

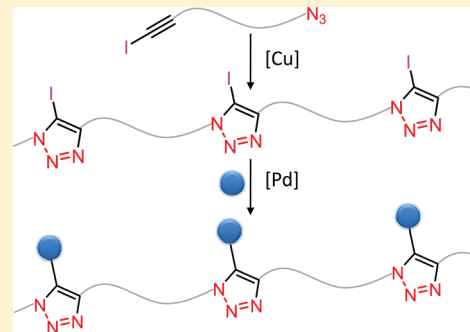
Synthesis and Postpolymerization Functionalization of Poly(5-iodo-1,2,3-triazole)s

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S Supporting Information

ABSTRACT: The step-growth, click polymerization of complementary azide and alkyne-containing monomers to produce polytriazoles (PTAs) has become a versatile and popular method of preparing structurally diverse high molecular weight polymers with a variety of useful functions. We describe here a new class of PTAs that contain 5-iodotriazole linkages prepared by the iodoalkyne version of the copper-catalyzed azide–alkyne cycloaddition (ⁱCuAAC) of an α -azido- ω -iodoalkyne (A–B) monomer. We found this monomer to be highly reactive in the ⁱCuAAC polymerization and show that the resulting poly(5-iodo-1,2,3-triazole) (iodo-PTA) can serve as a useful building block for further postpolymerization derivatization using palladium-catalyzed cross-couplings such as Suzuki and Heck reactions. The parent iodo-PTA and functionalized materials were successfully characterized by various spectroscopic techniques and shown to exhibit a wide range of chemical and thermal properties that are determined by the nature of functionalization at the 5-position of the triazole ring. This data suggests a certain tunability of PTA properties and offers potential for the development of a multitude of useful triazole-based materials based on this postpolymerization functionalization strategy.



INTRODUCTION

The fidelity and versatility of the copper-catalyzed azide–alkyne cycloaddition reaction (CuAAC)¹ have been widely exploited across multiple fields including bioconjugations,² materials science,³ and polymer chemistry.⁴ The features of this process—experimental simplicity, nearly quantitative yield, selectivity, and compatibility with a broad range of functional groups and reaction conditions—are ideally suited for polymer synthesis and modification. In polymer chemistry, CuAAC has led to the construction of a variety of macromolecular architectures (e.g., block, star, graft, dendritic, and polymeric networks) by utilizing polymers possessing either chain-end or side-chain azide/alkyne functionality.⁵ Using A–A/B–B or A–B monomers containing complementary azide and alkyne functionality, CuAAC also provides a facile and effective route toward the synthesis of step-growth poly(triazole)s (PTAs),^{6,7} many containing higher level functionality such as peptides⁸ and fluorinated subunits,⁹ as well as advanced architectures such as helical¹⁰ and dendronized polymers.¹¹ For example, the Reek and Bunz groups have synthesized semiconducting PTAs by clicking together π -conjugated subunits and studying the resulting energy transfer properties of these materials.¹² In another example, Reineke and co-workers synthesized high molecular weight, cationic glycopolymers (MW > 30 kDa) through click polymerization of diazido trehalose and dialkyne oligoamine comonomers and demonstrated their effectiveness at binding and *in vitro* transfection of nucleic acids in both the absence and presence of serum.¹³

Recently, our group demonstrated that 1-iodoalkynes react with azides in the presence of copper(I) catalyst and an amine

ligand (e.g., tris((1-*tert*-butyl-1*H*-1,2,3-triazolyl)methyl)amine (TTTA)), forming 5-iodo-1,2,3-triazoles as exclusive products in excellent yields.^{14,15} Furthermore, the obtained iodotriazole is a versatile intermediate for subsequent postfunctionalization using transition-metal-catalyzed transformations. We hypothesized that PTAs prepared from 1-iodoalkyne monomers, and thus bearing an iodo functionality at the C-5 position of the triazole ring, might have useful properties both as stand-alone materials and as a platform for the construction of a multitude of side-chain-functionalized PTAs prepared by similar catalytic cross-coupling reactions.¹⁶

Herein, we describe initial efforts toward the synthesis and postpolymerization functionalization of poly(5-iodo-1,2,3-triazole)s (iodo-PTAs). Specifically, the A–B monomer, 3-iodo-prop-2-ynyl-11-azidoundecanoate, was synthesized and polymerized by step-growth polymerization using a CuI–TTTA catalyst system. We observed qualitatively that this α -azido- ω -iodoalkyne monomer displays enhanced reactivity toward azides during polymerization, and the resulting iodopolytriazoles are significantly more soluble than a comparable proto-polytriazole prepared from prop-2-ynyl-11-azidoundecanoate. We demonstrate that the iodo-PTA can be further functionalized using palladium-catalyzed Suzuki coupling with phenylboronic acid or by Heck coupling with acrylonitrile and methyl vinyl ketone. Saponification and subsequent analysis by mass spectrometry

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assisted in the determination of the extent of postpolymerization functionalization, which was nearly quantitative for the Heck reaction. Thermal analyses by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed marked changes in glass transition temperatures (T_g) and thermal stabilities of the functionalized PTAs, suggesting that postpolymerization functionalization of iodo-PTAs may serve as a useful method to tailor the properties of traditional proto-PTAs.

EXPERIMENTAL SECTION

General. All solvents and reagents were purchased from commercial sources and used as received, unless otherwise stated. All reactions were carried out at room temperature under ambient atmosphere, except for the postpolymerization functionalization, which was performed under a nitrogen atmosphere using standard Schlenk techniques. Column chromatography was performed using silica gel (40–60 μ m) purchased from Merck. TLC analyses were carried out on silica 60 F₂₅₄-coated glass plates from Merck, and the compounds were visualized using KMnO₄. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker MER-300 instrument operating at 300 and 75 MHz, respectively, unless otherwise stated. Attenuated total reflectance FT-infrared (ATR-FTIR) spectra were recorded on a Perkin Spectrum 100 spectrometer. Mass spectrometry analyses were performed on an Agilent ES-TOF instrument. LC-MS experiments utilized an Agilent 1100 SL mass spectrometer, eluting with water containing 0.1% trifluoroacetic acid and acetonitrile containing 0.05% trifluoroacetic acid. Molecular weights and molecular weight distributions were measured using a Shimadzu Prominence GPC system with CHCl₃ as mobile phase (elution rate = 1.0 mL/min) and referenced against linear polystyrene standards. The system utilizes two Phenomenex Phenogel linear columns (10 μ m, 300 \times 7.80 mm), a refractive index detector, and photodiode array detector. Thermal gravimetric analysis (TGA) was performed on a Mettler 851e TGA under an argon atmosphere at a ramp rate of 10 $^{\circ}$ C/min. Differential scanning calorimetry (DSC) utilized a TA Instruments DCS 2920 at a ramp rate of 5 $^{\circ}$ C/min.

Synthesis. 11-Azidoundecanoic acid¹⁷ and 3-iodoprop-2-yn-1-ol¹⁸ were synthesized according to literature procedures.

3-Iodoprop-2-ynyl-11-azidoundecanoate (1). 11-Azidoundecanoic acid (1.5 g, 6.6 mmol) and 3-iodoprop-2-yn-1-ol (1.32 g, 7.2 mmol, 1.1 equiv) were dissolved in CH₂Cl₂ (100 mL). Diisopropylethylamine (DIPEA; 0.94 mL, 7.3 mmol, 1.1 equiv) and *N,N*-dimethylaminopyridine (DMAP; 0.15 g, 1.23 mmol, 0.2 equiv) were added to this solution. The mixture was cooled to 0 $^{\circ}$ C and 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC; 1.39 g, 7.3 mmol, 1.1 equiv) was added, and the reaction was allowed to stir for 12 h. The reaction mixture was concentrated to dryness *in vacuo*, and the product was dissolved in CHCl₃ (200 mL). The solution was subsequently washed with an aqueous citric acid solution (10% (w/w), 200 mL), H₂O (200 mL), an aqueous sodium carbonate solution (10% (w/w), 200 mL), and H₂O (200 mL). The organic layer was dried (Na₂SO₄), concentrated, and subjected to column chromatography (1% MeOH in CH₂Cl₂), yielding 2.2 g (85%) of **1** as a slightly yellow oil. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 4.78 (s, 2H, OCH₂C \equiv CI), 3.23 (tr, 2H, J = 6 Hz, N₃CH₂), 2.27 (tr, 2H, J = 6 Hz, CH₂CO₂), 1.57 (m, 4H, CH₂CH₂CH₂CO₂), 1.3–1.2 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 172.9 (C=O), 88.2 (CH₂C \equiv CI), 53.2 (OCH₂C \equiv CI), 51.5 (N₃CH₂), 34.0 (CH₂C=O), 29.4, 29.3, 29.2, 29.1, 29.0, 28.9, 26.7, 24.8 (CH₂), 4.3 (CH₂C \equiv CI). FT-IR (cm⁻¹, ATR): 2926, 2854 (CH, CH₂, CH₃), 2195 (C \equiv CI), 2092 (N₃), 1740 (C=O). MS-ESI m/z = 392 [M + H]⁺. HRMS for C₁₄H₂₃IN₃O₂: Calcd 392.0829. Found: 392.0844.

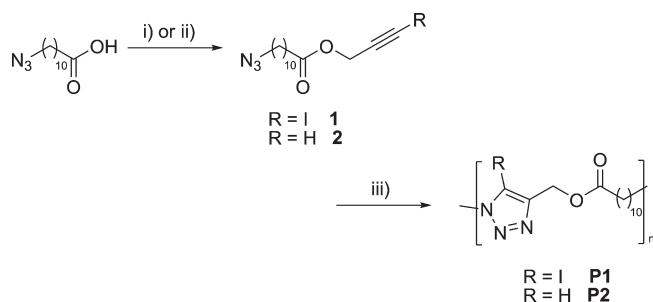
Prop-2-ynyl-11-azidoundecanoate (2). Following a similar procedure as described for 3-iodoprop-2-ynyl-11-azidoundecanoate (**1**), **2**

was obtained as a colorless oil (yield: 79%) that solidified at lower temperatures (-20 $^{\circ}$ C). ¹H NMR (δ ppm, CDCl₃, 300 MHz): 4.67 (d, 2H, J = 2.4 Hz, OCH₂C \equiv CH), 3.25 (tr, 2H, J = 6.9 Hz, N₃CH₂), 2.27 (tr, 1H, J = 2.4 Hz, OCH₂C \equiv CH), 2.34 (2H, J = 7.2 Hz, CH₂CO₂), 1.61 (m, 4H, CH₂CH₂CH₂CO₂), 1.3–1.2 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 173.0 (C=O), 78.9 (CH₂C \equiv CH), 74.8 (CH₂C \equiv CH), 51.8 (OCH₂C \equiv CH), 51.6 (N₃CH₂), 34.0 (CH₂C=O), 30.3, 29.5, 29.4, 29.1, 29.0, 28.9, 26.8, 24.9 (CH₂). FT-IR (cm⁻¹, ATR): 3295 (C \equiv CH), 2926, 2855 (CH, CH₂, CH₃), 2120, 2093 (C \equiv C, N₃), 1738 (C=O). MS-ESI m/z = 266 [M + H]⁺. HRMS for C₁₄H₂₄N₃O₂: Calcd 266.1863. Found: 266.1866.

CuAAC Polymerization of 3-Iodoprop-2-ynyl-11-azidoundecanoate (P1). CuI (41.9 mg, 0.22 mmol, 0.05 equiv) and TTTA (94 mg, 0.22 mmol, 0.05 equiv) were combined in CH₂Cl₂ (4 mL) at room temperature and stirred for 15 min to obtain a homogeneous solution. The catalyst solution was then added to a solution of **1** (1.7 g, 4.4 mmol) in CH₂Cl₂ (1.1 mL). The dark yellow, viscous solution was stirred for 3 h, after which time it was precipitated into a mixture of MeOH and NH₄OH(aq) (550 mL, 10:1 (v/v)). The polymer was isolated by filtration, dissolved in CHCl₃ (50 mL), and washed first with an aqueous EDTA solution (10 g/L, 50 mL) and then with deionized H₂O (100 mL). The organic layer was isolated, dried over Na₂SO₄, and concentrated to dryness. The polymer was taken up in a minimal amount of CHCl₃ and precipitated by dropping into MeOH (500 mL). The product was isolated by filtration, washed with MeOH, and dried *in vacuo* to give 1.3 g (75%) of polymer **P1** as a white powder. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 5.14 (s, 2H, OCH₂C=CI), 4.35 (tr, 2H, J = 7.5 Hz, CH₂N), 2.33 (tr, 2H, J = 7.5 Hz, CH₂CO₂), 1.88 (m, 2H, CH₂CH₂N), 1.62 (m, 2H, CH₂CH₂CO₂), 1.35–1.25 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 173.5 (C=O), 146.6 (IC=C), 80.8 (IC=C), 57.6 (IC=CCH₂), 51.0 (CH₂N), 34.1 (CH₂C=O), 30.0, 29.4, 29.3, 29.2, 29.0, 26.5, 24.9 (CH₂). FT-IR (cm⁻¹, ATR): 2925, 2854 (CH, CH₂, CH₃), 1736 (C=O).

CuAAC Polymerization of Prop-2-ynyl-11-azidoundecanoate (P2). Following a similar procedure as described for **P1**, polymer **P2** was obtained as a white powder in 76% yield. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.58 (s, 1H, OCH₂C=CH), 5.20 (s, 2H, OCH₂C=CH), 4.33 (tr, 2H, J = 7.2 Hz, CH₂N), 2.31 (tr, 2H, J = 7.2 Hz, CH₂CO₂), 1.89 (m, 2H, CH₂CH₂N), 1.59 (m, 2H, CH₂CH₂CO₂), 1.35–1.25 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 173.8 (C=O), 143.0 (HC=C), 123.6 (HC=C), 57.6 (HC=CCH₂O), 50.5 (CH₂N), 34.2 (CH₂C=O), 30.4, 29.4, 29.3, 29.2, 29.1, 26.6, 24.9 (CH₂). FT-IR (cm⁻¹, ATR): 2922, 2851 (CH, CH₂, CH₃), 1733 (C=O).

Postpolymerization Functionalization of P1 with Phenylboronic Acid (P3). Polymer **P1** (220 mg, 0.56 mmol), phenylboronic acid (206 mg, 1.68 mmol, 3 equiv), and K₂CO₃ (234 mg, 1.69 mmol, 3 equiv) were suspended in a solution of dimethylformamide (DMF) (5 mL) under N₂. The mixture was heated to 80 $^{\circ}$ C, Pd(OAc)₂ (13 mg, 0.06 mmol, 0.1 equiv) was subsequently added as a solid, and the mixture was stirred overnight. After cooling to room temperature, an aqueous ammonium chloride solution (10% (w/w), 100 mL) was added, and the polymer was extracted with CHCl₃ (200 mL). The organic layer was washed first with an aqueous sodium diethyl thiocarbamate solution (10 g/L, 50 mL) and then with deionized H₂O (100 mL). The organic layer was collected, dried over Na₂SO₄, concentrated, and passed through a short plug of silica (8% MeOH in CHCl₃). After extensive washing with MeOH and drying *in vacuo*, 170 mg of polymer **P3** was obtained as a yellow sticky solid. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.50 (m, 3H, ArH meta and para to C=C), 7.30 (m, 2H, ArH ortho to C=C), 5.08 (s, 2H, C=COCH₂), 4.22 (tr, 2H, J = 7.2 Hz, CH₂N), 2.24 (tr, 2H, J = 7.2 Hz, O₂CCH₂), 1.76 (m, 2H, CH₂CH₂N), 1.53 (m, 2H, O₂CCH₂CH₂), 1.25–1.15 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 173.5 (C=O), 140.08 (C=C), 136.9, 129.9, 129.5, 129.2, 126.4 (ArC, C=C), 57.2 (CH₂C=C), 48.5

Scheme 1. Synthesis of P1 and P2^a

^aReagent and conditions: (i) EDC, DIPEA, 3-iodoprop-2-yn-1-ol, CH₂Cl₂ (**1**, 85%); (ii) EDC, DIPEA, propargyl alcohol, CH₂Cl₂ (**2**, 79%); (iii) 0.05 equiv of CuI/TTTA, CH₂Cl₂ (**P1**: 75%; **P2**: 76%).

(CH₂N), 34.1 (CH₂C=O), 30.1, 29.3, 29.1, 29.1, 28.9, 26.4, 24.8 (CH₂). FT-IR (cm⁻¹, ATR): 2926, 2852 (CH, CH₂, CH₃), 1737 (C=O), 1602, 1494 (C=C).

Postpolymerization Functionalization of P1 with Acrylonitrile (P4). Polymer **P1** (165 mg, 0.42 mmol), acrylonitrile (0.18 mL; 2.7 mmol, 5.7 equiv), NaHCO₃ (213 mg, 2.5 mmol; 6 equiv), and tetrabutylammonium bromide (54 mg, 0.17 mmol, 0.4 equiv) were suspended in a solution of DMF (5 mL) under N₂. The mixture was heated to 70 °C, Pd(OAc)₂ (9.5 mg, 0.1 equiv) was added as a solid, and the mixture was stirred overnight. After cooling to room temperature, aqueous ammonium chloride (10% (w/w), 100 mL) was added, and the polymer was extracted with CHCl₃ (200 mL). The organic layer was washed first with an aqueous sodium diethyl thiocarbamate solution (10 g/L, 50 mL) and then with deionized H₂O (100 mL). The organic layer was collected, dried over Na₂SO₄, concentrated, and passed through a short plug of silica (8% MeOH in CHCl₃). The glassy solid was dissolved in a minimal amount of CHCl₃, and the polymer was precipitated by dropping into a vigorously stirred beaker containing MeOH (400 mL). The product was isolated by filtration, washed with MeOH, and dried *in vacuo* to give 111 mg of polymer **P4** as a yellow sticky solid. The polymer was obtained in a 7:3 *E:Z* ratio. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.36 (dd, 1H, *J*₁ = 16.5 Hz, *J*₂ = 3.9 Hz, *E*: CNCH=CH), 7.17 (d, 1H, *J* = 11.7 Hz, *Z*: CNCH=CH), 6.03 (d, 1H, *J* = 16.5 Hz, *E*: CNCH=CH), 5.90 (d, 1H, *J* = 11.7 Hz, *Z*: CNCH=CH), 5.27, 5.25 (s, 2H, OCH₂), 4.37, 4.30 (tr, 2H, *J* = 7.2 Hz, CH₂N), 2.32 (m, 2H, O₂CCH₂), 1.87 (br, 2H, CH₂CH₂N), 1.60 (br, 2H, O₂CCH₂CH₂), 1.35–1.1 (br, 12 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 173.2 (C=O), 142.2, 134.0, 133.0, 130.3 (C=C), 116.8 (CN), 105.3, 103.1 (C=C), 57.2 (C=CCH₂O), 49.3 (CH₂N), 34.0 (CH₂C=O), 30.1, 29.3–29.1, 26.4, 24.8 (br, CH₂). FT-IR (cm⁻¹, ATR): 2926, 2855 (CH, CH₂, CH₃), 2222 (CN), 1736 (C=O ester), 1638 (C=C).

Postpolymerization Functionalization of P1 with Methyl Vinyl Ketone (P5). Following a similar procedure as described for **P4**, polymer **P5** was obtained as a dark yellow sticky solid. ¹H NMR (δ ppm, CDCl₃, 300 MHz): 7.41 (d, 1H, *J* = 16.2 Hz, CH₃COHC=CH), 6.67 (d, 1H, *J* = 16.2 Hz, CH₃COHC=CH), 5.27 (s, 2H, OCH₂C=C), 4.38 (tr, 2H, *J* = 7.2 Hz, CH₂N), 2.36 (s, 3H, CH₃CO), 2.32 (tr, 2H, *J* = 7.5 Hz, O₂CCH₂), 1.85 (m, 2H, CH₂CH₂N), 1.60 (m, 2H, O₂CCH₂CH₂), 1.25–1.1 (br, 16 H, CH₂). ¹³C NMR (δ ppm, CDCl₃, 75 MHz): 196.6 (C=O ketone), 173.4 (C=O ester), 142.0, 131.2, 124.5, 104.9 (C=C), 57.3 (C=CCH₂O), 49.2 (CH₂N), 34.1 (OCCH₂), 30.2, 29.3–29.1, 29.1, 28.9, 26.6, 24.9 (CH₂). FT-IR (cm⁻¹, ATR): 2925, 2854 (CH, CH₂, CH₃), 1737 (C=O ester), 1698 (C=O ketone), 1675, 1618 (C=C).

RESULTS AND DISCUSSION

Step-growth polymerizations that utilize A–A/B–B monomers are inherently dependent on precise stoichiometric control

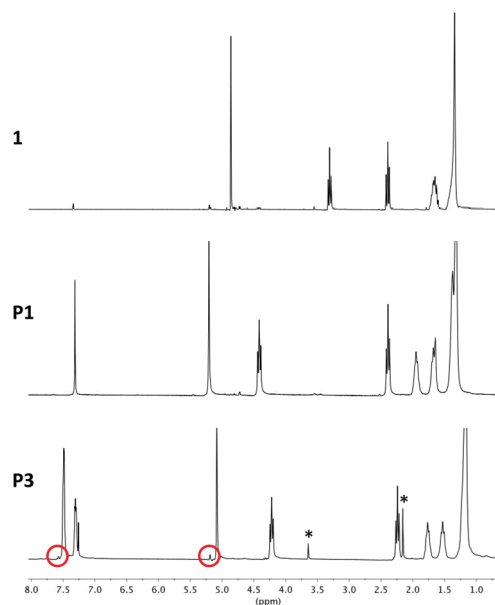


Figure 1. ¹H NMR spectra of **1**, **P1**, and **P3** in CDCl₃. The circled peaks show the presence of **P2** as side product in the Suzuki cross-coupling reaction between **P1** and phenylboronic acid. Asterisk denotes residual solvent impurities.

to achieve very high degrees of polymerization. To simplify the initial study, we prepared A–B monomers containing azide/alkyne functionality for the preparation of the PTAs.¹⁹ Furthermore, since it was previously observed that the triazole heterocycle could reduce solubility of the polymer, and thus preclude preparation of high molecular PTAs, we prepared α-azido-ω-alkyne monomers with decane spacers to maintain solubility in organic solvents. As shown in Scheme 1, 11-azidoundecanoic acid was reacted with either 3-iodoprop-2-yn-1-ol or propargyl alcohol using standard EDC coupling conditions to furnish iodoalkyne monomer **1** and proto-alkyne monomer **2** in 85% and 79% yield, respectively. Both monomers are shelf stable when stored at –20 °C as no coupling products have been observed after several months of storage.

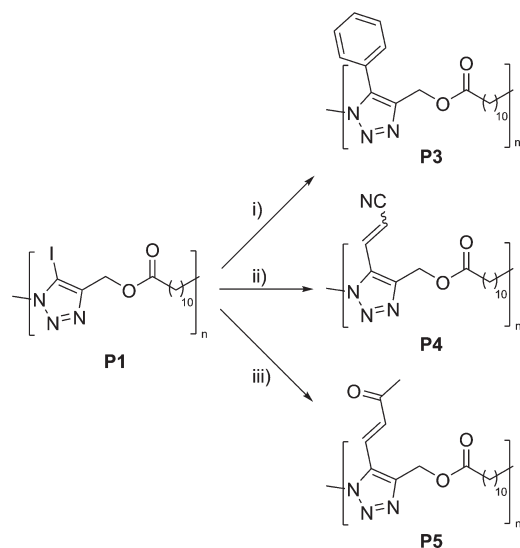
The polymerizations of **1** and **2** were carried out using CuI and TTTA (0.05 equiv) in dichloromethane at a relatively high monomer concentration (~0.8 M) to suppress the formation of cyclic structures. Upon addition of the catalyst mixture to the solution of **1**, the reaction immediately turned yellow and became visually viscous within ~15 min. In contrast, the polymerization of the proto-monomer **2** under similar conditions proceeded slower, and a similar viscosity (determined visually) was not obtained until after ~45 min. These visual observations were supported by TLC analysis of the two polymerizations, which showed that monomer **1** was completely consumed within 15 min while some amount of monomer **2** was still present 45 min after the catalyst was added. These preliminary investigations suggest that the reactivity of 1-iodoalkynes surpasses that of terminal alkynes under these particular polymerization conditions.¹⁵ Interestingly, prolonged reaction time (~24 h) of **2** led to the precipitation of a white solid, whereas the polymerization of **1** remained completely homogeneous, even after several days. We hypothesize that this precipitate is high molecular weight polymer **P2**, and thus, iodo-PTA **P1** is likely more soluble than its proto analogue. Although we do not know the precise origin of the observed

Table 1. Characteristics of Polytriazoles P1–P5

compound	M_n (g mol ⁻¹) ^a	M_w (g mol ⁻¹)	PDI	T_g (°C)	T_m (°C)
P1	13 400	28 600	2.13	3	— ^b
P2	18 100	49 200	2.72	−17	112 ^c
P3	14 400	29 800	2.01	−4	—
P4	13 500	25 900	1.92	3	—
P5	22 000	40 000	1.82	13	—

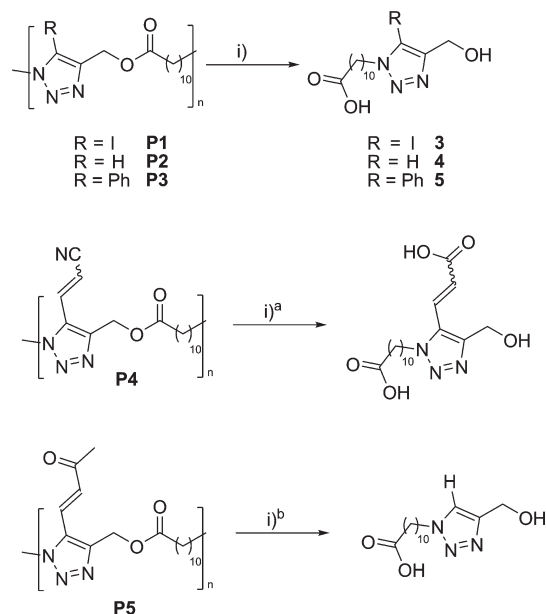
^a Obtained by GPC analysis in CHCl₃ and referenced against polystyrene standards. ^b No T_m could be detected between −20 and 180 °C.

^c Maximum T_m .

Scheme 2. Synthesis of P3–P5^a

^a Reagents and conditions. (i) PhB(OH)₂, K₂CO₃, Pd(OAc)₂, DMF, 80 °C; (ii) acrylonitrile, NaHCO₃, TBAB, Pd(OAc)₂, DMF, 70 °C; (iii) methyl vinyl ketone, NaHCO₃, TBAB, Pd(OAc)₂, DMF, 70 °C.

change in solubility, we speculate that the iodine substituent prevents aggregation by suppressing hydrogen bond formation between C(5)–H and N(1)/N(2) atoms of the triazole as well as by the increased lipophilicity and bulk imparted by the iodine. Reactions of monomer **1** were monitored, and the resulting polymer **P1** was characterized by ¹H NMR spectroscopy. As depicted in Figure 1, the resonances for the methylene protons adjacent to the alkyne and azide functionalities shifted from δ 4.78 and 3.23 ppm to δ 5.14 and 4.35 ppm, respectively, upon polymerization. That the reaction of **1** proceeded to completion was confirmed by ¹³C NMR analysis, which indicated the disappearance of the iodoalkyne carbon (C \equiv C–I) at δ 4.3 ppm and the appearance of the iodotriazole resonances at δ 146.6 ppm (I–C=C) and 80.8 ppm (I–C=C) of **P1**. The GPC analysis (Supporting Information, Figure S1) revealed a unimodal distribution for **P1** with a number-average molar mass (M_n) of ca. 13 400 g mol⁻¹ and a polydispersity index (PDI) of 2.13 (see Table 1), close to the theoretical value for a step-growth polymerization at full conversion. GPC analysis of the proto-polymer **P2** in CHCl₃ revealed a slightly higher M_n of ca. 18 000 g mol⁻¹ and a slightly broader PDI of 2.72. No oligomeric or cyclic structures were observed in the GPC chromatograms of **P1** and **P2** after work-up, indicating complete monomer conversion by the CuAAC step-growth polymerization reaction.

Scheme 3. Hydrolysis of P1–P5^a

^a Reagents and conditions: (i) 2 M NaOH(aq), 70 °C; 2 M HCl; i^a) hydrolysis of **P4** leads to a carboxylate-functionalized product, a result of base-catalyzed hydrolysis of the nitrile group; i^b) hydrolysis of **P5** results in a product with mass of 284 Da, which corresponds to hydrolysis product **4**.

The Suzuki reaction of aryl halides with aryl or vinyl boronic acids is a powerful and efficient method of carbon–carbon bond formation.²⁰ Since PTAs prepared from iodo-alkynes inherently possess an aryl halide functionality (i.e., 5-iodotriazole) in the polymer backbone, we sought to exploit this useful reaction as a means of postpolymerization functionalization. We initially tested the postpolymerization Suzuki reaction by suspending polymer **P1** in dimethylformamide (DMF) and subsequently adding phenylboronic acid, potassium carbonate (K₂CO₃), and palladium(II) acetate (Pd(OAc)₂) and stirring overnight at 80 °C under nitrogen (Scheme 2). The functionalized polymer, **P3**, was washed with an aqueous sodium diethyldithiocarbamate solution, subjected to a short plug of silica to remove residual palladium salts, and then extensively washed with MeOH.

5-Phenyltriazole-functionalized polymer **P3** generated in this way was characterized by ¹H NMR spectroscopy, IR spectroscopy, GPC, DSC, and TGA to evaluate property changes following the postpolymerization reaction. In the ¹H NMR spectrum of **P3**, shown in Figure 1, characteristic resonances for the introduced phenyl group are clearly visible at δ 7.50 and 7.30 ppm, indicating the success of the cross-coupling reaction. Upon careful inspection of the spectrum of **P3**, two resonances at δ 7.59 and 5.15 ppm (circled in Figure 1) were observed and attributed to small amounts of a proto-triazole compound formed during the cross-coupling reaction.

To quantify the extent of postpolymerization functionalization, polymer **P3**, which contains backbone ester linkages, was saponified with NaOH, and products were characterized by mass spectrometry. To accomplish this, a small quantity of **P3** was stirred in an aqueous sodium hydroxide solution at 70 °C until a clear, homogeneous solution was obtained (Scheme 3). LC-MS analysis of this solution showed two peaks in a ~17:1 ratio. The

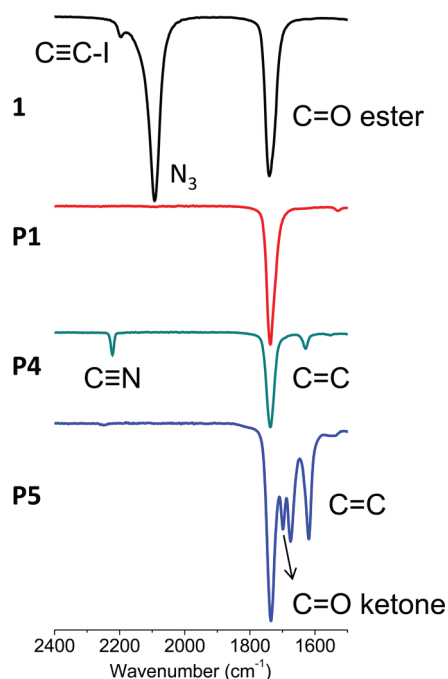


Figure 2. Infrared spectra of monomer **1** and polymers **P1**, **P4**, and **P5**.

predominant signal corresponds to a mass of 359 Da and can be attributed to the phenyl derivative **5**, indicating a >90% conversion of **P1** to **P3**. The minor signal corresponds to a mass of 283 Da, which corresponds to the proto-triazole **4**, as observed in the NMR spectrum of **P3** and verified by the independent hydrolysis of **P2** (Scheme 3).²¹ Mass signals corresponding to the iodo-functionalized, hydrolysis products of **P1** (i.e., 409 Da) were not observed, suggesting complete consumption of the aryl halide. It should be noted that hydrolysis of **P1** only yields one iodo-triazole product (**3**) with a mass of 409 Da, indicating that **4** is not formed during the hydrolysis of **P1** (Scheme 3).

Following the initial successful postpolymerization derivatization using Suzuki chemistry, we further explored the functionalization capabilities of **P1** by examining palladium-catalyzed Heck²² reactions with terminal alkenes. Using a Pd(OAc)₂/tetrabutylammonium bromide (TBAB) catalyst mixture and sodium bicarbonate as a base,²³ **P1** was functionalized with styrene with a conversion of 60% being obtained as determined by mass spectroscopy analysis of the hydrolyzed polymer. Unfortunately, the resulting functionalized polymer was completely insoluble in most common organic solvents, making further characterization impossible. In contrast, reaction of acrylonitrile or methyl vinyl ketone with **P1** (shown in Scheme 2) resulted in soluble polymers **P4** and **P5**, respectively. IR spectroscopic analysis of monomer **1** and the polymers **P1**, **P4**, and **P5** is shown in Figure 2 and confirms the complete consumption of azide at $\nu = 2092\text{ cm}^{-1}$ during the polymerization of **1** to **P1** and incorporation of acrylonitrile and methyl vinyl ketone by postpolymerization Heck reaction, as evidenced by the presence of the nitrile stretch at $\nu = 2222\text{ cm}^{-1}$ in **P4** and the carbonyl and vinylic stretches at $\nu = 1698$ and 1675 cm^{-1} in **P5**. The ¹H NMR spectrum of **P4** showed resonances from two sets of vinylic protons at δ 7.36 (*E*), 7.17 (*Z*), 6.03 (*E*) and 5.90 ppm (*Z*) in a 7:3 ratio. On the basis of the coupling constants (16.5 vs 3.9 Hz), it can be inferred that acrylonitrile is incorporated predominantly in the *E*-configuration of **P4**. In contrast, the conformation of the double bond δ 7.41 and 6.56 ppm in **P5** ($J = 16.5\text{ Hz}$) was shown

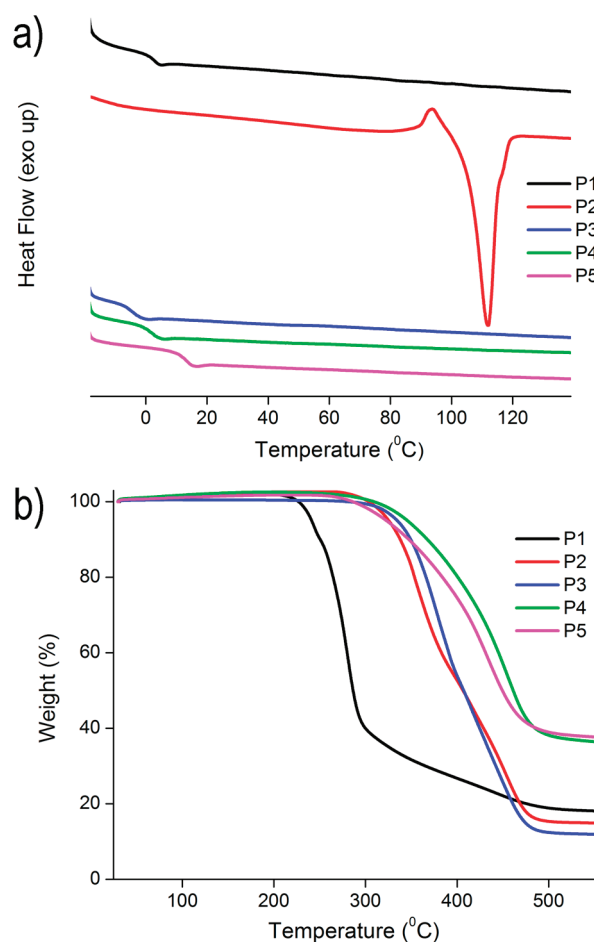


Figure 3. (a) DSC thermograms and (b) TGA curves of polytriazoles **P1–P5**.

to be entirely in the *E*-configuration. The ¹H NMR spectra of both **P4** and **P5** do not show any resonances related to the formation of the proto-polymer **P2**. Polymers **P4** and **P5** were independently subjected to hydrolysis in order to quantify the efficiency of the Heck reaction. For **P4**, one signal with a mass of 353 Da was obtained, corresponding to a subunit in which the cyano group has been transformed to a carboxylate (Scheme 3), suggesting quantitative conversion of the Heck coupling and base-catalyzed hydrolysis of the nitrile during saponification. Unfortunately, hydrolysis of **P5** led to a product with a mass of 283 Da (equivalent to the mass of the hydrolyzed product of **P2**), and thus, the reaction could not be quantified in this way (Scheme 3). The formation of a product with a mass of 283 Da might be explained by the conjugate addition of hydroxide to the double bond, thereby forming an enolate. After acidification, subsequent elimination of 3-hydroxybut-3-en-2-one yields the proto-triazole **4**. ¹H NMR spectroscopy proved useful in this case for quantifying the postpolymerization functionalization of **P5** by comparing the integration for methylene protons α to the triazole (δ 4.38 ppm) and vinylic protons (δ 6.70 and 7.40 ppm) of the introduced methyl vinyl ketone functionality. The integration ratio of 2:1 between the polymer chain methylene protons and vinylic protons suggests a near-quantitative conversion of **P1** to **P5** (¹H NMR spectra are shown in the Supporting Information).

The functionalized polymers **P3** and **P4** showed average molar masses and molecular weight distributions similar to **P1** (see Table 1) as determined by GPC, indicating that this postpolymerization functionalization does not significantly influence the size and solution properties of these polymers. In the case of **P5**, however, a significantly higher average molar mass was observed (i.e., 22K for **P5** versus 13.4K for **P1**). This observation might result from differing solution properties of **P5** in CHCl_3 as compared to **P1** or, more likely, due to solubility changes and fractionation of the lower molecular species during precipitation, as suggested by the accompanying decrease in polydispersity.

In order to compare the material properties of the synthesized PTAs and to study the effect of different functionalization reactions on the triazole, polymers **P1–P5** were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC analysis of the iodotriazole polymer, **P1**, shows the polymer to be amorphous in the temperature range between -20 and 180 °C with a glass transition temperature (T_g) of 3 °C (Figure 3a). Interestingly, the prototriazole analogue, **P2**, is semicrystalline with a melting temperature (T_m) of 111 °C and a (barely visible) T_g of -17 °C. This semicrystalline behavior is consistent with related polytriazoles (see Figure S2 in the Supporting Information for the molecular structures) reported by the Drockenmüller⁷ and Takasu²⁴ groups, who observed melting transitions at 115 and 125 °C. Compared to polyesters with a comparable carbon main chain (T_g of -80 °C for C_{11} polyester),²⁵ the T_g values of **P1** and **P2** are slightly higher, which might be attributed to the interchain hydrogen bonding interactions of the triazole ring.⁷ Similar interactions also influence the crystal packing of the polymers, as indicated by the T_m of **P2**, which cannot be attributed to crystallization of the C_{12} segment alone. Since many iodo compounds have a higher melting point as compared to their proto analogues, the melting temperature of **P1** may be higher than the upper limit of the experimental temperature range (i.e., 180 °C) and approaching or exceeding its degradation temperature of 220 °C (see Figure 3b). Alternatively, the bulky iodo side group may sterically inhibit crystallization, although it should be noted that both **P1** and **P2** are visually identical (i.e., white powders), suggesting that **P1** is, in fact, semicrystalline. Following postpolymerization functionalization, polymers **P3–P5** are all rendered amorphous with distinct glass transition temperatures observed at -4 , 3 , and 13 °C, respectively and, in contrast to **P1** and **P2**, are all tacky solids at room temperature.

TGA analysis of polymers **P1–P5** was performed under inert atmosphere at a ramp rate of 10 °C/min and showed, not surprisingly, that iodo-PTA, **P1**, is much less stable than the proto- and functionalized PTA analogues **P2–P5**. Specifically, the degradation temperature of **P1** was calculated to be ~ 220 °C, whereas the onset of degradation for polymers **P2–P5** starts at much higher temperatures ranging from 340 to 370 °C. This reduction in thermal stability can be rationalized by considering the lability of the carbon–iodine bond, as compared to the carbon–carbon bonds in polymers **P3–P5**. As seen in Figure 3, the weight loss varies significantly between the five polymer samples, as the char yield, defined as the weight remaining at 500 °C, was found to be $\sim 40\%$ for **P4** and **P5** and $\sim 20\%$ for **P1–P3**. These examples exemplify the variability and control by which the T_g of these polymers can be altered and hints at the importance of iodo-PTAs as a useful building block to prepare a

multitude of polytriazoles with distinct properties through metal-mediated cross-coupling reactions.

CONCLUSION

A new family of PTAs, poly(5-iodo-1,2,3-triazole)s, is now available via step-growth $^1\text{CuAAC}$ polymerization of α -azido- ω -iodoalkyne monomer **1**. The polymerization reaction proceeded remarkably fast with high molecular weight polymer obtained within a 1 h. We demonstrated that the iodo-PTA, **P1**, can serve as a useful platform for further functionalization by palladium-catalyzed cross-coupling reactions with phenylboronic acid or alkenes, such as acrylonitrile and methyl vinyl ketone. The resulting functionalized polymers show varying thermal properties when compared to the iodo- and proto-PTAs. For example, the functionalized PTAs are amorphous with varying glass transition temperatures, as can be seen from DSC, and show distinct differences in mass loss when compared to the parent iodo-PTA, **P1**. The selectivity and robustness of the chemistry and the ready availability and stability of the starting materials open a way to a new class of triazole-based polymeric materials with properties that can be tuned as desired based on the type and extent of side-chain functionalization. In addition, the iodotriazole functionalization strategies described here may complement and expand the diversity of biosourced,²⁶ oligomeric and cyclic,²⁷ or dendritic²⁸ triazole-based materials.

ASSOCIATED CONTENT

S Supporting Information. Experimental details and characterization of hydrolysis products of **P1**, **P2**, and **P3**, GPC chromatograms of **P1–P5** (Figure S1), Figure S2 and ^1H and ^{13}C NMR spectra of polymers **P1–P5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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