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Electrospinning as a New Method for Preparing Pure Polymer Complexes

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ABSTRACT: We demonstrate that electrospinning is a simple and efficient method of preparing pure polymer complexes. Such complexes are often difficult to prepare by conventional methods because of the kinetically favored crystallization of small molecules. As proof-of-concept examples, nanofibers of the complexes of poly(ethylene oxide) with hydroquinone and sodium thiocyanate (NaSCN) were produced. Infrared spectroscopy, X-ray diffraction, and differential scanning calorimetry were used to confirm the purity of the electrospun complexes and to establish the general applicability of this new strategy. It is concluded that the fast solvent evaporation is the critical factor enabling pure complex formation. This work should enable a better study of host/guest polymer complexes, for instance in the context of ionic conduction in the solid state.

Introduction

Electrospinning is a technique that allows fabrication of continuous polymer fibers with small diameters typically in the range of a few hundred nanometers. These nanofibers are already applied in many technological areas where a high surface-to-volume ratio is desirable, for instance in wound dressing, high-performance filters, drug delivery, and sensor technology.[1] The intense electric field, elongational forces, and rapid solvent evaporation that occur during the electrospinning process sometimes lead to unusual or metastable crystalline forms of polymers. For instance, electrospinning poly(vinylidene fluoride) promotes the formation of β-phase crystals, whereas other methods primarily yield α and γ crystals.[2] The electrospinning of nylon-6[3] and poly-1-butene[4] has also been shown to lead to unusual or metastable structures. Electrospinning could therefore become a simple yet powerful means of preparing desirable structures if it could be performed in a reliable and predictable way. This is particularly true for systems where there is a kinetic competition between the crystallization of different compounds or polymorphs.

Polymer complexes with small organic or inorganic molecules, which are self-assembled through electrostatic forces, hydrogen bonding, or van der Waals interactions, constitute a class of materials that suffers from such a kinetic competition.[5] Indeed, many polymer complexes present a phase diagram with an incongruent melting point and can only form partially by melt-cooling or cocrystallization because of the much faster crystallization of the small molecule (or of another stoichiometric complex).[6,7] In a recent paper, we have observed that electrospinning can be used to prepare pure samples of the β complex between poly(ethylene oxide) (PEO) and urea.[8] In contrast, conventional methods such as solvent casting, melt-cooling, and cocrystallization all lead to various mixtures. It was revealed that the pure β complex is thermodynamically stable rather than metastable as suggested in previous studies.[9] The preparation of pure complexes by electrospinning could therefore yield much deeper insight into their phase behavior.

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In this work, we demonstrate that electrospinning is widely applicable to the preparation of thermodynamically stable but kinetically prevented polymer complexes. As proof-of-concept examples, pure fibers are prepared and characterized for two peritectic PEO complexes: the PEO−hydroquinone complex assembled through hydrogen bonds and the PEO−NaSCN complex held by electrostatic interactions. In both cases, pure samples could not be obtained by melt-cooling, cocrystallization, or solvent casting but were readily prepared by electrospinning.[7,10]

Experimental Section

Sample Preparation. PEO with an average molecular weight of 400 000 g/mol (Scientific Polymer Products) and NaSCN (Fisher Scientific) were used as received and stored under vacuum. Hydroquinone (Fisher Scientific) easily degrades when exposed to light, oxygen, or humidity and becomes pinkish at the onset of degradation. When necessary, it was recrystallized twice in acetone to form a 1:1 hydroquinone:acetone complex, and acetone was evaporated under reduced pressure. Pure hydroquinone was stored under a constant nitrogen flow and shielded from light with an aluminum foil. Methanol (Fisher Scientific) was used without purification. Unless specified otherwise, solutions were prepared by dissolving 0.2 g of PEO and either 0.2255 g of hydroquinone or 0.1226 g of NaSCN in 5.5 mL of methanol. This leads to solutions with 3.6% m/v of the polymer and a 2:1 or 3:1 PEO:host stoichiometry for the hydroquinone and NaSCN complexes, respectively. For comparison, electrospinning was also conducted using solutions of the PEO−hydroquinone system with other PEO w/v fractions (0.5%, 1%, 5%, and 7%), always maintaining the appropriate stoichiometry.

The solutions were introduced in a 5 mL glass syringe equipped with a flat-ended needle. A voltage of 15 ± 2 kV was applied on the needle using a CZE 100R high-voltage power supply (Spellman High Voltage Electronics) while a −2 kV potential was imposed on a two-rod collector with a 3 cm gap. The working distance between the collector and the needle was 15 cm, and the flow rate was adjusted using a PHD 2000 syringe pump (Harvard Apparatus). Electrospinning was performed under constant nitrogen flow to reduce the relative humidity below 25% since the fibers are hygroscopic. Only a wet gel was collected on the rods when the relative humidity level

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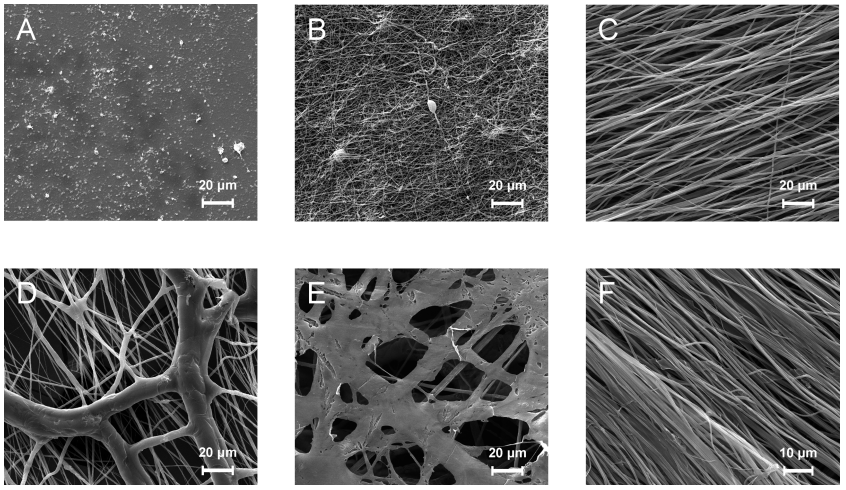

Figure 1. SEM images of PEO−hydroquinone samples electrospun from solutions with 0.5%, 1%, 3.6%, 5%, and 7% m/v of PEO in methanol (A to E, respectively) and of a PEO−NaSCN electrospun sample (F).

exceeded ~30%. All fibers were prepared at room temperature. For comparison, thin films were also prepared by solvent-casting and spin-coating the 3.6% solutions in methanol under a constant nitrogen flow.

Methanol was selected for this study because it is a good solvent for PEO, hydroquinone, and NaSCN, and its low boiling point allows for good fiber formation. Electrospinning was also attempted for the PEO−hydroquinone system using other solvents, but we faced problems of insufficient solubility at the stoichiometric ratio (chloroform), limited electrospinnability (diethyl ether, ethanol), and hydroquinone degradation (water). The best results were obtained by electrospinning solutions in acetone, for which fused ribbons could be prepared. IR spectroscopy revealed that they were essentially composed of pure complex, as will be shown for the methanol solutions (vide infra).

Characterization. Scanning electron microscopy (SEM) images were recorded using a FEI Quanta 200 FEG environmental scanning electron microscope. A thin layer of gold (sputter coater, Agar Scientific) was deposited on the samples to improve image quality. Infrared spectra with a 4 cm^{-1} resolution were recorded using a Tensor 27 FT-IR spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled HgCdTe detector and a MIRacle (Pike Technologies) attenuated total reflection (ATR) accessory. Differential scanning calorimetry (DSC) measurements were carried out using TA Instruments Q1000 or Perkin-Elmer DSC7 calorimeters calibrated with ultrapure indium. The heating rate was 10 °C/min, and the cooling rates varied between 5 and 100 °C/min. Wide-angle X-ray diffraction (XRD) measurements were performed using a Bruker AXS diffractometer (Siemens Kristalloflex 780 generator) operated at 40 kV and 40 mA. The Cu Kα (0.1542 nm) radiation was collimated by a 0.5 mm pinhole and a graphite monochromator. A HI-STAR detector was used to capture the diffraction patterns. A scattering background was subtracted from the collected patterns.

Results and Discussion

PEO−Hydroquinone Complex. The phase diagram of the PEO−hydroquinone complex shows a single complex with a 2:1 molar stoichiometry.[10] This complex melts incongruently at 79 °C to yield hydroquinone crystals in a liquid phase, which makes it hard to prepare pure and homogeneous complex samples. For instance, Paternostre et al. reported that samples obtained by cooling melts of PEO and hydroquinone contained residual hydroquinone crystals.[10] A rapid quench reduced hydroquinone crystallization but did not suppress it completely.

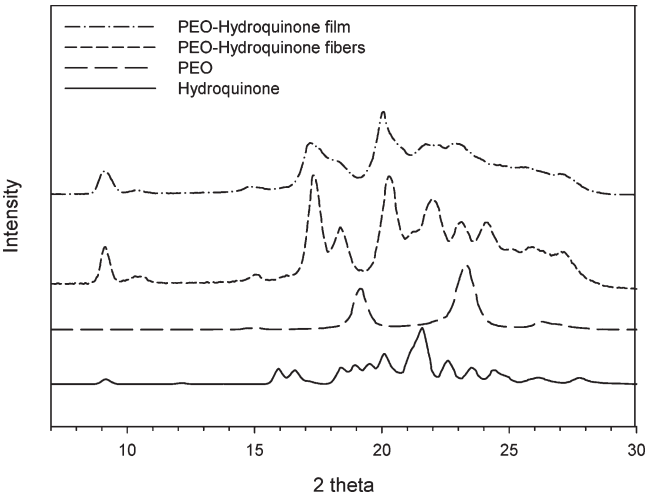

Figure 2. X-ray diffraction profiles of the PEO−hydroquinone film and fibers and of the pure products.

Solutions of PEO and hydroquinone with the appropriate stoichiometric molar ratio were electrospun to prepare nanofibers. Figure 1 shows representative SEM images of the samples obtained when electrospinning solutions at various concentrations in methanol, a volatile solvent. As expected, a very low concentration (0.5%) led to electrospray rather than electrospinning because of the lack of entanglements in the solution. A 1% solution led to the formation of nanofibers with occasional beads, while a 3.6% solution produced smooth and bead-free fibers with an average diameter of 1.2 ± 0.2 μm. Beyond this concentration electrospinning yielded a mixture of partially interconnected fibers with thick, filmlike ribbons. These ribbons and interconnections are likely due to incomplete solvent evaporation during electrospinning. The wet fibers are flattened upon impact with the collector, forming thick ribbons.[11] Based on these observations, the characterization was primarily focused on the 3.6% solutions in methanol, unless otherwise mentioned.

Figure 2 compares the XRD pattern recorded for the fibers with those of the starting products and of a solvent-cast film. It can be observed that the fibers are composed of the inclusion complex, as revealed by the most intense peaks at 17.4° and 20.4°, and that they do not contain a significant amount of residual crystalline starting products. This is confirmed by the absence of the characteristic peaks of pure

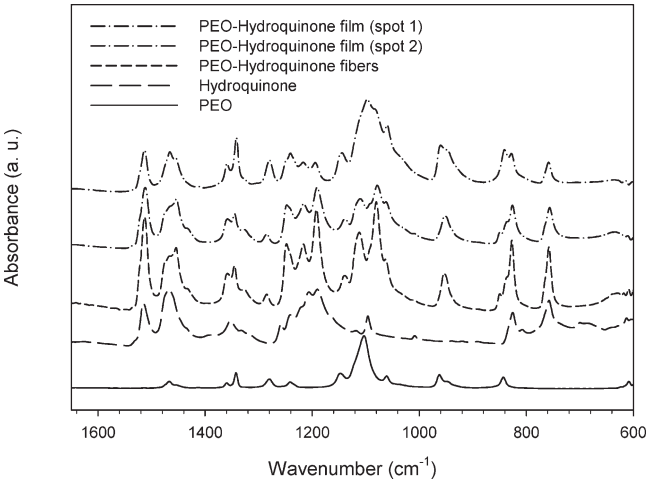

Figure 3. Infrared spectra of the PEO−hydroquinone film and fibers and of the pure products.

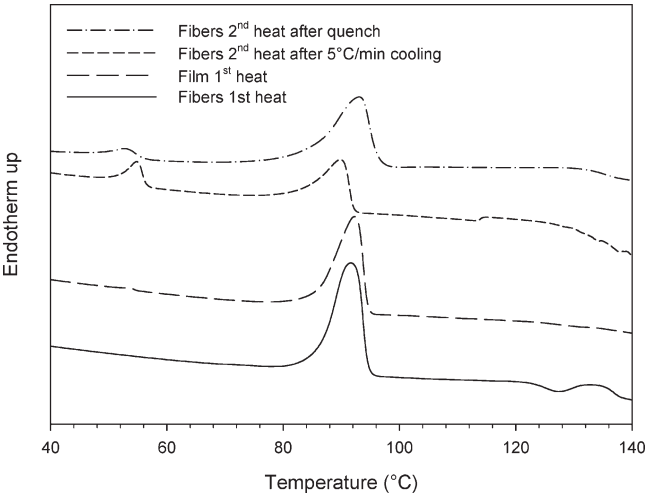

Figure 4. DSC thermograms of a PEO−hydroquinone film and of fibers exposed to different thermal histories.

PEO and hydroquinone at 19.2° and 19.6°, respectively. The IR spectra of Figure 3 confirm the formation of the complex in the nanofibers. In particular, a significant shift of the C−O−C stretching band from 1103 cm^{-1} in pure PEO to 1083 cm^{-1} in the complex reveals the formation of new hydrogen bonds between the PEO ether and the hydroxyl groups of hydroquinone. A shift of the OH stretching band from 3183 to 3355 cm^{-1} (not shown) suggests that these new H bonds are weaker than those in pure hydroquinone. The homogeneity of the nanofibers was confirmed by observing identical IR spectra and XRD patterns at different spots on the fiber bundles.

In contrast with the nanofibers, peaks due to both the complex and pure hydroquinone are present in the XRD pattern (Figure 2) for the solvent-cast film. These are highly overlapped, in particular in the 20°−24° region. The two-dimensional patterns (not shown) contain a series of discrete diffraction spots that confirm the presence of small hydroquinone crystals dispersed in the film. The lack of a significant peak at 19.2° suggests that the residual PEO is mostly present in an amorphous phase or in small PEO crystals. Figure 3 shows that the IR spectra recorded in different regions of the film are clearly different, indicating inhomogeneity within the sample. While one spectrum (spot 2) is quite similar to that of the nanofibers, indicating good complex purity, the other (spot 1) shows intense bands due to uncomplexed PEO such as those at 1103 and 840 cm^{-1}.

Figure 4 shows the DSC thermograms recorded for PEO−hydroquinone nanofibers and film during the first heating scan as well as subsequent heating scans following a slow cooling at 5 °C/min or a quench at 100 °C/min. The first heating curve for the fibers shows an endothermic peak around 89 °C due to the incongruent melting of the complex but no PEO melting peak (which should be around 53 °C), as expected from the XRD pattern of Figure 2. The peritectic reaction leads to the formation of hydroquinone crystals dispersed in a PEO-rich liquid phase. Melting (or solubilization) of these new crystals occurs over a broad temperature range up to around 135 °C. In contrast, the first heating scan for the film shows the presence of a weak but significant PEO melting event at 54 °C, confirming the presence of crystalline PEO as revealed by the IR spectra of Figure 3.

The second heating thermograms both show a significant PEO melting peak around 53 °C, proving that the complex does not re-form completely by melt-crystallization even at a rapid (100 °C/min) cooling rate. Indeed, upon cooling from the liquid state, the system must go through a region of the phase diagram where the equilibrium species are solid hydroquinone and a PEO-rich melt. As the crystallized hydroquinone molecules do not contribute to complex formation, residual PEO chains are able to crystallize when a sufficiently low temperature is reached. A faster cooling rate limits hydroquinone crystallization but does not completely suppress it. As a consequence, the PEO melting peak is noticeably smaller after the quench, in agreement with the results of Paternostre et al.[10] This confirms that melt-cooling is not an appropriate method for preparing pure samples of the PEO−hydroquinone complex. In addition, the thermal stability of hydroquinone is limited and partial degradation was observed even for relatively short periods of time at temperatures close to or above its melting point, further limiting the applicability of this method.

Electrospinning involves the application of a large electric field, of mechanical forces, and a rapid solvent evaporation that occurs on a millisecond time scale due to the very high surface/mass ratio of nanofibers. It is the latter that explains why the complex can form easily by electrospinning and poorly with other methods such as solvent casting or melt-cooling. The ultrafast solvent evaporation can be likened to an extremely fast temperature quench that almost completely prevents the formation of hydroquinone crystals. This interpretation is well supported by the IR spectra recorded for the various samples shown in Figure 1A−E. The spectra of samples prepared from 0.5% to 5% solutions were all indicative of complex formation with little or no residual starting products. In contrast, the spectrum recorded for the highest concentration (7%) showed signs of inhomogeneity, albeit to a much lesser extent than the solvent-cast film in Figure 3. This is reasonable since Figure 1E showed that this sample is composed of filmlike bundles of ribbons which are caused by solvent trapping in the electrospinning jet.[11] The solvent evaporation rate is therefore slower than for the other spun samples but not as slow as during the solvent casting process which led to highly inhomogeneous samples.

It is noteworthy that the complex readily formed during the electrospraying of the most diluted methanol solution, indicating that the ultrarapid solvent evaporation is the determining factor and not the formation of fibers. This interpretation can be further validated by spin-coating a stoichiometric PEO−hydroquinone solution with the objective of reaching an evaporation rate similar to that during electrospinning. As hypothesized, the IR spectrum was

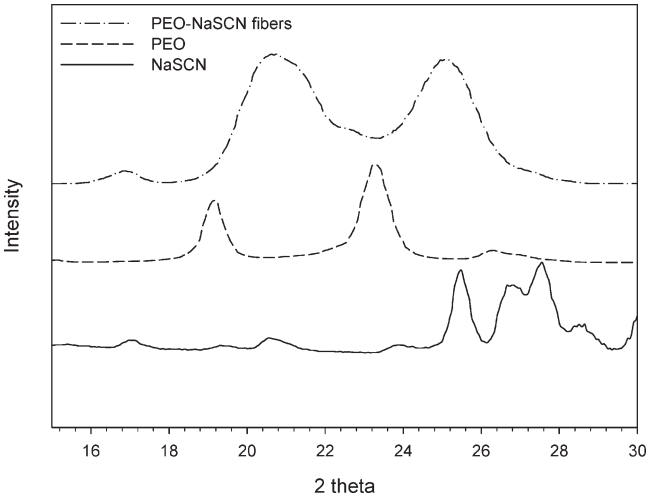

Figure 5. X-ray diffraction profiles of the PEO−NaSCN complex and of the pure products.

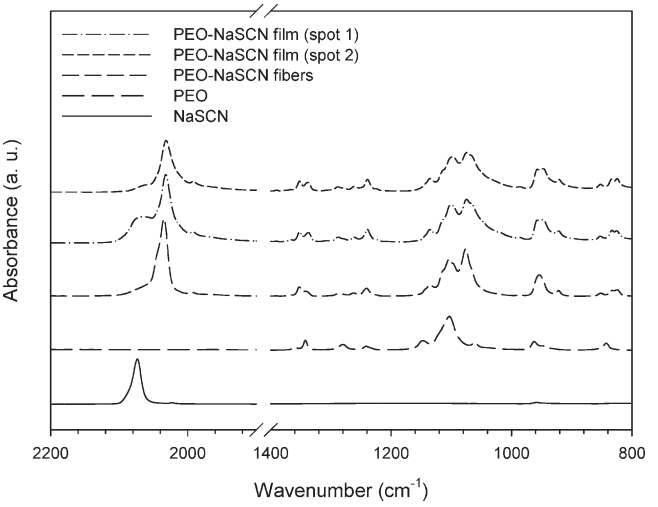

Figure 6. Infrared spectra of the PEO−NaSCN complex and of the pure products.

identical to that of the fibers shown in Figure 3, revealing the formation of a pure complex. Spin-coating therefore constitutes a simple alternative method to electrospinning or electrospraying to produce pure complex samples. Its main limitation is that it does not produce the bulk samples required for XRD or DSC characterization, so that both methods can be complementary for characterizing the structure and morphology of polymer complexes.

PEO−NaSCN Complex. In order to demonstrate more generally the potential of electrospinning for the preparation of pure polymer complexes, fibers of the PEO−NaSCN complex were also studied. This complex presents a 3:1 PEO:NaSCN molar ratio and is stabilized by electrostatic interactions.[12] Robitaille et al. showed that the pure complex can be prepared by solvent-casting when using low molecular weight (4000 g/mol) PEO but that the entanglement network prevents it for high molecular weight PEO such as the one used in this work.[7] For instance, highly heterogeneous films with a low degree of crystallinity were obtained by Lee and Crist when using 600 000 g/mol PEO, leading to an erroneous determination of the complex stoichiometry.[7,13] Pure complex could not be obtained by melt-cooling a stoichiometric blend since large crystals of NaSCN form during the first peritectic melt of the blends. These crystals are subsequently encapsulated in the complex and cannot participate in the formation of further complex.[7] A partial degradation is also observed when heating at temperatures close to or above the NaSCN melting point, further limiting the potential of this method.

As for the PEO−hydroquinone system, the electrospinning of a stoichiometric solution of PEO (3.6% w/v) and NaSCN in methanol yields pure and homogeneous fibers. Figure 1F shows an SEM image of the PEO−NaSCN nanofiber bundles. The fibers are mostly smooth with an average diameter of 0.8 ± 0.1 μm, but occasional ribbons with a diameter as high as 2.5 μm can be observed. Figure 5 shows that the XRD pattern of the electrospun nanofibers is completely different from those of the starting constituents, indicating formation of the PEO−NaSCN complex. The absence of the characteristic PEO (19.2°) and NaSCN (27.6°) peaks shows that the fibers do not contain a significant amount of residual crystalline PEO or NaSCN. It is noteworthy that the fiber peaks are very broad, suggesting that the complex crystals are small and/or contain defects. We are currently investigating the possibility of improving the crystal quality by annealing the fibers.

The IR spectra of Figure 6 confirm the complex formation in the nanofibers. The CN stretching band shifts from 2072 cm^{-1} in pure NaSCN to 2035 cm^{-1} (with a shoulder at 2045 cm^{-1}) in the nanofibers, as previously reported for the complex.[12] Only a weak band appears at 2072 cm^{-1} in the nanofibers spectrum, indicating that they contain a limited amount of uncomplexed NaSCN. In contrast, this band is clearly present in some sections of solvent-cast films (see in particular spot 1) due to incomplete complex formation when using high molecular weight PEO. The bands due to PEO also show large differences upon complexation, for instance the appearance of a strong C−O−C stretching band at 1076 cm^{-1} due to the interactions between the lone electron pairs with the Na^+ ions. The CH_2 wagging vibration, which is split at 1357 and 1341 cm^{-1} in pure PEO, becomes dominated by a single mode at 1352 cm^{-1} in the complex. This suggests a significant departure from the trans−gauche−trans conformation found in pure crystalline PEO and is consistent with the wrapping of the Na^+ ions in the PEO helix in the PEO−NaSCN complex.[12] Because of the rapid solvent evaporation, electrospinning suppresses most NaSCN crystallization and allows obtaining practically pure samples even for high molecular weight PEO.

Conclusion

This work has demonstrated that electrospinning is a simple and efficient method of preparing pure polymer complexes. The method appears to be generally applicable to challenging samples such as polymer complexes presenting an incongruent melting point. This ability to make pure and homogeneous nanofibers could become very useful both for fundamental studies of the complexes and for potential applications. In particular, PEO−salt binary systems are heavily studied for applications as solid polymer electrolytes and could beneficiate from this novel preparation method.

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