Supporting Information:

**Block Copolymer-Ferroelectric Nanoparticle Nanocomposites**

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**Table S1.** Molecular weights of amphiphilic star-like PAA-b-PS diblock copolymers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>$M_n,_{\text{PAA}}^a$</th>
<th>$M_n,_{\text{PS}}^b$</th>
<th>$M_w/M_n^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-1</td>
<td>4,500</td>
<td>4,100</td>
<td>1.13</td>
</tr>
<tr>
<td>Sample-2</td>
<td>8,400</td>
<td>5,200</td>
<td>1.10</td>
</tr>
<tr>
<td>Sample-3</td>
<td>28,100</td>
<td>29,680</td>
<td>1.18</td>
</tr>
</tbody>
</table>

$^a$ Number average molecular weight, $M_n$ of each PAA block calculated from the molecular weight difference between PmBA block (before hydrolysis) and PAA block (after hydrolysis) based on $^1$H-NMR spectra. $^b$ $M_n$ of each PS arm calculated from $^1$H NMR data. $^c$ Polydispersity index, PDI determined by GPC.
Scheme S1. Schematic representation of the synthesis of amphiphilic star-like PAA-\textit{b}-PS diblock copolymers by sequential atom transfer radical polymerization (ATRP) of \textit{tert}-butyl acrylate and styrene.$^1$

Figure S1. $^1$H-NMR spectrum of BaTiO$_3$ permanently capped with PS chains (sample-a, $D = \sim 6$ nm, solvent: CDCl$_3$). Inset: digital image of PS-functionalized BaTiO$_3$ NP toluene solution ($c = 10$mg/mL).
**Figure S2.** (A-C) The thermogravimetric analysis of PS-functionalized BaTiO$_3$ NPs with different sizes by using different star-like PAA-$b$-PS as templates (i.e., sample-1, sample-2, and sample-3 in Table S1, respectively). Weight fractions of polymers are 23.93 % in A ($D = \sim 6$ nm); B=13.92 % ($D = \sim 11$ nm); and C=15.48 % ($D = \sim 27$ nm).
Figure S3. (A-C) XRD patterns of PS-functionalized BaTiO$_3$ NPs with different sizes by using different star-like PAA-$b$-PS as templates (i.e., sample-1, sample-2 and sample-3 in Table S1, respectively). The diameters of NPs are $D = \sim 6$ nm in A; $D = \sim 11$ nm in B; and $D = \sim 27$ nm in C.
Figure S4. (A-C) EDS spectra of PS-functionalized BaTiO$_3$ NPs with different sizes by using different star-like PAA-$b$-PS as templates (i.e., sample-1, sample-2, and sample-3 in Table S1, respectively). The diameters of NPs are $D = \sim 6$ nm in A; $D = \sim 11$ nm in B; and $D = \sim 27$ nm in C.
Figure S5. The thermogravimetric analysis of nanocomposites by mixing PS-functionalized BaTiO$_3$ NPs ($D = \sim 11$ nm) and PS-$b$-PMMA ($M_{PS}=45,900$ and $M_{PMMA}=138,000$) at the different volume fractions of NPs: 11.5% in A and 16.3% in B.
Figure S6. AFM and TEM images of pure PS-\(b\)-PMMA (\(M_{\text{PS}}=315,000\) and \(M_{\text{PMMA}}=785,000\)) thin film. (A) AFM height and (B) phase images of as-prepared PS-\(b\)-PMMA (\(M_{\text{PS}}=315,000\) and \(M_{\text{PMMA}}=785,000\)); image size= 10.0\(\times\)10.0\(\mu\)m\(^2\), Z range= 30 nm for (A) and 36.9\(^\circ\) for (B). (C)-(D) TEM images of PS-\(b\)-PMMA thin film formed after the acetone vapor annealing for 6 h. The PS nanodomains appeared dark in the bright PMMA matrix. The average diameter of the PS nanocylinders is estimated to be 161.7 \(\pm\) 12.5 nm, obtained by using standard image analysis software \textit{ImageJ}. The film thickness is 46 nm.
Figure S7. TEM images of thin film of PS-\textit{b}-PMMA (M_{PS}=315,000 and M_{PMMA}=785,000)/PS-functionalized BaTiO$_3$ NP ($D \approx 6$ nm) nanocomposites formed after the acetone vapor annealing for 6h. The volume fraction of BaTiO$_3$ NPs was 10.8%. The vertically oriented arrays of PS nanodomains containing BaTiO$_3$ NPs appeared dark. The average diameter of the PS nanocylinders after the addition of BaTiO$_3$ NPs is estimated to be 206.4±31.2 nm, obtained by using standard image analysis software \textit{ImageJ}. The film thickness is 56nm. The average number of BaTiO$_3$ NPs in the PS nanocylinders is approximately 306, calculated based on the volume fraction of BaTiO$_3$ NPs and the size of the PS nanocylinders.
**Figure S8.** TEM images of thin film of PS-\(b\)-PMMA (\(M_{PS}=315,000\) and \(M_{PMMA}=785,000\))/PS-functionalized BaTiO\(_3\) NP (\(D = \sim 6\) nm) nanocomposites formed after the acetone vapor annealing for 6h. The volume fraction of BaTiO\(_3\) NPs was 16.8\%. The vertically oriented arrays of PS nanodomains containing BaTiO\(_3\) NPs appeared dark. The average diameter of the PS nanocylinders after the addition of BaTiO\(_3\) NPs is estimated to be \(220.8\pm25.3\) nm, obtained by using standard image analysis software *ImageJ*. The film thickness is 61 nm. The average number of BaTiO\(_3\) NPs in the PS nanocylinders is approximately 461, calculated based on the volume fraction of BaTiO\(_3\) NPs and the size of the PS nanocylinders.

**Figure S9.** TEM images of thin film of PS-\(b\)-PMMA (\(M_{PS}=315,000\) and \(M_{PMMA}=785,000\))/PS-functionalized BaTiO\(_3\) NP (\(D = \sim 11\) nm) nanocomposites formed after the acetone vapor annealing for 6h. The volume fraction of BaTiO\(_3\) NPs was 15.9\%. The vertically oriented arrays of PS nanodomains containing BaTiO\(_3\) NPs appeared dark. The average diameter of the PS nanocylinders after the addition of BaTiO\(_3\) NPs is estimated to be \(218.2\pm28.6\) nm, obtained by using standard image analysis software *ImageJ*. The film thickness is 58 nm. The average number of BaTiO\(_3\) NPs in the PS nanocylinders is approximately 239, calculated based on the volume fraction of BaTiO\(_3\) NPs and the size of PS nanocylinders.
Figure S10. Thermogravimetric analysis of star-like PAA-b-PS (sample-1 in Table S1) and PS-b-PMMA (M_{PS}=45,900 and M_{PMMA}=138,000).

Reference