Colloid Polym Sci (2008) 286:897–905
DOI 10.1007/s00396-008-1845-7

ORIGINAL CONTRIBUTION

Liquid crystal fibers produced by using electrospinning technique

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Received: 9 August 2007 / Revised: 7 December 2007 / Accepted: 28 January 2008 / Published online: 26 February 2008

Abstract This paper investigates the electrospinning process of liquid crystalline polysiloxane with cholesterol as side chain (LCPC) and the influence on the morphology of the formed fibers by mixing LCPC solution with small-molecule liquid crystal, triethylamine, and poly(ethylene oxide)(PEO). The mechanical properties of single fibers were characterized by a novel approach. The results indicate that, under appropriate conditions, fine liquid crystal fibers can be obtained and the preferable mechanical properties can be achieved, especially after annealing. WXRD was used to investigate the orientation of polymer molecules in the formed fibers, suggesting that strong interaction exists between LCPC and PEO molecule in the resulting composite fibers, and polymer molecular tends to arrange regularly during electrospinning processing. This research work provides a new and facile method of using electrospinning to prepare liquid crystal fibers, which would be useful for designing the related high-performance materials.

Keywords Electrospinning · Electrospun · Liquid crystal · Polysiloxane

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Introduction

One-dimensional (1D) structure with the diameter from several micrometers down to tens of nanometers is of considerable interest for various kinds of applications [1], such as for filter applications [2]. The fiber mats produced from biocompatible polymers can be used as drug delivery platforms [3], tissue engineering scaffolds [4], and reinforcing component in composite systems. In this respect, the fibers produced from polymer molecules with special structure or strong interconnect can be used for high-strength materials [5]. A larger number of synthetic fabrication methods have been demonstrated for generating 1D nanostructure in the forms of fibers, wires, belts, tubes, rods, and spirals from various materials [6–13]. Among these methods, electrospinning approach has many advantages, such as the high fibers production rate, the simplicity of the setup, the unique ability to simultaneously produce nanofibers of different materials in fibrous assemblies, etc. These features make electrospinning highly attractive to both academia and industry [14]. Using this method, a variety of nanofibers was made for applications in energy storage, healthcare, biotechnology, environmental engineering, and defense and security [15]. In the electrospinning process, polymer solution is poured into a syringe equipped with a needle tip. When a high electric field is applied between the tip of the needle and the counter electrode (collector), a thin polymer jet would be initiated from the tip of the needle and travels to the collector as the electrical force reaches a critical value to overcome the surface tension of the polymer solution [16]. The main factors that affect the morphology of the formed fibers are those including characters of polymers, solvent, value of voltage, distance between the tip and the collector, solution viscosity, surface tension, and net charge density induced by electrospinning [17].

Side-chain liquid crystalline polymers have been extensively studied because of their technological potential and scientific challenges. Normally, the side-chain liquid crystalline polymer is composed of polymer backbone, flexible spacer, and mesogenic unit [18]. Among these side-chain liquid crystalling polymers, liquid crystal polysiloxane polymers with cholesterol (LCPC) in the side chain have been investigated actively because the flexible polysiloxane backbone is propitious to improve the flexibility of polymer. Furthermore, cholesterol moiety on the side chain is beneficial to arrange regularly the polymer molecule. These features make LCPC have good optical and mechanical properties and can be used in many fields [19]. The unique structure of LCPC, namely the polysiloxane backbone with cholesteric side group and flexible alkyl spacer, endows this polymer with a relatively low-melt viscosity, and thus, the orientation of the LCPC domain can be easily achieved in elongational flow during processing. These characteristics make LCPC suitable for the preparation of ultra-high-strength fibers and as enhanced component for the fabrication of high-performance engineering plastics [20]. Generally, conventional melt spinning method is employed, and special equipment and processing are required. As a promising alternative, in this paper, we report on the use of electrospinning to conveniently and straightforwardly produce liquid crystal fibers. In this paper, the feasibility of using electrospinning for the preparation of liquid crystal fibers was first examined, and LCPC fibers were prepared by using this new method. Additionally, the factors that influence on the morphology of the formed fibers were investigated, and the mechanical property of the fibers was measured.

Experimental

Materials

Poly(ethylene oxide) (PEO; Mn 1000000) was kindly supplied by Beijing Guoren Yikan Technology. Liquid crystal polysiloxane with cholesterol (LCPC) poly((methyl-(4-propoxybenzoic acid cholesterol ester)siloxane)-co-(methyl-(4-acetoxyphenyl-4-propoxybenzoate)siloxane)) (**1a**) [21] and small molecular liquid crystal (SMLC; 4′-cyanobiphenyl-4-yl 4′-propylbi(cyclohexane)-4-carboxylate) (**1b**) [22] (Fig. 1) were kindly supplied by Professor Tang Hong, Department of Chemistry, and Tsinghua University, China. Chloroform and triethylamine (99% containing 0.5% H_2O) were purchased from Sinopharm Chemical Reagent Co., Ltd., and all materials were used without any further purification.

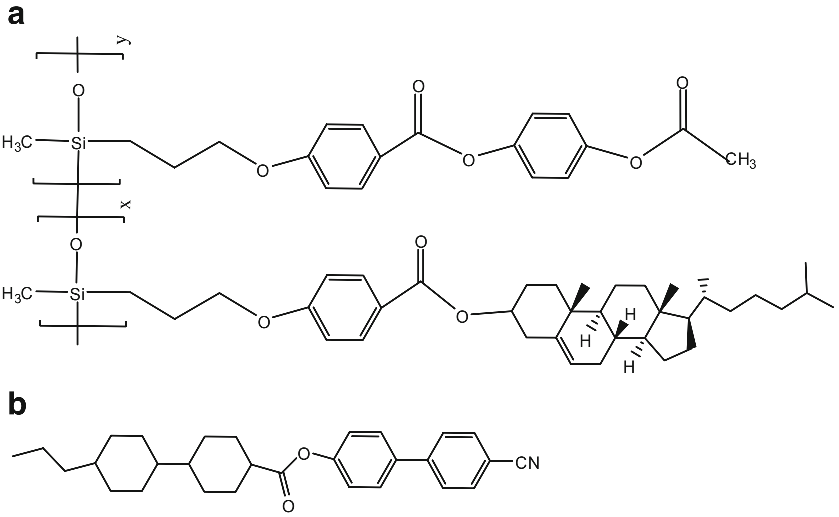
Sample preparation

Chloroform solution of liquid crystal (33%, viscosity is 643cP) was prepared by dissolving 10 g LCPC into 20 g chloroform, resulting in a clear solution at room temperature. PEO solution was prepared by dissolving 2 g PEO into 8 g chloroform to increase the spinnability of LCPC solution. A series of homogeneous mixture was obtained by mixing different volumes of LCPC and PEO solution.

Electrospinning process

The configuration of the electrospinning setup used in this study is shown in Fig. 2, which consists of an adjustable DC power supply (Gamma High Voltage Research, USA) capable of generating DC voltage in a range of 0–40 kV and

Fig. 1 The molecular structures of LCPC (**1a**) and small-molecule liquid crystal (**1b**)



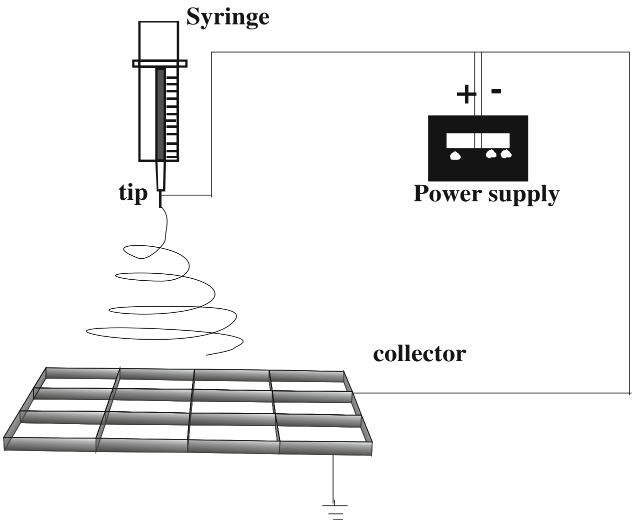


Fig. 2 The setup for the electrospinning

a 20-ml syringe that is connected to a stainless steel needle using a Teflon tube having an inner diameter of around 1.0 mm as the positive electrode. The collection screen is a 15×15 cm copper meshwork placed 20 cm horizontally from the tip of the syringe as the grounded counter electrode. The potential difference between the syringe and the counter electrode used to electrospin the mixed solution is imposed. To compare the properties of LCPC made with other methods with electrospinning process, fibers were also fabricated by drawing the same mixed solution with a needle without voltage. In addition, a casting film was also obtained by casting the same mixed solution with a blade. The obtained specimens were dried in a desiccator for 24 h.

Characterization

The morphology of the fibers collected on the meshwork on the glass substrates was observed under cross-polarized light using a polarized optical microscope (Olympus, Tokyo, Japan, ×10 magnification). Wide-angle X-ray diffraction (WAXD) studies of samples were conducted using a MAC Science X-ray unit operated at 35 kV and 30 mA with Cu K_α radiation and scan from 0° to 40° with a scan speed of 4°/min. The thermal behavior of the formed fibers was measured with a Shimadzu DSC60 differential scanning calorimeter (DSC, Kyoto, Japan) at a heating scan rate of 10 °C/min. Solution viscosities of polymer solutions were determined by a rheometer (DV III, Brookfield Co., USA) at 25 °C with a SH47 spindle at 80 rpm. Scanning electron microscopy measurements were carried out on various as-spun and heat-treated fibers using a Hitachi S-800 microscope operated at 20 kV. All samples were coated using a gold sputter coater.

Mechanical characterization

Mechanical characterization of the prepared fibers was performed by employing the setup built by ourselves with 500 mN load range and 50 nN load resolution, as shown in Fig. 11a. In this study, the specimen was prepared in the following way. First, a white paper template was cut as shown in Fig. 11b, and double-side tapes were glued onto the top and bottom areas of one side. Then, the well-aligned fibers were glued on the template just like the sketch map in Fig. 11b. Finally, the template adhered with fibers was glued onto both sides of the apparatus, and the template was put along the vertical lines before measuring. The tensile tests were performed under a crosshead speed of 10 mm/min at room temperature. Average Young modulus was calculated using the equation: $E = \frac{\Delta\sigma}{\Delta\varepsilon}$ where E is the Young modulus, σ is the representation of stress, and ε is the representation of strain.

Results and discussion

The pure LCPC solutions are not suitable for producing electrospun fibers, probably due to the rigid structure of liquid crystal (Fig. 1) and the strong tendency to form aggregation after the evaporation of solvent. In this work, various preparation conditions, including different solvents, different concentrations, different voltages, and different distance between the syringe and the collector were used, but no fibers or only short and beaded fibers were produced. Figure 3 displays the typical images of the electrospun materials from pure LCPC with different concentrations and different solvents. It is reported that the solution concentration, viscosity, surface tension, and net charge induced by the electrospinning are the main factors that influence the formation and the morphology of fibers prepared by electrospinning method. Therefore, to obtain uniform and well-defined liquid crystal fibers by electrospinning, the following experiments with the focus of adjusting the rigid property of liquid crystal molecule were performed.

Effect of small liquid crystal molecule

SMLC **1b** was first chosen to change the solution viscosity and the electrospinnability of LCPC solution. The pure LCPC solution (33% in $CHCl_3$) has a viscosity of 643 cp. With the addition of the molecule **1b** to LCPC solution, the viscosity of the resulting mixture decreases gradually. For example, the LCPC solution that contains 5%, 7.5%, and 10% molecule **1b** have a viscosity of 567, 507, and 456 cp, respectively. Indeed, compared to the pure LCPC solution, the spinnability was increased considerably when

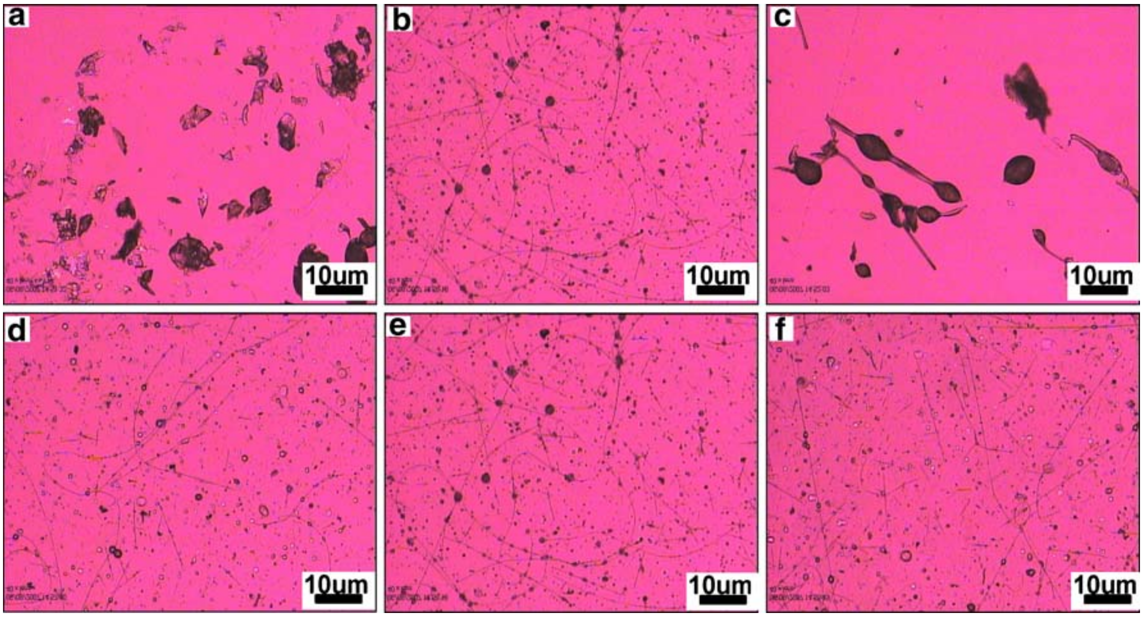


Fig. 3 Optical polarized photographs of the formed fibers using different LC concentrations (dissolved in $CHCl_3$), **a** 20%, **b** 33%, and **c** 40%, and different solvents used to dissolve LC polymer, **d** CH_2Cl_2, **e** $CHCl_3$, and **f** CH_2ClCH_2Cl

a little amount of molecule **1b** was added, although there are still some beads on the resulting fibers (Fig. 4b–d). The birefringence of the formed fibers is still apparent, indicating the presence of chain orientation and/or crystallization of LCPC to certain extent. It is found that the morphology and the birefringence of the resulting fibers are strongly dependent on the amount of the added molecule. The more molecules **1b** were added, the fewer beads were found in the resulting fibers. However, the diameter of the fibers was increased from 1 to 10 μm with the increasing content of small-liquid crystal. When 5% compound **1b** was used in polymer solution, relative fine fibers with a diameter of about 1 μm were obtained. Nevertheless, the bead and the friable problems in the fabricated fibers still exist. The possible reason is the inherent rigidity of LCPC and the lower plastic effect of small molecule.

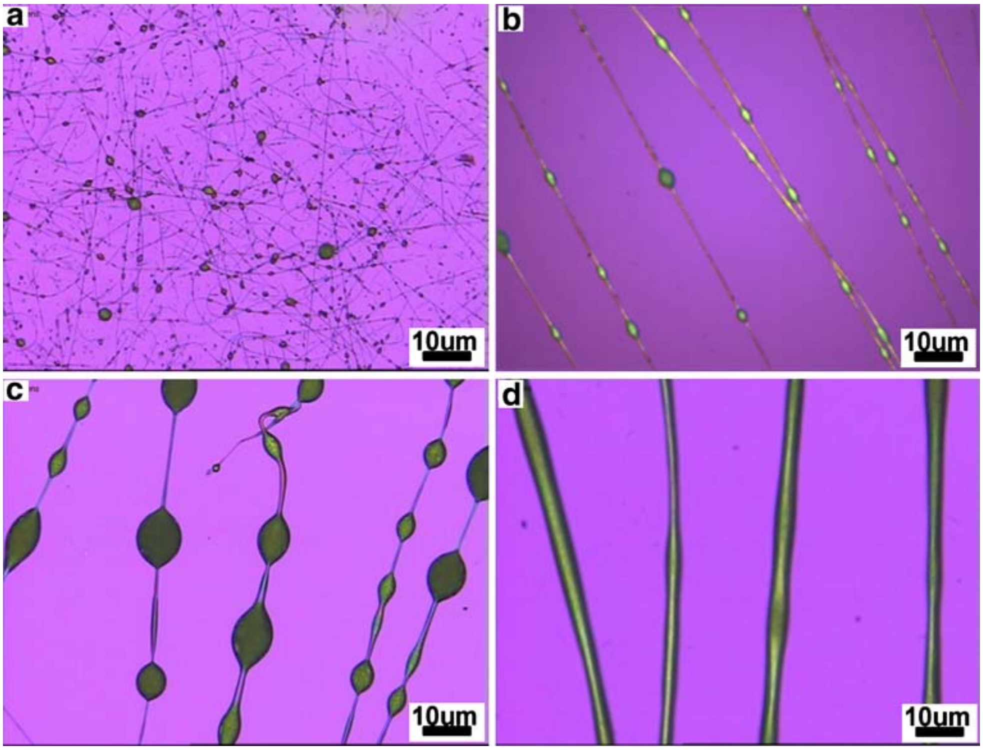


Fig. 4 Optical polarized photographs of the formed fibers by using pure LCPC solution (**a**) and different LCPC mixture containing **b** 5%, **c** 7.5%, **d** 10% SMLC

Effect of triethylamine molecule

Net charge density carried by the jet during the electrospinning process is an important parameter for the formation of well-defined fibers and is affected by the conductivity of the used solution. Generally, higher electrolyte concentration will result in higher conductivity and thus fine spinnability. However, too high electrolyte concentration will reduce solution viscosity and spinnability. To get desired fibers, the validity of adding appropriate content of triethylamine (containing 0.5% H_2O) was checked. In this case, due to the presence of trace water in the used Et_3N, the Et_3N is protonated to form Et_3NH^+ and serves as an electrolyte. The effect of Et_3N addition on the formation of electrospun LCPC fibers was shown in Fig. 5a–f. It is clearly seen that the birefringence and the morphology of the resulting LCPC fibers were apparently improved when Et_3N was added into LCPC solution. When 0.05 ml Et_3N was added in 5 ml LCPC solution, the diameter of the fibers was reduced from 1.3 to 1 µm. Unfortunately, more addition of Et_3N cannot produce improved results. When the addition of Et_3N exceeds 0.1 ml, a large numbers of beads on the resulting fibers occurred (Fig. 5b–f). Although a little amount of Et_3NH^+ can improve the formation of fiber from LCPC solution, we found that the formed fibers are rather brittle as observed in scanning electron microscopy (SEM; Fig. 9a) and not suitable for mechanical characterization. Interestingly, we also found that when anhydrous Et_3N was added to LCPC solution, the LCPC solution could not be electrospun to produce fibers.

Effect of PEO addition

The negative or not satisfying results described above force us to examine the effect of polymer additives. It is known that high molecular weight of PEO can give rise to higher intermolecular interaction of the polymer in the solution. Therefore, PEO is often used in spinning solution to increase polymer spinnability. In this study, a different amount of PEO was added into LCPC solution, and after stirring 1 h at room temperature, the resulting homogeneous mixture solutions were used for electrospinning process. Compared to the approaches described above, the addition of PEO can dramatically enhance the spinnability of LCPC molecule. Figure 6 displays the effect of PEO content on the morphology and birefringence of the resulting fibers prepared by electrospinning. Obviously, the beads in the fibers were decreased, and the formation of uniform thin fibers was dramatically increased and eventually became smooth fibers with the addition of PEO. Dependent on the ratio of LCPC to PEO in the mixed polymer solution, the diameter of the resulting fibers varies between 0.5 and 2 µm. It is found that, when the ratio of LCPC solution and PEO solution (*v*/*v*) is 20:1, the morphology and birefringence of the produced liquid crystal fibers are the best (Fig. 6b). In agreement with this observation, SEM measurement shows the similar results (Fig. 9b and c).

Effect of the applied voltage

Based on the above-mentioned findings, the effect of the electric field strength on electrospinning process was

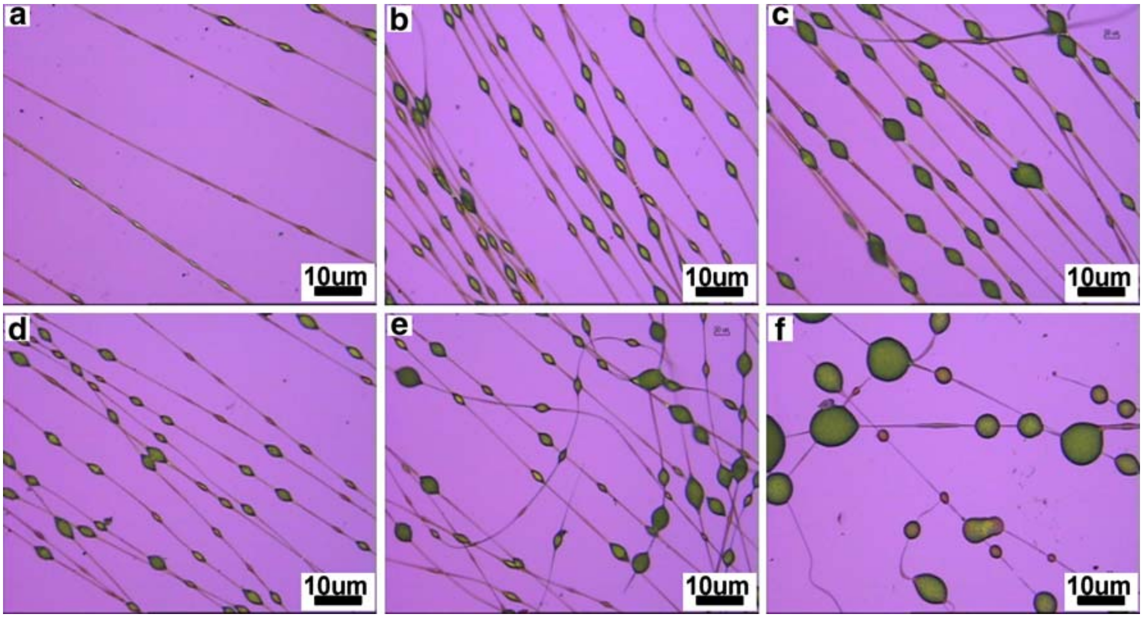


Fig. 5 Optical polarized photographs of the formed fibers by using different contents of Et_3N in the LCPC solution: **a** 0.05 ml, **b** 0.25 ml, **c** 0.45 ml, **d** 0.75 ml, **e** 1 ml, and **f** 1.25 ml

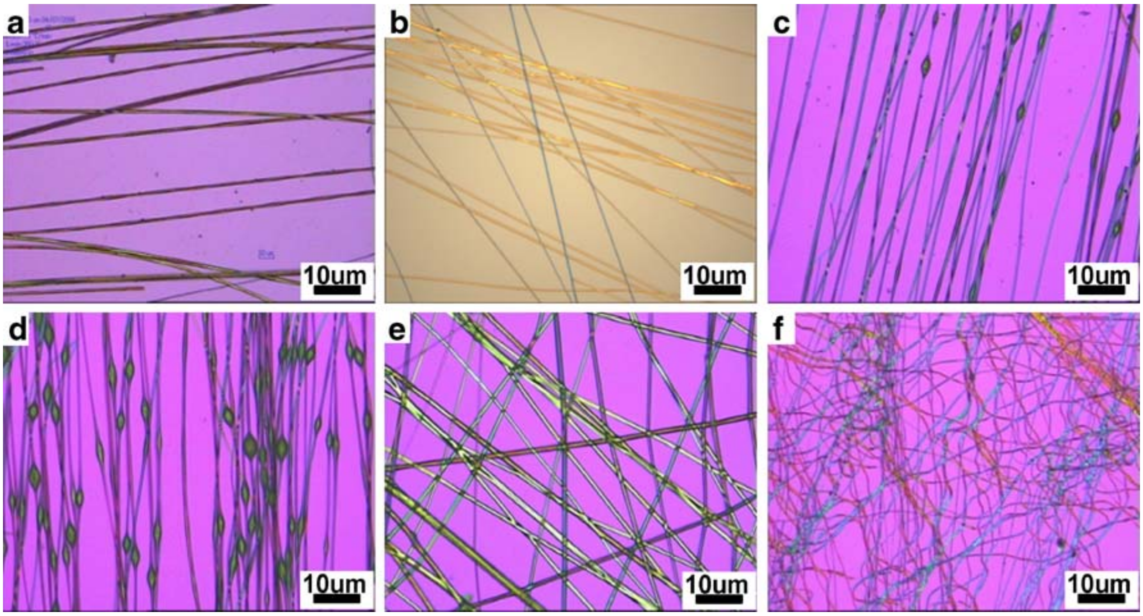
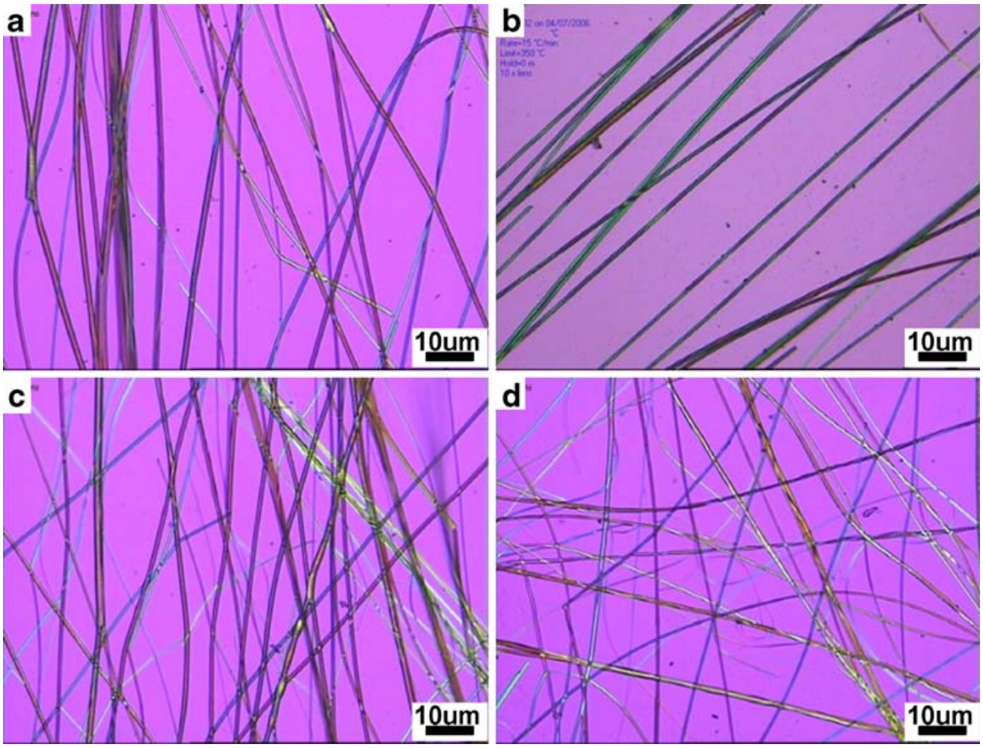


Fig. 6 Optical polarized photographs of the formed fibers by using LCPC/PEO blends with different compositions: **a** 30:1, **b** 20:1, **c** 10/1, **d** 3:1, **e** 1:1, and **f** PEO

investigated in the system of LCPC/PEO (20:1) to obtain fine fibers with controlled diameters. It is known that increasing the electric field strength will enhance the electrostatic repulsive force on the fluid jet that favors the thinner fiber formation. On the other hand, with the increase of the applied voltage, the solution will be removed from the capillary tip more quickly as jet is ejected from Taylor cone, and as consequence, the fiber diameter increases. To get fine desired fibers during the process of electrospinning, appropriate electric field should be put on the tip of the syringe. In our case, a series of experiments were carried out when applied voltage was varied from 12 to 22 kV, and the tip to target distance was held at 20 cm. Optical polarized photographs of the formed fibers under different voltages are shown in Fig. 7. The results indicated that, in the used system, the dependence of the

Fig. 7 Optical polarized photographs of the formed fibers of LCPC/PEO prepared under different voltages: **a** 12 kV, **b** 14 kV, **c** 18 kV, and **d** 22 kV



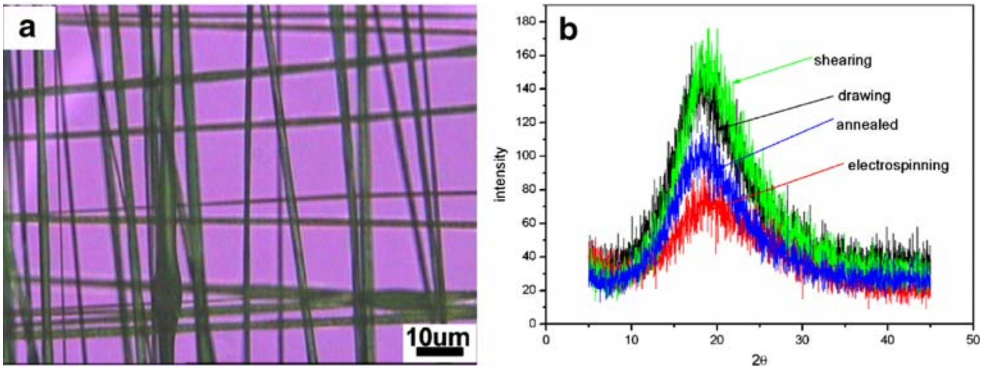


Fig. 8 **a** Optical polarized photographs of the drawn fibers, **b** WXRD patterns of the drawn, electrospun, annealed fibers, and shear-induced film

diameter of the formed fibers on the applied voltage is not strong; only a slight increase in fiber average diameter with increasing applied electric field was detected. The fibers produced under the voltage of 12, 14, 18, and 22 kV exhibits an average diameter of 1.1, 0.9, 1.2, and 1.1 μm, respectively. A narrow distribution of fiber diameters was observed at a voltage of 14 kV, while broad distribution of the fibers diameter was obtained at other applied voltages (12, 18, and 22 kV). Beyond the range between 12 to 22 kV, Corona discharge was observed, making electrospinning impossible.

Structure characterization

The optimized preparation conditions (system, LCPC/PEO=20:1; voltage, 14 kV; distance, 20 cm) were employed to produce liquid crystal fibers, and the structure of the resulting fibers was characterized using different methods. The LCPC molecule orientation induced by electrospinning, and the interaction between PEO molecules and the LCPC molecules were studied by WAXD, as shown in Fig. 8b. To compare the degree of the LCPC molecule orientation in the resulting fibers after the electrospinning process, fibers were also fabricated by drawing the same mixed solution with a needle without voltage (Fig. 8a). In addition, a casting film was also obtained by casting the same mixed solution with a blade. The obtained specimens were dried in a desiccator for 24 h and then investigated with WXRD (Fig. 8b).

If the LCPC and the PEO molecules have poor interaction or no interaction in the blends, each component has its own crystal region in the blend fibers, and X-ray diffraction patterns should express as simply mixed patterns of LCPC and PEO with the same ratios as those for mechanical blending [23]. In fact, the single peak in these graphs in Fig. 8b indicated that strong interaction occurred

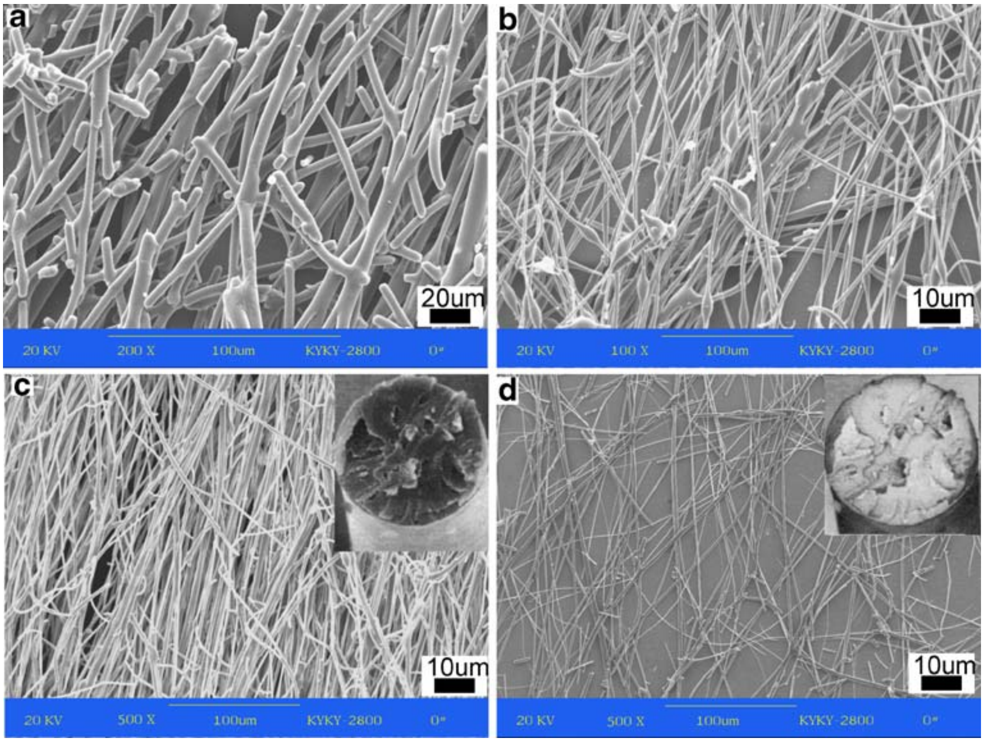


Fig. 9 SEM images of the fibers. **a** 0.05ml $(Et)_3N$ added into 5 ml chloroform solution of LCPC, **b** 5% small liquid crystal molecule added into 5 ml chloroform solution of LCPC. **c** LCPC/PEO=20:1; **d** LCPC/PEO=20:1 annealed at 70 °C for 20 min. *Inset* is the cross-section of the produced fibers

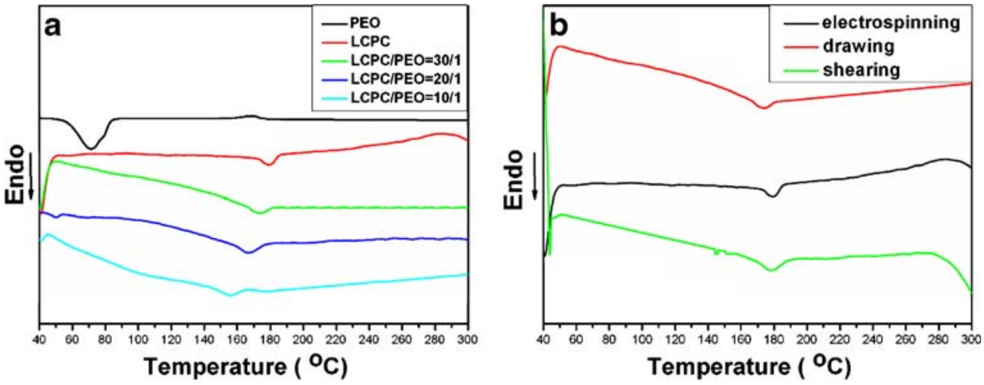


Fig. 10 DSC thermogram of **a** different contents of PEO, **b** different processing methods of LCPC/PEO=20:1

between LCPC and PEO molecule in the blends. In agreement with this observation, the SEM measurement also revealed no evidently phase separation between LCPC and PEO, and no apparently skin-core structure of the fibers (Fig. 9c, d). The crystal intensities of LCPC and PEO blends decreased as the processing method used shifted from shear-induced to electrospinning. A liquid crystal molecule that tends to arrange regularly uses the shear-induced method has been reported in many places [24]. The crystal intensity of the fibers produced by elctrospinning is relatively lower than that by conventional drawing method, probably due to the very fast evaporation of the solvent during the process of high-speed electrospinning, so that the liquid crystal molecules do not have enough time for molecular organization. Interestingly, after annealing of electrospun fibers at 70 °C for 20 min, the intensity of WXRD of the treated fibers increases nearly 50% (Fig. 8b), indicating that the annealing process induces the further arrangement of polymer chains in the fibers.

The DSC thermograms of the different fiber samples were presented in Fig. 10. Pure PEO exhibited a relatively large endothermic peak at about 70 °C (Fig. 10a). LCPC have no apparent melt peaks but have a clear temperature (T_m) at about 180 °C. The T_m was reduced from 180 °C to 155 °C when the ratio of LCPC/PEO decreased from 30:1 to 10:1. The T_m changed little when different methods are used to produce the fibers from the mixture of LCPC/PEO= 20:1; the T_m of the resulting fibers remains nearly the same (Fig. 10b).

Mechanical properties of the prepared liquid crystal fibers

Because of the small diameter of the electrospun fibers, the mechanical properties are usually measured only for mats or yarns rather than for individual fibers [25]. The mechanical properties measured in this way depend strongly on fiber orientation within the material, bonding between fibers, and slip of one fiber over another. Taken

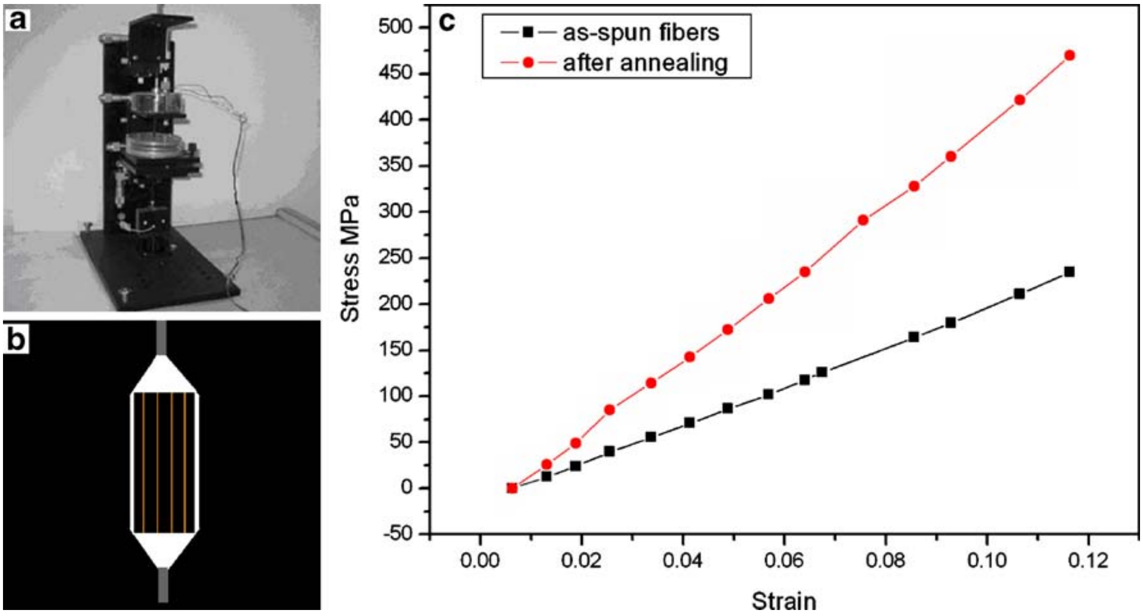


Fig. 11 Mechanical properties measurement: **a** the setup, **b** the sketch map of fibers substrate, and **c** the measured strain-stress curve of the formed fiber

together, these effects can easily mask the material-specific properties of the nanofibers that compose the mat or yarn. Furthermore, the modulus and strength of the materials cannot be calculated accurately due to the difficulty in determining the cross-sectional area of the mat or yarn due to porosity. Therefore, knowledge of mechanical properties of single fibers is desirable as a starting point in optimization of electrospinning conditions for specific fiber mechanical properties as well as for the design of useful materials composed of these fibers [26]. Using the apparatus as shown in Fig. 11a, the prepared sample like that in Fig. 11b can be used to calculate mechanical properties of single fibers accurately. Figure 11c shows the strain stress curves of the prepared liquid crystal fiber. The fact that the curves fit the line well demonstrates that the as-spun fibers from LCPC/PEO=20:1 and annealed fibers are flexible. The Young modulus of as-spun fibers is 2 GPa. Consistent with the WXRD results, after annealing, the Young modulus of the treated fibers reaches 3.98 GPa, which is nearly doubly higher compared to that of the as-spun fibers.

Conclusion

Electrospinning technique is a straightforward, convenient, and inexpensive method of preparing polymer fibers at nano- and submicron scales. Due to liquid crystal, nanofibers have their unique mechanical and optical properties; using electrospinning to prepare liquid crystal fibers seems to be a promising approach. By using this method, polymer fibers of polysiloxane liquid crystal (LCPC) were successfully fabricated with diameters ranging from 1 to 10 μm. Although the pure solution of liquid crystal polymer is not suitable for electrospinning, the spinnability of the polymer solution was enhanced dramatically by the addition of additive molecule like triethylamine or PEO. Compared to small molecule, macromolecule PEO is most effective to influence the formation of LCPC fibers. When the ratio of 20 of LCPC/PEO was used, well-defined smooth was achieved by electrospinning. WXRD measurements indicated that the orientation of the polymer molecular chains within the electrospun fibers occurred during the electrospinning process but was relatively lower than that prepared by conventional drawing process. The probable reason is that the rapid evaporation of solvent during the electrospinning process makes it difficult for molecules to organize themselves. Annealing under appropriate conditions could induce further arrangement of polymer chains in fiber and hence improve the mechanical properties remarkably. Young modulus of single fiber was measured by a designed method, and the strain–stress curve indicated that the prepared fibers were elastic and is promising as high-performance fibers.

To the best of our knowledge, this is the first report that describes the fabrication of side-chain polysiloxane liquid crystalline fibers by using electrospinning technique. Using LCPC as model liquid crystal, this research work not only confirms the feasibility of using electrospinning for the preparation of liquid crystal fibers but also provides a new method of preparing liquid crystal fibers, which would be useful for designing the related high-performance materials.

Acknowledgment The authors thank the National Science Foundation of China (20473044, 20533050 and 50673048) and the 973 Program (2006 CB806200) for the financial support.

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