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A Versatile New Monomer Family: Functionalized 4-Vinyl-1,2,3-Triazoles via Click Chemistry

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The field of polymer science has undergone a renaissance in recent years as the ability to design, construct, and functionalize macromolecules to fit targeted applications develops.[1] While these applications are diverse, the majority of the polymer structures are based on polymerization or functionalization of vinyl monomers derived from a limited range of families.[2] Classic examples include the extensively studied and widely used styrenic, acrylate, or α-olefin-based monomer systems. The development of a new vinyl monomer family that combines the attractive features of thermal and chemical stability, yet having functional handles for compositional versatility, would represent a significant advance in the area of functionalized materials.

Key considerations in the design of a novel type of vinyl monomer include the synthetic accessibility of the basic monomer unit and its ease of functionalization. Recently, the advantages of using the "click" chemistry concept and, specifically, the Cu(I)-catalyzed cycloaddition of azides and alkynes as a powerful tool in the design and synthesis of materials have been demonstrated.[3] The benign reaction conditions, functional group tolerance, quantitative yields, and broad applicability of this chemistry make it ideal for the development of unique vinylic monomers based on a triazole nucleus. In this report, we describe the first examples of an expanding library of triazole-based monomers, which are certain to have importance as polar and chemically versatile components for materials development.

As shown in Figure 1, 4-vinyl-1,2,3-triazole monomers are expected to possess many of the outstanding features of traditional monomers, such as styrenics, vinyl pyridines, and acrylates. These features include an aromatic nucleus, stability to both acid and base treatment, a large dipole moment, and access to structural diversity through substitution at N-1. We now report the synthesis of a family of functionalized 4-vinyl-1,2,3-triazole monomers[4] that combine into a single structure many of the desirable features found in established monomers.

Two distinct synthetic methods were examined for the preparation of 4-vinyl-1,2,3-triazoles. An initial one-pot approach was driven by the orthogonality of "click" chemistry which allows multiple chemical transformations to occur in solution without interference.[5] Coupling of a mixture of 1-trimethylsilyl-2-vinyl acetylene, **1**, and an alkyl/aryl halide leads in one pot to the desired 4-vinyl-1,2,3-triazole derivatives. This is illustrated in Scheme 1 for iodobenzene, **2**, which undergoes an in situ azidation by reaction with sodium azide and L-proline in the presence of Cu(I) to give azidobenzene, **3**. Concurrently, **1** undergoes reaction with tetra-*n*-butylammonium fluoride to give the active terminal acetylene, **4**. In situ coupling of **3** and **4**, again by Cu(I) catalysis, then leads to 1-phenyl-4-vinyl-1,2,3-triazole, **5**, in 73% overall yield (Scheme 1).

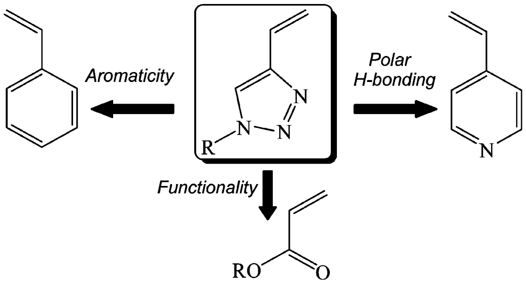
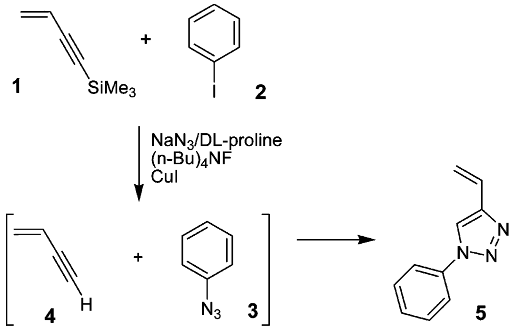
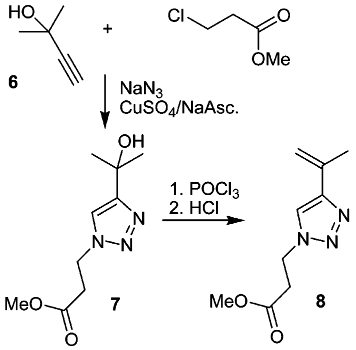


Figure 1. Structural similarities between the 4-vinyl-1,2,3-triazole monomer family and traditional vinyl systems.

Scheme 1. One-Pot Synthesis of 1-Phenyl-4-vinyl-1,2,3-triazole, **5**



Scheme 2. Two-Step Synthesis of 1-(3′-Methyl propionate)-4-α-methylvinyl-1,2,3-triazole, **8**



The modular nature of "click" chemistry can also be exploited in an alternative two-step approach for the preparation of vinyl triazole derivatives that involves cheap and readily available butynol starting materials, such as 2-methylbut-3-yn-2-ol, **6**, or but-3-yn-1-ol. This approach is illustrated in Scheme 2 with the synthesis of α-methyl triazole derivatives which can be considered the functional

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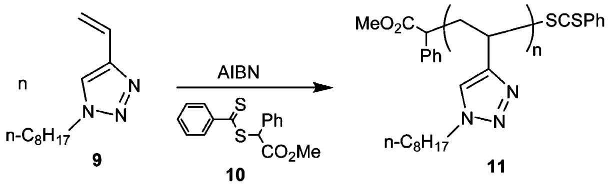
Scheme 3. Polymerization of 1-Octyl-4-vinyl-1,2,3-triazole, **9**, to Give the Corresponding Homopolymer, **11**



equivalent of methacrylate or α-methyl styrene systems. The first step involves in situ generation of an azide derivative (Caution)[6] followed by formation of the triazole nucleus. The resulting hydroxy functionalized triazole, **7**, can then be readily dehydrated with $POCl_3$ to afford a high yield of the desired 1-substituted-4-α-methylvinyl-1,2,3-triazole, **8** (Scheme 2). The corresponding vinyl derivatives could be prepared easily by applying the same strategy to but-3-yn-1-ol.

An important aspect of these synthetic strategies is the inherent versatility in the range of alkyl/aryl halides or mesylates that can be used as precursors. Moreover, both pathways alleviate the need for synthesis and isolation of organic azides, which further increases the range of possible structures while at the same time decreasing safety concerns.[6] As shown in Figure 2, these approaches have provided access to a spectrum of triazole-based functional monomers with the substituent at N-1 ranging from alkyl/aryl to heteroatom-containing (cf. meth/acrylate systems).

Polymerization of the triazole monomers to give both homopolymers as well as copolymers was examined under reversible addition fragmentation chain transfer (RAFT) conditions.[7] For example, RAFT polymerization of a 500:1 mixture of **9** and an initiating system consisting of dithioester, **10**, and 20 mol % of AIBN (relative to **10**) in DMF at 70 °C resulted in a living polymerization system with excellent control over molecular weight and polydispersity ($M_{\mathrm{n(exp)}} = 44.9$ kDa; $M_{\mathrm{n(theor)}} = 44.0$ kDa; PDI $= 1.08$). Homopolymerization and copolymerization of all the triazole monomers shown in Figure 2 under RAFT conditions proceed with a high degree of control to give materials with a wide range of physical properties. Significantly, the physical properties of these homo/copolymers were found to be dramatically influenced by incorporation of the triazole monomer. To illustrate this point, the homopolymer based on polymerization of the *n*-octyl derivative, **11**, displays significantly different properties when compared to those of comparable styrenic, vinyl pyridine, or acrylate-based materials.

For example, the glass transition temperature of **11** is 23 °C, while the T_g values for poly(*n*-octyl acrylate) and poly(4-octylstyrene) are -65 and -45 °C, respectively.[8] The dramatic influence of the polar nature of the triazole nucleus on the physical properties of **11** is also evident in the solubility of **11**, which is fully soluble in methanol, in sharp contrast to the corresponding octyl-substituted polymers based on styrene, acrylate, or vinyl pyridine monomers which are totally insoluble in methanol. Similarly enhanced properties were observed for the homopolymer based on the phenyl monomer, **5**, which showed a T_g of 148 °C and solubility in ethanol.

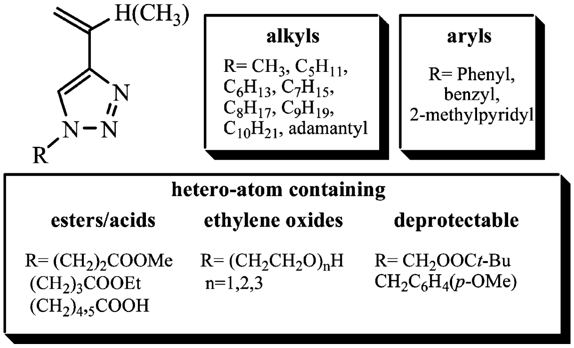


Figure 2. Structure and functional diversity in the 4-vinyl-1,2,3-triazole monomer library.

In summary, we have introduced a new monomer family based on 1,2,3-triazole-4-vinyl monomers synthesized via highly modular synthetic approaches that permit a wide range of derivatives with various functional groups to be prepared in high yields. Subsequent homo- and copolymerization of these novel functionalized monomers was achieved under “living” conditions utilizing RAFT techniques to give polymeric materials with unique physical properties, combining many attractive features of more established systems. It is anticipated that this new family of vinyl monomers will significantly extend the range of functional materials that can be prepared when compared to traditional monomers, such as styrene, vinylpyridine, and meth/acrylates.

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Supporting Information Available: Experimental details and spectroscopic/analytical data for monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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