Structure−Properties Relationship of Biosourced Stereocontrolled Polytriazoles from Click Chemistry Step Growth Polymerization of Diazide and Dialkyne Dianhydrohexitols

Céline Besset, Jean-Pierre Pascault, Etienne Fleury, Eric Drockenmuller,* and Julien Bernard*

Université de Lyon, INSA-Lyon, Université Claude Bernard Lyon 1, Ingénierie des Matériaux Polymères (UMR-CNRS 5223), F-69621 Villeurbanne Cedex, France

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The design of dialkyne and diazide functionalized dianhydrohexitol stereoisomers (**1**−**6**) afforded a new family of starch-based polytriazoles (**7**−**15**) with defined stereochemistry through $A_2 + B_2$ CuAAC step growth polymerization. The present strategy gave rise to polytriazoles having a high biosourced weight fraction (superior to 60% wt) and exhibiting relatively high molar masses (M_n = 8−17 kg/mol) that could be easily dissolved in DMF or DMSO. The obtained materials were amorphous and displayed high transition temperatures (T_g = 125−166 °C) as well as good resistance to thermal degradation (T_{d10} = 325−347 °C). Monomer stereochemistry proved to be a crucial parameter aiming at generating polymers with high T_g. Thus, optimal thermal properties were obtained with monomers having *RR* absolute configuration of the C-2 and C-5 carbon atoms (isomannide configuration).

Introduction

The fossil resources depletion and rising costs are at present driving a renewal of interest toward the development of high performance materials derived from biomass feedstock. In this context, increasing attention has been dedicated to the generation of innovative and sustainable materials from the chemical modification of inexpensive and abundant natural polymers such as cellulose, starch, chitosan, or lignin, as well as their derivatives.[1] A second promising route to biorenewable materials relies on the polymerization of natural or biosourced monomers. For instance, extensive research efforts have been devoted to the preparation of a broad array of macromolecular materials derived from tannins,[2] vegetable oils,[3] furans,[4] and sugars.[5] One of the most spectacular achievements in the field of biosourced polymers is probably related to the production of starch-based polylactide, an industrial commodity polymer with applications in biomaterials, packaging, or fiber technology.[6] Unfortunately, the applicability of these biorenewable polyesters is currently limited by their relatively low glass transition temperature (T_g = 50−60 °C) as well as their poor toughness, and it is, therefore, of keen interest to develop a panel of new biosourced materials exhibiting improved thermal properties and tunable functionalities.

In regard to their nontoxicity, chirality, and rigidity, 1,4:3,6-dianhydrohexitols, that is, isosorbide, isomannide, and isoidide, constitute another promising class of biosourced monomers.[7] These diols generally issued from cereal-based polysaccharides have been thoroughly investigated in step growth polymerization processes to generate polymers having enhanced and tunable thermal and mechanical properties. As the secondary alcohols of dianhydrohexitols display a relatively low reactivity that depends on their configuration and hydrogen bonding nature, significant efforts have also been paid to the preparation of derivatives with enhanced reactivity.[7] For instance, amine, isocyanate, primary alcohol, and carboxylic acid derivatives have been reported by Thiem,[8] Bortolussi,[9] and Brandenburg.[10]

Consequently, a large panel of amorphous and semicrystalline dianhydrohexitol-based materials, that is, polyamides, polyesters, poly(ester-imide)s, poly(ether-sulfone)s, polyurethanes, poly(ether-urethane)s, poly(ester-amide)s, or polycarbonates, has been generated in the last decades by copolymerizing 1,4:3,6-dianhydrohexitol derivatives with a broad range of aliphatic or aromatic comonomers whose chemical nature hence strongly guided the final properties of the polymers.[7,8,11] In contrast, materials generated from the exclusive polymerization of dianhydrohexitol-based monomers and thus displaying a high biosourced weight fraction have been scarcely reported to date.[7,8,12] To our knowledge, only semicrystalline polythiourea (T_g not detected, T_m = 270 °C), polyurea (T_g not detected, T_m = 185−191 °C), polythiourethane (T_g not detected, T_m = 158 °C), polyurethane (T_g = −20−118 °C, T_m = 120−194 °C), and amorphous polycarbonate (T_g = 163 °C) have been described in the literature and the influence of monomer stereochemistry has not been systematically discussed.

An alternative fruitful route to materials having high dianhydrohexitol weight fraction relies on the design of derivatives suitable for step growth polymerization through the highly efficient, orthogonal and regiospecific copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC).[13] So far, this reaction constitutes one of the most reliable illustrations of the "click chemistry" philosophy,[14] and several examples have notably shown its potential to obtain functional polymer materials through step growth polymerization.[15] The CuAAC polyaddition of natural, bioanalogous, or biosourced monomers has also been lately explored.[16] Recently, we described the synthesis of α-azide-ω-alkyne dianhydrohexitol stereoisomers and the investigation of their polyaddition by CuAAC in solution or by

* To whom correspondence should be addressed. E-mail: julien.bernard@insa-lyon.fr; eric.drockenmuller@univ-lyon1.fr.

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solvent and copper-free thermal Huisgen polyaddition, as well as the formation of biosourced polymer networks.[17] These approaches afforded high T_g linear polytriazoles or networks as a consequence of the rigidity promoted by the combined presence of 1,2,3-triazole and dianhydrohexitol heterocyclic moieties. In the case of linear polytriazoles, monomer stereochemistry and to some extent polyaddition regiospecificity (exclusively 1,4- or mixtures of 1,4- and 1,5-disubstituted 1,2,3-triazoles) were shown to affect the physicochemical properties of the resulting materials. However, contrary to the thermal bulk polyaddition process, the catalyzed polyaddition process was somewhat limited by the physical gelation of the polymerization media and the very poor solubility of the resulting polymers in common organic solvents.

In the present study, we expand on our earlier work by studying the $A_2 + B_2$ CuAAC step growth polymerization of tailor-made diazide (A_2) and dialkyne (B_2) dianhydrohexitol stereoisomers and by examining the structure/properties relationship of the resulting polytriazoles. Particularly, the impact of monomer stereochemistry on the physicochemical properties, that is, M_n, T_g, T_{d10}, or solubility, of these biosourced linear polytriazoles are discussed and compared to the polytriazoles generated through the AB approach.

Experimental Section

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%), and triethylamine (Fluka, 98%) were used as received. Isosorbide, isomannide, and isoidide were provided by Roquette Frères (France). Copper iodide triethylphosphite[18] and 2,5-diazide-1,4:3,6- dianhydrohexitol stereoisomers **1**−**3**[8a] were synthesized as previously described.

Characterization Methods. NMR spectra were recorded on a Bruker AC spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C. High resolution mass spectrometry (HRMS) was performed on a ThermoFinnigan spectrometer at the Centre de Spectrométrie de Masse of the 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 viscosimeter) operating at 120 °C and using DMSO as the mobile phase at a flow rate of 1 mL/min. Molar masses were evaluated by means of a relative and universal method based on PMMA standards.[19] Differential scanning calorimetry (DSC) experiments were 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.

General Procedure for the Synthesis of Dialkyne Monomers. *Synthesis of 1,4:3,6-Dianhydro-2,5-di-O-propargyl-D-mannitol,* **4.** NaH (680 mg, 17 mmol) was added to a solution of isomannide (510 mg, 3.5 mmol) in 15 mL of dimethylformamide maintained at 0 °C under argon. After hydrogen was entirely emitted, propargyl bromide (1.9 mL, 17 mmol) and 18-crown-6 (11 mg, 0.03 mmol) were added and the mixture was then stirred 2 h at room temperature. After neutralization of residual NaH by distilled water (5 mL), the solvents were evaporated under reduced pressure and the residue was extracted with dichloromethane (3 × 30 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 7:3 mixture of petroleum ether and ethyl acetate, giving after evaporation of the solvents a yellow solid (745 mg, 96%). ^{1}H NMR (C_2D_6SO): δ 4.52−4.53 (m, H-3, H-4, 2H), 4.12−4.29 (m, H-2, H-5, H-a, 6H), 3.88−3.93 (m, H-1a, H-6a, 2H), 3.43−3.48 (m, H-1b, H-6b, H-c, 4H); ^{13}C NMR (C_2D_6SO): δ 80.0 (C-3, C-4), 79.7 (C-b), 78.4 (C-2, C-5), 77.3 (C-c), 70.1 (C-1, C-6), 56.8 (C-a). HRMS *m*/*z* Calcd for $C_{12}H_{14}O_6$ (*m*/*z*+H), 223.0970; found, 223.0970.

Synthesis of 1,4:3,6-Dianhydro-2,5-di-O-propargyl-D-sorbitol, **5.** The general procedure for alkylation was applied to isosorbide (510 mg, 3.5 mmol), NaH (700 mg, 17.5 mmol), and propargyl bromide (1.9 mL, 17 mmol) to obtain a yellow oil (747 mg, 96%). ^{1}H NMR (C_2D_6SO): δ 4.57 (t, J = 4.6 Hz, H-3, 1H), 4.47 (d, J = 4.6 Hz, H-4, 1H), 4.05−4.30 (m, H-2, H-5, C-a, 6H), 3.71−3.90 (m, H-1a, H-6a, H-6b, 3H), 3.43−3.47 (m, H-1b, H-c, 3H); ^{13}C NMR (C_2D_6SO): δ 85.1 (C-3), 82.5 (C-2), 80.0 (C-b), 79.7 (C-4), 78.4 (C-5), 77.3 (C-c), 72.3 (C-1), 69.4 (C-6), 55.9−56.8 (C-a). HRMS *m*/*z* Calcd for $C_{12}H_{14}O_6$ (*m*/*z*+H), 223.0970; found, 223.0970.

Synthesis of 1,4:3,6-Dianhydro-2,5-di-O-propargyl-L-iditol, **6.** The general procedure for alkylation was applied to isoidide (510 mg, 3.5 mmol), NaH (700 mg, 17.5 mmol), and propargyl bromide (1.9 mL, 17 mmol) to obtain a yellow solid (765 mg, 98%). ^{1}H NMR (C_2D_6SO): δ 4.52 (s, H-3, H-4, 2H), 4.22 (d, J = 2.4 Hz, H-a, 4H), 4.07−4,08 (m, H-2, H-5, 2H), 3.68−3,82 (m, H-1a, H-1b, H-6a, H-6b, 4H), 3.46 (t, J = 2.4 Hz, H-c, 2H); ^{13}C NMR (C_2D_6SO): δ 84.4 (C-3, C-4), 81.9 (C-2, C-5), 80.0 (C-b), 77.3 (C-c), 71.1 (C-1, C-6), 56.0 (C-a). HRMS *m*/*z* Calcd for $C_{12}H_{14}O_6$ (*m*/*z*+H), 223.0968; found, 223.0968.

General Procedure for the Synthesis of Polytriazoles by Copper-Catalyzed Azide−Alkyne Cycloaddition in DMSO. *Synthesis of* **7.** Triethylamine (0.36 mL, 1.5 mmol) and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) were sequentially added to a stoichiometric mixture of diazide **1** (98 mg, 0.48 mmol) and dialkyne **4** (102 mg, 0.48 mmol) in 0.94 mL of dimethylsulfoxide. After 15 h at 60 °C, the reaction media was precipitated into ethanol (30 mL). The solid was filtered and dried and residual DMSO was extracted by stirring the resulting powder for 12 h in water (4 × 15 mL) and acetone (2 × 15 mL). Compound **7** was dried under vacuum and recovered as an orange solid (164 mg, 83%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.25 (s, H-c, 2H), 5.43−5.48 (m, H-2, H-5, 2H), 4.96−4.98 (m, H-3, H-4, 2H), 4.56−4.76 (m, H-3′, H-4′, H-a, 6H), 4.30−4.33 (m, H-2′, H-5′, 2H), 3.43−4.14 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-6a′, H-6b′, 8H); ^{13}C NMR (C_2D_6SO): δ 144.0 (C-b), 124.3 (C-c), 82.4 (C-3, C-4), 79.8 (C-3′, C-4′), 79.0 (C-2′, C-5′), 70.3 (C-1′, C-6′), 69.4 (C-1, C-6), 62.2 (C-2, C-5), 61.8 (C-a).

Synthesis of **8.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **2** (100 mg, 0.5 mmol) and dialkyne **4** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol) and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a yellow solid (189 mg, 93%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.25 (s, H-c, 1H), 8.17 (s, H-c, 1H), 5.37−5.40 (m, H-2, H-5, 2H), 5.01−5.05 (m, H-3, H-4, 2H), 4.53−4.71 (m, H-3′, H-4′, H-a, 6H), 3.42−4.41 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-2′, H-5′, H-6a′, H-6b′, 10H); ^{13}C NMR (C_2D_6SO): δ 144.0 (C-b), 124.4 (C-c), 123.4 (C-c), 87.3 (C-4), 81.8 (C-3), 79.8 (C-3′, C-4′), 79.0 (C-2′, C-5′), 73.1 (C-6), 70.3 (C-1′, C-6′), 68.6 (C-1), 65.5 (C-5), 62.6 (C-a), 61.9 (C-2).

Synthesis of **9.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **3** (100 mg, 0.5 mmol), dialkyne **4** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a yellow solid (188 mg, 93%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.19 (s, H-c, 2H), 5.36−5.38 (m, H-2, H-5, 2H), 5.12−5.14 (m, H-3, H-4, 2H), 4.52−4.68 (m, H-3′, H-4′, H-a, 6H), 4.31−4.36 (m, H-2′, H-5′, 2H), 3.41−4.17 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-6a′, H-6b′, 8H); ^{13}C NMR (C_2D_6SO): δ 145.2 (C-b), 123.4 (C-c), 87.0 (C-3, C-4), 79.8 (C-3′, C-4′), 79.0 (C-2′, C-5′), 72.0 (C-1, C-6), 70.2 (C-1′, C-6′), 64.9 (C-2, C-5), 62.5 (C-a).

Synthesis of **10.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **1** (100 mg, 0.5 mmol) and dialkyne **5** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol) and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a light brown solid (142 mg, 70%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.26 (s, H-c, 2H), 5.41−5.48 (m, H-2, H-5, 2H), 4.97−4.99 (m, H-3, H-4, 2H), 4.50−4.74 (m, H-3′, H-4′, H-a, 6H), 3.40−4.33 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-2′,

H-5′, H-6a′, H-6b′, 10H); ^{13}C NMR (C_2D_6SO): δ 144.0 (C-b), 124.4 (C-c), 85.2 (C-3′), 82.9 (C-2′), 81.9 (C-3, C-4), 79.6 (C-4′), 78.8 (C-5′), 72.2 (C-6, C-1′), 69.4 (C-1, C-6′), 62.4 (C-a), 62.0 (C-2, C-5), 61.5 (C-a).

Synthesis of **11.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **2** (100 mg, 0.5 mmol), dialkyne **5** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2.4 mg, 0.007 mmol) to obtain a brown solid (166 mg, 78%).^{1}H NMR (C_2D_6SO): δ 8.26 (s, H-c, 1H), 8.17 (s, H-c, 1H), 5.37−5.39 (m, H-2, H-5, 2H), 5.03−5.10 (m, H-3, H-4, 2H), 4.48−4.74 (m, H-3′, H-4′, H-a, 6H), 3.70−4.49 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-2′, H-5′, H-6a′, 9H), 3.39−3.44 (m, H-6b′, 1H); ^{13}C NMR (C_2D_6SO): δ 140.4 (C-b), 137.7 (C-b), 124.5 (C-c), 123.4 (C-c), 87.2 (C-3′), 85.4 (C-2′), 83.1 (C-3), 81.8 (C-4), 79.7 (C-4′), 78.9 (C-5′), 73.1 (C-1′), 72.5 (C-6′), 69.4 (C-1), 68.6 (C-6), 65.6 (C-2), 62.5 (C-a), 61.9 (C-5), 61.6 (C-a).

Synthesis of **12.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **3** (100 mg, 0.5 mmol), dialkyne **5** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a light brown solid (146 mg, 72%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.19 (s, H-c, 2H), 5.36−5.37 (m, H-2, H-5, 2H), 5.11−5.15 (m, H-3, H-4, 2H), 4.46−4.70 (m, H-3′, H-4′, H-a, 6H), 4.32−4.37 (m, H-2′, H-5′, 2H), 3.38−4.18 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-6a′, H-6b′, 8H); ^{13}C NMR (C_2D_6SO): δ 144.1 (C-b), 126.8 (C-c), 123.4 (C-c), 86.9 (C-3, C-4), 85.4 (C-4′), 83.1 (C-5′), 79.7 (C-3′), 78.9 (C-2′), 72.4 (C-6′), 72.0 (C-1, C-6), 69.3 (C-1′), 64.9 (C-2, C-5), 62.5 (C-a), 61.6 (C-a).

Synthesis of **13.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **1** (98 mg, 0.48 mmol), dialkyne **6** (102 mg, 0.48 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a yellow solid (188 mg, 93%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.25 (s, H-c, 2H), 5.40−5.47 (m, H-2, H-5, 2H), 4.96−4.97 (m, H-3, H-4, 2H), 4.53−4.62 (m, H-3′, H-4′, H-a, 6H), 4.26−4.32 (m, H-2′, H-5′, 2H), 3.70−4.07 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-6a′, H-6b′, 8H); ^{13}C NMR (C_2D_6SO): δ 149.4 (C-b), 124.4 (C-c), 84.6 (C-3′, C-4′), 82.4 (C-3, C-4), 82.0 (C-2′, C-5′), 71.2 (C-1′, C-6′), 69.4 (C-1, C-6), 62.2 (C-2, C-5), 61.8 (C-a).

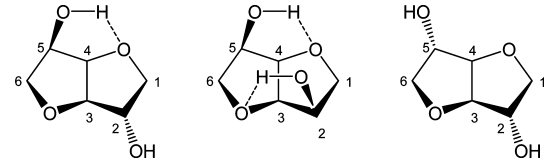
Synthesis of **14.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **2** (100 mg, 0.5 mmol), dialkyne **6** (103 mg, 0.5 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a slightly brown solid (191 mg, 94%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.26 (s, H-c, 1H), 8.16 (s, H-c, 1H), 5.36−5.43 (m, H-2, H-5, 2H), 5.01−5.05 (m, H-3, H-4, 2H), 4.51−4.61 (m, H-3′, H-4′, H-a, 6H), 3.69−4.41 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-2′, H-5′, H-6a′, H-6b′, 10H); ^{13}C NMR (C_2D_6SO): δ 143.4 (C-b), 124.8 (C-c), 124.4 (C-c), 87.2 (C-4), 84.7 (C-3′, C-4′), 82.4 (C-3), 81.7 (C-2′, C-5′), 73.0 (C-6), 71.2 (C-1′, C-6′), 68.5 (C-1), 65.5 (C-5), 61.8 (C-2), 61.7 (C-a).

Synthesis of **15.** The general procedure for CuAAC polyaddition in DMSO was applied to diazide **3** (90 mg, 0.46 mmol), dialkyne **6** (100 mg, 0.46 mmol), triethylamine (0.36 mL, 1.5 mmol), and $CuIP(OEt)_3$ (2 mg, 0.006 mmol) to obtain a colorless solid (182 mg, 96%). ^{1}H NMR (C_2D_6SO, 300 MHz): δ 8.18 (s, H-c, 2H), 5.37−5.39 (m, H-2, H-5, 2H), 5.07−5.13 (m, H-3, H-4, 2H), 3.70−4.59 (m, H-1a, H-1b, H-6a, H-6b, H-1a′, H-1b′, H-2′, H-3′, H-4′,H-5′, H-6a′, H-6b′, H-a, 16H); ^{13}C NMR (C_2D_6SO): δ 144.0 (C-b), 124.4 (C-c), 86.9 (C-3, C-4), 84.7 (C-3′, C-4′), 82.0 (C-2′, C-5′), 72.0 (C-1, C-6), 71.2 (C-1′, C-6′), 64.8 (C-2, C-5), 61.8 (C-a).

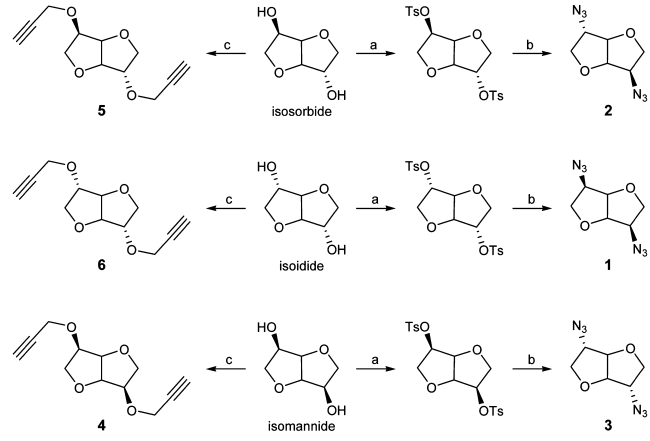
Results and Discussion

Synthesis of Diazide and Dialkyne Dianhydrohexitol Stereoisomers. Dianhydrohexitol stereoisomers, that is, isosorbide, isomannide, and isoidide, can serve as a platform to generate a library of alkyne and azide functionalized biosourced monomers with controlled stereochemistry suitable for $A_2 + B_2$ CuAAC step growth polymerization. These starting diol materials, which are composed of two *cis*-fused tetrahydrofuran rings, nearly planar and V-shaped with a 120° angle between rings, differ from the absolute configuration of the C-2 and C-5 carbon atoms (Scheme 1). The alcohol groups can indeed be positioned either inside (endo position) or outside (exo position) the polar and hydrogen bonding heterocyclic rings. When the hydroxyl groups are in endo position (at C-5 for isosorbide and at C-2 and C-5 for isomannide), hydrogen bonding association with the cyclic ether groups decreases their reactivity.[7b] The configuration of the different stereoisomers is also expected to impact the rigidity and the association of the resulting polytriazoles and thus their physicochemical properties.

Scheme 1. 3D Structure of Isosorbide (*SR*), Isomannide (*RR*), and Isoidide (*SS*) Dianhydrohexitol Starting Materials (from Left to Right)



Scheme 2. Synthesis of Diazide and Dialkyne Dianhydrohexitol Monomers **1**−**6** Suitable for $A_2 + B_2$ CuAAC Step Growth Polymerization



a) TsCl, pyridine, R.T.; b) NaN_3, DMF, 140 °C; c) Propargyl bromide, NaH, 18-crown-6, DMF, R.T.

To investigate in detail the structure/properties relationship of the dianhydrohexitol-based polytriazoles targeted herein and evaluate the influence of monomer stereochemistry, two series of diazide (**1**−**3**) and dialkyne (**4**−**6**) biosourced dianhydrohexitol stereoisomers have been prepared (Scheme 2). The structure of these complementary monomers was also designed to allow incorporating in the resulting polymers a high fraction of both biosourced dianhydrohexitols and triazole rings that possess interesting adhesion and hydrogen bonding properties.

Following a previously described procedure,[8a] 2,5-diazide-1,4:3,6-dianhydrohexitols **1**−**3** having, respectively, *RR*, *SR*, and *SS* absolute configurations of the C-2 and C-5 carbon atoms were conveniently synthesized in two steps, respectively, from isoidide, isosorbide, and isomannide. This synthetic pathway involved tosylation of the alcohol groups and subsequent nucleophilic substitution by sodium azide which proceeds through a configuration inversion of the C-2 and C-5 carbon atoms. Diazide monomers **1**−**3** were obtained as colorless oils in moderate to relatively high yield (34, 60, and 77%, respectively) as a result of the competition between the targeted nucleophilic substitution and the elimination side reaction occurring during the azidation step. The latter is particularly significant when the tosylate is in exo position. The comple-

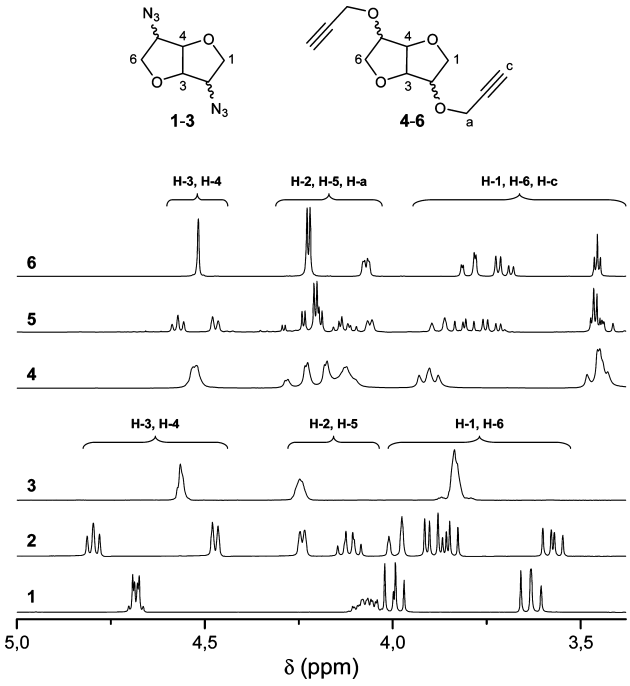
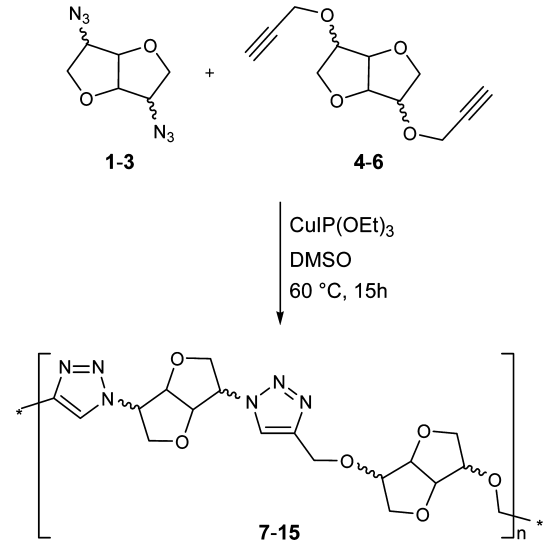


Figure 1. ^{1}H NMR of diazide and dialkyne dianhydrohexitol monomers **1**−**6**.

mentary 2,5-di-*O*-propargyl-1,4:3,6-dianhydrohexitol monomers **4**−**6** having, respectively, *RR*, *SR*, and *SS* absolute configuration of the C-2 and C-5 carbon atoms were readily obtained in a single step in quantitative yields (96−98%), respectively, from isomannide, isosorbide, and isoidide, by alkylation of the hydroxyl groups using propargyl bromide. Compounds **4** and **6** were obtained as yellow solids, whereas **5** was recovered as a yellow oil reflecting the influence of stereochemistry on the monomer physical state. After purification, monomers **1**−**6** were characterized by ^{1}H and ^{13}C NMR (Figure 1 and Figure S1 in the Supporting Information) as well as high resolution mass spectrometry (HRMS) showing the high purity of the obtained materials. Interestingly, the chemical shifts, multiplicity, and splitting constants of most of the proton signals are significantly impacted by the configuration of the diazide and dialkyne monomers. For each series of monomers, an identical single peak was obtained in HRMS spectra, confirming the formation of stereoisomer derivatives. To prevent their thermal or UV degradation, monomers **1**−**3** were stored at −20 °C in the dark and under these conditions no alteration could be observed after several months of storage.

CuAAC Step Growth Polymerization of Diazide and Dialkyne Monomers. Screening every possible combination of complementary monomers **1**−**6**, dianhydrohexitol-based polytriazoles **7**−**15** were generated through CuAAC polyaddition of stoichiometric mixtures of diazides **1**−**3** and dialkynes **4**−**6** in DMSO (Scheme 3). The cycloaddition reaction was catalyzed by copper iodide triethylphosphite ($CuIP(OEt)_3$, 0.01 equiv, according to azide or alkyne functionalities) as it is soluble in DMSO and prevents the loss of azide chain ends observed in the presence of the commonly used $Cu(PPh_3)_3Br$ through a Staudinger side reaction.[20] Therefore, the polyaddition process resulted exclusively in the formation of 1,4-disubstituted 1,2,3-triazole linkages, whereas the initial stoichiometry of the dianhydrohexitol moieties remained unchanged. Triethylamine (TEA, 1.5 equiv, according to azide or alkyne functionalities) was used instead of diisopropylethylamine (DIPEA) as the latter is not miscible with DMSO. In addition, polymerizations were

Scheme 3. Synthesis of Polytriazoles **7**−**15** by CuAAC Step Growth Polymerization of Diazides **1**−**3** and Dialkynes **4**−**6**



performed at relatively high monomer concentrations of about 1 M in order to decrease the possible formation of low molar mass cyclic species.

Conversely to the AB CuAAC polyaddition of α-azide-ω-alkyne-dianhydrohexitols and independently of monomer stereochemistry,[17a] polymerization of each dialkyne/diazide mixture proceeded under homogeneous conditions throughout the process. This trend may reflect the less-ordered microstructure of the polytriazoles obtained through $A_2 + B_2$ strategy (vs AB strategy), in agreement with the significant solubility enhancement observed in the case of polytriazoles generated through nonregioselective AB thermal Huisgen step-growth polymerization.[17a]

Polytriazoles **7**−**15** were precipitated twice in ethanol, subsequently dispersed in water and then acetone to remove DMSO traces, and recovered in high to excellent yields (70−96%), confirming the occurrence of monomer polyaddition (Table 1). The lower yields observed for **10**, **11**, or **12** are probably due to polymer fractionation during the workup. Whereas materials generated from AB α-azide-ω-alkyne-dianhydrohexitols exhibited extremely poor solubility, especially when the polyaddition was performed with a monomer having an azide in the *R* configuration,[17a] all the polytriazoles generated using an $A_2 + B_2$ approach could be readily dissolved in DMSO and DMF at room temperature.

^{1}H NMR analysis clearly corroborated the formation of dianhydrohexitol/1,2,3-triazole, based polymers with the appearance of characteristic 1,4-disubstituted triazole (C*H*═C−N) broad singlets and the concomitant disappearance of the alkyne signals ($CH_2C{\equiv}CH$), as well as the typical displacement of the protons adjacent to the initial alkyne ($CH_2C{\equiv}CH$) and azide (CHN_3) groups. Depending on the stereochemistry of the monomers, either one or two triazole signals were observed at 8.15−8.19 ppm and 8.25−8.26 ppm (Figure 2). The presence of two peaks evidenced for polytriazoles **8**, **11**, and **14** can be correlated to the configuration of diazide **2** (*SR*), which results in the formation of two nonequivalent C═C*H*−*N* triazole protons. Conversely, it is worth noting that, except in the case of polyaddition with **2**, polytriazoles generated in the presence of dialkyne **5** (*SR*) exhibited one single triazole peak. This tendency probably stems from the presence of freely rotating methylene segments surrounding the dianhydrohexitol moiety of the dialkyne monomer.

Table 1. Properties of Polytriazoles **7**−**15** Obtained by CuAAC Step Growth Polymerization of Diazides **1**−**3** and Dialkynes **4**−**6**

No.	diazide (stereo.)	dialkyne (stereo.)	yield (%)	M_n[a] (g/mol)	DP_n[a]	PDI[a]	T_g (°C)	T_{d10}[b] (°C)
7	**1** (*RR*)	**4** (*RR*)	83	9000	41	1.6	166	331
8	**2** (*SR*)	**4** (*RR*)	93	13300	61	2.4	161	324
9	**3** (*SS*)	**4** (*RR*)	93	17200	79	3.8	150	325
10	**1** (*RR*)	**5** (*SR*)	70	10400	48	3.2	146	347
11	**2** (*SR*)	**5** (*SR*)	78	12100	56	2.3	126	342
12	**3** (*SS*)	**5** (*SR*)	72	8200	38	2.8	121	332
13	**1** (*RR*)	**6** (*SS*)	93	9000	40	2.6	151	334
14	**2** (*SR*)	**6** (*SS*)	94	12500	58	5.7	141	342
15	**3** (*SS*)	**6** (*SS*)	96	16800	78	3.3	125	334

[a] From SEC dual detection (RI/viscosimetry) in DMSO at 120 °C. [b] Temperature at 10 wt % loss.

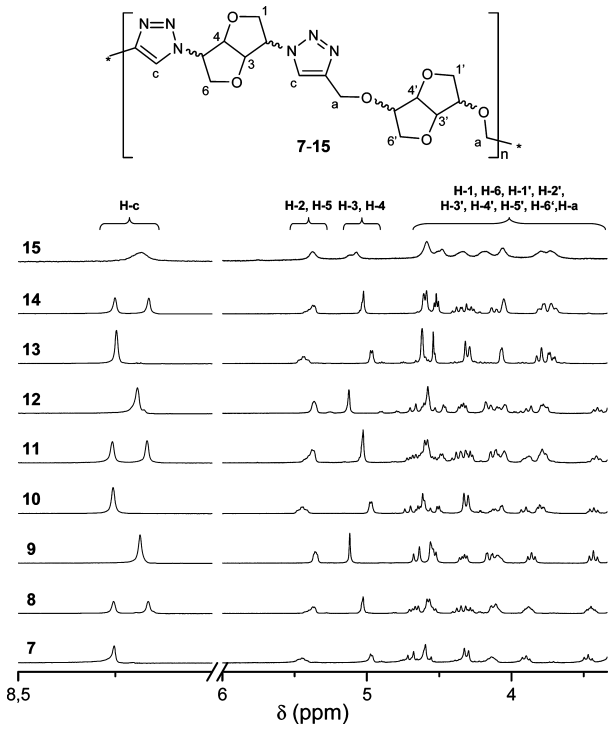


Figure 2. ^{1}H NMR spectra (DMSO-d_6) of polytriazoles **7**−**15** obtained by CuAAC step growth polymerization of diazides **1**−**3** and dialkynes **4**−**6**.

SEC analysis using universal calibration (120 °C in DMSO, dual detection RI/viscosimetry) further confirmed the generation of polymers through CuAAC polyaddition (Figure 3). Interestingly, polymerization of stoichiometric dialkyne/diazide mixtures afforded polytriazoles **7**−**15** with degrees of polymerization (DP_n) ranging from 38 to 79 and polydispersity indices (PDI) varying from 1.6 to 5.7 (Table 1). In regard to the polymerization process, several polytriazoles exhibited unexpectedly high values of PDI (for instance, PDI (**9**) = 3.8 and PDI (**14**) = 5.7). The broadening of the molar mass distribution may originate from the additional presence of high molar mass species due to the formation of aggregates in hot DMSO (see Figure 3) and of low molar masses cyclic species. As a comparison, CuAAC step growth polymerization in DMSO of α-azide-ω-alkyne-dianhydrohexitols provided polytriazoles displaying lower DP_n ranging from 33 to 36 and very high values of PDI ranging from 21 to 29. Such discrepancy between the two polyaddition systems may arise from the physical gelation of the polymerization medium observed in the AB polyaddition method and a stronger association of the resulting polymer chains driven by their superior degree of stereoregularity.

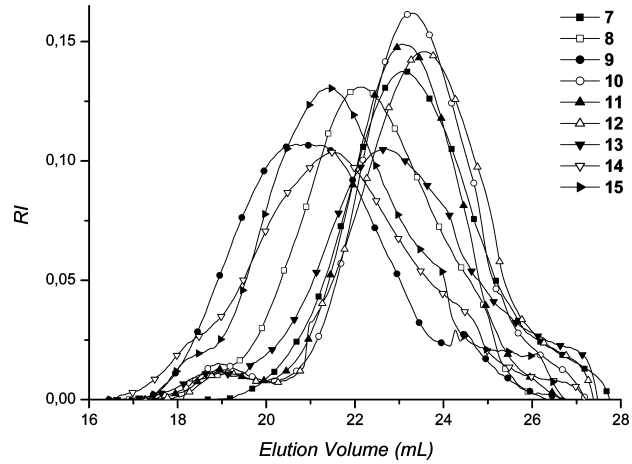


Figure 3. SEC traces (DMSO, 120 °C) of polytriazoles **7**−**15** obtained by CuAAC step growth polymerization of diazides **1**−**3** and dialkynes **4**−**6**.

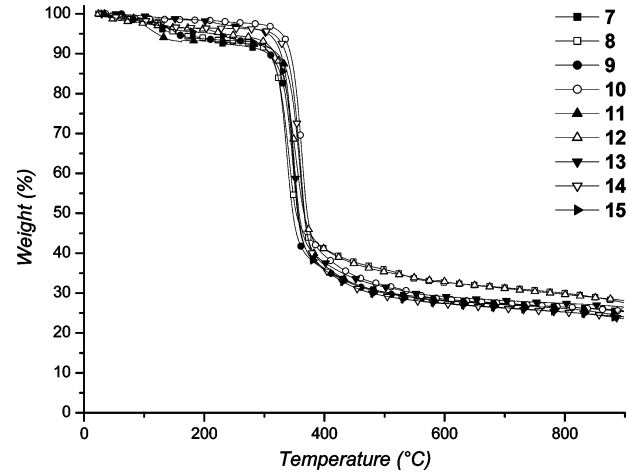


Figure 4. TGA traces of polytriazoles **7**−**15**.

Structure/Thermal Properties Relationship of Dianhydrohexitol-Based Polytriazoles. Thermal analyses of polytriazoles **7**−**15** were subsequently performed. First, their thermal resistance was evaluated by TGA measurements performed under nitrogen (Figure 4). Independently of monomer stereochemistry, all polytriazoles exhibited a high resistance to thermal degradation with T_{d10} varying from 324 to 347 °C and amounts of residual ashes of 25−30 wt %.

Furthermore, DSC experiments clearly demonstrated the amorphous behavior of all the polymers with the exclusive presence of a glass transition temperature (T_g) for every polytriazole derivatives. As a result of the relatively high rigidity of dianhydrohexitol and triazole heterocyclic moieties, high T_g values ranging from 121 to 166 °C were observed (Table 1).

These values were slightly lower than those obtained for the CuAAC polyaddition of α-azide-ω-alkyne-dianhydrohexitols, possibly due to the use of dialkyne and diazide monomers with different stereochemistry and to the presence on the dialkyne monomers of two methylene segments surrounding the dianhydrohexitol heterocycle, which could confer an enhanced mobility to the polytriazole chains and thus alter their overall rigidity. Monomers having C-2 and C-5 carbon atoms with *R* absolute configuration were the best candidates aiming at preparing polytriazoles with high T_g ($T_{g(7)} = 166$ °C obtained from **1** + **4**), and the stereochemistry of the diazide monomer appeared to be the key parameter to optimize the T_g of the resulting dianhydrohexitol/triazole-based polymers. Interestingly, this configuration corresponds to the isomannide derivative, which is the less reactive dianhydrohexitol, as both secondary alcohols are involved in hydrogen bonding associations. Inversely, the introduction of dianhydrohexitol units with *S* configuration at C-2 and/or C-5 in the polytriazole backbone resulted in a drastic decrease of T_g. A close comparison of polymers **7** and **9**, **10** and **12**, or **13** and **15** stressed that, for a given configuration of the dialkyne monomer, the T_g of the polytriazoles obtained with diazides **1** (*RR*), **2** (*SR*), and **3** (*SS*) decreases in the following order: **1** > **2** > **3**. A similar influence of monomer stereochemistry was noted in the case of polytriazoles generated from the step growth polymerization of α-azide-ω-alkyne dianhydrohexitol stereoisomers.[17a]

Conclusions

A series of diazide and dialkyne biosourced monomers with controlled stereochemistry (*RR*, *SR*, and *SS* absolute configuration of the C-2 and C-5 carbon atoms) have been designed from 1,4:3,6-dianhydrohexitols (isosorbide, isoidide and isomannide). The step growth polymerization of the different stoichiometric combinations of these complementary diazide and dialkyne stereoisomers through copper(I)-catalyzed azide−alkyne cycloaddition afforded a library of nine dianhydrohexitol-based polytriazoles with defined stereochemistry allowing a fine investigation of their structure/properties relationship. In contrast with the previously reported AB CuAAC step growth polymerization strategy, the $A_2 + B_2$ synthetic approach resulted in the generation of polytriazoles exhibiting all at once relatively high molar masses ($M_n = 8-17$ kg/mol), high glass transition temperatures ($T_g = 121-166$ °C), and good resistance to thermal degradation ($T_{d10} = 325-347$ °C), as well as solubility in DMSO and DMF at room temperature. Interestingly, monomer stereochemistry was shown to significantly impact the T_g of the resulting polytriazoles and, in regard to thermal properties, monomers having *RR* absolute configuration of the C-2 and C-5 carbon atoms were the best candidates aiming at preparing linear polytriazoles with high T_g.

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Supporting Information Available. ^{13}C NMR of monomers **1**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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