Supporting Information

One-component nanocomposites made from diblock copolymer grafted cellulose nanocrystals

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Figure S24. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce CNC-g-PMA$_{35}$ ([MA]:[Initiator]:[Cu$^{II}$]:[Ligand] = 1000:1:0.05:0.25, solvent:monomer ratio of 1:1 v/v) after 30 min. The spectrum was recorded in CDCl$_3$. 
Figure S25. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce CNC-g-PMA5 ([MA]:[Initiator]:[Cu$^{II}$]:[Ligand] = 100:1:0.05:0.25, solvent:monomer ratio of 1:1 v/v) after 60 min. The spectrum was recorded in CDCl$_3$. 
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Figure S27. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce PMA$_{15}$ after a reaction time of 0 min and measured in CDCl$_3$. The signal at 5.26 ppm is associated with the 5 $\mu$L of dichloromethane that was added as an internal standard. The signal at 2.14 ppm is associated with an acetone impurity. The reaction conditions were [Monomer]:[Initiator]:[Cu$^{II}$]:[Ligand] of 200:1:0.05:0.25, a solvent:monomer ratio of 1:4 v/v.
Figure S28. $^1$H NMR spectrum of an aliquot PMA$_{15}$ taken @ 1h and measured in CDCl$_3$. The signal at 5.25 ppm is associated with the 5 μL of dichloromethane that was added as an internal standard. The signal at 2.14 ppm is associated with an acetone impurity. The reaction conditions were [Monomer]:[Initiator]:[Cu$^{II}$]:[Ligand] of 200:1:0.05:0.25, a solvent:monomer ratio of 1:4 v/v.
Figure S29. $^1$H NMR spectrum of an aliquot of CNC-g-PMA$_{15}$ taken at $t_0$ and measured in CDCl$_3$. The signal at 5.25 ppm is associated with the 5 µL of dichloromethane that was added as an internal standard. The signal at 2.26 ppm is associated with an acetone impurity. The reaction conditions were [Monomer]:[Initiator]:[Cu$^{II}$]:[Ligand] of 200:1:0.05:0.25, a solvent:monomer ratio of 1:4 v/v.
Figure S30. $^1$H NMR spectrum of an aliquot of CNC-g-PMA$_{15}$ taken @ 1h and measured in CDCl$_3$. The signal at 5.25 ppm is associated with the 5 µL of dichloromethane that was added as an internal standard. The signal at 2.25 ppm is associated with an acetone impurity. The reaction conditions were [Monomer]:[Initiator]:[Cu$^{II}$]:[Ligand] of 200:1:0.05:0.25, a solvent:monomer ratio of 1:4 v/v.
Figure S31. $^1$H NMR spectrum of an aliquot of CNC-g-PMA$_{15}$ taken @ 2h and measured in CDCl$_3$. The signal at 5.25 ppm is associated with the 5 µL of dichloromethane that was added as an internal standard. The signal at 2.25 ppm is associated with an acetone impurity. The reaction conditions were [Monomer]:[Initiator]:[Cu$^{II}$]:[Ligand] of 200:1:0.05:0.25, a solvent:monomer ratio of 1:4 v/v.
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Figure S36. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce CNC-g-PMA$_8$-b-PMMA$_2$ just before the reaction was quenched. The spectrum was recorded in CDCl$_3$. 
Figure S37. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce CNC-$\text{g-PMAs}-b$-PMMA$_7$, just before the reaction was quenched. The spectrum was recorded in CDCl$_3$. 
Figure S38. $^1$H NMR spectrum of CNC-g-PMA$_8$-b-PMMA$_2$ (isolated after a reaction time of 120 + 60 min and purified by dialysis against THF) that was redispersed in CDCl$_3$. 
Figure S39. $^1$H NMR spectrum of CNC-g-PMA$_8$-b-PMMA$_7$ (isolated after a reaction time of 120 + 120 min and purified by dialysis against THF) that was redispersed in CDCl$_3$. 
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Figure S41. $^1$H NMR spectrum of an aliquot taken from the reaction mixture to produce CNC-$g$-PMA$_5$-$b$-PMMA$_{12}$ just before the reaction was quenched. The spectrum was recorded in CDCl$_3$. 
Figure S42. $^1$H NMR spectrum of CNC-g-PMA$_5$-b-PMMA$_7$ (isolated after a reaction time of 60 + 60 min and purified by dialysis against THF) that was redispersed in CDCl$_3$. 
Figure S43. $^1$H NMR spectrum of CNC-g-PMAs-b-PMMA$_{12}$ (isolated after a reaction time of 60 + 120 min and purified by dialysis against THF) that was redispersed in CDCl$_3$. Signals at 3.73-3.76 ppm and 1.84-1.87 ppm are related to residual THF.
Figure S44. Thermogravimetric analysis (TGA) traces of PMA\textsubscript{15} and PMMA\textsubscript{40} recorded at a heating rate of 10 °C min\textsuperscript{-1}.
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**Figure S48.** Magnification of portions of the FT-IR spectra of CNC-g-PMA₈ and CNC-g-PMA₈-b-PMMA₇.
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**Figure S50.** Picture of a film of CNC-g-PMA<sub>15</sub> after hot pressing.
Figure S51. Picture of a film of CNC-g-PMA₈-b-PMMA₇ after hot pressing.

Figure S52. DMA traces of PMA-b-PMMA block copolymers.
Figure S53. Tensile tests of CNC-g-PMA. The graph shows a magnification of the low-strain regime. Tests were conducted at 50 % min\(^{-1}\) at room temperature.

Figure S54. Tensile tests of the PMA-b-PMMA reference free-polymers conducted at 50 % min\(^{-1}\) and at room temperature.
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Figure S57. Characterization of the CNC-Br, CNC-g-PMA, and CNC-g-PMA-b-PMMA by X-ray scattering. Small- and wide-angle scattering profile of CNC-Br was recorded in a powder state with Kapton as the reference material. Measurements of CNC-g-PMA and CNC-g-PMA-b-PMMA were conducted after the nanocomposites were pressed into 250 µm thick films.
2 Supplementary Tables S1-3

Table S1. Reaction conditions and composition of PMA, PMMA, and PMA-\textit{b}-PMMA reference polymers.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Reaction times PMA/PMMA block (h)</th>
<th>Equivalents MA/MMMA in feed (-)</th>
<th>PMA/PMMA fraction in polymer(^a) (mol / mol)</th>
<th>PMA/PMMA (M_n) NMR (kg mol(^{-1}))(^b)</th>
<th>PMA/PMMA (M_n) SEC(^c) (kg mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA(_{15})</td>
<td>1 / -</td>
<td>200 / -</td>
<td>100 / 0</td>
<td>15.9</td>
<td>15.7</td>
</tr>
<tr>
<td>PMMA(_{40})</td>
<td>(c,d)</td>
<td>(c,d)</td>
<td>0 / 100(^d)</td>
<td>-</td>
<td>40.2</td>
</tr>
<tr>
<td>PMA(_{15})-\textit{b}-PMMA(_4)</td>
<td>1 / 1</td>
<td>200 / 400</td>
<td>75 / 25</td>
<td>15 / 4</td>
<td>15.5 / 41.8</td>
</tr>
<tr>
<td>PMA(<em>{15})-\textit{b}-PMMA(</em>{11})</td>
<td>1 / 2</td>
<td>200 / 400</td>
<td>61 / 39</td>
<td>15 /11</td>
<td>16.1 / 51.2</td>
</tr>
<tr>
<td>PMA(_{8})-\textit{b}-PMMA(_7)</td>
<td>1 / 1</td>
<td>100 / 400</td>
<td>53 / 47</td>
<td>8 / 7</td>
<td>44.6</td>
</tr>
<tr>
<td>PMA(<em>{8})-\textit{b}-PMMA(</em>{10})</td>
<td>1 / 2</td>
<td>(100 / 400)</td>
<td>43 / 57</td>
<td>8 / 10</td>
<td>29.7</td>
</tr>
</tbody>
</table>

\(^a\)Determined from the ratio of the integrals of the methyl group signals of PMA (3.66 ppm) and PMMA (3.60 ppm) in the \(^1\)H NMR spectrum of a sample taken from the reaction mixture just before quenching the reaction. 
\(^b\)Calculated using Eqs. S1 and S2 from the monomer conversion, which was determined from the integrals of signals associated with monomer (6.36, 6.07, 5.75 ppm) and polymer (3.66 ppm) in the \(^1\)H NMR spectrum of a sample taken from the reaction mixture just before quenching the reaction. 
\(^c\)Measured by SEC of the isolated polymer. 
\(^d\)Commercial sample.

Table S2. Mechanical and thermomechanical properties of PMA, PMMA, and PMA-\textit{b}-PMMA reference polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_y)(^a) (MPa)</th>
<th>(\sigma_{UTS})(^a) (MPa)</th>
<th>(\varepsilon)(^a) (%)</th>
<th>Tensile Toughness(^a) (MJ m(^{-3}))</th>
<th>(E^\prime) at -60 (^\circ)C(^b) (MPa)</th>
<th>(T_g,1)(^b) (°C)</th>
<th>(T_g,2)(^b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA(_{15})</td>
<td>9 ±0.6</td>
<td>0.15 ±0.02</td>
<td>265 ±29</td>
<td>0.17 ±0.0</td>
<td>2590 ±380</td>
<td>26.2 ±0.5</td>
<td>-</td>
</tr>
<tr>
<td>PMMA(_{40})</td>
<td>1770 ±280</td>
<td>47 ±7</td>
<td>4 ±1</td>
<td>1.1 ±0.4</td>
<td>4700 ±120</td>
<td>-</td>
<td>120 ±1</td>
</tr>
<tr>
<td>PMA(_{15})-\textit{b}-PMMA(_4)</td>
<td>360 ±20</td>
<td>7 ±1</td>
<td>120 ±30</td>
<td>0.68 ±0.0</td>
<td>4150 ±430</td>
<td>46.5 ±3</td>
<td>n.d.(^e)</td>
</tr>
<tr>
<td>PMA(<em>{15})-\textit{b}-PMMA(</em>{11})</td>
<td>550 ±70</td>
<td>16 ±0.3</td>
<td>58 ±5</td>
<td>0.95 ±0.1</td>
<td>4300 ±370</td>
<td>31.4 ±3</td>
<td>131 ±2</td>
</tr>
<tr>
<td>PMA(_{8})-\textit{b}-PMMA(_7)</td>
<td>650 ±70</td>
<td>18 ±3</td>
<td>9 ±1</td>
<td>0.96 ±0.2</td>
<td>4450 ±290</td>
<td>37.6 ±1</td>
<td>134 ±3</td>
</tr>
<tr>
<td>PMA(<em>{8})-\textit{b}-PMMA(</em>{10})</td>
<td>1190 ±150</td>
<td>17 ±0.3</td>
<td>2 ±0.2</td>
<td>0.02 ±0.0</td>
<td>4500 ±370</td>
<td>44.5 ±5</td>
<td>131 ±2</td>
</tr>
</tbody>
</table>

\(^a\)Determined by tensile tests. \(^b\)Determined by dynamic mechanical analysis; \(T_g\) values represent the maxima of the \(\tan \delta\) curves. Not detected, as the sample fails.
Table S3. Monomer conversion determined by $^1$H NMR analysis through an internal standard (IS) versus comparing the monomer to polymer integrals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion based on IS$^a$ (%)</th>
<th>$M_n$ (IS) (kg mol$^{-1})^b$</th>
<th>Conversion based on Polymer Formed$^b$ (%)</th>
<th>$M_n$ (Based on Polymer Formed) (kg mol$^{-1})^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA$_{15}$ (1h)</td>
<td>84</td>
<td>14.5</td>
<td>87</td>
<td>15.0</td>
</tr>
<tr>
<td>CNC-g-PMA$_{15}$ (1h)</td>
<td>66</td>
<td>11.5</td>
<td>68</td>
<td>11.8</td>
</tr>
<tr>
<td>CNC-g-PMA$_{15}$ (2h)</td>
<td>85</td>
<td>14.7</td>
<td>82</td>
<td>14.1</td>
</tr>
</tbody>
</table>

$^a$Determined using equation S4 and S5. $^b$Determined using equation S3 and S4.
Supplementary Equations S1-5

SSA = \frac{m_{\text{CNC}}}{\rho_{\text{cellulose}}} \frac{2\pi H + 4(W - H)}{\pi WH} \quad \text{Eq. S1}

Equation S1. Equation for calculating the specific surface area (SSA) of CNCs. Further details can be found in the experimental section.

\[ \sigma_i = \frac{w_i}{M W_i} \times \frac{N_A}{(1 - w_i) \times SSA \times 10^{18}} \quad \text{Eq. S2} \]

Equation S2. Equation for calculating the initiator grafting density. Further details are can be found in the experimental section.

\[ \% \text{ Conversion} = \left( \frac{\int \text{Polymer @ } \tau_x}{\# \text{H, polymer}} \div \frac{\int \text{Monomer @ } \tau_x}{\# \text{H, monomer}} \right) \times 100 \quad \text{Eq. S3} \]

Equation S3. The conversion of monomer into polymer was calculated on the basis of the integration of \(^1\text{H} \) NMR signals associated with monomer and polymer. \#H, polymer (3) and \#H, monomer (3) indicate the number of protons associated with the signals observed at chemical shifts of 6.36, 6.07, and 5.75 ppm for the polymer. \( \int \text{Polymer @ } \tau_x \) = integral of the signal at 3.66 ppm, \( \int \text{Monomer @ } \tau_x \) = integral of signals at 6.36, 6.07, and 5.75 ppm; this value was set to 1.

\[ M_{n \text{NMR}} = M_{\text{monomer}} \times (\text{Monomer Eq.}) \times \left( \frac{\% \text{Conversion}}{100} \right) + M_{\text{initiator}} \quad \text{Eq. S4} \]

Equation S4. The \( M_{n \text{NMR}} \) was calculated from the Conversion determined with Eq. S1 assuming living conditions. \( M_{\text{monomer}} \) and \( M_{\text{initiator}} \) are the molecular weights of the monomer (MA, 85.01 g mol\(^{-1}\)) and initiator (195.05 g mol\(^{-1}\)). Monomer Eq. represents the equivalence of the monomer to the initiator.

\[ \% \text{ Conversion} = [1 - \frac{\int \text{IS @ } \tau_x}{\int \text{IS @ } \tau_0}] \times 100 \quad \text{Eq. S5} \]

Equation S5. The conversion of monomer into polymer was calculated on the basis of the integration of \(^1\text{H} \) NMR signals associated with monomer and dichloromethane (DCM, 2.52 ppm) that was used as an internal standard. Aliquots of the reaction mixture were filtered through alumina before 5 µL of DCM were added for \(^1\text{H} \) NMR analysis. \( \int \text{Monomer @ } \tau_x \) = integral of signals at 6.37, 6.07, and 5.78 ppm. \( \int \text{IS @ } \tau_x \) and \( \int \text{IS @ } \tau_0 \) are integrals at 5.25 ppm that were set to 1.