8886 *Macromolecules* **2006,** *39,* 8886−8888

Highly Oriented Electrospun Fibers of Self-Assembled Inclusion Complexes of Poly(ethylene oxide) and Urea

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Received November 3, 2006
Revised Manuscript Received November 22, 2006

Introduction. Electrospinning is a technique that allows production of polymeric fibers with diameters ranging from nanometers to a few microns and thus with an inherent high surface-to-volume ratio.[1−3] These fibers are finding potential applications in drug delivery, tissue engineering, membranes, nanocomposites, etc. While electrospinning was initially used to prepare disordered mats, it is now possible to produce aligned fibers using various collectors.[1,2,4] However, it is important to control not only the macroscopic alignment of fibers but also their molecular orientation because it strongly influences most mechanical, optical, and electrical properties of polymers.[5] Conventional spinning methods allow the production of fibers with a very large molecular orientation, leading to ultrahigh modulus, but these are typically several microns or tens of microns in diameter.[5] In contrast, the molecular orientation is generally modest in electrospun nano- or microfibers.[2,6−8]

An independent method for preparing highly structured materials is the self-assembled formation of inclusion complexes (IC) of polymeric guests inside a small molecule host matrix. For instance, poly(ethylene oxide) (PEO) has been complexed with urea,[9−11] mercuric chloride,[12] cyclodextrins,[13] etc. In their urea inclusion complexes, polymers are packed in one-dimensional channels constructed from an essentially infinite three-dimensional network of hydrogen-bonded urea molecules.[14] The polymer chains are thus highly extended at the molecular scale, but they are not aligned at the macroscopic level.

In this work, we have used electrospinning to prepare highly oriented and well-aligned fibers of the self-assembled inclusion complex between urea and high molecular weight (400 000 g/mol) PEO. The IC was prepared by a cocrystallization method, and the resulting 20% w/v suspension was electrospun, under a 17 kV potential difference, onto a target composed of two metallic counter electrodes separated by a 5 cm gap. The details of the sample preparation, electrospinning conditions, and sample characterization are provided in the Supporting Information. To our knowledge, it is the first time that such IC fibers were prepared and characterized.

Results and Discussion. Figure 1 shows a crossed-polarized optical micrograph of a sample obtained by electrospinning the PEO−urea IC suspension. Cylindrical fibers having a 1−2 μm diameter are observed, clearly demonstrating that the PEO−urea inclusion complex can form fibers in spite of its rather poor film-forming properties. The fibers do not show any beading and are mostly continuous over the 5 cm gap between the counter electrodes. A few breakage points can nevertheless be observed, most likely because of a high level of crystallinity (vide infra) that makes the material brittle. The fibers transmit light when observed under crossed polarizers, indicating that they possess a significant level of molecular orientation.

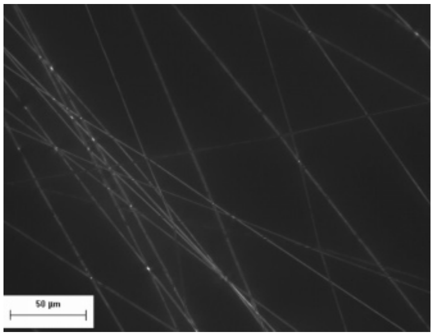

Figure 1. Crosssed-polarized optical micrograph of electrospun fibers of the PEO−urea inclusion complex.

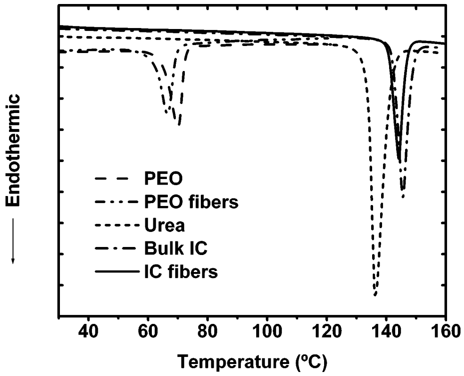

Figure 2. DSC thermograms of the bulk PEO, urea, and inclusion complex (IC) as well as those of the pure PEO and PEO−urea IC electrospun fibers.

For comparison, control PEO fibers electrospun under similar conditions had a diameter in the 400−700 nm range. This significant difference can be explained by the large concentration difference necessary to reach a similar viscosity, 5% for pure PEO vs 20% for the inclusion complex. It is well accepted that higher concentrations lead to fibers with larger diameters.[15] Interestingly, thermogravimetric analysis (see Supporting Information) revealed a 3:1 urea:PEO mass ratio, thus suggesting a similar PEO concentration in both solutions. This corresponds to a ~9:4 urea:PEO molar ratio, in agreement with the reported value for this complex.[9]

Figure 1 shows that fibers can be electrospun, but it does not establish that they are composed of the inclusion complex. Figure 2 compares the DSC thermograms of the bulk PEO, urea, and IC as well as those of the pure PEO and IC electrospun fibers. A single endothermic peak, attributed to the melting of the crystalline phase, can be observed for all samples. The melting temperature of the bulk inclusion complex is found at 146 °C, clearly above those of pure PEO (69 °C) and pure urea (136 °C) and in agreement with the literature value.[11] The melting peak is observed at ~144 °C for the fibers electrospun from the IC suspension, very close to that of the bulk sample. It is thus a good indication that the fibers are truly composed of the inclusion complex. The melting temperature difference between the fibers and bulk IC is similar to that (1−3 deg) observed between the fibers and bulk of pure PEO.

These conclusions are supported by infrared spectroscopy measurements (see Supporting Information). Indeed, the infrared spectra of the bulk IC and the electrospun IC fibers are very

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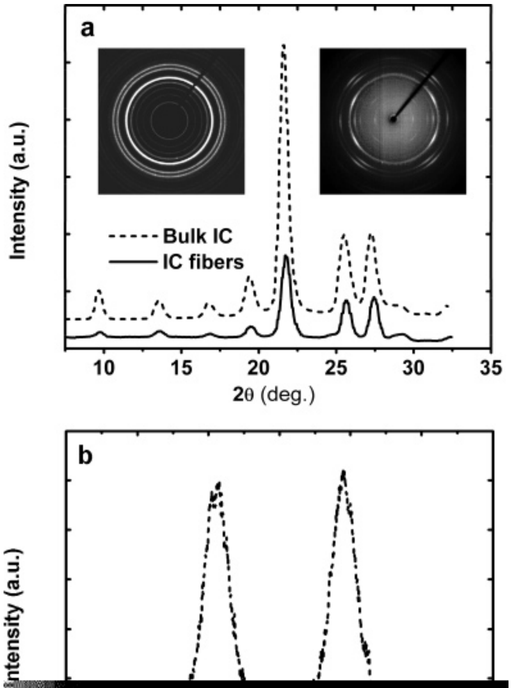

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Figure 3. (a) Wide-angle X-ray diffraction 2θ diagrams for the bulk and electrospun fibers of the PEO−urea inclusion complex (IC) and two-dimensional diffraction patterns of bulk IC (left inset) and electrospun fibers (right inset). (b) Azimuthal profile of the WAXD pattern for electrospun PEO−urea IC at $2\theta = 21.6°$.

similar but are markedly different from those of pure PEO and urea. Tonelli et al. studied the infrared spectra of bulk PEO−urea IC and suggested that the urea bands are modified by the new hydrogen-bonding network and that PEO chains adopt a more extended conformation than the usual trans−gauche−trans (TGT) conformation found in pure crystalline PEO around the O−C−C−O linkages.[11]

It can be observed in Figure 2 that the thermograms of the bulk IC and of the fibers do not present any significant transition at the melting temperatures of either pure PEO or urea. This indicates that the sample preparation procedure removed most if not all free urea and PEO from the inclusion complex. In addition, thermogravimetric analysis (see Supporting Information) of the fibers shows that the electrospinning process does not alter the composition of the inclusion complex. The crystallinity level could not be determined quantitatively because the melting enthalpy of the 100% crystalline IC is not known. However, the absence of a glass transition temperature and of a crystallization exotherm suggests that the degree of crystallinity is large for both IC samples.

The two-dimensional WAXD patterns and 2θ diagrams obtained for the bulk and electrospun IC are shown in Figure 3a. Very similar 2θ diagrams can be observed, indicating that the crystalline structure remains essentially the same after electrospinning. Both samples show intense and narrow diffraction peaks and no significant amorphous halo, further suggesting a high crystallinity level. It is noteworthy that the most intense diffraction peaks of pure PEO (23.5°) and urea (22.5°) are not observed in the X-ray diagrams, confirming that no residual pure (crystalline) products are present.

Table 1. WAXD Characterization of the Degree of Orientation for PEO−Urea Inclusion Complex Electrospun Fibers

2θ peak (deg)	21.6	25.5	27.2
fwhh[a] (deg)	13	13	13
$\langle P_2(\cos\varphi)\rangle_c$	0.90	0.91	0.85
plane attribution[b]	102; 201; 012; 021	210; 120	211; 121

[a] Full width at half-height of the diffraction peaks in the azimuthal scan. [b] Calculated based on the unit cell data reported in ref 9.

In addition to providing structural information, X-ray diffraction can be used to probe the molecular orientation in polymers. While a uniform azimuthal intensity distribution is observed for the bulk IC (left inset of Figure 3a), the electrospun fibers present a highly inhomogeneous diffraction intensity distribution (right inset). The azimuthal scan for the $2\theta = 21.6°$ diffraction plane of the electrospun fibers is shown in Figure 3b. A narrow peak with a full width at half-height (fwhh) of ~13° can be observed because of the strongly anisotropic distribution of the crystals in the fibers. Similar values are obtained for the other intense 2θ diffraction peaks, as shown in Table 1.

The second-order moment of the orientation distribution function of the c-axis, $\langle P_2(\cos\varphi)\rangle_c$, was calculated to quantify the molecular orientation in the fibers. Because the (00l) reflection plane is not available, the orientation function was calculated from other reflection planes, assuming uniaxial symmetry, as

$$\langle P_2(\cos\varphi)\rangle_c = \frac{2}{3\cos^2\sigma - 1}\,\frac{3\langle\cos^2\varphi\rangle - 1}{2} \tag{1}$$

where σ is the angle between the normal to the (hkl) plane and the c-axis. Because the assignment of the (hkl) is not unique for most diffraction peaks, the azimuthal angle of the peak maximum was taken as σ. The average $\langle\cos^2\varphi\rangle$ was calculated by integrating the intensity of specific 2θ diffraction peaks along the azimuthal angle, φ, as

$$\langle\cos^2\varphi\rangle = \frac{\int_0^\pi I(\varphi)\cos^2\varphi\,\sin\varphi\,d\varphi}{\int_0^\pi I(\varphi)\sin\varphi\,d\varphi} \tag{2}$$

Table 1 shows that an average $\langle P_2(\cos\varphi)\rangle_c$ value of 0.89 is obtained for the electrospun fibers of the inclusion complex. This unusually large molecular orientation is very close to the maximum theoretical value of 1 that would be obtained for a sample perfectly oriented along the reference direction.[5] In contrast, a $\langle P_2(\cos\varphi)\rangle_c$ value of ~0 would be obtained for an isotropic sample, as for the bulk IC.

To the best of our knowledge, it is the first time that such high orientation level is reported not only for self-assembled inclusion complexes but also for polymers in electrospun fibers. The largest quantitative values we have found in the literature were obtained by Reneker and Cheng et al. for nanocomposite fibers of poly(acrylonitrile) (PAN) and multiwalled carbon nanotubes (MWCNT).[16] $\langle P_2(\cos\varphi)\rangle$ values of 0.62 and 0.90 were obtained for the PAN and MWCNT, respectively. It should be noted that a rotating collector was used in these experiments and imposed an ~8.4 m/s linear velocity on the fibers. It was shown for pure PAN fibers that increasing the take-up speed from 0 to 9.84 m/s increases the orientation function from 0 to 0.23,[7] partly because of better macroscopic alignment but also because of drawing. In contrast, the PEO−urea IC fibers prepared in this work were collected between two static metallic rods, ensuring that no force acted on the fibers apart from the electrospinning process itself. Low molecular orientation values were observed for electrospun fibers in most other studies. For instance, Dersch et al. reported no orientation in poly(lactic acid) fibers,[2] while a modest orientation function of 0.092 was found in electrospun silk fibroin.[8]

It is worth noting that the orientation functions of Table 1 were calculated assuming that all fibers are perfectly aligned during the WAXD measurements, although Figure 1 shows that this is not the case. The values obtained here are thus low estimates of the molecular orientation. In future work, we will attempt determining the orientation of single fibers, thus avoiding the uncertainties due to imperfect fiber alignment.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), the Fonds Québécois de Recherche sur la Nature et les Technologies (FQRNT), and the Canada Foundation for Innovation (CFI) is acknowledged. We also thank S. Essiembre for his technical assistance.

Supporting Information Available: Details of the sample preparation, electrospinning conditions, and sample characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0625408