Janus Long-Chain Hyperbranched Copolymer of PSt and POEGMA
from Self-Assembly Mediated Click Reaction

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Synthesis of alkynyl-(PSt-N$_3$)$_2$ and alkynyl-(POEGMA-N$_3$)$_2$

Figure S1 shows $^1$H-NMR spectrum of alkynyl-(PSt-N$_3$)$_2$. Two meso-protons of phenyl groups of styrene units have the signal in the range of 6.3–6.9 ppm. The signals of methylene protons and methine proton of PSt backbone are located in the range of 1.0–2.3 ppm. Importantly, the signal of methylene protons from propargyl group appears at 4.52 ppm and that of methine proton next bromo end-group at 3.94 ppm.
**Figure S1.** $^1$H-NMR spectrum of alkynyl-(PSt-N$_3$)$_2$ seesaw macromonomer

POEGMA with one alkynyl group at the chain center and two azido groups at each chain end [alkynyl-(POEGMA-Br)$_2$] was prepared through atom transfer radical polymerization (ATRP) of OEGMA with PBMPMP as the initiator and the conversion of bromo end groups into azido end groups. Figure S2 shows $^1$H-NMR spectrum of alkynyl-(POEGMA-N$_3$)$_2$. Based on the integral heights of the signal at 3.67 ppm (methylene protons from OEG) and that at 4.25 ppm (methylene protons from propargyl group), real number-averaged molecular weight ($M_{n,NMR}$) of alkynyl-(POEGMA-N$_3$)$_2$ is 15000.

![Figure S1](image1.png)

**Figure S2.** $^1$H-NMR spectrum of alkynyl-(POEGMA-N$_3$)$_2$ seesaw macromonomer

**Contact angle imaging of different copolymer films**

Different $\mu$-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ films were obtained by casting real solution in THF and micelle dispersion in one selective solvent. Contact angles to water ($CA_w$) and oil ($CA_o$) were imaged with digital camera, as shown in Figure S3.
Figure S3. Contact angles of $\mu$-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$ films casting from different solvents [$CA_w$: THF (a), methanol (b), cyclohexane (c); $CA_o$: THF (d), methanol (e), cyclohexane (f)]

Camera images of different $\mu$-(lhb-POEGMA)(PSt-N$_3$)$_2$ films are shown in Figure S4.

Figure S4. Contact angles of $\mu$-(lhb-POEGMA)(PSt-N$_3$)$_2$ films from THF (a: $CA_w$, d: $CA_o$), methanol (b: $CA_w$, e: $CA_o$) and cyclohexane (c: $CA_w$, f: $CA_o$)

Camera images of different $\mu$-(lhb-POEGMA)(lhb-PSt) films are shown in Figure Ss.
Figure S5. Contact angles of $\mu$-(lhb-POEGMA)(lhb-PSt) films casting from different solvents THF (a: $CA_w$, d: $CA_o$), methanol (b: $CA_w$, e: $CA_o$) and cyclohexane (c: $CA_w$, f: $CA_o$)

Table S1. Contact angles of different copolymer films cast from different solvents

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<tr>
<th>sample</th>
<th>THF</th>
<th></th>
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<th>CH$_3$OH</th>
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<th>cyclohexane</th>
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<tr>
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<td>$CA_w$</td>
<td>$CA_o$</td>
<td>$CA_w$</td>
<td>$CA_o$</td>
<td>$CA_w$</td>
<td>$CA_o$</td>
</tr>
<tr>
<td>$\mu$-(PSt-N$_3$)$_2$(POEGMA-N$_3$)$_2$</td>
<td>50.0°</td>
<td>65.6°</td>
<td>39.8°</td>
<td>82.5°</td>
<td>89.5°</td>
<td>56.4°</td>
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<td>70.3°</td>
<td>19.9°</td>
<td>98.7°</td>
<td>79.1°</td>
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<td>65.9°</td>
<td>42.4°</td>
<td>83.1°</td>
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