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ARTICLE

Synthesis and Characterization of Isomeric Vinyl-1,2,3-triazole Materials by Azide–Alkyne Click Chemistry

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ABSTRACT: The synthesis of isomeric, functionalized 4-vinyl-1,2,3-triazole and 5-vinyl-1,2,3-triazole monomers is demonstrated using heterogeneous copper (copper-in-charcoal)-catalyzed azide–alkyne cycloaddition (CuAAC) or homogeneous ruthenium (Ru)-catalyzed azide–alkyne cycloadditions (RuAAC) "click" protocols. These reactions are regiospecific, exclusively forming 1,4- and 1,5-disubstituted triazoles as determined by ^{1}H NMR, ^{13}C NMR, and X-ray crystallography analysis. Polymerizations were performed using living free radical procedures to yield materials with divergent properties. In the case of the 1,5-triazole materials, glass transition temperature were significantly higher that for the 1,4-derivatives while solubility was decreased.

Introduction

Understanding structure–property relationships is one of the key challenges in polymer science as the physicochemical properties of polymers are intrinsically related to their molecular structure, especially the nature of the repeat unit. In order to meet the world's constantly evolving demands for materials with superior performance, new functionalized monomer families need to be developed.[1] However, the need for these new building blocks is offset by significant challenges such as efficient monomer synthesis, control of functional group incorporation, and orthogonal reactivity. If all of these issues can be addressed, these new monomers would allow for the preparation of well-defined materials with control over the number and nature of multiple reaction sites on the polymer backbone.[2]

One approach to address these issues is based on the concept of "click" chemistry[3] which provides the basis for efficient and orthogonal synthetic strategies leading to the preparation and modification of a wide range of polymeric materials. The Cu(I)-mediated Hüisgen-type [3 + 2] cycloaddition reaction between an organic azide and a terminal alkyne, resulting in a 1,4-disubstituted triazole,[3,4] is one of the most thoroughly studied reactions based on the click chemistry philosophy. This highly efficient reaction takes place under benign conditions and tolerates a wide range of functional groups. As a result, "click" strategies have emerged as important and general methodologies for constructing materials and have found use in many applications in a relatively short period of time. For example, click reactions have been extremely successful in the synthesis of nanostructures, protein conjugates, and polymeric materials[5–19] due to the regiospecificity and chemoselectivity of the alkyne/azide reaction. This allows for highly efficient and modular synthetic approaches, accessible to nonexperts, to be developed.

If the discovery of efficient click reactions for materials synthesis has been a major new development in polymer chemistry, equally important in recent years is the study of the polymerization of vinyl monomers under living free radical conditions. Considerable effort has been directed toward preparing functionalized materials with well-controlled properties based on vinyl monomers, with the majority of the attention directed toward derivatives of conventional monomers such as acrylates and styrenic copolymers. These monomers are relatively easy to incorporate into polymeric structures but often lack desired properties such as chemical stability for acrylates or structural diversity for styrenic derivatives.[20] To address this issue and alleviate the scarcity of new vinyl monomer families, 4-vinyl-1,2,3-triazoles have been designed to take advantage of the 1,2,3-triazole subunit and combine the features found in classical monomers, such as aromaticity, polarity, and structural diversity inherent to styrenics, vinylpyridines, and acrylates, respectively, into a single building block.[21] In combining the major research themes of click chemistry and living free radical polymerization, a wide variety of 4-vinyl-1,2,3-triazoles have been prepared utilizing the highly efficient Cu(I)-catalyzed Hüisgen type [3 + 2] cycloaddition reaction[22,23] and readily polymerized by free radical and living free radical polymerization techniques. Examination of these 1,2,3-triazole-based polymers showed unique physical properties, demonstrating increased stability due to the aromatic triazole ring, a large dipole moment, and significant hydrogen-bonding character.[24]

The modular nature of the 4-vinyl-1,2,3-triazole synthesis combined with the interesting physical properties for the resulting polymers raises the interesting possibility of examining isomers of the parent 4-vinyl derivatives. To this end, Fokin and Jia have recently reported that the Ru-mediated reaction of azides and alkynes regioselectively complements the Cu-catalyzed reaction and leads to the exclusive formation of 1,5-triazoles.[25] This ability to selectively prepare regioisomers by utilizing either a Cu(I)[25] or Ru(I) catalyst provides an unique

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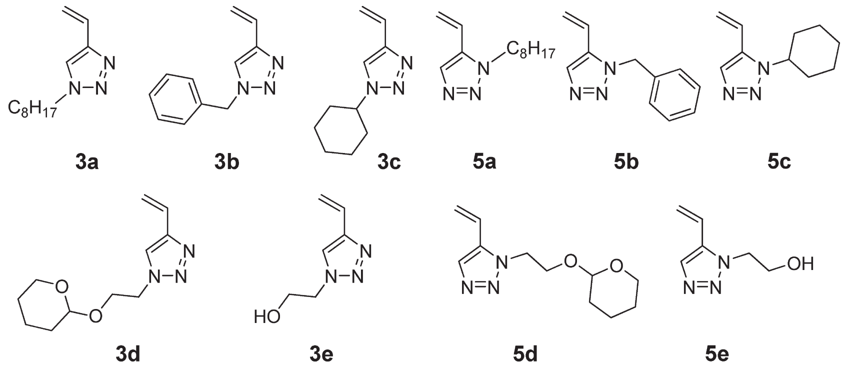
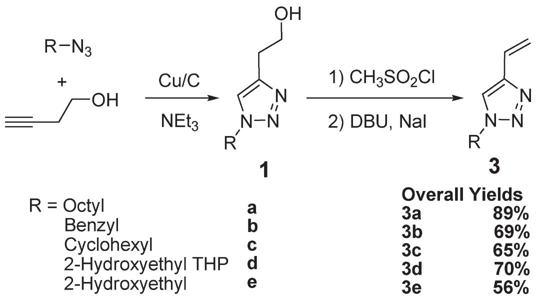


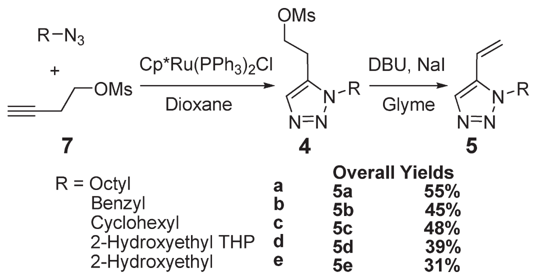
Figure 1. Structural libraries of 1-substituted-4-vinyl triazoles, **3a–e**, and 1-substituted-5-vinyl triazoles, **5a–e**, monomers.

opportunity to develop rigorous structure/property relationships and to study the effects of various pendent groups on polymeric properties. Herein, we report the synthesis of isomeric, substituted 5-vinyl-1,2,3-triazoles and 4-vinyl-1,2,3-triazoles monomers and subsequent polymerization to give a library of isomeric homopolymers, copolymers, and block copolymers (Figure 1).

Scheme 1



Scheme 2



Results and Discussion

1-Substituted-4-vinyl-1,2,3-triazoles. The common starting material for the synthesis of all 1-substituted-4-vinyl-1,2,3-triazoles was but-3-yn-1-ol, which was coupled to a variety of different azides in the presence of the recently introduced heterogeneous Cu/C catalyst system.[26] Interestingly, Cu/C is a bench stable solid that offers many advantages, such as the ability to use a wide range of solvents, recyclability of the catalyst, and most importantly rapid isolation of the desired triazole products. Through the use of Cu/C, a library of the desired 1,4-disubstituted-triazoles, **1**, were obtained in excellent yield (>95%) with only minimal purification (Scheme 1). The corresponding 4-vinyltriazoles, **3**, were then prepared by conversion of the alcohol to the mesylate, **2**, followed by elimination with sodium iodide in combination with 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU). While the yields for the last two steps were slightly lower, overall yields for the 4-vinyltriazoles range from 65% to 89%, which combined with the robust nature of the method offers a facile strategy for the syntheses of these highly functional monomers. In the case of the 2-hydroxyethyl derivative, **3e**, introduction of a hydroxyl-containing substituent required protection due to the mesylation step used in formation of the vinyl group. To address this, tetrahydropyran (THP) was found to be a suitable protecting group with deprotection of **3d** being carried out using *p*-toluenesulfonic acid (*p*-TSA) in methanol to yield **3e** in 56% yield over four steps.

1-Substituted-5-vinyl-1,2,3-triazoles. For the isomeric 5-vinyltriazoles, initial attempts to couple azides with but-3-yn-1-ol gave very low yields, presumably due to deactivation of the Ru catalyst by the hydroxyl group. As a result, a more advanced starting material, the mesylated alkyne, **7**, with the hydroxyl group masked as a mesylate was coupled with organic azides in anhydrous dioxane using a catalytic amount of Cp*RuCl(PPh_3)$_2$. In contrast to the hydroxyl derivative, the yields significantly increased with the triazole derivatives, **4**, being obtained in good yields, though still consistently lower than for the Cu/C system (Scheme 2). As will be shown below, the use of the Ru catalyst, while not a click reaction in terms of efficiency and quantitative yield, did provide access to the pure 1,5-isomer, which is significant and allows the desired 5-vinyl derivatives, **5**, to be regiospecifically obtained as discrete isomers of the traditional 1,4-triazoles obtained through CuAAC click chemistry.

The regiospecificity of both the Ru and Cu catalyzed cycloaddition reactions was confirmed using a combination of spectroscopic techniques. High-resolution mass spectrometry revealed the same molecular ions for the corresponding members of each library, showing that the materials have the same molecular formula. Perhaps more diagnostic was a comparison of the NMR spectra for the triazoles obtained from the Ru and Cu procedures. As shown in Figure 2, ^{1}H NMR spectral analysis of 1-octyl-4-vinyltriazole, **3a**, and 1-octyl-5-vinyltriazole, **5a**, reveal distinct resonances for the triazole ring proton at 7.49 and 7.73 ppm, respectively, with significant changes also observed for the protons of the vinyl groups. A similar difference was also observed in the ^{13}C NMR spectra with significant variations in the aromatic/vinyl region fully consistent with the 1,4- and 1,5-substitution patterns (Figure 3). These results clearly demonstrate both the isomeric purity obtained for each catalyst system and the structural similarity between the monomer families. More importantly, a similar trend was observed for the other vinyl triazole derivatives with the difference between the two series being consistent.

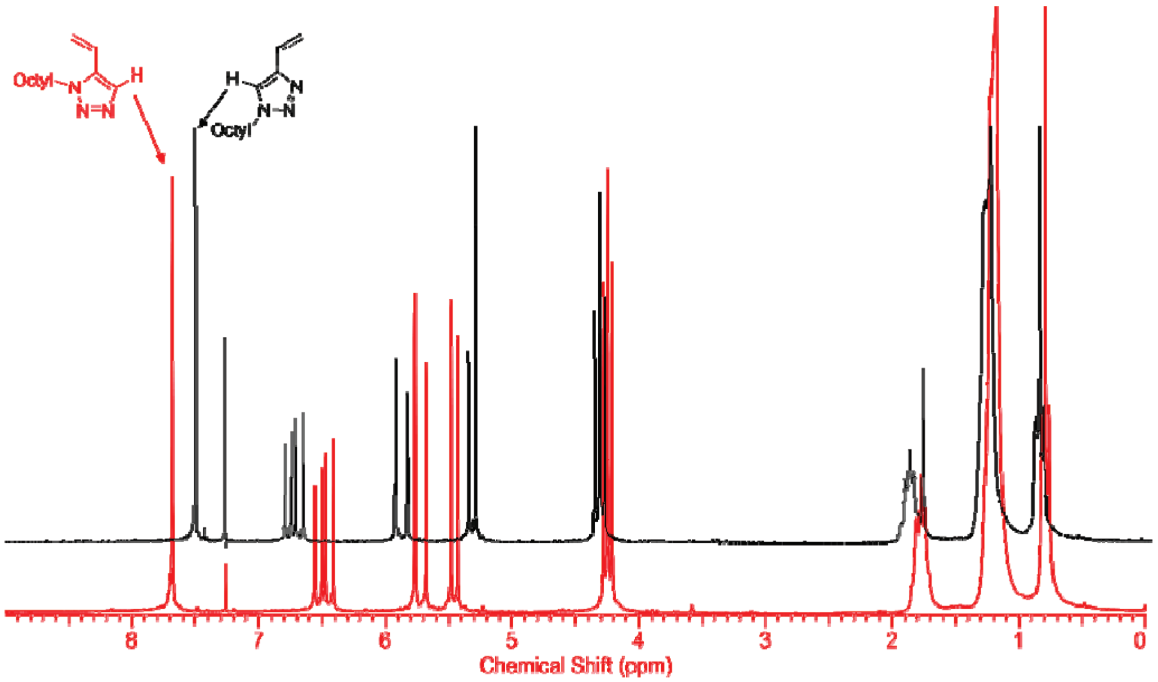


Figure 2. Comparison of ^{1}H NMR spectra for 1-octyl-4-vinyl-1*H*-1,2,3-triazole (**3a**, top) and 1-octyl-5-vinyl-1*H*-1,2,3-triazole (**5a**, bottom).

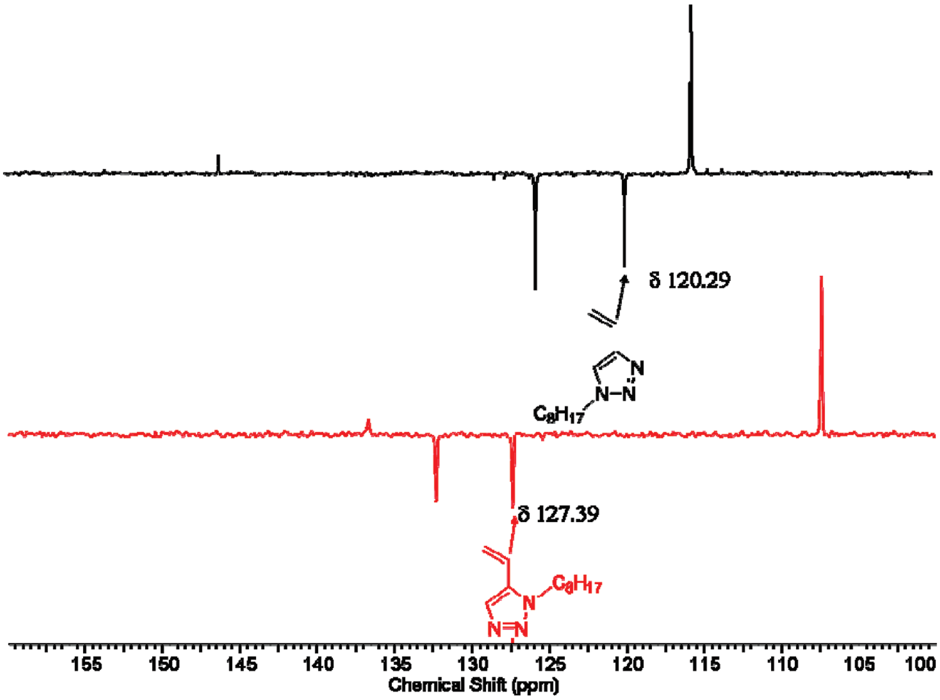


Figure 3. Comparison of ^{13}C NMR spectra for 1-octyl-4-vinyl-1*H*-1,2,3-triazole (**3a**, top) and 1-octyl-5-vinyl-1*H*-1,2,3-triazole (**5a**, bottom).

Conclusive structural characterization was then obtained from X-ray analysis of single crystals of 2-(4′-vinyl-1*H*-1′,2′,3′-triazol-1′-yl)ethanol (**3e**) and 2-(5′-vinyl-1*H*-1′,2′,3′-triazol-1′-yl)ethanol (**5e**). These results clearly confirm the regiospecificity of the Ru- and Cu-catalyzed reactions with the correct assignment of the 1,5-substituted triazole ring to the Ru reaction and the 1,4-substituted triazole ring to the Cu system (Figure 4). Interestingly, the crystal structures also showed the presence of strong hydrogen bonding between the hydroxyl group and N-3 of the triazole ring of adjacent monomers with a distance of 2.84 Å for **3e** and 2.85 Å for **5e**,[27,28] fully consistent with the significant H-bonding character of the triazole ring.

Having demonstrated the regiospecificity of the Ru- and Cu-catalyzed formation of the triazole monomers, a unique opportunity therefore exists to evaluate the steric and electronic effect of 1,4- vs 1,5-substitution for these novel monomers and to develop structure/property relationships for the corresponding macromolecular isomers. To address this, the polymerization of isomeric vinyl triazole monomers was investigated using NMP and RAFT living free-radical polymerization techniques.[29] For RAFT-mediated

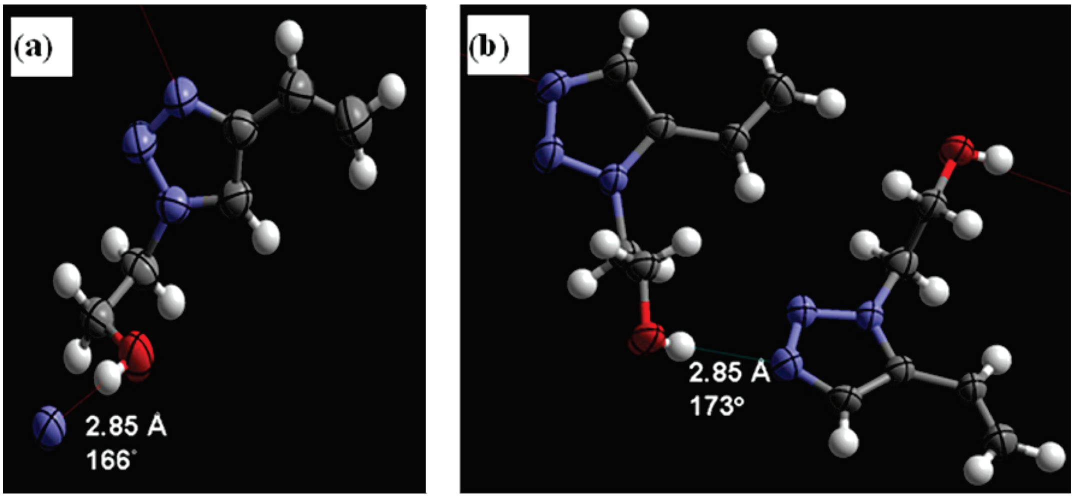


Figure 4. Crystal structures of (a) 2-(4′-vinyl-1*H*-1′,2′,3′-triazol-1′-yl)ethanol, **3e**, and (b) 2-(5′-vinyl-1*H*-1′,2′,3′-triazol-1′-yl)ethanol, **5e**.

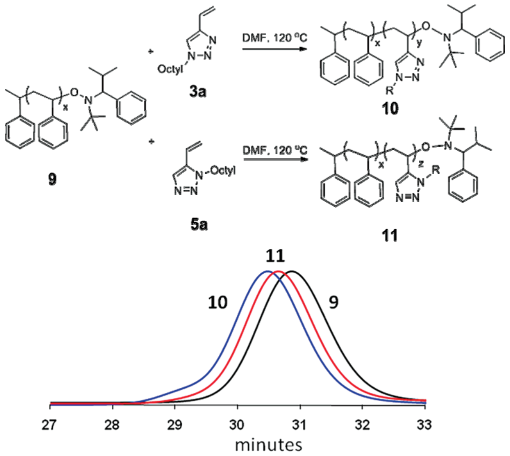


Figure 5. GPC traces for the starting polystyrene macroinitiator, **9** (black, M_n = 12 400 amu, PDI = 1.12), polystyrene-*b*-1-octyl-4-vinyltriazole, **10** (blue, M_n = 18 800 amu, PDI = 1.13), and polystyrene-*b*-1-octyl-5-vinyltriazole, **11** (red, M_n = 16 400 amu, PDI = 1.10) synthesized by NMP polymerization.

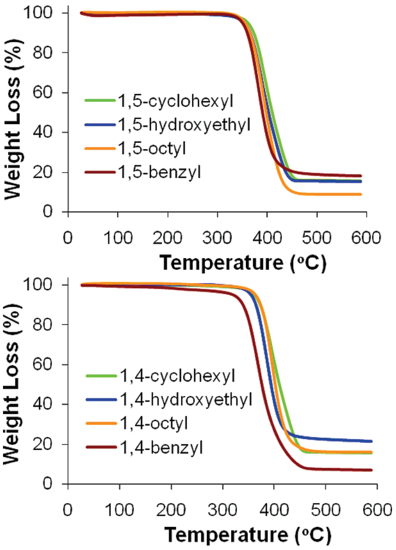


Figure 6. Thermogravimetric analyses of substituted poly(vinyltriazole)s in nitrogen at a heating rate of 10 °C/min.

polymerization, control over the polydispersity (PDI < 1.15) was observed for both the 1,4- and 1,5-monomers with kinetic studies showing that the 1,5-disubstituted monomer polymerized significantly faster than its 1,4-counterpart. This was unexpected due to the steric hindrance of the vinyl substituent for the 1,5-isomer. However, the increased reactivity can be attributed to the electronic environment of the 4-vinyl and 5-vinyl groups with the lower electron density on the β-carbon of 1-octyl-5-vinyl-triazole, **5a**, being demonstrated by the downfield shift of the ^{13}C NMR resonance for the β-carbon of **5a** (127.39 ppm) compared to the resonance for **3a** (120.29 ppm) (Figure 3). This lower electron density facilitates the electron transfer from the polymer radical to the monomer, consequently leading to higher reactivities for the 1,5-triazole monomers.[30]

Having demonstrated RAFT homopolymerization for both the 1,4- and 1,5-substituted monomers with accurate control over both molecular weight and polydispersity, the formation of well-defined block copolymers by nitroxide-mediated procedures was then examined. Starting from a polystyrene macroinitiator, **9**, reinitiation and block copolymer formation with both 1-octyl-4-vinyl and 1-octyl-5-vinyl monomers were observed to be a living process in DMF at 120 °C with symmetrical low-polydispersity block copolymers, **10** and **11**, being obtained in each case (Figure 5).

The availability of homopolymers and block copolymers based on isomeric vinyltriazole derivatives allows the influence of regiochemistry on physical properties to be addressed in these systems. As can be seen in Figure 6, the thermogravimetric analysis (TGA) traces for all the functionalized triazole polymers have similar onsets of weight loss around 320 °C with only minor differences depending on substituent and isomer structure.

In contrast, major differences in the glass transition temperatures, as measured by DSC, were observed between the isomeric families of similarly functionalized poly(vinyltriazole)s (Figure 7). In each case, the T_g of the 1,5-isomer was significantly amplified when compared to the corresponding 1,4-isomer, with the 1,5-isomers having glass transition temperatures ≈70−100 °C higher. Of particular note are poly(1-cyclohexyl-5-vinyltriazole) **5c** with a glass transition temperature of 220 °C (cf. poly(1-cyclohexyl-4-vinyltriazole) **3c**, T_g of 105 °C) and poly(1-octyl-5-vinyltriazole) **5a**, with a T_g of 95 °C (cf. poly(1-octyl-4-vinyltriazole) **3a**, T_g of 7 °C). These results demonstrate the significant influence that the sterically more encumbered 1,5-isomer has on the mobility of the polymer backbone coupled with the overall

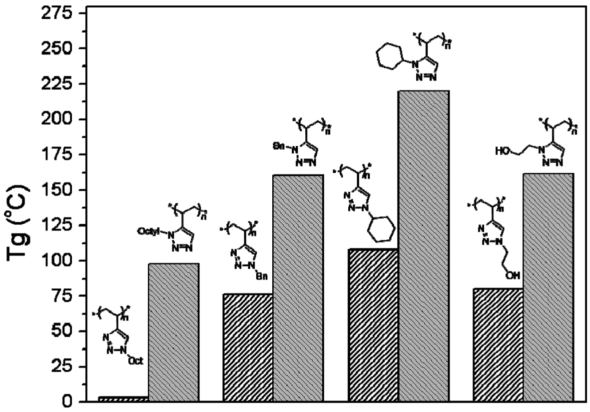


Figure 7. Glass transition temperatures for isomeric poly(1,4-vinyltriazole) and poly(1,5-vinyltriazole) derivatives. Molecular weights were approximately $M_n = 20\,000$ amu and PDI < 1.20 in all cases.

Table 1. Solubility Properties of Isomeric 1,4- and 1,5-Substituted Poly(vinyltriazole) Derivatives[a]

R	MeOH		DMF		THF		Chloroform		DCM	
	1,4	1,5	1,4	1,5	1,4	1,5	1,4	1,5	1,4	1,5
2-Hydroxyethyl	+	+	+	-	-	-	-	-	-	-
Cyclohexyl	-	-	+	-	+	-	+	+	+	-
Octyl	+	-	+	+	+	+	+	+	+	+
Benzyl	-	-	+	-	+	-	+	+	+	-

[a] Molecular weights were approximately $M_n = 20\,000$ amu and PDI < 1.20 in all cases. "+" indicates solubility of ~10 mg/mL while "−" indicates no detectable solubility even at 0.1 mg/mL.

influence that the polar, aromatic 1,2,3-triazole ring has on the glass transition temperature. For example, the octyl-substituted derivatives with T_g's of 7 and 95 °C, respectively, are both dramatically enhanced when compared to other vinyl polymers bearing octyl substituents, such as poly(4-octylstyrene) (−45 °C) and poly(*n*-octyl acrylate) (−65 °C).

The influence of the triazole ring and its substitution pattern on the physical properties of the resulting homopolymers was also observed in the solubility behavior of the two isomeric series of derivatives. As shown in Table 1, for poly(1-substituted-4-vinyltriazole)s and poly(1-substituted-5-vinyltriazole)s with similar molecular weights and polydispersities, the 1,4-derivatives were generally more soluble than their 1,5-counterparts with the latter being soluble in a limited range of solvents. For example, poly(1-cyclohexyl-4-vinyltriazole) **3c** was soluble in a wide range of solvents (DMF, THF, $CHCl_3$, and CH_2Cl_2) whereas the isomeric poly(1-cyclohexyl-5-vinyltriazole) **5c** was only soluble in $CHCl_3$, even though the molecular weight and polydispersity of the two polymers are almost identical.

Conclusions

Isomeric 1-substituted-4-vinyl-1,2,3-triazole and 1-substituted-5-vinyl-1,2,3-triazole monomers have been successfully synthesized under regiospecific conditions by taking advantage of recently developed Cu(I)- and Ru(I)-catalyzed "click" chemistry methodologies. These monomers were shown to undergo controlled polymerization to give the corresponding homopolymers and block copolymers with distinct property differences depending on both the substituent and the isomer configuration. It was shown that the 1,5-isomers had significantly higher glass transition temperatures, up to 220 °C for the cyclohexyl derivative, and decreased solubilities when compared to the corresponding 1,4-isomers. These studies further expand the modular nature of azide−alkyne coupling chemistry for the preparation of novel vinyltriazole monomers and demonstrate that these modular systems have great potential for imparting "tunable" properties in polymeric materials due to their unique thermal nature, synthetic accessibility, and functional group tolerance. It is anticipated that these isomeric vinyltriazole families will become valuable and versatile building blocks in materials research for the construction and functionalization of well-defined macromolecules and nanostructures.

Experimental Section

General Procedures and Materials. Unless otherwise stated, ACS reagent grade chemicals and solvents were purchased from Aldrich and used without further purification. All reactions were carried out under ambient conditions unless specified. All organic azides,[31] Cu/C,[26] $Cp^*RuCl(PPh_3)_2$,[24] and the RAFT initiator,[32] were synthesized according to literature procedures (Cu/C is now commercially available from Aldrich; CAS# 70910-7).

Analytical thin layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF254 (0.24 mm thick). Flash column chromatography was carried out either by using silica gel (Merck Kieselgel 60 (230−400 mesh, ASTM)) or on Biotage SP1 system using 40+M and 65i columns. ^{1}H NMR (500 and 200 MHz) and ^{13}C NMR (162 and 60 MHz) analysis was completed using Bruker AC 500 and 200 spectrometers, respectively, with the chemical shift reported in ppm and referenced to signals from residual protons of the solvents. These data were processed on ACD laboratories Version 11 software. Size exclusion chromatography (SEC) was carried out at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer and six Waters Styragel columns (five HR-5 μm and one HMW-20 μm) using THF as eluent (flow rate: 1 mL/min). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The molecular weights of the polymers were calculated relative to linear polystyrene standards. Differential scanning calorimetry (DSC) measurements took place using a TA Instruments DCS 2920 at a ramp rate of 10 deg/min. A Mettler TGA/DTA 851e was used for thermal gravimetric analysis (TGA) measurements, mass spectral analyses data were collected with a PE Sciex API Qstar Pstar instrument, and infrared spectroscopic experiments were completed on a Perkin-Elmer Spectrum 100 Fourier transform infrared spectrometer (FTIR). Typically, 32 scans at a resolution of 4 cm^{-1} were recorded on each sample by using an ATR (attenuated total reflection) apparatus. The crystal structures were determined by mounting crystals on glass fibers and transferred to a Bruker CCD platform diffractometer. The SMART1 program was used to determine the unit cell parameters and data collections (15 s/frame, 0.3 deg/frame for a sphere of diffraction data). The data were collected at room temperature with Mo Kα radiation. The raw frame data were processed using SAINT2 program. Empirical absorption corrections were applied beads on Psi scan method. Subsequent calculations were carried out using SHELXTL3 program, and the structures were solved by direct methods and refined on F2 by full-matrix least-squares techniques. Mass spectral data were collected on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer (ESI-MS) or on an Applied Biosystems TF4800 MALDI-TOF mass spectrometer.

General Procedure for Synthesis of 1,4-Triazoles Using Heterogeneous Cu/C Catalyst System: 2-(1-octyl-1*H*-1,2,3-triazol-4-yl)ethanol (1a). A 250 mL round-bottom flask, equipped with a magnetic stir bar, was charged with octyl azide (9.97 g, 64.2 mmol), triethylamine (32.00 g, 320 mmol), 1,4-dioxane (130 mL), 3-butyn-1-ol (4.50 g, 64.2 mmol), and copper on charcoal (0.20 g). The reaction mixture was stirred for 3 h at 60 °C, and the reaction was monitored by TLC. The reaction mixture was filtered over Celite and concentrated under reduced pressure to give 14.00 g of essentially pure 2-(1-octyl-1*H*-1,2,3-triazol-4-yl)ethanol, **1a**, as a white waxy solid, in 97% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (s, 1H), 4.32 (t, $J = 7.3$ Hz, 2H), 3.95 (t, $J = 5.9$ Hz, 2H), 2.95 (t, $J = 5.8$ Hz, 2H), 1.89 (m, 3H), 1.28 (m, 10H), 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$): δ145.65, 121.52, 61.79, 50.45, 31.86, 30.46, 29.19, 29.12, 28.87, 26.67, 22.75, 14.22. ESI mass spec: Calculated for [$C_{12}H_{23}N_3O$]: 225.18. Found: 225.18.

General Procedure for Mesylation: Synthesis of 2-(1-Octyl-1*H*-1,2,3-triazol-4-yl)ethyl methanesulfonate (2a). Compound **1a** (1.00 g, 4.8 mmol) was placed in a 100 mL round-bottom flask containing 50 mL of CH_2Cl_2, to which triethylamine (3.00 g 29 mmol) was added. The flask was cooled in an ice bath, and methanesulfonyl chloride (0.70 g, 6.1 mmol) added dropwise. The reaction was then allowed to warm to room temperature, stirred for an additional 3 h, poured into a separatory funnel, and washed with 1 M HCl and brine (2 × 50 mL each). The organic layer was dried over $MgSO_4$, filtered, and concentrated to yield 1.25 g (96%) of compound **2a**, which was used without any further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.43 (s, 1H), 4.53 (t, $J = 6.4$ Hz, 2H), 4.33 (t, $J = 7.3$ Hz, 2H), 3.19 (t, $J = 6.4$ Hz, 2H), 2.97 (s, 3H), 1.89 (m, 2H), 1.26 (m, 10H), 0.88 (m, 3H).

1-Cyclohexyl-4-vinyl-1*H*-1,2,3-triazole (3c). Compound **1c** (14.60 g, 74.8 mmol), *p*-toluenesulfonic acid (1.5 g, 8.72 mmol), and DMF (200 mL) were added to a 500 mL round-bottom flask, equipped with a reflux condenser. The reaction mixture was heated to 140 °C for 1 h and then poured into 500 mL of water, and the pH of the solution was adjusted to 7. The product was then extracted with CH_2Cl_2 (3 × 150 mL), and the combined organic layers were washed repeatedly with water, brine solution, dried over $MgSO_4$, filtered, and concentrated to dryness. The product was further purified by column chromatography (ethyl acetate (EA):hexanes (Hex)) (1:1) yielding 8.75 g of **3c** as a colorless oil in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (s, 1H), 6.71 (dd, $J = 17.90$, 11.03 Hz, 1H), 5.85 (d, $J = 17.65$ Hz, 1H), 5.30 (dd, $J = 11.35$, 1.26 Hz, 1H), 4.31−4.52 (m, 1 H), 1.17−2.27 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.87, 125.91, 117.78, 115.47, 59.95, 33.51, 25.12. ESI mass spec for $C_{10}H_{15}N_3$ Calculated: 177.13. Found $(M + H)^+$: 178.13.

One-Pot Procedure for Synthesis of 1-(2-(Tetrahydro-2*H*-pyran-2-yloxy)ethyl)-4-vinyl-1*H*-1,2,3-triazole (3d) Using Heterogeneous Cu/C Catalyst. To a 250 mL round-bottom flask filled with 60 mL of gylme, compound **7** (5.6 g, 38.7 mmol), (6.47 g, 38.7 mmol) of 2-(2-azidoethoxy)tetrahydro-2*H*-pyran, triethylamine (11.47 g, 113 mmol), and 100 mg of Cu/C were added. The reaction vessel was heated to 45 °C and stirred overnight. The reaction was monitored via TLC to completion, and a small amount (50 mg) of butylated hydroxytoluene (BHT) and sodium iodide (11.3 g, 76.0 mmol) were added, and the reaction vessel was heated to reflux for 1.25 h. After cooling, the reaction mixture was filtered, concentrated under vacuum, and dissolved in 200 mL of ethyl acetate. The organic solution was then washed with water (2 × 100 mL), 1 M HCl (2 × 100 mL), and brine and dried over $MgSO_4$. The crude product was then concentrated and further purified by column chromatography using EA:Hex (1:2) as eluent to give 5.91 g of **3e** in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (s, 1H), 6.69 (dd, $J = 17.75$, 11.16 Hz, 1H), 5.85 (d, $J = 17.74$ Hz, 1H), 5.29 (d, $J = 11.15$ Hz, 1H), 4.46−4.58 (m, 3H), 4.07 (dd, $J = 10.92$, 2.52 Hz, 1H), 3.75 (dd, $J = 10.84$, 3.20 Hz, 1H), 3.57−3.68 (m, 1H), 3.42 (s, 1H), 3.45 (t, $J = 4.99$ Hz, 1H), 1.60−1.77 (m, 2H), 1.43−1.57 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.14, 125.67, 121.19, 115.62, 98.95, 65.63, 62.22, 50.27, 30.31, 25.12, 19.26. ESI mass spec: $C_{11}H_{17}N_3O_2$ Calculated: 223.13. Found: 224.14.

Synthesis of But-3-ynyl Methanesulfonate (7). 3-Butyn-1-ol (0.50 g, 7.1 mmol) and triethylamine (2.17 g, 21.4 mmol) were added to a 250 mL round-bottom flask containing 90 mL of CH_2Cl_2. After cooling this mixture in an ice bath, methanesulfonyl chloride (1.06 g, 9.23 mmol) was added dropwise over a period of 30 min. The reaction mixture was then allowed to warm to the room temperature and stirred for 16 h. Upon completion, the reaction mixture was washed with 1 M HCl solution and brine, and the organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 1.02 g (96%) of **7** as an orange oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.23 (t, $J = 6.6$ Hz, 2H), 3.00 (S, 3H), 2.59 (dt, $J = 6.6$, 2.6 Hz, 2H), 2.05 (t, $J = 2.6$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 78.83, 71.03, 67.36, 37.50, 19.63. ESI mass spec for $C_5H_8N_3O_3S$ Calculated: 148.02. Found $(M + H)^+$: 149.04.

Synthesis of 2-(2-Azidoethoxy)tetrahydro-2*H*-pyran (8). A 50 mL round-bottom flask equipped with a magnetic stirring bar was charged with 2-chloroethanol (1.00 g, 12.4 mmol), 3,4-dihydro-2*H*-pyran (0.36 g, 4.3 mmol), CH_2Cl_2 (26.50 g, 20.08 mL), and pyridinium *p*-toluenesulfonate (0.080 g 0.33 mmol). After 4 h of vigorous stirring, the reaction mixture was concentrated and redissolved in diethyl ether and poured into a separatory funnel containing 80 mL of deionized water and extracted 4 times with 80 mL of diethyl ether. The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude 2-(2-chloroethoxy)tetrahydro-2*H*-pyran was then dissolved in 10 mL of DMF, 3 g of sodium azide was added, and the reaction mixture was stirred for 24 h. The solution was filtered, and the crude product was extracted with pentanes and concentrated in vacuum to yield 2-(2-azidoethoxy) tetrahydro-2*H*-pyran, **8**, in quantitative yield as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.50−4.68 (m, 1H), 3.30−3.98 (m, 6H), 1.37−1.88 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 98.75, 66.27, 61.94, 50.82, 30.34, 25.34, 18.97.

General Procedure for the Synthesis of 1,5-Triazoles by RuACC: Synthesis of 2-(1-Octyl-1*H*-1,2,3-triazol-5-yl)ethyl Methanesulfonate (4a). A 250 mL Schlenk flask was charged with Cp*Ru(PPh_3)$_2$ (0.96 g, 1.21 mmol), and the flask was evacuated and backfilled with argon three times. Dry dioxane (89.0 mL), (6.00 g, 40.5 mmol) of but-3-ynyl methanesulfonate, **7**, and 1-azidooctane (6.91 g, 44.5 mmol) were then added in that order. The reaction mixture was allowed to stir at 70 °C for 6 h and monitored to completion using TLC. The dioxane was removed under reduced pressure, and the crude product was purified by flash column chromatography eluting with 2:3 (EA:Hex) to give 7.7 g of **4a** in 63% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.57 (s, 1H), 4.45 (t, $J = 6.54$ Hz, 2H), 4.28 (t, $J = 7.33$ Hz, 2H), 3.14 (t, $J = 6.11$ Hz, 2H), 1.78−1.98 (m, 2H), 2.99 (s, 3H), 1.22−1.38 (m, 10H), 0.87 (t, $J = 6.32$ Hz, 3H). ESI mass spec for $C_{12}H_{21}N_3$ Calculated: 303.42. Found $(M + H)^+$: 304.20.

General Procedure for the Synthesis of 1,5-Vinyltriazoles: Synthesis of 1-Octyl-5-vinyl-1*H*-1,2,3-triazole (5a). A 250 mL round-bottom flask, equipped with a magnetic stir bar and reflux condenser, was charged with **4a** (1.00 g, 4.60 mmol) and glyme (44 g, 50 mL). To this mixture was added NaI (3.00 g, 20 mmol), followed by DBU (1.00 g, 7.69 mmol), and the reaction was heated to reflux for a period of 45 min. The solution was then evaporated to dryness and redissolved in CH_2Cl_2, washed with water (2 × 150 mL) and brine, and dried over $MgSO_4$. The excess solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography (1:1 EA:Hex) to yield **5a** as a viscous transparent oil in 88% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.73 (s, 1H), 6.52 (dd, $J = 17.6$, 11.2 Hz, 1H), 5.77 (dd, $J = 17.6$, 0.9 Hz, 1H), 5.50 (dd, $J = 11.2$, 0.9 Hz, 1H), 4.29 (t, $J = 7.3$ Hz, 2H), 1.82 (t, $J = 7.0$ Hz, 2H), 1.04−1.43 (m, 12H), 0.73−0.98 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 135.7$, 131.7, 121.1, 120.6, 48.7, 32.2, 30.7, 30.7, 29.6, 29.5, 27.0, 23.1, 14.6, 14.3. ESI mass spec for $C_{12}H_{21}N_3$ Calculated: 207.17. Found $(M + H)^+$: 208.18. IR (ATR): ν (cm^{-1}) 2925, 2856, 1635, 1540, 1465, 1375, 1310, 1225, 1120, 1085, 1045, 975, 720.

General Procedures for Polymerization of Substituted Vinyltriazoles. Ampules equipped with a magnetic stirring bar, monomer, initiator, and DMF (50 wt % monomer concentration) was subjected to four cycles of freeze−pump−thaw process and then sealed under vacuum. The monomer (typically 200 mg) to initiator ratio was 200:1, and the polymerization reaction was conducted at 125 °C for NMP and 70 °C for RAFT procedures for 16 h typically. The viscous reaction mixture was cooled to room temperature, dissolved in dichloromethane (30 mL), and precipitated in methanol (800 mL) to give the desired homopolymer as a white solid. All materials were characterized by GPC, IR, ^{1}H NMR, and ^{13}C NMR.

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Supporting Information Available: Synthesis and characterization data for monomers and intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

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