Electronic Supplementary Information

Metal-Free Click Polymerizations of Activated Azide

and Alkynes

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Fig. S1 ¹⁹F NMR spectra of chloroform-*d* solutions of perfluorobenzophenone **1** (A) and diazide monomer **2** (B).



Fig. S2 HRMS spectra of monomer 2 (calcd 408.0006).



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.

no.	monomer	polymer	$M_{ m w}{}^{ m b}$	PDI ^b	yield
1	3a + 4	PIIa	1800	1.00	trace
2	3b + 4	₽ IIb	1900	1.01	trace
3	3a + 5	PIIc	/	/	/

^{*a*} Reactions were carried out in DMF at 100 °C under nitrogen for 12 h at a monomer concentration of 0.4 M. ^{*b*} Weight-average molecular weight (M_w) and polydispersity index (PDI = M_w/M_n) were estimated by gel permeation chromatography (GPC) in DMF/0.05 M LiBr solution on the basis of a PMMA calibration.



Fig. S3 FT-IR spectra of monomers 2 (A), 3b (B) and polymer PIb (C).



Fig. S4 FT-IR spectra of monomers 2 (A), 3c (B), and polymer PIc (C).



Fig. S5 ¹N NMR spectra of DMF- d_7 solution of monomer **3b** (A), polymer PIb (B). The solvent peaks are marked with asterisks.



Fig. S6 ¹N NMR spectra of DMF- d_7 solution of monomer **3c** (A), polymer PIc (B). The solvent and water peaks are marked with asterisks.



Fig. S7 ¹³C 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.



Fig. S8 ¹³C NMR spectra of DMF- d_7 solution of monomer **3b** (A), diazide **2** (B) and polymer PIb (C). The solvent and water peaks are marked with asterisks.



Fig. S9 ¹³C 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.