Computational Details. In this study, 12 host α-CD molecules that were aligned in a column with an internal channel were examined. In order to obtain 1:1 stoichiometric ratios, the required number of repeat units of PLLA, PCL, N-6, N-11 chains are 28, 12, 12, and 7 respectively (Figure 1). All of the structures were built using the Materials Studio 5.0 software package\textsuperscript{2} with the Discover and Amorphous cell modules and the simulations were performed with the LAMMPS\textsuperscript{3} molecular dynamics package employing the second generation force field PCFF\textsuperscript{3}. An NVT (constant number of molecules, volume, and temperature) ensemble at 300 K was used with no applied pressure. A timestep of 1 fs was used for a total simulation time of 1 ns.

Results and Discussion

In order to observe competitive IC formation of N-6 and N-11, N-6-α-CD-IC powder was added to an N-11 solution. Under these conditions, it is expected that the N-11 chains will replace N-6 chains and form an IC with the α-CD channel, since N-11 chains are more hydrophobic.

In the FTIR spectra in Figure 2a, both characteristic nylon and α-CD peaks are observed, indicating IC formation.\textsuperscript{3} However, it is difficult to decipher from these results whether the guest polymer of this IC is N-6 or N-11.

To make this identification, we remove the α-CD by washing it with water to obtain just the coalesced polymer.\textsuperscript{3} This coalesced polymer has an FTIR spectra (Fig. 2b) similar to N-11, which means that competitive IC formation occurs between N-6 and N-11, with N-11 chains dislodging N-6 chains.

Further DSC characterization was done for the coalesced and un-included polymers. As observed in Figure 3a, the coalesced polymer has a melting point of 186.5 °C, which is very similar to the $T_m$ of N-11. This result indicates that the N-11 chains replace most of the N-6 chains. The DSC for the un-included polymer (Figure 3b) has a melting point of 206.5 °C, which is slightly lower than melting point of N-6 possibly due to un-included N-11 chains. Because the IC never dissolves, this observation indicates that guest N-6 chains migrate into the solution from the crystalline α-CD channels as N-11 chains push them out and become included inside the α-CD cavities.

These experiments indicate that competitive IC formation occurs not only between PCL and PLLA, but also between N-6 and N-11. In light of these observations, we performed some molecular dynamics (MD) simulations for some additional insights. In our preliminary simulations, we calculated the interaction energies between four different guest polymer chains, which are depicted in Figure 1, when they are threaded through and covered by the 12 host α-CDs. So far, simulations were only performed for polymer chains when they are outside the α-CD channel. We are in the process of performing further simulations for unthreaded chains outside the CD channels in the presence of solvent.
Figure 3. DSC scans of (a) coalesced nylon and (b) un-included nylon, after evaporating the solvent.

Table I. Interaction energies of ICs of various polymers within the α-CD channel.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Number of Repeat Units</th>
<th>Average Interaction Energies (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>12</td>
<td>-997.1</td>
</tr>
<tr>
<td>PLLA</td>
<td>28</td>
<td>-1041.1</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>12</td>
<td>-949.5</td>
</tr>
<tr>
<td>Nylon 11</td>
<td>7</td>
<td>-1019.4</td>
</tr>
</tbody>
</table>

The calculated interaction energies from the MD simulations between each polymer and the CD cavity are given in Table 1. The negative interaction energies imply that all of these polymers can form ICs with α-CD from an energetic standpoint. However, there is not a large energy difference between either PCL and PLLA or N-6 and N-11. Therefore we cannot conclude that the driving force of competitive IC formation is a result of differences in the energies of these guest polymers inside the CD cavity.

To attempt to determine the reason for this interesting phenomenon, we will conduct other simulations, where the effects of the solvents are also included. We will also calculate the interaction energies between these polymer chains and α-CDs when they are outside the α-CD channels, which is a hydrophilic environment due to the hydroxyl groups on the exterior rims of α-CD. These hydroxyl groups might cause higher repulsive forces in the case of more hydrophobic polymers (PCL and N-11) and might be the driving force of this competitive IC formation.

Conclusion

This study experimentally identifies the competitive IC formation between N-6 and N-11. When N-11 is introduced into a suspension of N-6-α-CD-IC, N-11 dislocates the N-6 chains without dissolution of the IC. The MD simulations reveal that neither PCL nor N-11 have significantly different interaction energies than PLLA or N-6, respectively, when they are inside the α-CD channel. Thus the principal reason for competitive IC formation has yet to be revealed, but further MD simulations should assist in achieving this goal.

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