Supporting Information

Amphiphilic Quasi-Block Copolymers and Their Self-Assembled Nanoparticles via Thermally Induced Interfacial Absorption in Miniemulsion Polymerization

Xianbo Xu, Guorong Shan*, Pengju Pan

State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China

*Corresponding Author
Tel.: +86-571-87951334; e-mail: shangr@zju.edu.cn
**Figure S1** $^1$H NMR spectra of homopolymer (sample PSMA, A) and copolymer (sample NP11, B).

$^1$H NMR was carried out to confirm the chemical structure and composition. Figure S1(A) shows the $^1$H NMR spectrum of PSMA homopolymer. The signal within $\delta = 0.76$–$0.90$ ppm corresponds to the protons of methyl groups and the peak at $\delta$ = 1.20–1.40 ppm (e) can be ascribed to the long chain methylene bands. The chemical shift at 1.52–1.67 ppm (d) and 1.80–1.92 ppm (b) are attributed to the protons of methylene adjacent to the methylene connected to the oxygen atom of stearyl (-OCH$_2$-) and the protons of methylene in the backbone, respectively. The protons of methylene group adjacent to the oxygen atom of stearyl shows a chemical shift of 3.80–4.10 ppm. Figure S1 (B) exhibits the typical $^1$H NMR spectrum of PNIPAM/PSMA quasi-block copolymer. Compared with Figure S1(A), all the
signals corresponding to the protons in PSMA copolymer can be found. The characteristic signals of PNIPAM moiety can be seen as follows. The signals around $\delta = 1.15$ (k) can be attributed to the methyl protons of isopropyl units and the signal at $\delta = 5.9$–$6.9$ ppm (i) corresponds to the imido group adjacent to the carbonyl group. The chemical shift of protons of methine in the backbone appears at $\delta = 2.3$ ppm.

**Figure S2** Molecular weights ($M_n$) and content of SMA in copolymers with different polymerization temperature and feed ratio.

$^a$Content refers to mole ratio, and was calculated from $^1$H NMR spectra.

Figure S2 (A) shows the plots of the molecular weight ($M_n$) vs polymerization temperature. The molecular weight was decreased and the content of SMA in copolymers was relatively decreased due to the faster polymerization and termination rate at higher temperatures. The feed ratio of SMA had a bigger influence on $M_n$ (Figure S2 (B)). $M_n$ values increased linearly with SMA. As the proportion of NIPAM was quite low, PNIPAM oligomers were not enough to coat the oil droplets. This could be attributed that the PNIPAM oligomers not only acted as a thermo-sensitivity moiety copolymerized with a hydrophobic monomer, but also as a stabilizer to stabilize the resultant particles during polymerization.
Figure S3 GPC traces of all polymers.

Figure S4 The nanoparticles sizes vs reaction time with different content of $n$-hexane: (a) $n$-hexane =0 g; (b) $n$-hexane = 5.0 g; (c) $n$-hexane = 8.0 g (Table 1, NP70A, NP11, NP70B).
Figure S5 Dependence of nanoparticle sizes in water on temperature and monomer molar ratio (Table 1, NP21, NP11, NP12, NP13 and NP14).

Table S1 Oil-water partition coefficient of NIPAM in \(n\)-hexane and SMA at different temperatures

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>partition coefficient\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)-hexane/water</td>
</tr>
<tr>
<td>30</td>
<td>0.02748</td>
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<tr>
<td>50</td>
<td>0.04361</td>
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<tr>
<td>70</td>
<td>0.06138</td>
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</tbody>
</table>

\textsuperscript{a}The partition coefficient was calculated with \(P = C_{\text{oil}} / C_{\text{water}}\).

NIPAM monomer has a small partition in oil phase. The oil-water partition coefficient of NIPAM in \(n\)-hexane and SMA shows that NIPAM is slightly soluble in oil phase and its solubility in oil droplets of \(n\)-hexane and SMA increases with temperature obviously. This
indicates that, increasing temperature would increase the incorporation of hydrophilic monomer into copolymer; this will lead to the copolymerization of the hydrophobic and hydrophilic monomers inside droplets and the formation of amphiphilic copolymers.