Supporting Information for:

Copper Catalyzed vs Thermal Step Growth Polymerization of Starch-Derived α-Azide-ω-Alkyne Dianhydrohexitol Stereoisomers: to Click or not to Click?

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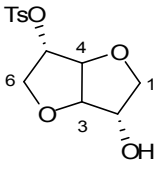
Materials. Sodium hydride (Aldrich, 60% dispersion in mineral oil), propargyl bromide (Aldrich, 80 wt% in toluene), 18-*crown*-6 (Aldrich, 99%), sodium azide (Alfa Aesar, 99%), dimethylformamide (DMF, Aldrich, 99%), dimethylsulfoxide (DMSO, Aldrich, 99%), dimethylsulfoxide-d_6 (DMSO-d_6, Aldrich, 100%), triethylamine (Fluka, 98%) were used as received. Isosorbide, isomannide and isoidide were provided by Roquette Frères (France). Copper iodide triethylphosphite,[1] 1,4:3,6-dianhydrohexitol monotosylates **1**,**3**,**4**,[2,3] and 1,4:3,6-dianhydrohexitol monoazide **5**,[4] were synthesized as described previously.

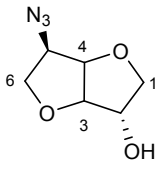
Characterization methods. NMR spectra were recorded on Bruker AC spectrometers at 300 MHz for ^{1}H and 75 MHz for ^{13}C. High resolution mass spectra (HRMS) were recorded on a ThermoFinnigan spectrometer at the Centre de Spectrométrie de Masse de l'Université Claude Bernard Lyon 1. SEC experiments were performed using a system consisting of a Waters apparatus (alliance GPVC 2000 with three PL gel-mixed columns Styragel HT2-HT4-HT6) and dual detection (refractive index and viscometer) operating at 120 °C and using DMSO as the mobile phase at a flow rate of 1 mL/min. Number average molar masses were evaluated by means of a relative and universal method based on PMMA standards. Differential scanning calorimetry (DSC) was performed under nitrogen using a DSC 2920 (TA Instruments) at a heating rate of 20 °C/min. Thermal gravimetric analysis (TGA) measurements were performed under nitrogen using a TGA 2950 (TA Instruments) at a heating rate of 10 °C/min.

Nomenclature. The general nomenclature used for α-azide-ω-alkyne dianhydrohexitol stereoisomers described in this article is **MYNZ**, where Y indicates the propargyl group, Z indicates the azide functionality, M indicates the configuration of the carbon bearing the propargyl group (R or S) and N indicates the configuration of the carbon bearing the azide functionality (R or S).

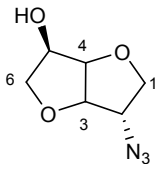


Synthesis of 1,4:3,6-dianhydro-5-O-toluenesulfonyl-L-iditol, 2. *p*-Toluenesulfonyl chloride (7.2 g, 38 mmol) was added to a stirred solution of isoidide (5.0 g, 34 mmol) in pyridine (30 mL). After 48h at 50 °C, the reaction was diluted with dichloromethane (150 mL) and sequentially washed with 1 M HCl (100 mL), water (100 mL), and a saturated solution of K_2CO_3 (100 mL). The organic layer was then dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel, eluting with a 1:1 mixture of heptanes and ethyl acetate giving after evaporation of the

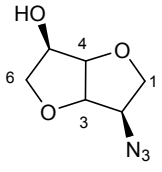
solvents **2** as a yellow liquid (6.0 g, 59%). ^{1}H NMR ($CDCl_3$): δ 7.79 (d, 2H, J = 8.3 Hz, C**H**CSO_2), 7.36 (d, 2H, J = 8.3 Hz, C**H**CCH_3), 4.87 (d, 1H, J = 3.6 Hz, H-5), 4.63 (d, 1H, J = 3.6 Hz, H-4), 4.54 (d, 1H, J = 3.6 Hz, H-3), 4.31-4.33 (m, 1H, H-2), 3.75-3.78 (m, 4H, H-1a, H-1b, H-6a, H-6b), 2.46 (s, 3H, CH_3), 1.84 (d, 1H, J = 4.5 Hz, OH); ^{13}C NMR ($CDCl_3$): δ 145.3 (**C**CH_3), 133.0 (**C**SO_2), 130.0 (**C**$HCSO_2$), 127.7 (**C**$HCCH_3$), 87.5 (C-3), 84.7 (C-5), 83.0 (C-4), 75.5 (C-1), 74.6 (C-2), 71.8 (C-6), 21.6 (**C**H_3). HRMS: m/z calcd for $C_{13}H_{16}O_6S$ (m/z+H): 323.0565; Found: 323.0565.



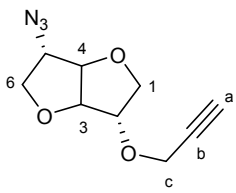
General procedure for azidation. Synthesis of 1,4:3,6-dianhydro-5-azido-5-deoxy-D-sorbitol, 6. A suspension of 1,4:3,6-dianhydro-5-O-toluenesulfonyl-L-iditol **2** (5.4 g, 18 mmol) and sodium azide (3.5 g, 54 mmol) in dimethylformamide (50 mL) was heated at 140 °C for 18h. *Caution! Sodium azide is highly toxic by inhalation and ingestion, yields highly toxic hydrazoic acid under acidic conditions and may react with lead or copper to form highly explosive metal azides.* Excess sodium azide was filtered and the solution was concentrated under vacuum. The residue was diluted with dichloromethane (150 mL) and washed with water (2 × 100 mL). The combined organic phases were dried with $MgSO_4$, filtered and concentrated under vacuum. The residue was then purified by column chromatography on silica gel, eluting with a 7:3 mixture of heptanes and ethyl acetate giving after evaporation of the solvents **6** as a yellow liquid (1.6 g, 52%). ^{1}H NMR ($CDCl_3$): δ 4.72 (t, 1H, J = 4.3 Hz, H-4), 4.30 (d, 1H, J = 4.3 Hz, H-3), 4.18-4,20 (m, 1H, H-2), 3.78-3.84 (m, 4H, H-1a, H-1b, H-5, H-6a), 3.49-3.56 (m, 1H, H-6b); ^{13}C NMR ($CDCl_3$): δ 88.1 (C-3), 82.0 (C-4), 75.6 (C-2), 75.3 (C-1), 69.2 (C-6), 61.7 (C-5). HRMS: m/z calcd for $C_9H_9N_3O_3$ (m/z+H): 172.0722; Found: 172.0721.



Synthesis of 1,4:3,6-dianhydro-2-azido-2-deoxy-D-sorbitol, 7. The general procedure for azidation was applied to 1,4:3,6-dianhydro-2-O-toluenesulfonyl-D-mannitol **3** (4.8 g, 16 mmol) and sodium azide (3.1 g, 48 mmol) to obtain a yellow liquid (2.6 g, 94 %). ^{1}H NMR ($CDCl_3$): δ 4.56 (t, 1H, J = 4.7 Hz, H-4), 4.43 (d, 1H, J = 4.7 Hz, H-3), 4.21-4.28 (m, 1H, H-5), 4.00-4.04 (m, 2H, H-1a, H-2), 3.90-3.94 (m, 1H, H-1b), 3.80-3.85 (m, 1H, H-6a), 3.54-3.57 (m, 1H, H-6b); ^{13}C NMR ($CDCl_3$): δ 86.0 (C-3), 81.8 (C-4), 73.6 (C-6), 72.5 (C-1), 72.0 (C-5), 66.1 (C-2). HRMS: m/z calcd for $C_9H_9N_3O_3$ (m/z+H): 172.0722; Found: 172.0721.

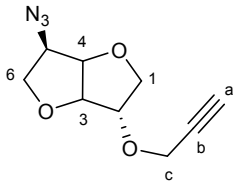


Synthesis of 1,4:3,6-dianhydro-2-azido-2-deoxy-D-mannitol, 8. The general procedure for azidation was applied to 1,4:3,6-dianhydro-2-O-toluenesulfonyl-D-sorbitol **4** (0.51 g, 1.7 mmol) and sodium azide (0.33 g, 5.1 mmol) to obtain a yellow liquid (0.16 g, 54 %). ^{1}H NMR ($CDCl_3$): δ 4.67 (t, 1H, J = 5.0 Hz, H-3), 4.52 (d, 1H, J = 5.0 Hz, H-4), 4.29-4.38 (m, 1H, H-5), 4.27 (dd, 1H, J = 6.2 Hz, J = 9.6 Hz, H-6a), 4.10 (dd, 1H, J = 6.7 Hz, J = 8.4 Hz, H-1a), 3.85-3.92 (m, 1H, H-2), 3.76 (t, 1H, J = 8.4 Hz, H-1b), 3.67 (dd, 1H, J = 6.6 Hz, J = 9.6 Hz, H-6b); ^{13}C NMR ($CDCl_3$): δ 82.5 (C-3), 82.2 (C-4), 74.1 (C-6), 72.4 (C-5), 70.4 (C-1), 62.2 (C-2). HRMS: m/z calcd for $C_9H_9N_3O_3$ (m/z+H): 172.0722; Found: 172.0721.

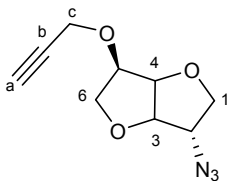


General procedure for alkylation. Synthesis of 1,4:3,6-dianhydro-5-azido-2-O-propargyl-5-deoxy-L-iditol, 9. NaH (1.8 g, 44 mmol) was added to a solution of azide **5** (5.0 g, 29 mmol) in 60 mL of dimethylformamide maintained at 0 °C under argon. After hydrogen was entirely emitted, propargyl bromide (4.2 mL, 44 mmol) and 18-*crown*-6 (110 mg, 0.29 mmol) were added and the mixture was stirred for

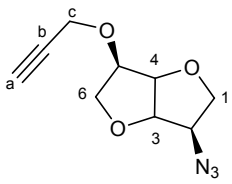
12h at room temperature. After neutralization of residual NaH by distilled water (10 mL), the solvents were evaporated under reduced pressure and the residue was extracted with dichloromethane (3 × 100 mL). The organic layer was dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with a 85:15 mixture of petroleum ether and ethyl acetate giving after evaporation of the solvents **9** as a yellow liquid (5.7 g, 94%). ^{1}H NMR (C_2D_6SO): δ 4.57 (d, 1H, J = 4.1 Hz, H-3), 4.50 (d, 1H, J = 4.1 Hz, H-4), 4.23 (d, 2H, J = 2.4 Hz, H-c), 4.20-4.21 (m, 1H, H-5), 4.09-4.10 (m, 1H, H-2), 3.72-3.85 (m, 4H, H-1a, H-1b, H-6a, H-6b), 3.49 (t, 1H, J = 2.4 Hz, H-a); ^{13}C NMR (C_2D_6SO): δ 85.1 (C-4), 84.6 (C-3), 82.8 (C-2), 79.9 (C-b), 77.4 (C-a), 70.8-71.6 (C-1, C-6), 65.1 (C-5), 56.1 (C-c). HRMS: m/z calcd for $C_9H_{11}N_3O_3$ (m/z+H): 210.0879; Found: 210.0880. T_g = -62 °C.



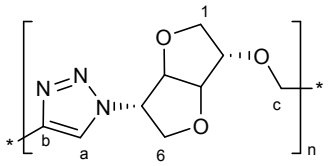
Synthesis of 1,4:3,6-dianhydro-5-azido-2-O-propargyl-5-deoxy-D-sorbitol, 10. The general procedure for alkylation was applied to monazide **6** (0.85 g, 5.0 mmol), NaH (0.30 g, 7.5 mmol) and propargyl bromide (0.71 mL, 7.5 mmol) to obtain a yellow solid (0.87 g, 84%). ^{1}H NMR (C_2D_6SO): δ 4.73 (t, 1H, J = 4.6 Hz, H-4), 4.49 (d, 1H, J = 4.6 Hz, H-3), 4.23 (d, 2H, J = 2.4 Hz, H-c), 4.11-4,12 (m, 1H, H-2), 3.94-4.10 (m, 2H, H-1b, H-5), 3.79-3.87 (m, 2H, H-1a, H-6a), 3.51-3.57 (m, 1H, H-6b), 3,49 (t, 1H, J = 2.4 Hz, H-a); ^{13}C NMR (C_2D_6SO): δ 85.5 (C-4), 82.4 (C-3), 82.3 (C-2), 78.9 (C-b), 77.3 (C-a), 69.0-72.4 (C-1, C-6), 61.4 (C-5), 56.0 (C-c). HRMS: m/z calcd for $C_9H_{11}N_3O_3$ (m/z+H): 210.0879; Found: 210.0880. M_p = 74 °C.



Synthesis of 1,4:3,6-dianhydro-2-azido-5-O-propargyl-2-deoxy-D-sorbitol, 11. The general procedure for alkylation was applied to monazide **7** (2.6 g, 15 mmol), NaH (0.90 g, 22 mmol) and propargyl bromide (2.2 mL, 22 mmol) to obtain a yellow liquid (2.7 g, 86%). ^{1}H NMR (C_2D_6SO): δ 4.64 (t, 1H, J = 4.6 Hz, H-4), 4.47 (d, 1H, J = 4.6 Hz, H-3), 4.13-4.31 (m, 4H, H-2, H5, H-c), 3.80-4.93 (m, 3H, H-1a, H-1b, H-6a), 3.46-3.53 (m, 2H, H-6b, H-a); ^{13}C NMR (C_2D_6SO): δ 85.8 (C-3), 80.0 (C-4, C-b), 78.1 (C-5), 77.2 (C-a), 70.0-72.1 (C-1, C-6), 65.5 (C-2), 56.9 (C-c). HRMS: m/z calcd for $C_9H_{11}N_3O_3$ (m/z+H): 210.0879; Found: 210.0878. T_g = -72 °C.

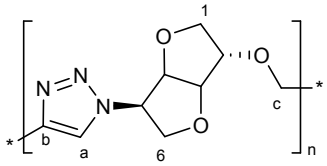


Synthesis of 1,4:3,6-dianhydro-2-azido-5-O-propargyl-2-deoxy-D-mannitol, 12. The general procedure for alkylation was applied to monazide **8** (0.52 g, 3.0 mmol), NaH (0.18 g, 4.5 mmol) and propargyl bromide (0.44 mL, 4.5 mmol) to obtain a yellow liquid (0.55 g, 86%). ^{1}H NMR (C_2D_6SO): δ 4.67 (t, 1H, J = 4.6 Hz, H-3), 4.54 (t, 1H, J = 4.6 Hz, H-4), 4.14-4,30 (m, 3H, H-5, H-c), 3.91-4.01 (m, 3H, H-1a, H-2, H-6a), 3.48-3.60 (m, 3H, H-1b, H-6b, H-a); ^{13}C NMR (C_2D_6SO): δ 82.5 (C-3), 80.3 (C-4), 80.0 (C-b), 78.4 (C-5), 77.4 (C-a), 69.7-70.3 (C-1, C-6), 61.3 (C-2), 56.9 (C-c). HRMS: m/z calcd for $C_9H_{11}N_3O_3$ (m/z+H): 210.0879; Found: 210.0878. T_g = -67 °C.

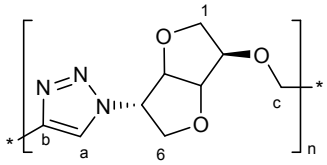


General procedure for the synthesis of polytriazoles by copper catalyzed azide-alkyne cycloaddition in DMSO, synthesis of 13. Triethylamine (0.09 mL, 0.7 mmol) and CuI.P(OEt)$_3$ (2 mg, 0.006 mmol) were sequentially added to a solution of **9** (0.1 g, 0.5 mmol) in 0.5 mL of dimethylsulfoxide. After 15h at 60 °C, the resulting physical gel was solubilized in DMSO and precipitated twice into ethanol (15 mL). The solide residue was filtered, dried and DMSO traces

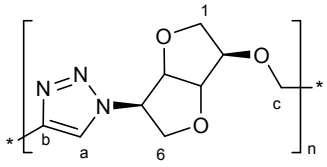
were extracted by stirring the resulting powder for 12 hours in water (4 × 15 mL) and acetone (2 × 15 mL). The suspension wasthen filtered and dried under vacuum yielding **13** as a colorless powder (93 mg, 95%). ^{1}H NMR (C_2D_6SO): δ 8.16 (s, 1H, H-a), 5.19-5.21 (m, 1H, H-5), 4.77-4.84 (m, 2H, H-3, H-4), 4.60-4.62 (m, 2H, H-c), 4.07-4.17 (m, 3H, H-2, H-6a, H-6b), 3.88-3.90 (m, 2H, H-1a, H-1b). The solubility of polytriazoles **13**-**20** in DMSO at room temperature is below the concentration required to perform ^{13}C NMR.



Synthesis of 14. The general procedure for CuAAC polyaddition in DMSO was applied to monomer **10** (0.1 g, 0.5 mmol), triethylamine (0.09 mL, 0.7 mmol) and CuI.P(OEt)$_3$ (2 mg, 0.006 mmol) to obtain an orange solid (93 mg, 95%). ^{1}H NMR (C_2D_6SO): δ 8.18 (s, 1H, H-a), 5.26-5.33 (m, 1H, H-5), 4.78-4.81 (m, 1H, H-4), 4.70-4.71 (m, 1H, H-3), 4.59-4.61 (m, 2H, H-c), 3.89-4.30 (m, 5H, H-1a, H-1b, H-2, H-6a, H-6b).

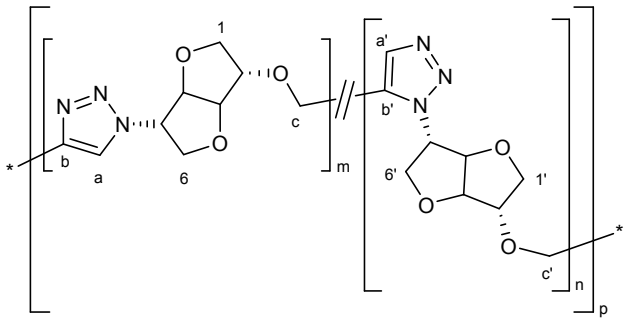


Synthesis of 15. The general procedure for CuAAC polyaddition in solution was applied to monomer **11** (0.1 g, 0.5 mmol), triethylamine (0.09 mL, 0.7 mmol) and CuI.P(OEt)$_3$ (2 mg, 0.006 mmol) to obtain a brown solid (96 mg, 94%). ^{1}H NMR (C_2D_6SO): δ 8.15 (s, 1H, H-a), 5.20-5.22 (m, 1H, H-5), 4.58-4.82 (m, 4H, H-3, H-4, H-c), 3.59-4.17 (m, 5H, H-1a, H-1b, H-2, H-6a, H-6b).

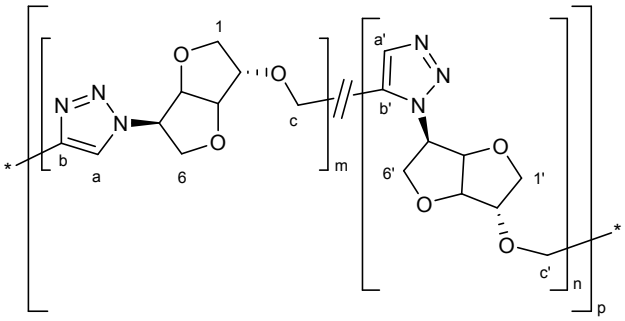


Synthesis of 16. The general procedure for CuAAC polyaddition in DMSO was applied to monomer **12** (0.9 g, 0.4 mmol), triethylamine (0.08 mL, 0.6 mmol) and CuI.P(OEt)$_3$ (2 mg, 0.006 mmol) to obtain a yellow solid (81 mg, 88%). ^{1}H NMR (C_2D_6SO): δ 8.17 (s, 1H, H-a), 5.27-5.34 (m, 1H, H-5),

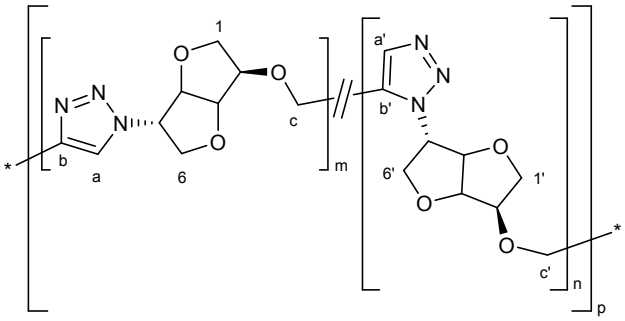
4.56-4.81 (m, 4H, H-3, H-4, H-c), 4.30-4.36 (m, 1H, H-2), 3.54-4.23 (m, 4H, H-1a, H-1b, H-6a, H-6b).



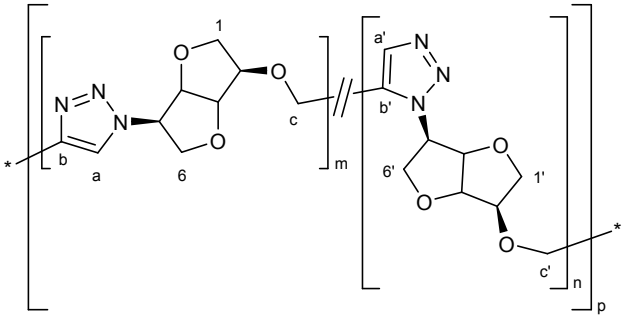
General procedure for the synthesis of polytriazoles by catalyst free azide-alkyne cycloaddition in bulk, synthesis of 17. Polymer **17** was obtained quantitatively as a slightly brown solid by heating monomer **9** (10-50 mg) from room temperature to 200 °C at a heating rate of 20 °C/min in a vial. The safe polyaddition of larger quantities monomer **9** (0.05-2 g) requires a precure step at an intermediate temperature. First, monomer **9** was heated in a vial at 50 °C for 2 hours to form solid reactive oligomers ($DP_n \sim 3$). The temperature was then increased to 200 °C for 10 minutes to afford **17** as a slightly brown solid in quantitative yield. Alternatively, films of polytriazole **17** were generated by heating **9** or higher generation oligomers under a hot press at 200 °C and 2900 psi for 30 seconds. The pressure and the film large surface area favour the energy dissipation and a precure step is not necessary in this case. ^{1}H NMR (C_2D_6SO): δ 8.16-8.17 (m, 1H, H-a), 7.76-7.77 (m, 1H, H-a'), 5.21-5.23 (m, 1H, H-5), 5.12-5.14 (m, 1H, H-5'), 4.78-4.89 (m, 6H, H-3, H-4, H-3', H-4', H-c'), 4.58-4.67 (m, 2H, H-c), 3.86-4.17 (m, 10H, H-1a, H-1b, H-2, H-6a, H-6b, H-1a', H-1b', H-2', H-6a', H-6b'). 1,4/1,5 Ratio of 2.0:1.0 as determined by integration of Ha and Ha' signals.



Synthesis of 18. The general procedure for polyaddition in bulk was applied to monomer **10** yielding **18** as a brown solid. ^{1}H NMR (C_2D_6SO): δ 8.16-8.18 (m, 1H, H-a), 7.74-7.75 (m, 1H, H-a'), 5.27-5.33 (m, 1H, H-5), 5.08-5.12 (m, 1H, H-5'), 4.51-4.86 (m, 8H, H-3, H-4, H-c, H-3', H-4', H-c'), 3.64-4.30 (m, 10H, H-1a, H-1b, H-2, H-6a, H-6b, H-1a', H-1b', H-2', H-6a', H-6b'). 1,4/1,5 Ratio of 1.9:1.0 as determined by integration of Ha and Ha' signals.



Synthesis of 19. The general procedure for polyaddition in bulk was applied to monomer **11** yielding **19** as a brown solid. ^{1}H NMR (C_2D_6SO): δ 8.14-8.16 (m, 1H, H-a), 7.78-7.79 (m, 1H, H-a'), 5.22-5.26 (m, 2H, H-5, H-5'), 4.58-4.90 (m, 8H, H-3, H-4, H-c, H-3', H-4', H-c'), 3.59-4.22 (m, 10H, H-1a, H-1b, H-2, H-6a, H-6b, H-1a', H-1b', H-2', H-6a', H-6b'). Ratio 1,4/1,5 = 1.8/1.0 as determined by integration of Ha and Ha' signals.



Synthesis of 20. The general procedure for polyaddition in bulk was applied to monomer **12** yielding **20** as a brown solid. ^{1}H NMR (C_2D_6SO): δ 8.16-8.17 (m, 1H, H-a), 7.77-7.78 (m, 1H, H-a'), 5.27-5.34 (m, 1H, H-5), 5.18-5.25 (m, 1H, H-5'), 4.57-4.90 (m, 8H, H-3, H-4, H-c, H-3', H-4', H-c'), 4.30-4.39 (m, 2H, H-2, H-

2'), 3.41-4.24 (m, 8H, H-1a, H-1b, H-6a, H-6b, H-1a', H-1b', H-6a', H-6b'). Ratio 1,4/1,5 = 1.8/1.0 as determined by integration of Ha and Ha' signals.

General procedure for kinetic monitoring of the polyaddition by DSC. Several DSC capsules containg *ca.* 5 mg of monomer **9** or **12** were sealed off under ambient conditions. A first capsule of each monomer was heated in the DSC apparatus from -90 °C to 300 °C at a heating rate of 20 °C/min (t = 0 in Figure S1) to obtain monomer glass transition temperature (T_g) and total bulk polyaddition enthalpy (ΔH_{total}). Then, different capsules were heated in an oven at temperatures ranging from 70 °C to 140 °C during times ranging from 10 to 240 minutes before being quenched at room temperature and directly analyzed by DSC to access T_g of the formed polytriazoles and residual polyaddition enthalpy ($\Delta H_{residual}$).

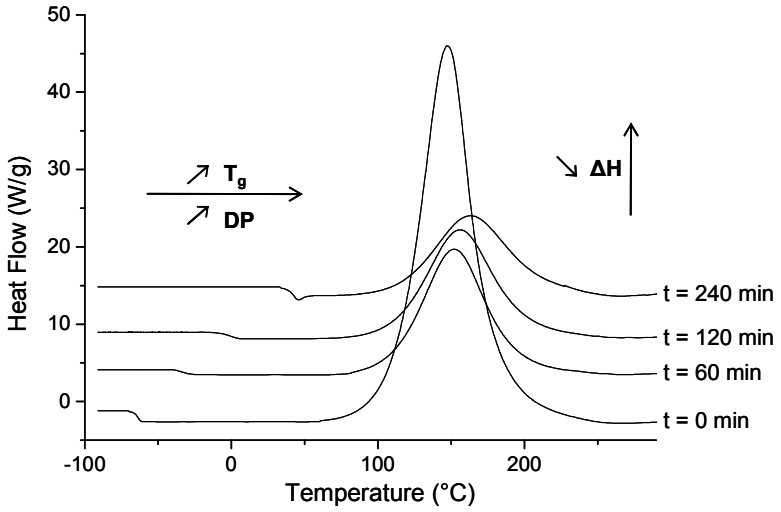


Figure S1. Evolution of DSC traces with time at 70 °C during the catalyst free polyaddition of **9** in bulk**.**

For each sample, monomer conversion (ρ) and theoretical number average polymerization degrees (DP_n) were calculated using Equations S1 and S2, respectively.

$$\rho = (\Delta H_{total} - \Delta H_{residual})/\Delta H_{total} \qquad \text{(Eq. S1)}$$

$$DP_n = 1/(1 - \rho) \qquad \text{(Eq. S2)}$$

Also by combining DSC kinetics performed at different temperatures (Figure S2 left), the evolution of T_g with M_n ($M_n = DP_n \times 209$) shows the adequation with the Flory-Fox relation (Equation S3) for polytriazoles having a DP_n higher than 12 which corresponds to an average molar mass of 2500 g/mol (Figure S2 right).

$$T_g = T_{g\infty} - K_g/M_n \qquad \text{(Eq. S3)}$$

where $T_{g\infty}$ is the bulk glass transition temperature and K_g a polymer-specific constant.

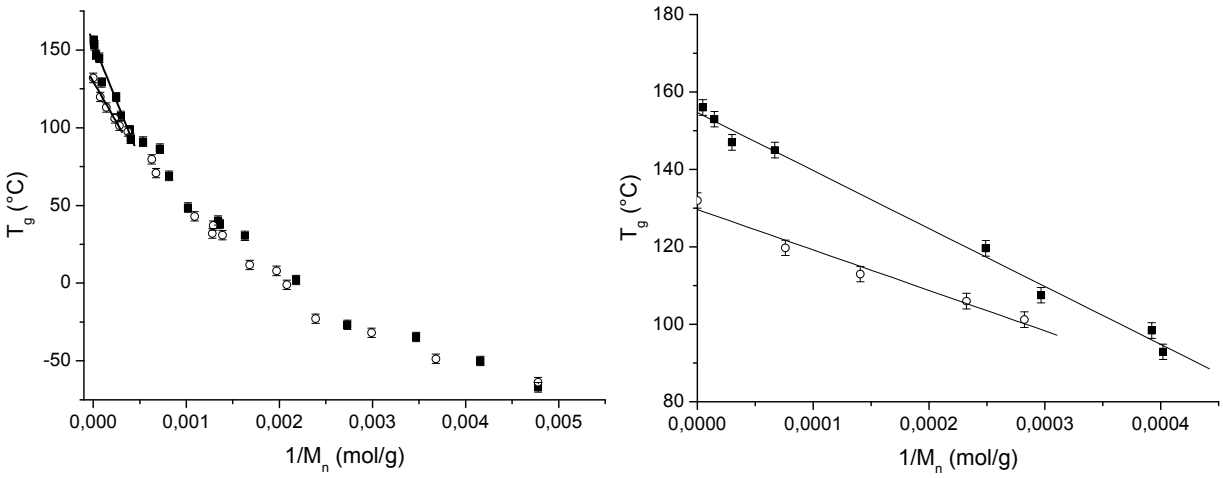


Figure S2. Full (left) and partial (right) evolution of glass transition temperature versus inverse of number average molar mass (Flory-fox plot) for the catalyst free polyaddition of **9** (○) and **12** (■) in bulk.

General procedure for the determination of the polyaddition activation energy by DSC (Kissinger plot). This method allows the determination of the bulk polyaddition activation energy by DSC kinetic measurements. Several DSC capsules containg *ca.* 5 mg of monomer **9** or **12** were sealed off under ambient conditions. Each monomer was heated in the DSC apparatus from 0 °C to 300 °C at heating rates (Φ) of 5, 10, 15 and 20 °C/min (Figure S3 for **12**).

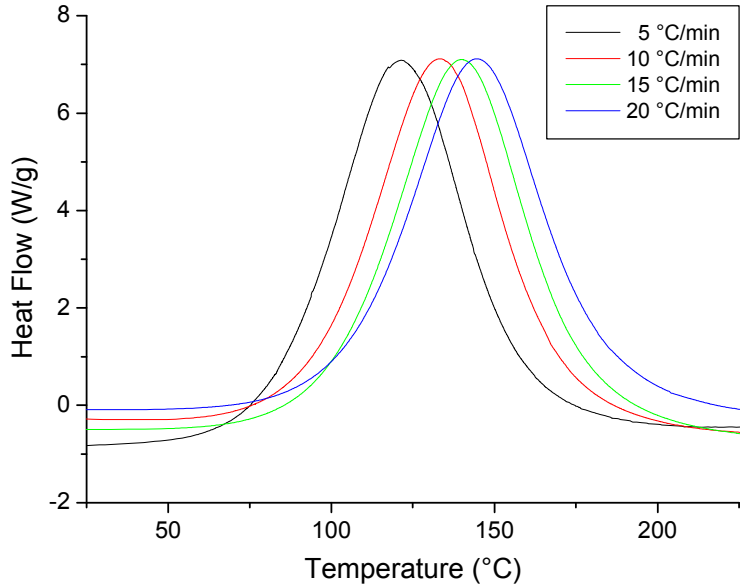


Figure S3. Evolution of DSC traces with heating rate during the catalyst free polyaddition of **12** in bulk**.**

The relation between the heating rate (Φ) and the peak exotherm (T_p) has been expressed by Kissinger in the form of Equation S4:[6]

$$\ln (\Phi/T_p^2) = \ln (AR/E_a) - E_a/(RT_p) \qquad \text{(Eq. S4)}$$

where Φ is the heating rate, T_p the peak exotherm, R the ideal gas constant and E_a the polyaddition activation energy. The values of E_a were obtained from the slopes of the curves plotted in Figure S4 (Kissinger plot).

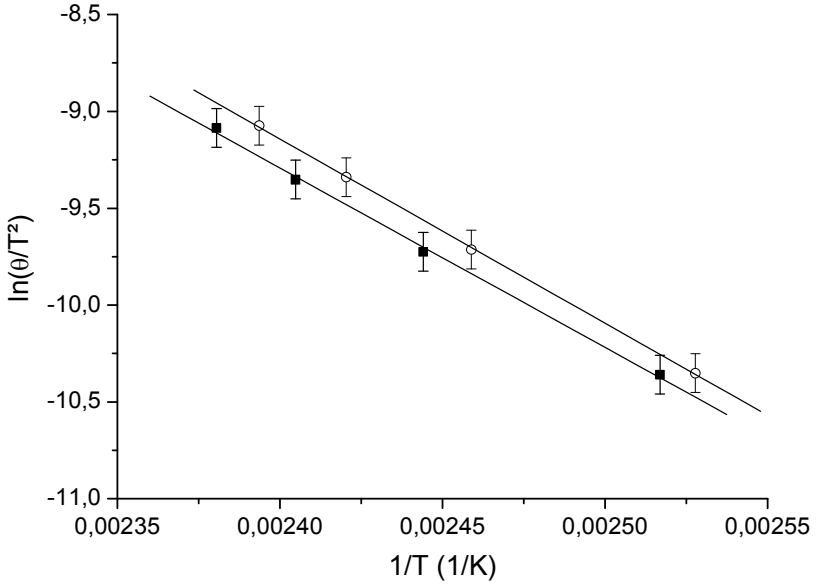


Figure S4. Kissinger plot for the catalyst free polyaddition in bulk of **9** (○) and **12** (■).

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