Macromol. Symp. **2011**, 303, 42–47 DOI: 10.1002/masy.201150506

Polymer Complexes with Congruent and Incongruent Fusion by Spin Coating

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Summary: We demonstrate that spin coating is an efficient method for preparing pure complexes between polymers and small molecules. Samples of the α and β complexes between poly(ethylene oxide) and urea were prepared as proof-of-concept examples since they show congruent and incongruent fusion, respectively. Infrared spectroscopy showed that pure complex of both types could be obtained by spin coating from solutions in various solvents. The ultrafast solvent evaporation appears to be the key factor in preventing the crystallization of the small molecule. These results suggest that this simple method could be generally applicable to a wide range of systems.

Keywords: infrared spectroscopy; polymer complex; poly(ethylene oxide); spin coating; urea

Introduction

Many polymers and small molecules can self-assemble through non-covalent interactions to form co-crystalline complexes.[1] These complexes sometimes present an incongruent fusion, in which case they typically melt to yield a polymer-rich peritectic liquid and crystals of the pure small molecule. This creates a challenge for the preparation of pure complex samples when using most common synthesis methods such as cocrystallization from concentrated solutions, melt-cooling, or solvent casting.[2–8] Indeed, the system has to pass through a region of the phase diagram where crystallization of the small molecule is thermodynamically favored and, as a consequence, samples often consist in mixtures of the complex with crystals of the small molecule and residual polymer. Examples of such complexes are those of poly(ethylene oxide) (PEO) with hydroquinone and NaSCN, for which the melting point of the complex is 64 and 100 °C below that of the small molecule (at the complex stoichiometry), respectively.[2,3]

Congruent complexes can also present preparation challenges for kinetic reasons, in particular if the melting temperature of the complex is only slightly above that of the pure small molecule. Indeed, the maximum crystallization rate for polymers and polymer-containing complexes often occurs tens of degrees below their melting point while small molecules usually require a smaller undercooling for crystallizing. As a consequence, crystallization of the small molecule can be kinetically favored even if thermodynamics would dictate the exclusive formation of the complex. As an example, the complex between poly(ε-caprolactone) (PCL) and urea melts congruently at 143 °C, as compared to 133 °C for pure urea.[6,7] In spite of this, pure samples have proven difficult to obtain because significant crystallization of urea occurs for kinetic reasons when using standard methods.

It is in principle possible to prevent small molecule crystallization, whether it occurs for kinetic or thermodynamic control, by quenching a melt with an appropriate stoichiometry. Unfortunately, this is often not applicable because of the degradation of one of the components or because the

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system require very high cooling rates that are technically impracticable. We have recently explored the alternative of ultrafast solvent evaporation to replicate such deep quench without facing these adverse thermal effects and technical limitations. We first realized that electrospinning, a technique used to prepare nanofibers by the application of a large electric field on a polymer solution,[9] is surprisingly efficient for preparing pure complexes.[10] This can be explained by the very large surface/volume ratio of the electrospun jet that enables very efficient solvent evaporation. This was first noted for the α complex between PEO and urea, a congruent complex, and then for the incongruent complexes between PEO and urea (β form) and thiourea.[10–12] We later generalized the approach by preparing pure samples of the incongruent complexes of PEO with hydroquinone and NaSCN.[13] Nevertheless, a limitation of electrospinning is the need to use well entangled, highly viscous solutions to prevent breakup of the jet. In the case of complexes, it implies finding a solvent that can dissolve several wt% of both the polymer and the small molecule.

In this paper, we show that spin coating, a widely used method for preparing thin or ultrathin films, is also an efficient method for preparing co-crystalline complexes between polymers and small molecules due to its ultrafast solvent evaporation. As a proof of concept, samples of the α (congruent) and β (incongruent) complexes between PEO and urea were prepared in various solvents and were found to be practically pure by infrared spectroscopy.

Experimental Part

PEO with a weight-average molecular weight of 400 000 g/mol (Scientific Polymer Products) and urea (Fisher Scientific) were used as received. Solutions for spin coating were prepared by dissolving 1 wt% of PEO and appropriate masses of urea in methanol, distilled water or dimethyl formamide (DMF). Spin coating was performed using a Headway Research EC-101 apparatus by depositing 1 ml of solution on infrared-transparent ZnSe windows at a rotation speed of 4000 rpm for 60 s. Solutions for electrospinning were prepared as above but with a higher concentration of 5 wt% of PEO and by heating at 60° until complete dissolution. Solutions were introduced in a glass syringe equipped with a flat-ended needle and were submitted to a 20 kV voltage using a CZE 100R power supply (Spellman High Voltage Electronics). A -2 kV potential was imposed on a two-rod collector counter-electrode. The working distance between the collector and the needle was 15 cm and the flow rate was maintained at 0.03 ml/min using a PHD 2000 syringe pump (Harvard Apparatus). 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. Polarized grazing angle attenuated total reflection spectra were recorded using a VariGATR accessory (Harrick Scientific). An Axioskop 2 from Carl Zeiss was used to observe the birefringence of the samples under crossed polarization with 20 and 100X objectives. A 550 nm wave plate was used to optimize the birefringence contrast.

Results and Discussion

The PEO-urea α complex possesses a 4:9 EO:urea stoichiometry and melts congruently at 145 °C, above the melting temperatures of both PEO (65 °C) and urea (135 °C).[14,15] It can be readily prepared by various methods, including co-crystallization and electrospinning from methanol, and has been very well characterized. Brisse and Chenite showed that it is an inclusion compound with channels formed by 6 urea molecules (per unit cell) in which 4 EO units and 3 urea molecules are included.[14] In contrast, the β complex has a 12:8 EO:urea stoichiometry and it is much more difficult to prepare because of its incongruent melting at 90 °C that yields a PEO-

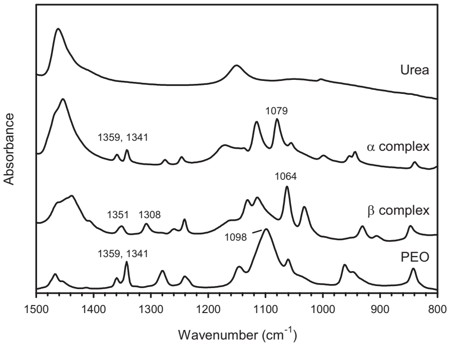

Figure 1.
Infrared spectra of the four compounds present in the PEO-urea phase diagram. The most characteristic bands used to determine composition are labeled.

rich liquid and crystals of the α complex.[12] It has most often been obtained by melt-quenching the α complex, but this process leads to a metastable mixture of β complex and urea.[4,5] We recently showed that the pure β complex prepared by electrospinning is thermodynamically stable and suggested an intercalated structure with layers of PEO and urea.[16]

Figure 1 shows IR spectra recorded for the pure components and for both complexes. Obvious differences can be observed between the spectra for the bands due to PEO, allowing determining rapidly the content of electrospun fibers or spin coated samples. These differences are, for the most part, due to the formation of new hydrogen bonds between PEO and urea. In particular, the C-O-C stretching band shifts from 1098 cm^{-1} in pure PEO (no hydrogen bonds) to 1079 cm^{-1} in the α complex and to 1064 cm^{-1} in the β complex. The CH_2 wagging band is also an explicit marker for the β complex since it appears as a single band at 1351 cm^{-1} as opposed to the doublet at 1359 and 1341 cm^{-1} found in pure PEO and in the α complex. A new band at 1308 cm^{-1} is also observed for the β complex. The CH_2 rocking modes are also quite dissimilar in the different species, with two bands appearing at 959 and 947 cm^{-1} for pure PEO, 954 and 944 cm^{-1} for the α complex, and 931 and 905 cm^{-1} for the β complex. The intense urea bands are strongly affected by complexation, in particular the intense Amide I, II, and III bands in the range between 1720 and 1400 cm^{-1}. Those are not shown here for clarity because pure urea was not observed in the spin coated samples and the narrower PEO bands are more direct indicators of complex formation.

The α complex was first spin coated since it was the most likely to yield pure complex thanks to its congruent fusion. Figure 2 shows crossed-polarized optical micrographs of ultrathin films prepared from a solution in methanol. Figure 2A shows that the sample consists of bundles of spreading fibrils propagating along a preferential direction over long distances. In some cases, the surface of the 2.5 cm diameter window was completely covered by a single spherulite so that this image corresponds to only one of the spherulite sectors. The crystalline growth is therefore extremely rapid as compared to the nucleation

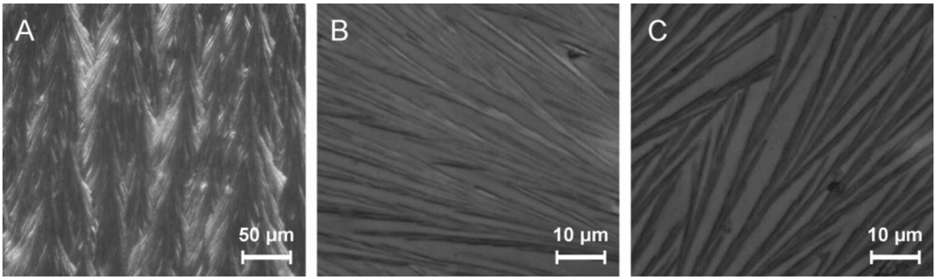

Figure 2.
Optical micrographs of α complex samples spin coated from methanol and recorded under crossed polarization with A) 20X magnification, and B) and C) 100X magnification with the insertion of a waveplate.

process. The α complex is known to produce such very large spherulites when slowly cooled from the melt state.[4,17] Figure 2B and 2C show images recorded with 100X magnification and using a waveplate to increase the birefringence contrast. The periodic branching of outgrowths from the main fibrils can be noted. Rotation of the sample at −45° and +45° from the analyzer direction shows the characteristic yellow and blue colors, respectively, that are characteristic of the positive birefringence which is observed in bulk spherulites of the α complex.[4,17]

IR spectra were recorded to confirm the formation of the α complex and to evaluate the presence of residual starting products. Figure 3 shows series of polarized spectra recorded for films spin coated from methanol, water, and DMF. They are all dominated by the α complex bands, such as the C-O-C stretch at 1079 cm^{-1}, and none of them features the bands characteristic of pure PEO (such as 1098, 959, and 947 cm^{-1}) or the β complex (1064, 931, and 905 cm^{-1}). It can therefore be concluded that spin coating is very efficient at producing practically pure samples of this inclusion complex. This conclusion holds even for solutions in DMF in spite of its high boiling temperature, 153 °C. For comparison, electrospinning was used to prepare fibers of the complex in the same solvents (spectra not shown). Pure complex was obtained from methanol solutions, as previously reported,[10] as well as from water, although good fibers could not be recovered. In contrast, electrospinning from DMF led to a gelatinous mixture containing the α and β complexes as well as residual urea.

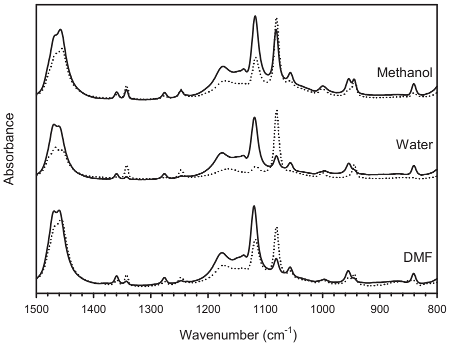

Figure 3.
Polarized infrared spectra recorded for ultrathin films of the α complex spin coated in methanol, water and dimethyl formamide. Full and dotted lines represent p- and s-polarized spectra, respectively.

The efficiency of electrospinning and spin coating as methods for preparing host/guest complexes can be ascribed to the ultrafast evaporation of the solvent due to the large surface/volume ratio of the charged jet or the ultrathin film. One therefore expects solvents with a low boiling point, such as methanol, to be more successful than others with a higher boiling point, such as DMF. Such effect is observed for the electrospun samples but not for the spin coated films, for which pure complex was obtained even in DMF. This is counterintuitive since the surface/volume ratio is higher in the electrospun fibers. In fact, the poor result obtained when electrospinning from DMF solutions is due to the gradual accumulation on the collector of fibers containing residual solvent. The fibers most likely crystallize as pure α complex during the flight of the jet, as with the other solvents, but they can partly dissolve on the collector due the continuous replenishment of residual DMF. Crystals of pure urea can then form during this slower evaporation process, depleting the amount of urea available for formation of the α complex and leading to some amount of the PEO-rich β complex. A similar process cannot happen during spin coating unless the atmosphere is saturated in DMF so that pure samples are readily produced.

An obvious observation from Figure 3 is that the infrared spectra of the spin coated samples recorded with p and s polarization are quite different from one another. This is due to the molecular orientation within the ultrathin films. Indeed, when performing a polarized ATR measurement, the s spectrum is only sensitive to functional groups oriented parallel to the surface of the substrate and perpendicular to the plane of incidence of the IR radiation. On the other hand, the p spectrum is sensitive to

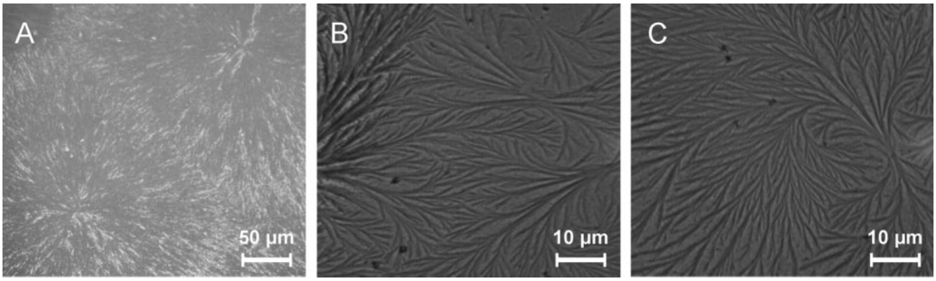

Figure 4.
Optical micrographs of β complex samples spin coated from methanol and recorded under crossed polarization with A) 20X magnification, and B) and C) 100X magnification with the insertion of a waveplate.

groups parallel to the surface (parallel to the plane of incidence) as well as those oriented normal (perpendicular) to the surface. It is thus possible to determine in which direction the inclusion channels are oriented based on the relative absorbance of bands in the p or s spectrum. For instance, we know from our studies of electrospun fibers that the two most intense bands at 1079 and 1116 cm^{-1} are orientated parallel and perpendicular to the channel direction, respectively.[12] In fact, all bands that are oriented along the fiber axis are dominant in the s spectrum of Figure 3, and all those that are perpendicular to the fiber axis appear predominantly in the p spectrum. It can therefore be concluded that the channels (and the included PEO chains) are strongly aligned parallel to surface of the film. This edge-on orientation of the lamellae justifies the significant positive birefringence observed in Figure 2B and C.

As a second (and more challenging) test, solutions of PEO and urea with a 12:8 molar ratio were spin coated to determine if the β complex could also be prepared using spin coating. Figure 4A shows a 20X cross-polarized optical image of a typical sample. In contrast with Figure 2A, complete spherulites can be observed in this case. It has been reported that the β complex does form much smaller spherulites than the α complex in the bulk state,[4,17] probably because of slower crystallization kinetics. Figure 4B and 4C show sheaflike structures when observed at higher magnification. Intriguingly, the birefringence contrast is very weak and appears to be positive, in contrast with the large negative birefringence observed for the β complex.[4,17]

IR spectra were again recorded to determine the composition of the samples. Figure 5 shows p- and s-polarized spectra obtained for films spin coated from methanol, water, and DMF. In all cases, the spectra are dominated by the bands associated with the β complex, such as the C-O-C stretch at 1064 cm^{-1}, the single CH_2 wagging at 1351 cm^{-1}, and the characteristic band at 1308 cm^{-1}. The spectra from samples spin coated from DMF show a very weak band at 1098 cm^{-1}, indicating a small amount of pure PEO. These results show that close to pure β complex samples can readily be obtained by a method as simple

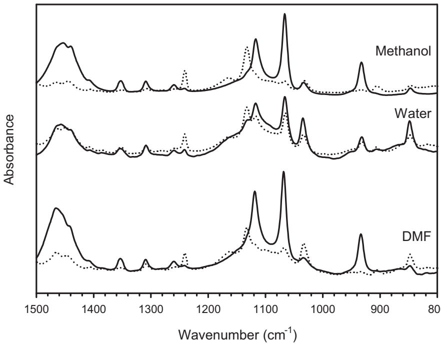

Figure 5.
Polarized infrared spectra recorded for ultrathin films of the β complex spin coated in methanol, water and dimethyl formamide. Full and dotted lines represent p- and s-polarized spectra, respectively.

and convenient as spin coating, in spite of its incongruent fusion that makes it difficult to prepare using most methods.

The difference between the polarized spectra can again be used to determine the direction of the crystals with respect to the substrate by reference to the results obtained when studying highly oriented electrospun fibers.[12] It is known, for instance, that the intense bands at 1132 and 1064 cm^{-1} are parallel to the c direction of the crystal, while those at 1240 and 1032 cm^{-1} have a perpendicular transition dipole direction. The former bands are prominent in the p spectrum of Figure 5 while the latter dominate the s spectrum. This clearly indicates that the c axis of the crystals is aligned normal to the surface of the sample and therefore that the lamellae have a flat-on orientation, in contrast with the edge-on structure observed for the α complex. This flat-on orientation explains the weak birefringence observed in Figure 4 for the ultrathin films in spite of the fact that bulk samples of the bulk β complex crystallizes into spherulites with a large negative birefringence.

Conclusion

This work demonstrates the efficiency of spin coating as a method for preparing supramolecular polymers complexes. Practically pure samples of the α and β complexes between poly(ethylene oxide) and urea could be readily prepared from three different solvents. The method is thus applicable to complexes with congruent and incongruent fusions, and to solvents with low or high boiling temperatures. The ultrathin films present a large level of molecular orientation, with lamellae adopting edge-on and flat-on morphologies for the α and β complexes, respectively.

Acknowledgements: This work was supported by a research grant and by an undergraduate scholarship (MRL) from the Natural Sciences and Engineering Research Council of Canada (NSERC).

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