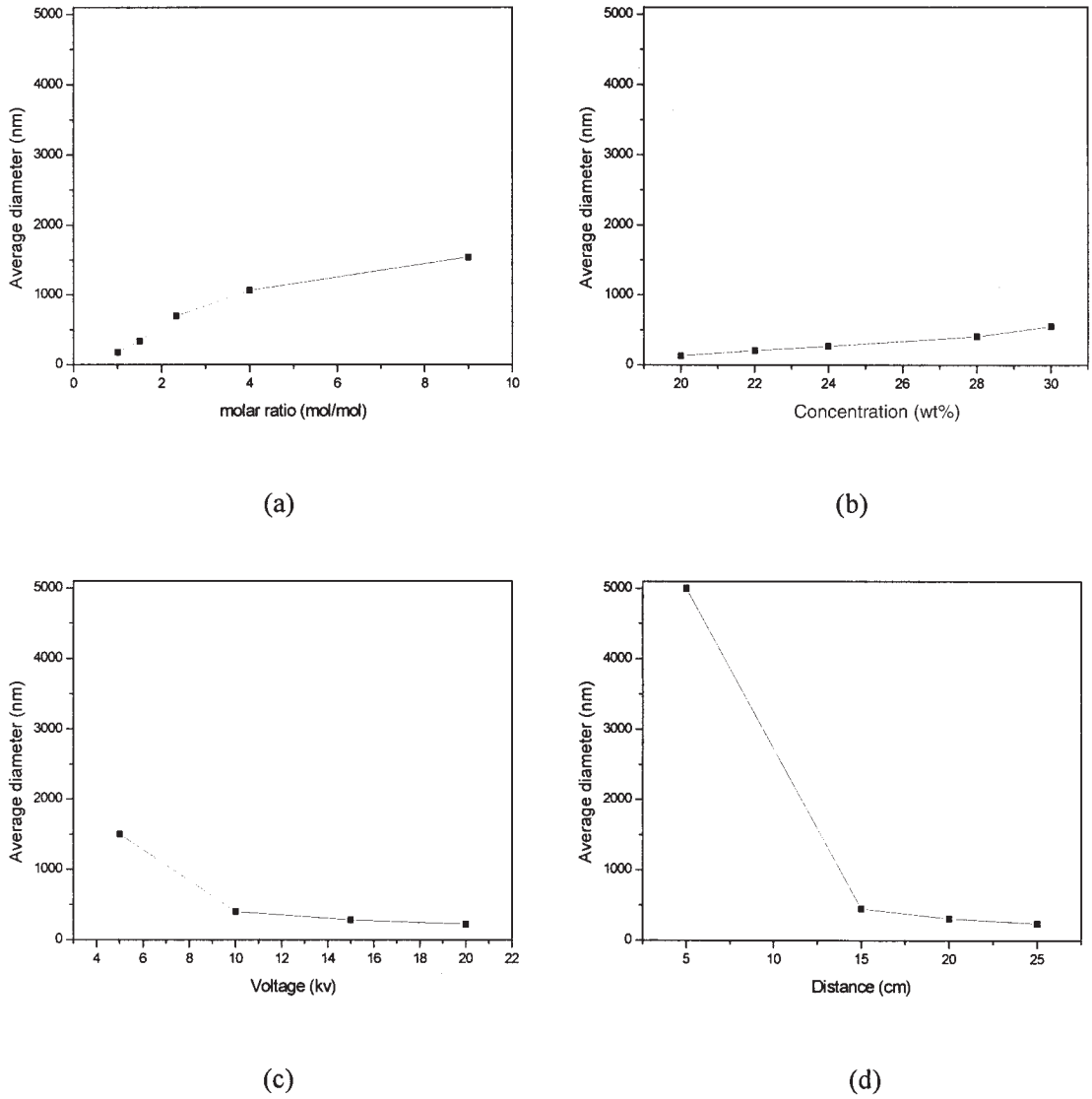


Figure 3 Average diameter changes with the processing parameters.

DSC analysis

Figure 7 provides DSC thermograms of the electrospun fibers dried under a vacuum at room temperature. It was observed that only one melting point existed in the DSC curve, and the melting point decreased with increasing TMC content in the copolymer. Obviously, the reason was that the polyTMC belonged to the amorphous domain and the PCL block belonged to the crystal domain. The increase of the amount of TMC in the block copolymer fibers gave worse conditions for crystallization.

Figure 8 contains DSC curves of the electrospun fibers and the corresponding films of the block copolymer. As shown in the figure, the melting point of electrospun fibers was higher than that of corresponding films for each molar ratio. The reason was that an extremely large effective draw ratio was enhanced during electrospinning, so the crystallinity and the melting point of the electrospun fibers both increased.

XRD study

Figure 9 show XRD patterns of the electrospun fibers of the block copolymer with different molar ratios of TMC/ε-CL. A intensity diffraction peak appeared at 2θ 21.4° for 90/10 fibers, 2θ 22° for 70/30 fibers, and 2θ 23.8° for 50/50 fibers, which was the characteristic peak of the crystallized PCL block in the copolymer fiber molecule chain.[2] The intensity of the peak decreased gradually with increasing TMC content in the copolymer. This indicated that the crystallinity of the block copolymer fibers decreased with increasing

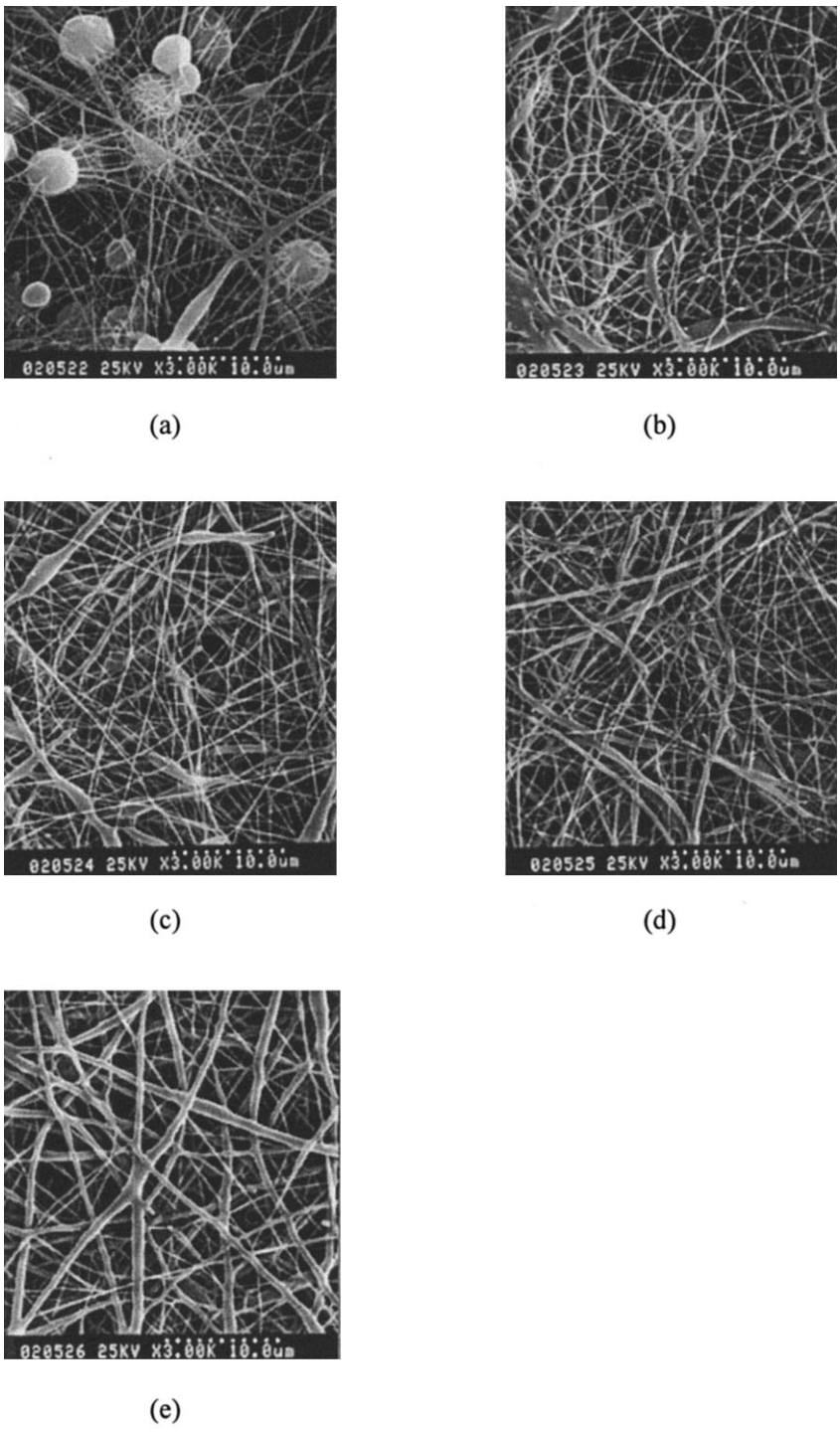


Figure 4 SEM photographs of the electrospun fibers as a function of the concentration (wt %): (a) 20, (b) 22, (c) 24, (d) 26, and (e) 28.

TMC content in the copolymer. This result was in good agreement with the results from the DSC analysis.

Figure 10 presents the XRD patterns of the electrospun fibers and the corresponding films of the block copolymers with different molar ratios of TMC/ε-CL. Compared with the films, the intensity of the electrospun fibers was more vigorous. This suggested that the electrospun fibers possessed higher crystallinity than that of corresponding films. This also agreed with the results of the DSC measurements.

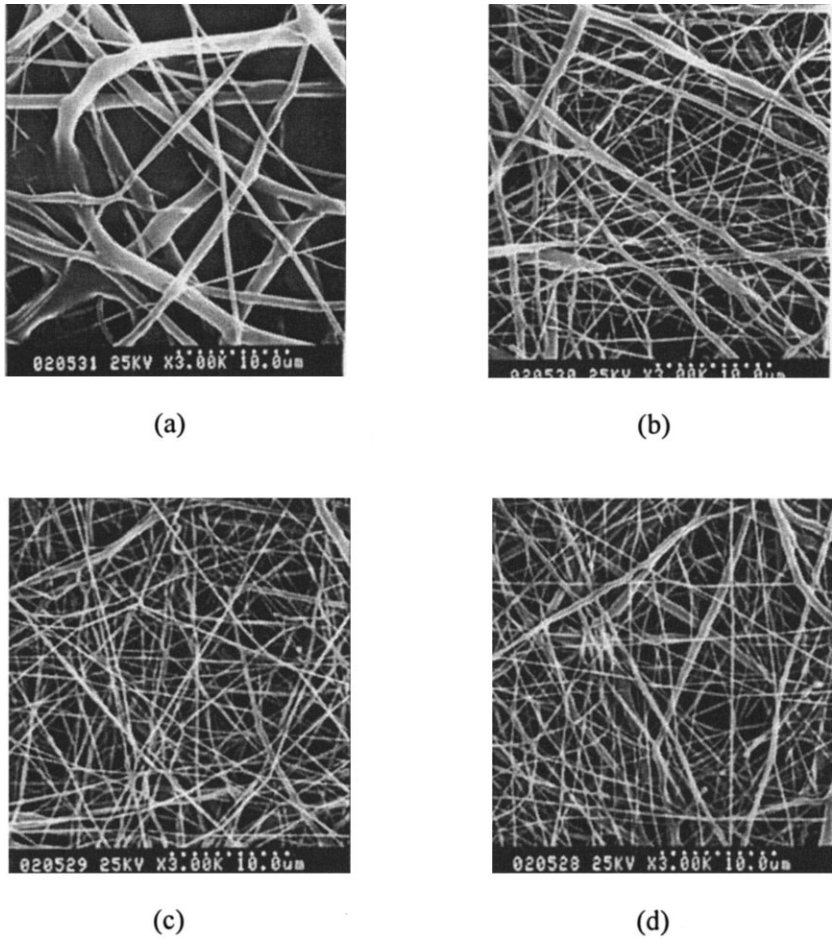


Figure 5 SEM photographs of the electrospun fibers as a function of the voltage (kV): (a) 5, (b) 10, (c) 15, and (d) 20.

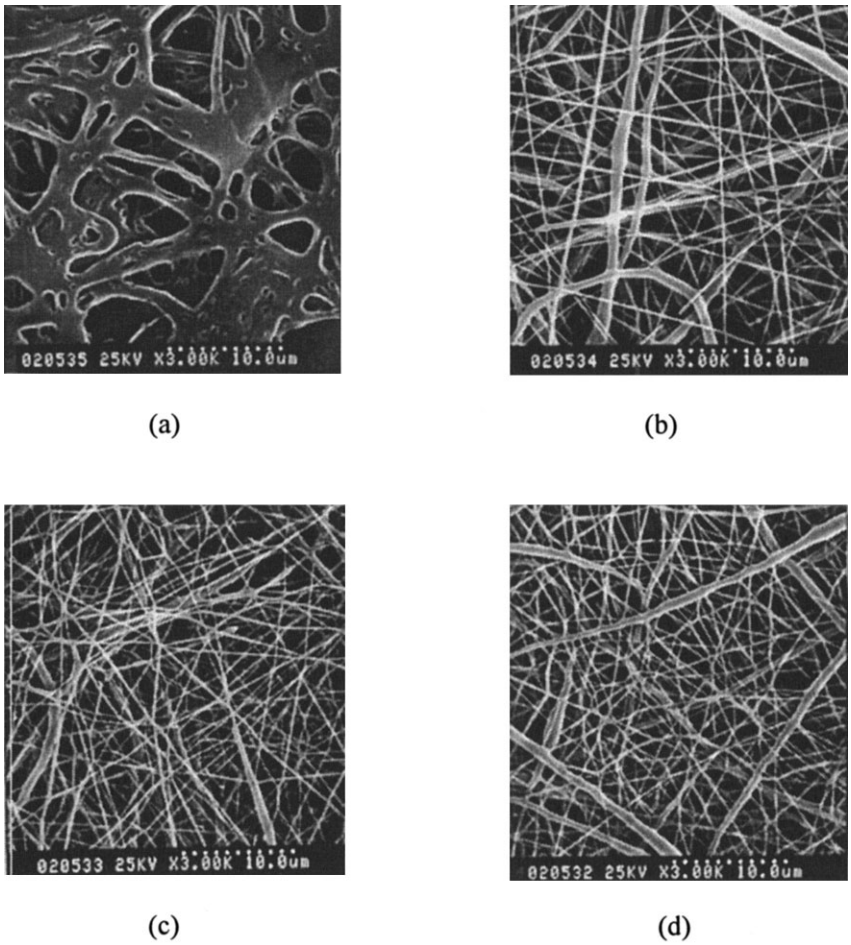


Figure 6 SEM photographs of the electrospun fibers as a function of the distance (cm): (a) 5, (b) 10, (c) 15, and (d) 20.

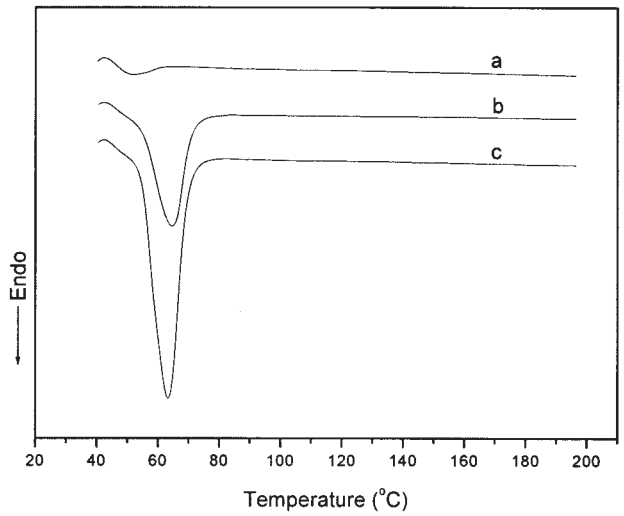


Figure 7 DSC curves of the electrospun fibers with different molar ratios of TMC/ε-CL: (a) 90/10, (b) 70/30, and (c) 50/50.

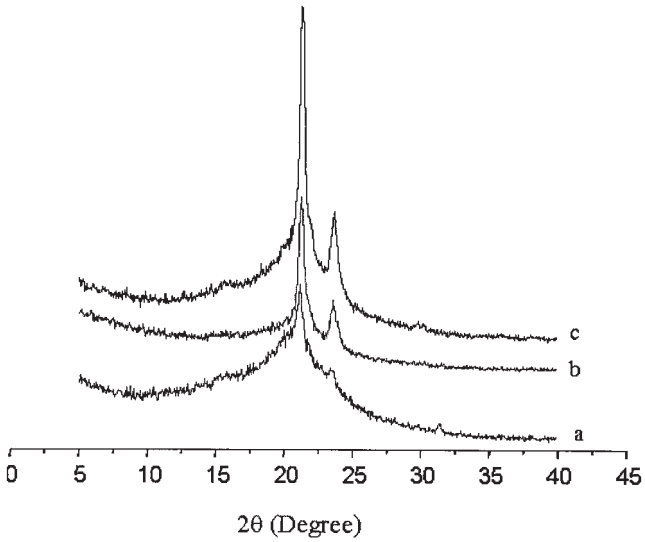
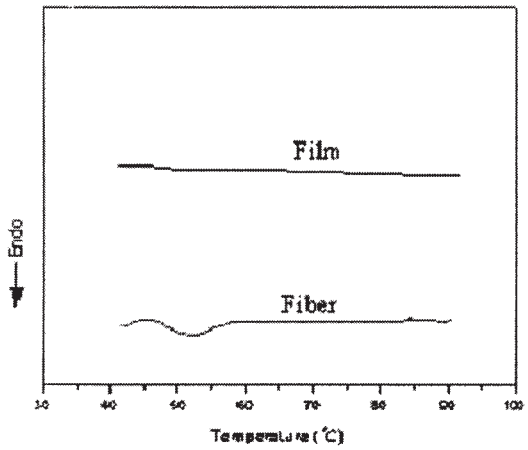
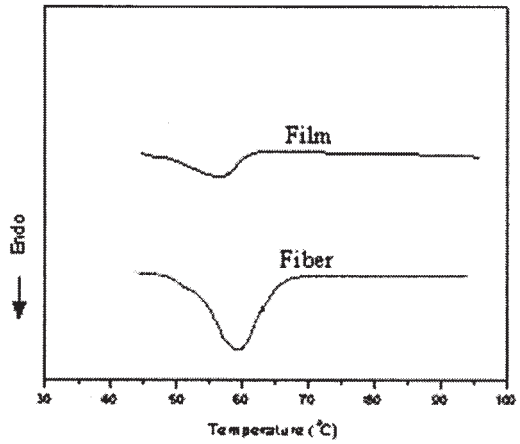


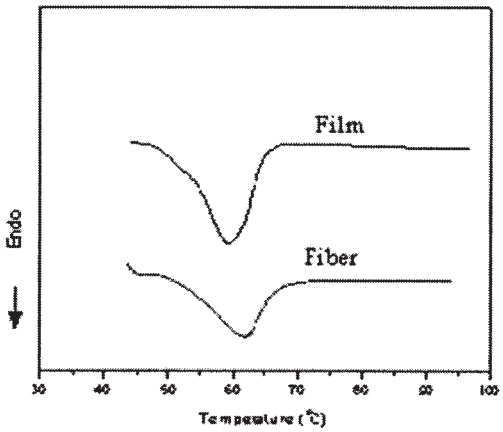
Figure 9 XRD patterns of the electrospun fibers with different molar ratios of TMC/ε-CL: (a) 90/10, (b) 70/30, and (c) 50/50.



(a)



(b)



(c)

Figure 8 DSC curves of the electrospun fibers and the corresponding films with different molar ratios of TMC/ε-CL: (a) 90/10, (b) 70/30, and (c) 50/50.

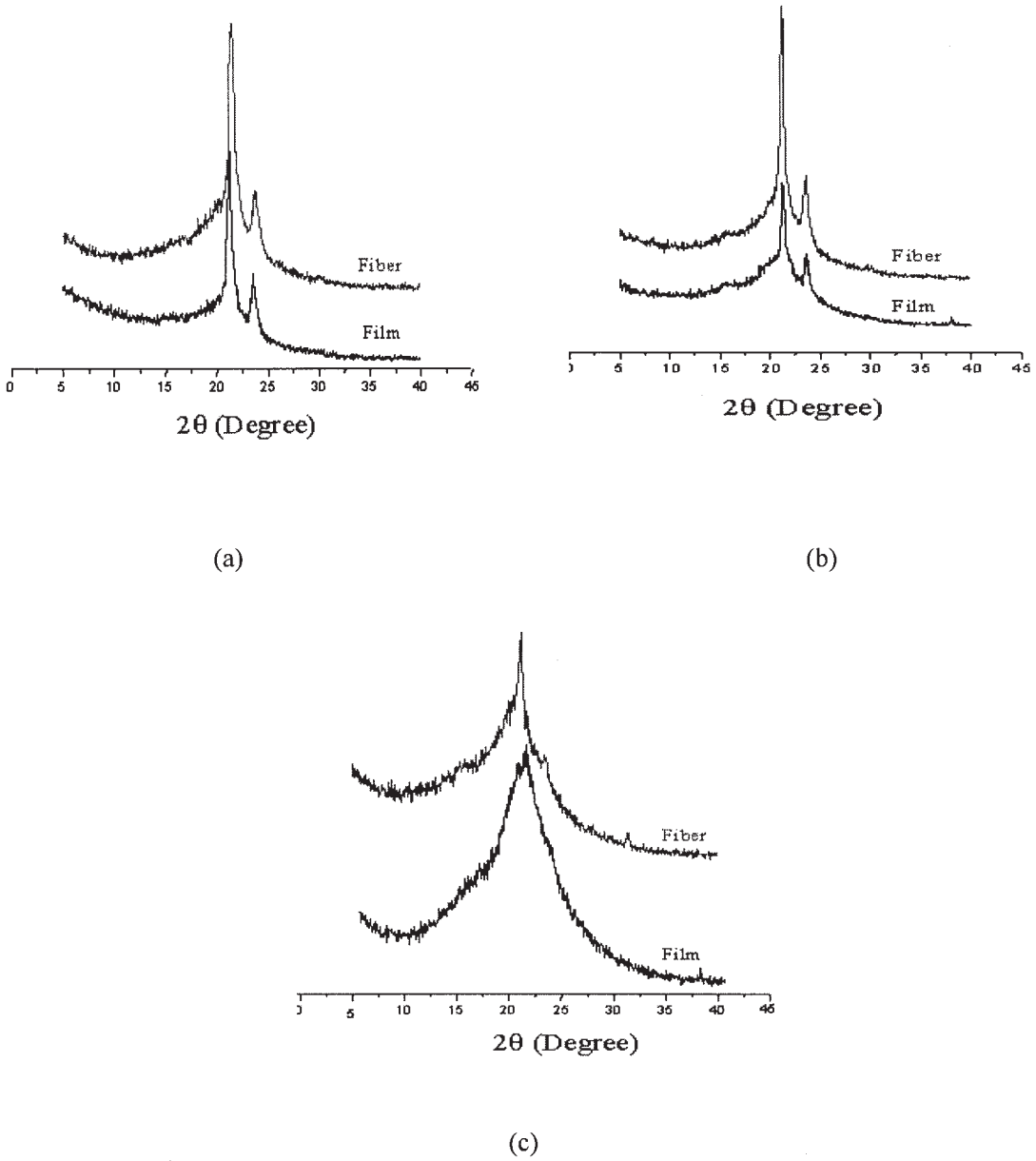


Figure 10 XRD patterns of the electrospun fibers and the corresponding films with different molar ratios of TMC/ε-CL: (a) 90/10, (b) 70/30, and (c) 50/50.

CONCLUSION

Block copolymer fibers of TMC and ε-CL were successfully prepared by the electrospinning technique. DMF, an effective additional solvent, was used in the electrospinning process. SEM photographs demonstrated that the diameter and morphology of electrospun block copolymer fibers depended on the blended solvent molar ratio of MC/DMF, the solution concentration, the strength of the voltage, and the TCD. The DSC and XRD results showed that the crystallinity and melting point of the block copolymer fibers decreased with increasing TMC content in the copolymer. Compared with that of the corresponding films, the crystallinity and melt point of the electrospun fibers obviously increased.

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