TUNABLE STIMULI-RESPONSIVE PROPERTIES OF PEG-PDMAEMA DIBLOCK COPOLYMERS

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Abstract
Thermo- and pH-responsive diblock copolymers of polyethylene glycol-block-poly((2-dimethylamino)ethyl methacrylate) (PEG-PDMAEMA) were synthesized using atom transfer radical polymerization to control polymer molecular weight and molecular weight distribution. Stimuli-responsive properties were tested using UV-Visible spectroscopy and dynamic light scattering. Cloud point, or the temperature at which the polymer solution becomes cloudy, was determined for each diblock copolymer. Factors affecting cloud point and self-assembly behavior of PEG-PDMAEMA diblock copolymers were determined to be polymer concentration, polymer molecular weight, pH, and ionic strength. Stimuli-responsive and self-assembly behavior of PEG-PDMAEMA diblock copolymers were tunable using polymer structure and solution properties, enabling applications ranging from smart coatings to stimuli-responsive dispersants.

Keywords
Polymers, Stimuli-responsive, Self-assembly

Introduction
Properties of polymeric materials depend on both polymer chemical functionality and polymer architecture. Both can be controlled during polymer synthesis to achieve materials that have properties arising from the combination of both polymer chemical functionality and polymer architecture. Smart polymer chemical functionality and diblock copolymer architecture have been chosen because these combine to create unique and switchable polymer properties (Cohen Stuart et al., 2010 and Roy et al., 2013). Smart polymers show a dramatic change in properties in response to external stimuli such as temperature or pH. These switchable polymer properties can be reversible or irreversible and include changes in solubility, viscosity, and self-assembly. Polymer architecture can be controlled during polymer synthesis to achieve diblock copolymers. Smart chemical functionality and diblock copolymer architecture can be combined to create polymer materials with unique and controlled switchable properties and self-assembly behavior. Being able to switch polymer behavior enables a wide range of applications where reversible properties are needed.

In order to tune polymer properties for applications, it is necessary to determine the effect of changing polymer structure on properties. Polyethylene glycol-block-poly((2-dimethylamino)ethyl methacrylate) (PEG-PDMAEMA) has been studied because it is both pH- and thermo-responsive. PDMAEMA is water-soluble at low temperature and becomes insoluble upon increasing the temperature. While a previous initial report by Han et al. (2013) has looked at how changing testing conditions affects stimuli-responsive behavior of specific PEG-PDMAEMA diblock copolymers, more detailed

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investigations into how polymer structure affects smart polymer properties is needed to understand the range of possible smart properties for PEG-PDMAEMA diblock copolymers.

**Results and Discussion**

A series of PEG-PDMAEMA diblock copolymers was synthesized using atom transfer radical polymerization (ATRP). The results for these copolymers is summarized in Table 1. The stimuli-responsive behavior of these diblock copolymers as a function of polymer molecular weight, polymer concentration, pH, and ionic strength were tested.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (NMR) (kDa)</th>
<th>Molar Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG(_{127})-Br</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>PEG(<em>{127})PDMAEMA(</em>{140})</td>
<td>26.8</td>
<td>1:1.1</td>
</tr>
<tr>
<td>PEG(<em>{127})PDMAEMA(</em>{278})</td>
<td>49.3</td>
<td>1:2.2</td>
</tr>
<tr>
<td>PEG(_{43})-Br</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>PEG(<em>{43})PDMAEMA(</em>{43})</td>
<td>8.7</td>
<td>1:1</td>
</tr>
<tr>
<td>PEG(<em>{43})PDMAEMA(</em>{87})</td>
<td>15.5</td>
<td>1:2</td>
</tr>
</tbody>
</table>

UV-Visible spectroscopy was used to determine cloud point, or the temperature at which the polymer solution becomes visibly cloudy. Dynamic light scattering was used to determine the aggregation behavior of the PEG-PDMAEMA diblock copolymers in solution.

**Conclusions**

A series of PEG-PDMAEMA diblock copolymers were synthesized using ATRP. Stimuli-responsive properties were tested using UV-Visible spectroscopy and dynamic light scattering to determine the impact of changing polymer structure on smart polymer properties.

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**References**

