Electronic Supplementary Information

Metal-Free Click Polymerizations of Activated Azide and Alkynes

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**Fig. S9** $^{13}$C NMR spectra of DMF-$d_7$ solution of monomer 3c (A), diazide 2 (B) and polymer P1c (C). The solvent and water peaks are marked with asterisks. (7)

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Scheme S1 Synthetic routes to polytriazoles by metal-free click polymerization of ordinary alkynes and azide.

Table S1 Reaction of ordinary aliphatic and aromatic azides 4 and 5 with alkynes 3a and 3b.

<table>
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<th>no.</th>
<th>monomer</th>
<th>polymer</th>
<th>$M_w$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>PDI&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>1</td>
<td>3a + 4</td>
<td>PIIa</td>
<td>1800</td>
<td>1.00</td>
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</tr>
<tr>
<td>2</td>
<td>3b + 4</td>
<td>PIIb</td>
<td>1900</td>
<td>1.01</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>3a + 5</td>
<td>PIIc</td>
<td></td>
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</table>

<sup>a</sup> Reactions were carried out in DMF at 100 °C under nitrogen for 12 h at a monomer concentration of 0.4 M. <sup>b</sup> Weight-average molecular weight ($M_w$) and polydispersity index (PDI = $M_w$/M<sub>n</sub>) were estimated by gel permeation chromatography (GPC) in DMF/0.05 M LiBr solution on the basis of a PMMA calibration.
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Fig. S4 FT-IR spectra of monomers 2 (A), 3c (B), and polymer P1c (C).
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**Fig. S6** $^1$N NMR spectra of DMF-$d_7$ solution of monomer 3c (A), polymer P1c (B). The solvent and water peaks are marked with asterisks.
Fig. S7 $^{13}$C NMR spectra of DMF-$d_7$ solution of monomer 3a (A), diazide 2 (B) and polymer PIa (C). The solvent and water peaks are marked with asterisks.

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**Fig. S9** $^{13}$C NMR spectra of DMF-$d_7$ solution of monomer 3c (A), diazide 2 (B) and polymer PIc (C).

The solvent and water peaks are marked with asterisks.