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## COMMUNICATION

# A dual stimuli responsive fluorescent probe carrier from double hydrophilic block copolymer capped with $\beta$ -cyclodextrin

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**A double hydrophilic block copolymer with  $\beta$ -cyclodextrin endgroups was prepared via RAFT polymerization and click reaction. The micelle formation of the polymer has been investigated as a function of temperature and pH values. The release of the encapsulated fluorescent probe pyrene from the polymer can be controlled by variation of temperature and addition of adamantanyl-NH<sub>3</sub>Cl.**

## Introduction

Stimuli responsive polymers are able to change their chain conformation, solubility, and intermolecular association in the presence of external stimulations such as temperature,<sup>1</sup> electrical field,<sup>2</sup> pH,<sup>3</sup> redox agents,<sup>4, 5</sup> and ionic strength.<sup>6</sup> Especially, responsive block copolymers have been widely studied because of their ability to self-assemble into micelles with hydrophobic core and hydrophilic shell during stimulation. These soft materials have been reported to have promising biomedical applications such as controlled drug and gene delivery, tissue engineering, and enzyme catalysis.<sup>7-9</sup> Stimuli responsive double hydrophilic block copolymers (DHBCs) are capable of forming various types of aggregates such as random aggregates, micelles, and more organized structure.<sup>10-13</sup> DHBCs typically contain thermosensitive blocks such as poly(*N*-isopropyl acrylamide) (PNIPAM)<sup>14</sup> and polypropylene oxide,<sup>15</sup> pH sensitive blocks such as poly(2-(diethylamino)ethyl methacrylate) (PDEA)<sup>11</sup> and poly(4-vinyl-pyridine),<sup>16</sup> or combination of thermosensitive and pH sensitive blocks.<sup>17</sup> PNIPAM is one of the most popular thermoresponsive polymers with phase transition temperature at 32 °C which is the result of entropy driven process of hydrophobic interactions between the isopropyl groups. Among pH sensitive polymers, PDEA is water-insoluble at neutral or alkaline pH, but becomes soluble at pH < 6.5 due to protonation of tertiary amine residues.<sup>17</sup> Solution properties of diblock copolymer (PDEAEMA-*b*-PNIPAM) with tunable hydrophilicity has been previously investigated.<sup>18</sup>

$\beta$ -Cyclodextrin ( $\beta$ -CD), with hydrophilic exterior and hydrophobic interior, is a native cyclic oligomer composed of 7 glucopyranose units linked by  $\alpha$ -1, 4-glycosidic bonds.<sup>19</sup> The hydrophobic cavity has been extensively utilized to serve as a host unit to construct host-guest delivery carriers and supramolecular assemblies.<sup>20, 21</sup> Over the

past few years, the combination of  $\beta$ -CD with stimuli-responsive polymers to form nanoscale micelles as drug carriers has gained a lot of attention.<sup>20-24</sup>  $\beta$ -CD can be attached to one end of linear polymer chains or serve as side groups of polymer chains while the assembly process takes place via inclusion complexation between  $\beta$ -CD moieties and other selected hydrophobic molecules bonded to polymer chains. For instance, Liu *et al.* reported the preparation of  $\beta$ -CD capped linear polymer  $\beta$ -CD-PNIPAM that was able to form complexation with adamantane capped pH responsive polymer Ad-PDEA in which the supramolecular diblock polymer had reversible micelle to vesicle transition behavior.<sup>14</sup> Zou *et al.* demonstrated that the inclusion complexation between the azobenzene group and  $\beta$ -CD unit at the end of linear polymer  $\beta$ -CD-PNIPAM could lead to vesicle formation tuned by light and temperature.<sup>25</sup> Linear polymer chains with both ends capped by  $\beta$ -CD are new building blocks for self-assemble process. Guo *et al.* reported the polyetherimide (PEI) with  $\beta$ -CD at the both ends in which PEI can self-assemble into vesicles in water. The vesicles were active in supramolecular chemistry because the  $\beta$ -CDs were equally distributed on both surfaces of the vesicles and adamantane-ended polyethylene glycol could non-covalently form inclusion complexes with  $\beta$ -CD.<sup>23</sup>

Although responsive block copolymers have been used as potential drug carriers and  $\beta$ -CD has been employed to modify the chain end of non-responsive homopolymer, no study has been performed on bonding  $\beta$ -CD to responsive DHBCs. We hypothesize that if the chain ends of stimuli responsive DHBCs are modified with  $\beta$ -CD, the polymer not only retain the multi-responsive properties but also have functional end groups that can be used for further assembly and modification. This may help to construct new structures of polymer assemblies and drug carrier species. Herein we report the synthesis and characterization of a dual stimuli-responsive DHBC capped with  $\beta$ -CD that can be loaded with a fluorescent probe at the both chain ends. The responses of the prepared block copolymer with  $\beta$ -CD terminal groups to variation of temperature and pH value have been investigated. Furthermore, we successfully demonstrated that the fluorescent probe can be released from the block copolymer by adding adamantanyl group containing molecules that have extremely high complexation constant with  $\beta$ -CD.<sup>26</sup>

The synthetic route employed for the triblock copolymer PDEA-*b*-PNIPAM-*b*-PDEA is illustrated in Scheme 1. The first step was to



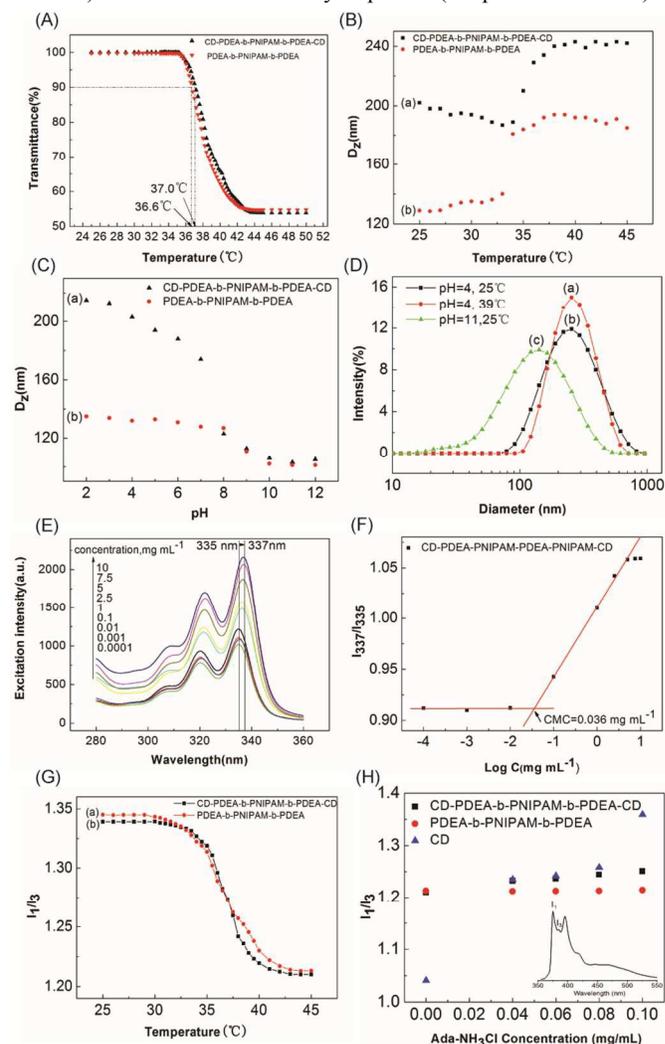
PDEA, and CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (Figure 2A). For PDEA (curve a), the wavenumber at 1730  $\text{cm}^{-1}$  can be assigned to the C=O stretching vibrational absorption of PDEA and 1254  $\text{cm}^{-1}$  belongs to C-N stretching vibrational absorption. For PDEA-*b*-PNIPAM-*b*-PDEA (curve b), absorption at 1554  $\text{cm}^{-1}$  comes from N-H bending vibration of NIPAM and 1643  $\text{cm}^{-1}$  arises from C=O absorption of NIPAM. In the case of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (curve c), absorptions at 1080  $\text{cm}^{-1}$  and 1031  $\text{cm}^{-1}$  are attributable to C-O and C-O-C stretching vibrational absorption in  $\beta$ -CD, respectively. Also, the peak at 1062  $\text{cm}^{-1}$  belongs to C=S bending vibrational absorption that results from the PDEA macro-chain transfer agent.  $^1\text{H}$  NMR was used to characterize the structure of pg-PDEA-*b*-PNIPAM-*b*-PDEA-pg (pg stands for propargyl group) (Figure 2B) and CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (Figure 2C). As shown in Figure 2B, chemical shift  $\delta$  at 1.92 was assigned to the proton of alkyne group at both ends of polymer chain while the chemical shift  $\delta$  at 5.15-5.25 in Figure 2C was resulted from protons of cyclodextrin units.  $^1\text{H}$  NMR results revealed that  $\beta$ -CD molecules were successfully bonded to polymer chain end via click reaction. It is estimated that 33% of the chain ends are functionalized.

Liu *et al.* synthesized diblock copolymer PDEA-*b*-PNIPAM using RAFT method and found that the low critical solution temperature (LCST) of this polymer was pH dependent (25  $^\circ\text{C}$  at pH=8 and 34  $^\circ\text{C}$  at pH=6).<sup>28</sup> In this study due to the presence of PDEA and CD, we hypothesized that the LCSTs of PDEA-*b*-PNIPAM-*b*-PDEA and CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD were higher than the LCST of PNIPAM. Figure 3A shows the UV transmittance as a function of temperature for PDEA-*b*-PNIPAM-*b*-PDEA and CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD. The LCST of PDEA-*b*-PNIPAM-*b*-PDEA was about 36.6  $^\circ\text{C}$ , which was obviously higher than that of PNIPAM, i.e. 32  $^\circ\text{C}$  because the hydrogen bond between the triblock copolymer and solution was strengthened when hydrophilic PDEA was incorporated into the copolymer.<sup>29</sup> Consequently, the hydrophilic component made it difficult for the triblock copolymer to dehydrate when temperature was raised.<sup>30</sup> For CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD, the LCST value was about 37  $^\circ\text{C}$ ; this can be explained by the hydrophilic feature of  $\beta$ -CD, which made polymer phase transition more difficult.

We characterized the Z-average particle size ( $D_z$ ) change of self-assembled aggregates as a function of temperature and pH using dynamic laser scattering (DLS). Before DLS measurement, PDEA was completely dissolved in hydrochloric acid solution to avoid chain aggregation in the solution.<sup>18</sup> Figure 3B shows the change in  $D_z$  of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD and PDEA-*b*-PNIPAM-*b*-PDEA as a function of temperature. In the case of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD,  $D_z$  ranged between 190 to 200 nm at low temperature (i.e.  $<34$   $^\circ\text{C}$ ). As the temperature increased above 34  $^\circ\text{C}$ , the  $D_z$  quickly increased and was stable at 240 nm, indicating the self-assemble process that was induced by the coil to globe transition of PNIPAM chain. Figure 3B also demonstrates a similar  $D_z$  trend for PDEA-*b*-PNIPAM-*b*-PDEA. Interestingly, the  $D_z$  remained between 130 and 137 nm at temperatures below 33  $^\circ\text{C}$  and increased to 192 nm as the temperature increased. These results revealed that the presence of  $\beta$ -CD units increased the  $D_z$  value.

We also characterized the changes of  $D_z$  of self-assembled aggregates for CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD group as a function of pH values (Figure 3C). At pH<6,  $D_z$  decreased from 215 to 173 nm, however, as pH increased beyond 7, the  $D_z$  significantly dropped to 121 nm and finally was stabilized at 105 nm, indicating the self-assemble process that was induced by the hydrophobic transition of PDEA chain. Figure 3C also presents the  $D_z$  for PDEA-*b*-PNIPAM-*b*-PDEA as a function of pH. For pH<8, the  $D_z$  slightly decreased from 135 to 129 nm, however, as pH elevated beyond 8 an

obvious decrease took place and finally the  $D_z$  was finally stable at 100 nm. The difference in trend of  $D_z$  as a function of pH and temperature might be explained by different self-assembly process in ABA triblock copolymers when block A becomes hydrophobic (pH induced) and block B becomes hydrophobic (temperature induced).<sup>31</sup>



**Figure 3.** A) UV transmission change curves of PDEA-*b*-PNIPAM-*b*-PDEA and CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (pH=4). B)  $D_z$  as a function of temperature for (a) CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD, and (b) PDEA-*b*-PNIPAM-*b*-PDEA (pH=4, 0.1 mg mL $^{-1}$ ). C)  $D_z$  as a function of pH for (a) CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD, and (b) PDEA-*b*-PNIPAM-*b*-PDEA (0.1 mg mL $^{-1}$ , 25  $^\circ\text{C}$ ). D)  $D_z$  distribution of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD solution (0.1 mg mL $^{-1}$ ) (a) pH=4, 39  $^\circ\text{C}$ , (b) pH=4, 25  $^\circ\text{C}$ , (c) pH=11, 25  $^\circ\text{C}$ . E) Fluorescence excitation spectra of pyrene in the presence of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (pH=4, 25  $^\circ\text{C}$ ). F) CMC determination of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD (pH=4, 25  $^\circ\text{C}$ ). G)  $I_1/I_3$  ratio from emission spectra of pyrene in the presence of (a) PDEA-*b*-PNIPAM-*b*-PDEA and (b) CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD. (pH=4, 0.1 mg mL $^{-1}$ ). H)  $I_1/I_3$  ratio from emission spectra of pyrene in the presence of PDEA-*b*-PNIPAM-*b*-PDEA, CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD, and CD as a function of Ada-NH $_3$ Cl concentration (the inset graph shows the emission peaks  $I_1$  and  $I_3$  at 0.04 mg/mL of Ada-NH $_3$ Cl).

Figure 3D shows the diameter distribution of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD self-assembled aggregates at different temperature and pH. When PNIPAM chain underwent phase transition and PDEA chain remained soluble (pH=4, 39  $^\circ\text{C}$ ), the  $D_z$  was 241 nm (red curve) and particle dispersion index (PDI) was 0.122. When both PDEA and PNIPAM chains were soluble in water (pH=4, 25  $^\circ\text{C}$ ) the  $D_z$  was reduced to 213 nm and PDI was 0.228

(black curve). When PDEA chain underwent phase transition but PNIPAM remained soluble in water (pH=11, 25 °C), the Dz value further decreased to 104 nm and PDI was 0.151 (green curve). The PDI values were in the range of 0.08-0.70, indicating that the particles' size had mid-range polydispersity.<sup>32</sup> Zeta potential was used to study the stability of colloids. When the absolute value of zeta potential is higher than 30 mV, the dispersion is stable.<sup>33</sup> Figure S2 (see Supporting Information) shows the zeta potential of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD as a function of temperature in an acidic solution. The zeta potential value was ~-52 mV at the beginning when the temperature was lower than 35 °C, then increased quickly as temperature was elevated above 35 °C at the rate of 0.2 °C min<sup>-1</sup>. Finally it was significantly slowed down after 41 °C. It could be inferred that these particles were stably dispersed in the solution.

Other group reported that DHBC would form micelles in solution when one block of DHBC became hydrophobic.<sup>34</sup> As indicated in Figure 3A, the LCST of CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD was determined to be about 37 °C. Therefore, there was no thermal induced micelle formation of PDEA-*b*-PNIPAM-*b*-PDEA at 25 °C. However, after bonding with  $\beta$ -CD we detected the micelle formation using fluorescence spectroscopy of probe molecule pyrene. Polymer was dissolved in  $6 \times 10^{-6}$  M pyrene solution with different concentrations. As depicted in Figure 3E, the fluorescence intensity increased as the polymer concentration increased from 0.0001 to 10 mg mL<sup>-1</sup>. There was a shift of the (0, 0) absorption band from 335 to 337 nm, indicating the formation of micelles.<sup>35</sup> In addition, the plot of fluorescence intensity ratio of  $I_{337}/I_{335}$  as a function of concentration (Figure 3F) further elucidates the critical micelle concentration (CMC) value to be 0.036 mg mL<sup>-1</sup>. We previously found that  $\beta$ -CD became less hydrophilic after mono-substitution modification.<sup>36</sup> It is possible that the presence of  $\beta$ -CD served as relatively hydrophobic units and induced the micelle formation.

The encapsulation of pyrene molecule into CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD was investigated using fluorescence spectroscopy. The intensity of the first emission peak to the third emission peak ratio ( $I_1/I_3$ ) can be used to characterize the micro-environment of pyrene. The smaller  $I_1/I_3$  value indicates the more hydrophobic environment for the pyrene molecule.<sup>37</sup> The hydrophobic cavity of  $\beta$ -CD can encapsulate pyrene molecule by forming complexation of pyrene into  $\beta$ -CD.<sup>38</sup> To minimize the disturbing effect of encapsulated pyrene, and make sure that the complexation process of pyrene into  $\beta$ -CD was in equilibrium, the pyrene/polymer solution was kept at room temperature for 1 day before measurement.<sup>23</sup> As shown in Figure 3G, at low temperature pyrene was in hydrophilic environment and  $I_1/I_3$  was stable. As temperature increased above 34 °C, there was a sharp decrease, indicating that pyrene molecules were in more hydrophobic area due to the phase transition of PNIPAM chain. Finally,  $I_1/I_3$  maintained at a stable value, indicative of the equilibrium of pyrene/PNIPAM interaction. It has been reported that hydrophobic adamantanyl (Ada) group and  $\beta$ -CD could be used for drug release experiments because of their significantly higher inclusion constant ( $5 \times 10^4$  M<sup>-1</sup>) compared with other guest molecules.<sup>21, 23</sup> In order to further explore the functionality of the  $\beta$ -CD end groups, Ada-NH<sub>3</sub>·Cl was added to the solution at 45 °C. As indicated in Figure 3H, as the concentration of Ada-NH<sub>3</sub>·Cl increased from 0 to 0.1 mg/mL, the value of  $I_1/I_3$  increased steadily for CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD group. However, for the group without  $\beta$ -CD the  $I_1/I_3$  value showed no obvious change when the Ada-NH<sub>3</sub>·Cl was added. The increase of  $I_1/I_3$  can be inferred that for the CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD group more pyrene molecules were expelled out of  $\beta$ -CD cavities to the hydrophilic environment by adding Ada-NH<sub>3</sub>·Cl. In the group

without  $\beta$ -CD, there were no  $\beta$ -CD units and nothing can be replaced by Ada-NH<sub>3</sub>·Cl, thus  $I_1/I_3$  value did not change. Also, it seems that pyrene exchange with CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD is less efficient than the exchange with pristine CD.

## Conclusions

In summary, the  $\beta$ -CD terminated triblock copolymer CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD with both hydrophilic temperature (PNIPAM) and pH (PDEA) responsive chains have been synthesized via RAFT polymerization and subsequent click reaction. Unique thermo and pH sensitive properties have been demonstrated in CD-PDEA-*b*-PNIPAM-*b*-PDEA-CD micelles when compared to PDEA-*b*-PNIPAM-*b*-PDEA. The diameter distribution (PDI) of these polymeric nanoparticles in the solution was found to be in the mid-range polydispersity. Pyrene molecules are encapsulated in the polymer assemblies and  $\beta$ -CD cavities and can be released by adding Ada-NH<sub>3</sub>·Cl molecules. We envision the extension of the strategy reported here as a proof of concept to develop novel drugs/biomolecules encapsulated  $\beta$ -CD terminated triblock copolymer. With enormous potential for sensing, tissue engineering, and drug delivery systems, we believe this technique can be used for different applications in sensors, scaffolding and other biomedical areas.

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