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REVIEW

Synthesis and polymerization of *C*-vinyl- and *N*-vinyl-1,2,3-triazoles

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Although they have been known for decades, the synthesis and polymerization of vinyl-1,2,3-triazoles have recently gained attention driven by the spectacular development of the copper-catalyzed azide-alkyne cycloaddition, the most widely applied example of the "click" chemistry philosophy. Indeed, a broad library of vinyl-1,2,3-triazole-based monomers and polymers carrying aliphatic, aromatic, heterocyclic or functional groups has been reported so far. However, their polymerization has been scarcely reported and is subjected to a broad development in the near future. This review describes the synthesis and polymerization of vinyl-1,2,3-triazole regioisomers with respect to emerging highly efficient, robust and orthogonal chemistries as well as properties of the resulting materials and their potential for the design of smart and stimuli-responsive macromolecular objects.

A Introduction

The constant need for functional materials with improved and/or unusual features is one of the most important driving forces for advanced macromolecular design. One key step in this quest for improvement of materials performance relies on the development of original building blocks and functional units capable to impart enhanced properties to the resulting polymers. One prerequisite for the design of attractive building blocks consists in the development of simple, modular and high yielding synthetic routes. The recent advent of the robust, efficient and orthogonal copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) has emphasized the exceptional features of the resulting 1,2,3-triazole rings. Triazoles are indeed highly stable heterocycles possessing an electron-rich aromatic ring prone to π–π interactions, nitrogen atoms available for hydrogen bonding or metal ion coordination and a strong dipole moment. Based on the

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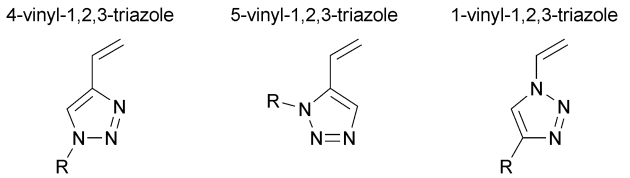
Imen Abdelhedi Miladi

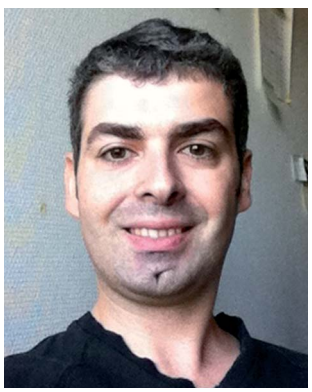
Imen Abdelhedi Miladi received her Masters degree in organic chemistry in 2010 from the Sciences University of Sfax, Tunisia. Now she is a PhD student in the group of Prof. H. Ben Romdhane at the Tunis Sciences University (Tunisia). Her main research interests focus on the synthesis of new polymers by copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC) issued from biomass or for the storage and conversion of the solar energy in collaboration with Prof. E. Drockenmuller from the University of Lyon 1, France.

outstanding properties of these heterocycles, much attention has recently been devoted to the design of a library of vinyl-1,2,3-triazole monomers and related polymers that offer the quite unique opportunity to combine most of the desirable features found in conventional monomers (styrenics, (meth)acrylates, vinyl pyridines) into one single building block and display a broad structural diversity through the existence of different regioisomers, diversity of substituents chemical nature and position of the polymerizable moiety (Scheme 1).



Scheme 1 Chemical structures of three vinyl-1,2,3-triazole regioisomers.

In this review, we aim to provide an exhaustive and comprehensive overview of the different chemical pathways developed for the synthesis of *C*-vinyl-1,2,3-triazole and *N*-vinyl-1,2,3-triazole derivatives (sections B and C, respectively). The polymerizations of this promising class of monomers by conventional free radical polymerization or controlled radical polymerization techniques and the properties of the resulting polymers are then described in detail (sections D and E). In an effort to provide a strong basis for the further development of this new category of macromolecules, the capability of 1,2,3-triazole-based monomers to impart highly tunable properties to polymer materials through their structural diversity (regiochemistry of the triazole ring, chemical nature of the R substituent and position of the vinyl group) is also discussed.



Daniele Addis

Daniele Addis was born in 1980 in Alghero (Italy). He studied at the Universities of Sassari (Italy) and Zaragoza (Spain). Afterwards, he joined the group of Prof. Matthias Beller at the Leibniz Institute for Catalysis (LIKAT) and started his PhD funded by the Leibniz Society in 2006 in the field of homogeneous iron catalysis. After finishing his PhD in 2010, he worked as a postdoctoral fellow for several months at the LIKAT. In early 2011, he took up a postdoctoral position in the group of Prof. E. Drockenmuller at the University of Lyon 1.

Julien Bernard

Julien Bernard was born in 1976 in Bordeaux (France). He studied chemistry at the University of Bordeaux 1 and received a PhD in 2003 in the field of macromolecular chemistry under the supervision of Dr A. Deffieux. He then moved to Australia to work as a research fellow on RAFT polymerization with Prof. M. Stenzel and Prof. T. Davis and finally completed his education with Prof. B. Charleux (Université Paris 6, France). He has been a CNRS researcher in the Polymer Materials Engineering Laboratory (Lyon, France) since 2006. His research interests include polysaccharides, glycopolymers, controlled radical polymerizations and supramolecular chemistry.

Hatem Ben Romdhane

Hatem Ben Romdhane received his PhD in 1989 from the Université Paris 6 (France) after working on acetylene-terminated resins. He conducted his postdoctoral research with Prof. R. Chaabouni (Tunis Sciences University, Tunisia) and Dr B. Sillion (Laboratoire des Matériaux Organiques à Propriétés Spécifiques, France) in the field of step growth polymerization. In 1997 he was promoted to Associate Professor of the Tunis Sciences University and Professor in 2008 leading the "Technical Polymers with Specific Properties" group. He has been a staff member since 2007 and was recently appointed vice-President of the national board of the Tunisian Chemical Society.

Eric Drockenmuller

Eric Drockenmuller was born in 1973 in Thionville (France), and received his PhD degree in 2002 from the University of Strasbourg (France) after working in the field of nitroxide-mediated radical polymerization. He then undertook a two year postdoctoral position with Prof. C. J. Hawker (IBM Almaden Research Center, California, USA) and Prof. T. P. Russell (University of Massachusetts, Amherst, USA) working on the synthesis and functionalization of nanostructured materials. In 2004 he was appointed assistant Professor at the University of Lyon 1 (France) and Professor in 2011. Since 2010 he has been a junior member of the "Institut Universitaire de France".

B Synthesis of *C*-vinyl-1,2,3-triazoles

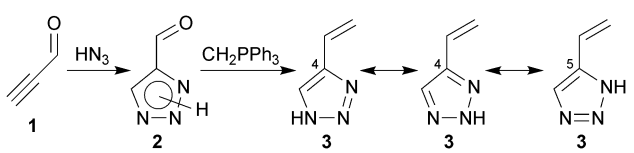
Synthesis of 4(5)-vinyl-1,2,3-triazole by a Wittig strategy

4(5)-Vinyl-1,2,3-triazole **3** is the most basic *C*-vinyl triazole monomer as it does not contain any substituent at the *N*-position but a hydrogen atom that is subjected to extremely fast tautomerism equilibrium at room temperature (Scheme 2). Therefore the position of the vinyl group (4 or 5) depends on the position of the hydrogen atom. Smets and co-workers reported the synthesis of **3** in 28% yield by Wittig reaction of 4(5)-formyl-1,2,3-triazole **2** with methylenetriphenylphosphorane.[1] Synthesis of **2** by hazardous and low yielding cycloaddition of propargyl aldehyde **1** and hydrazoic acid is the main limitation of this approach.[2,3]

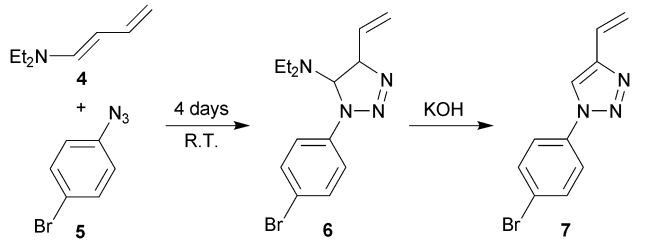
Synthesis of 4-vinyl-1,2,3-triazoles by a cycloaddition and elimination strategy

The first *N*-substituted-4-vinyl-1,2,3-triazole monomer has been synthesized by L'abbé and co-workers in 1972 (Scheme 3).[4] In this pioneering work, 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole **7** was prepared in two steps by 3 + 2 cycloaddition of *trans*-1-diethylamino-1,3-butadiene **4** with *p*-bromophenyl azide **5** to yield the triazoline intermediate **6**. Further elimination of diethylamine under basic conditions afforded the aromatic 1,2,3-triazole ring of **7**. Although successful, the first step of this approach is limited by the formation and purification of side-products (*e.g.* dimerized and aziridine adducts) and thus yields lower than 50% were obtained after long reaction times (4 days at room temperature). Moreover the selectivity, yield and efficiency of the cycloaddition reaction is strongly impacted by the structure of the azide substituent which limits the scope of this chemical pathway.

Owing to their very delicate preparation, 4-vinyl-1,2,3-triazole (4VT) monomers have not received attention from the polymer chemistry community with the exception of the report of the polymerization of **7** in 1982 by the same group.[1] Since then no new 4VT derivatives have been reported until recently. Indeed, after the spectacular craze for "click" reactions, specifically CuAAC coupling chemistry, the interest of polymer scientists in these functionalized monomers and more generally materials having 1,2,3-triazole rings in their repeating unit has dramatically increased.[5] This current interest is driven by the substantial efficiency and high tolerance of CuAAC coupling chemistry to a wide range of functional groups that has allowed the development of a broad library of functionalized 4VT monomers. A thorough investigation of the different synthetic approaches to the synthesis of 4VTs has been reported by Hawker and co-workers.[6–8] Three main chemical pathways, *i.e.* one-pot, Wittig and elimination-based strategies, have been particularly efficient to build-up the library of 4VT monomers **8–30** depicted in Scheme 4. All of these broadly accessible and efficient synthetic routes first rely on the CuAAC formation of the 1,2,3-triazole ring using an azide and an alkyne bearing respectively a substituent of interest and the vinyl group or a functional precursor that can be easily converted to a vinyl group to reach the targeted 1-substituted-4VT monomers. The principles, applications and limitations of these three major routes, are described below.



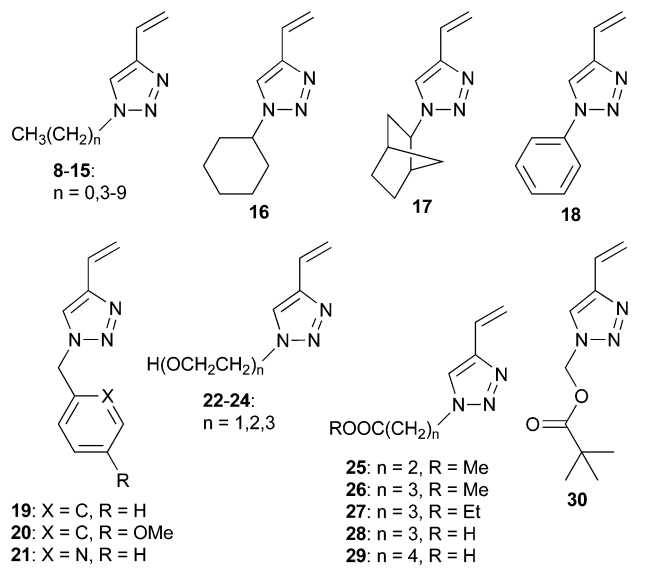
Scheme 2 Synthesis of 4(5)-vinyl-1,2,3-triazole **3** by a Wittig strategy.[1]



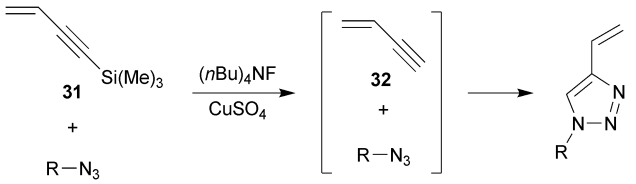
Scheme 3 Synthesis of 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole **7** by a 1,3-dipolar cycloaddition and elimination strategy.[3]

One-pot synthesis of 4-vinyl-1,2,3-triazoles

The first CuAAC-based method for the preparation of 4VTs is based on a one-pot approach driven by the orthogonal nature of "click" chemistry which allows multiple chemical transformations to occur in solution without interference. The key component in this approach is 1-trimethylsilyl-2-vinyl acetylene **31** (Scheme 5). Deprotection of **31** by tetra-*n*butylammonium fluoride ($(n\text{Bu})_4\text{NF}$) and tandem CuAAC coupling with the appropriate organic azides afforded 4VT derivatives **13**,**19**,**21**,**24**,**25**,**27** and **28** in a one-pot and two-step process. Furthermore, in order to avoid the handling of potentially hazardous low molar mass azide derivatives the level of complexity was increased to a one-pot and three-step system for the synthesis of 4VTs using a halide instead of an azide. For instance, *in situ* azidation of iodobenzene by reaction with sodium azide and DL-proline in the presence of Cu(I) afforded azidobenzene. Concurrently, **31** underwent reaction



Scheme 4 Library of 4-vinyl-1,2,3-triazoles reported by Hawker and co-workers.[6–8]



Scheme 5 One-pot and two-step approach for the synthesis of 4-vinyl-1,2,3-triazoles by *in situ* generation of vinyl-acetylene **32**.[6,7]

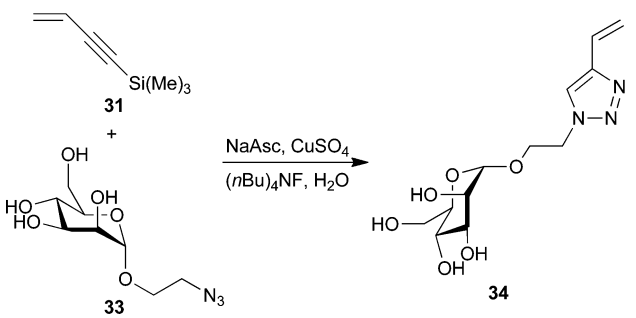
with $(n\text{Bu})_4\text{NF}$ to give 1-buten-3-yne **32**. *In situ* coupling of **32** and azidobenzene, again by Cu(I) catalysis, which led to 1-phenyl-4-vinyl-1,2,3-triazole **18** in 73% overall yield. The same one-pot and three-step approach was further applied to the synthesis of 4VTs **8**,**22** and **23**.

The one-pot and two-step approach developed by the group of Hawker was recently applied by Stenzel and co-workers to the synthesis of 4VT glycomonomer **34** with a mannose group at the 1-position of the triazole ring (Scheme 6).[9] This synthetic methodology relies on the *in situ* generation of **32** followed by the tandem CuAAC coupling with azidoethyl-functionalized mannose **33** in the presence of Cu(I) to afford **34** in 37% yield.

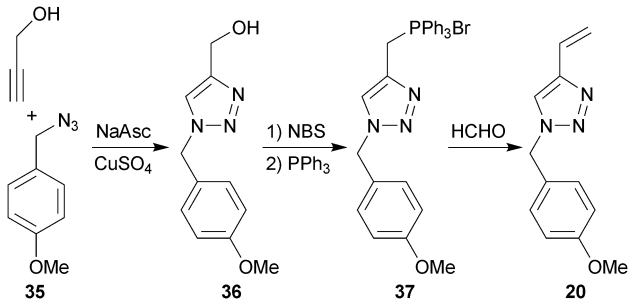
While successful, these one-pot synthetic strategies suffer from a number of drawbacks, primarily the difficulty in the synthesis and handling of **31** as well as the high cost of the starting materials. However, an important aspect of these one-pot synthetic strategies is the inherent versatility in the range of halides or azides that can be used as precursors. To overcome the above-mentioned drawbacks and enable widespread availability of 4VT monomers, alternative synthetic strategies have been thus developed. The two methods with the most wide scope are described below and involve Wittig or elimination reactions in the last step in order to generate the vinyl group. The choice of the alkyne derivative structure is of outmost importance as it requires an easy access to the vinyl group formation as well as a wide functional group tolerance to allow the CuAAC reaction to proceed in the presence of different functional organic azides.

Synthesis of 4-vinyl-1,2,3-triazole 20 by a Wittig strategy

The high tolerance to functional groups of CuAAC coupling chemistry allowed a Wittig-based synthetic strategy starting from the CuAAC coupling of *p*-methoxy-benzyl azide **35** with propargyl alcohol to be conducted (Scheme 7).[7] The alcohol group of the resulting triazole derivative **36** was then brominated and the



Scheme 6 One-pot synthesis of mannose-based 4-vinyl-1,2,3-triazole **34**.[9]



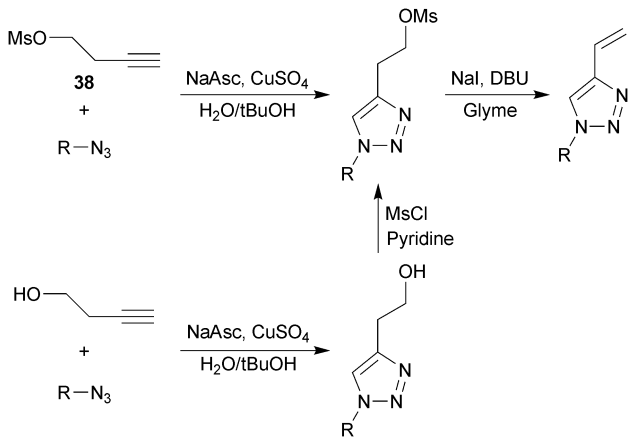
Scheme 7 Synthesis of 4-vinyl-1,2,3-triazole **20** by a Wittig strategy.[10]

resulting bromide was reacted with triphenylphosphine to afford the triazole-derived phosphine-ylide **37**. **20** could then be obtained in 80% yield by Wittig coupling of **37** with formaldehyde. It is worth noting that the reverse strategy, based on the Wittig reaction of the 4-aldehyde-1,2,3-triazole derivative and methyltriphenylphosphonium bromide provided only a very low yield (<10%) of the targeted 4VT **20**.

Synthesis of 4-vinyl-1,2,3-triazoles by elimination strategies

Elimination-based strategies are the most straightforward and wide in scope routes to 4VT monomers. A first approach relies on the introduction of a mesylated primary hydroxyethyl group at the 4-position of the 1,2,3-triazole ring and further elimination of the mesyl leaving group to yield the vinyl functionality (Scheme 8). Mesylated 1,2,3-triazoles could be obtained either in two steps by CuAAC coupling of 3-butyn-1-ol with an azide and further mesylation of the resulting alcohol, or in one step by direct CuAAC coupling of functional organic azides with the mesylated derivative of 3-butyn-1-ol **38**. In both cases elimination of the mesyl group occurred efficiently in the presence of sodium iodide (NaI) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to yield the 4VT derivatives.

Alternatively, a one-pot and two-step elimination procedure using mesyl chloride (MsCl), Et_3N and NaI in addition to the 4-hydroxyethyl-1,2,3-triazole intermediate was also found to give the desired 4VTs in good yield. Performing the elimination reaction using potassium *tert*-butoxide also gave excellent yields



Scheme 8 Synthesis of 4-vinyl-1,2,3-triazoles by elimination of a primary alcohol.[7,8]

with unfunctionalized hydrocarbon substituents but reduced efficiency with other functional groups. To circumvent the synthesis and handling of low molar mass azides, a one-pot alternative where the azide is generated *in situ*, was examined and found to give yields comparable with those obtained when the preformed azides were employed. All these elimination strategies involving mesylated primary alcohols allowed for the efficient formation of 4VT monomers **9–17**,**19**,**20**,**22** and **24** in excellent overall yields starting from a wide variety of organic azides. Although these elimination strategies are compatible with a wide range of functional groups, in the case of alcohol or amino substituents, unwanted mesylation occurs at these functionalities. To overcome this lack of chemoselectivity, protection/deprotection strategies of the protic groups (*e.g.* protection of alcohols with a tetrahydropyran group) is thus mandatory. The methyl-pivalate-functionalized 4VT **30** could be transformed into 4(5)-vinyl-1,2,3-triazole **3** in 65% yield by sequential reactions with NaOH and Dess–Martin reagent. This was shown to be a simpler and higher yielding procedure than previously decribed methods.[1]

In analogy with the work described earlier with 3-butyn-1-ol as the starting material, the isomeric 3-butyn-2-ol **39** could be used as an acetylene source for further elimination of the alcohol to yield the vinyl group (Scheme 9). A substantial advantage of this approach is that the secondary alcohol undergoes a more facile dehydration reaction when compared with the primary alcohol and therefore alleviates the necessity to form the intermediate mesylate derivative. For instance, the 4VT monomer **19** could be easily obtained in 80–90% yield by facile dehydration of the secondary alcohol-functionalized 1,2,3-triazole in the presence of *p*-toluenesulfonic acid (PTSA) or $POCl_3$/pyridine. Although not described, one-pot strategies involving *in situ* generation of the organic azide similar to those developed with primary alcohols are conceivable.

Synthesis of 4-(α-methyl-vinyl)-1,2,3-triazoles by an elimination strategy

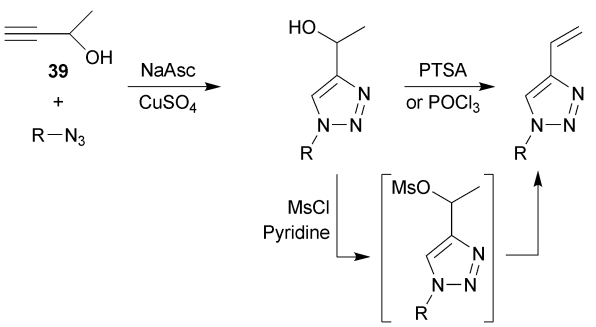
Besides 4VTs, 4-(α-methyl-vinyl)-1,2,3-triazoles (α-4VTs) are highly attractive from both an academic and industrial point of view. Indeed, similarly to the complementarity of acrylates and methacrylates, or styrene and α-methyl-styrene, the presence of the α-methyl group is expected to play a crucial role for tuning the properties of the resulting polymers. In 2004, Yamamoto and co-workers reported the copper(I) catalyzed synthesis of unsubstituted α-4VT derivative **40** (Scheme 10).[10] The reaction of 2-methyl-1-buten-3-yne and trimethylsilyl azide ($TMSN_3$) in the presence of CuI in a MeOH/DMF mixture afforded α-4VT **40** in 55% yield. However, this one-pot two-step process relies on the hazardous formation of hydrazoic acid by reaction of $TMSN_3$ with MeOH and concomitant cycloaddition with the conjugated alkyne catalyzed by CuI.

Hawker and co-workers adapted previously described elimination strategies using primary or secondary alcohols to tertiary alcohol derivatives to afford the preparation of α-4VTs monomers **42–47** (Scheme 11). Commercially available 2-methyl-3-butyn-2-ol **41** was thus coupled by CuAAC with different azides to give *N*-substituted-1,2,3-triazoles having a 2,2′-hydroxypropyl group in the 4-position. Then, reaction of the tertiary alcohol with mesyl chloride did not yield the corresponding mesylated derivative, instead the desired α-4VT was obtained in a single step regardless of the substituent on the triazole ring. Interestingly, other dehydration procedures such as $POCl_3$/pyridine that proved unsuccessful for the 2-hydroxyethyl triazole derivatives were high yielding reactions in this case and led directly to the dehydrated products. For example, reaction of the benzyl derivative, gave the α-4VT **42** in 98% yield after purification. Using the same strategy, α-4VTs **43–47** were obtained in excellent yields (above 90%).

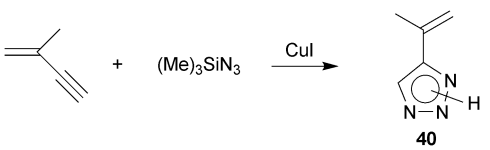
To further increase the availability of the α-4VT monomer family and avoid the use of organic azides, a one-pot click reaction starting from **41** and substituted alkyl halides was examined. The compatibility of the CuAAC coupling with other reaction conditions allows NaN_3 to be present which permits *in situ* generation of the alkyl azide and tandem CuAAC coupling. For example, reaction of methyl 3-bromopropionate with **41**, NaN_3 and $CuSO_4$ gave the corresponding triazole having a tertiary alcohol at the 4-position of the triazole ring which could be dehydrated in 90% yield with $POCl_3$/pyridine to give **45**.

Synthesis of 5-vinyl-1,2,3-triazoles by an elimination strategy

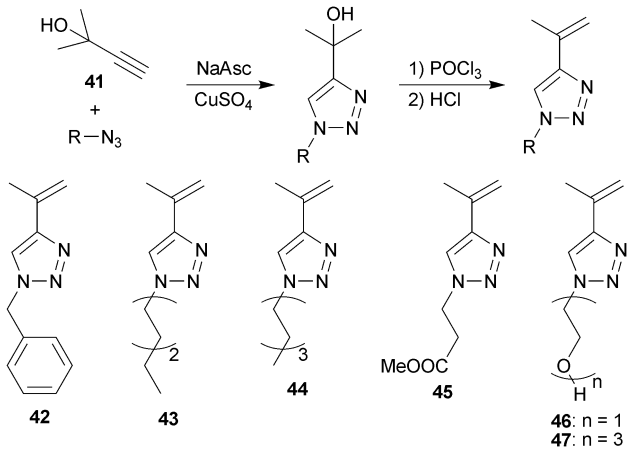
Fokin and Jia have recently reported that the Ru-mediated reaction of azides and alkynes regioselectively complements the Cu-catalyzed reaction and leads to the exclusive formation of 1,5-disubstituted-1,2,3-triazoles.[11] This ability to selectively prepare 5-vinyl-1,2,3-triazoles (5VTs) by Ru(I) catalysis provides an unique opportunity to develop regioisomers of the parent 4VT derivatives and to develop rigorous structure/property relationships to investigate the effects of the regiochemistry of various pendent groups on the properties of the resulting polymers (Scheme 12).[8] For instance, alkyne **38** possessing a hydroxyl group masked as a mesylate has been coupled with different organic azides using a catalytic amount of $Cp^*RuCl(PPh_3)_2$.



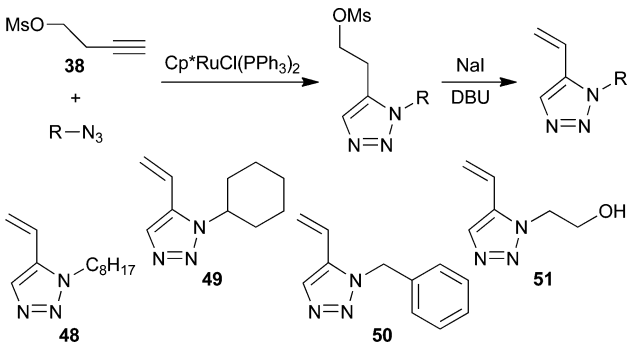
Scheme 9 Synthesis of 4-vinyl-1,2,3-triazoles by elimination of a secondary alcohol.[7]



Scheme 10 Synthesis of 4(5)-(α-methyl-vinyl)-1,2,3-triazole by a one-pot two-step cycloaddition strategy.[10]



Scheme 11 Synthesis of 4-(α-methyl-vinyl)-1,2,3-triazoles by elimination of a tertiary alcohol.[6,7]



Scheme 12 Synthesis of 5-vinyl-1,2,3-triazoles by RuAAC and elimination of a mesylated primary alcohol.[8]

Elimination of the mesyl group using NaI and DBU afforded 5VTs **48–51** in 72 to 88% yields. In contrast to the hydroxyl derivative, which deactivates the Ru catalyst and requires THP protection, other functionalized triazoles were obtained in relatively good yields (55–65%), though still consistently lower than for the Cu(I) system. 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-substituted monomers to be regiospecifically obtained as discrete isomers of the traditional 4VTs obtained through CuAAC click chemistry.[6,7] ^{1}H and ^{13}C NMR spectra of 5VTs **48–51** revealed distinct resonances for the vinyl and triazole ring protons compared to the corresponding 4VTs **9**,**16**,**19**,**22**. The hydrogen bonding nature of both 4VT and 5VT regioisomers was also confirmed by X-Ray analysis of single crystals.

C Synthesis of *N*-vinyl-1,2,3-triazoles

In parallel to 4VTs, several methods have been developed to synthesize 4-substituted 1-vinyl-1,2,3-triazoles (1VTs) of interest through direct incorporation of a vinyl group into the 1,2,3-triazole heterocycle, formation of the heterocycle at the vinyl group or formation of the vinyl group at the heterocycle. Early chemical pathways have focused on the introduction of the vinyl substituent on preformed 1-*H*-1,2,3-triazole. However, the CuAAC of alkynes and azides bearing precursors of the vinyl functionality has become lately the method of choice for the efficient synthesis of 1VT derivatives. Whereas the first approach suffers from low yields and the formation of different regioisomers issued from the different tautomers of 1-*H*-1,2,3-triazole, the latter takes advantage of the high yield, selectivity and functional group tolerance of CuAAC coupling reaction. This section provides an overview of the chemical pathways developed for the synthesis of polymerizable 1VT monomers.

Synthesis of 1-vinyl-1,2,3-triazoles by vinylation with acetylene

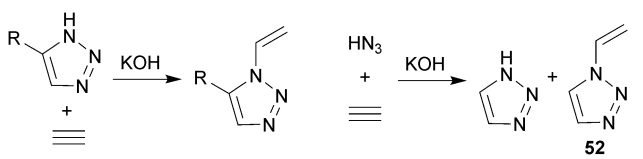
The direct vinylation of 1-*H*-1,2,3-triazole with acetylene is the traditional method for incorporating vinyl groups at the 1-position of 1,2,3-triazoles (Scheme 13). Whereas different 1,5-disubstituted-1-vinyl-1,2,3-triazoles could be prepared in yields up to 50% by the reaction of acetylene with the corresponding 5-substituted-1-*H*-1,2,3-triazoles in the presence of potassium hydroxide, the reaction of hydrazoic acid with acetylene afforded 1-vinyl-1,2,3-triazole **52** in only 8% yield together with 1-*H*-1,2,3-triazole.[12] However, experimental difficulties (high pressure, elevated temperature or handling of hazardous hydrazoic acid) together with the limited yields of targeted product (<50%) and complex purification of the crude products have restricted the preparative potential of these vinylation procedures.

Synthesis of 1-vinyl-1,2,3-triazoles by a vinyl exchange strategy

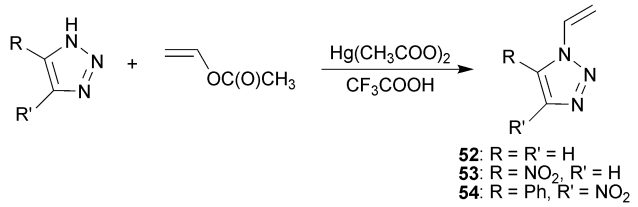
A versatile method for the incorporation of vinyl groups into the 1-position of 1,2,3-triazoles is the *trans*-vinylation reaction using vinyl acetate as vinylating agent and mercury acetate as catalyst (Scheme 14). Activation of the vinyl group by coordination with the mercury cation enables the vinyl exchange reaction to occur. Kizhnyaev and co-workers applied this method to selectively prepare 1VTs **52–54** with yields ranging from 70 to 88%.[12]

Synthesis of 1-vinyl-1,2,3-triazoles by a cycloaddition and Horner–Wadsworth–Emmons olefination strategy

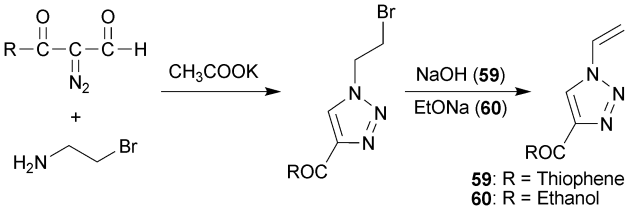
Sikora and Gajda combined thermal alkyne-azide 1,3-dipolar cycloaddition with Horner–Wadsworth–Emmons olefination for the synthesis of 1VT **58** (Scheme 15).[13] Initially, the 1,3-dipolar cycloaddition of diethylazidomethylphosphonate **55** and dimethyl acetylenedicarboxylate **56** afforded the 1,4,5-trisubstituted-1,2,3-triazole **57** in 92% yield. In the presence of sodium hydride and formaldehyde, formation of the vinyl group was achieved with the concomitent *in situ* decarboxylation of the resulting intermediate to obtain 1-vinyl-4-methoxycarbonyl-1,2,3-triazole **58** in 35% yield. Although successful, the scope of this approach is limited by the low availability and reactivity of other alkyne starting materials.



Scheme 13 Synthesis of 1-vinyl-1,2,3-triazoles by vinylation with acetylene.[12]



Scheme 14 Synthesis of 1-vinyl-1,2,3-triazoles by a vinyl exchange strategy.[12]



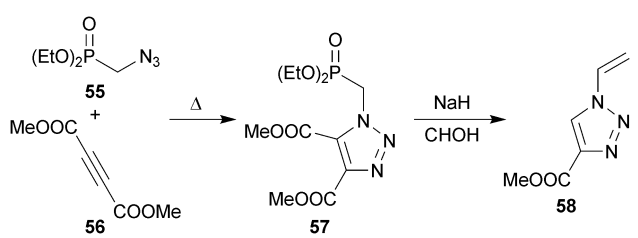
Scheme 16 Synthesis of 4-vinyl-1,2,3-triazoles by condensation and elimination strategies.[14]

Synthesis of 1-vinyl-1,2,3-triazoles by a condensation and elimination strategy

Dabak and Akar have reported the condensation of thiophene and ethyl ester functionalized α-diazo-β-oxoaldehyde derivatives with 2-bromoethyl-amine in the presence of potassium acetate to afford the corresponding 4-substituted-1-bromoethyl-1,2,3-triazoles (Scheme 16).[14] Further elimination of hydrobromic acid in the presence of NaOH or EtONa yielded respectively 1VTs **59** and **60** in 75% yield. However, the harsh conditions for the elimination step and the limited availability of α-diazo-β-oxoaldehydes significantly restrict the range of application of this chemical pathway.

Synthesis of 1-vinyl-1,2,3-triazoles by an elimination strategy

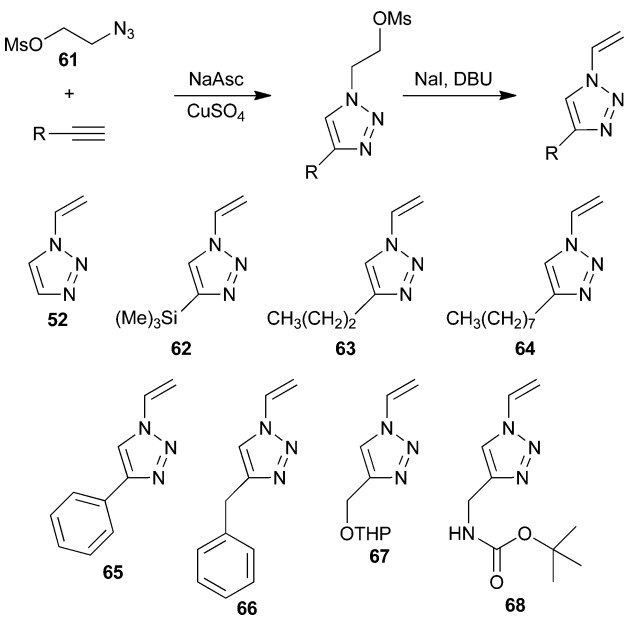
Taking advantage of the different chemical pathways developed for the synthesis of 4VTs, Hawker and co-workers applied a complementary elimination strategy for the efficient preparation of 1VT monomers (Scheme 17).[15] The key building block of this approach is 2-azidoethyl methanesulfonate **61** which serves as a precursor of the 1,2,3-triazole ring and the vinyl group. Indeed, CuAAC coupling of heterofunctional azide **61** with several alkynes afforded in almost quantitative yields 4-substituted-1,2,3-triazoles carrying a mesylated hydroxyethyl group in the 1-position. As earlier, the elimination of the mesyl group occurred efficiently in the presence of NaI and DBU to yield several 1VT monomers carrying trimethylsilyl (**62**), alkyl (**63**,**64**), aromatic (**65**,**66**) as well as THP-protected alcohol (**67**) or BOC-protected amine (**68**) groups in the 4-position. Similarly to the strategies developed for the synthesis of the parent 4VTs, protection of protic functionalities such as amines or alcohols was required. For instance, hydroxymethyl and aminomethyl 1VT monomers could be obtained by straightforward deprotection of the THP and BOC protecting groups of 1VTs **67** and **68**, respectively. Furthermore, 4-*H*-1-vinyl-1,2,3-triazole **52** could be obtained in 70% yield by deprotection of the trimethylsilyl group of 1VT **62** using (nBu$_4$)NF. This route to 1VT **52** is much more versatile, safer and efficient than those reported earlier (Scheme 13).[12]



Scheme 15 Synthesis of 1-vinyl-1,2,3-triazole **58** by a cycloaddition and Horner–Wadsworth–Emmons olefination strategy.[13]

D Synthesis and properties of poly(*C*-vinyl-1,2,3-triazole)s

As illustrated in the first sections of this paper, significant efforts have been paid over the past decades to design a broad library of *C*-vinyl- and *N*-vinyl-1,2,3-triazole monomers. However, surprisingly, the preparation of polymers thereof remains scarcely explored so far. The following sections provide an overview of the different polymerization methods that have been applied to this class of monomers. It must be pointed out that only part of the monomers described in the previous sections have been polymerized by either conventional or controlled radical polymerization methods. Whereas the former allowed to establish kinetic parameters of the polymerization of *C*-vinyl and *N*-vinyl triazole monomers and the peculiar properties of the resulting materials, the later focused on the conditions required to achieve the synthesis of polymers with well-defined properties using controlled radical polymerization methods, *i.e.* nitroxide mediated radical polymerization (NMRP) and reversible addition fragmentation chain transfer (RAFT) polymerization.



Scheme 17 Library of 1-vinyl-1,2,3-triazoles obtained by Hawker and co-workers using an elimination strategy.[15]

Owing to triazole rings ability to bind metal species,[16] atom transfer radical polymerization has not yet been applied to the synthesis of such materials.

Conventional radical (co)polymerization of 4-vinyl-1,2,3-triazoles

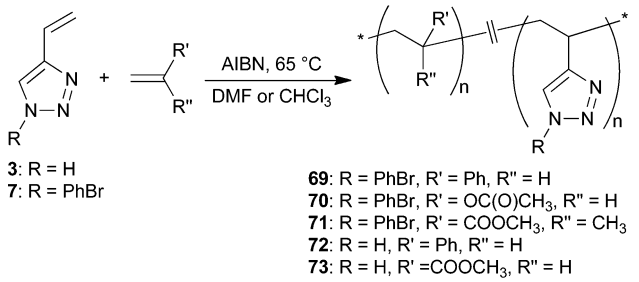
The first example of 4-vinyl-1,2,3-triazole-based polymers (P4VT) was reported by the group of Smets in the early eighties.[1] In this contribution, the authors first focused on the homopolymerization of 4(5)-vinyl-1,2,3-triazole **3** initiated by AIBN at 65 °C in dimethylformamide (DMF). The authors highlighted quite unusual polymerization kinetics such as a non linear concentration dependence of the polymerization rate with the monomer concentration and initiator. It was suggested that this atypical behavior could stem from *H*-bonding molecular interactions of triazole rings. These intermolecular associations were further studied in detail by ^{1}H and ^{13}C NMR measurements.[17]

The copolymerizations of 4(5)-vinyl-1,2,3-triazole **3** and 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole **7** with styrene (St), methyl methacrylate (MMA) and vinyl acetate (VOAc) were further investigated in DMF or $CHCl_3$ at 65 °C in presence of AIBN (Scheme 18).[1] Determination of the reactivity ratios for each comonomer system stressed a tendency toward alternation for MMA and St (**3**/St, $r_1 = 0.55$, $r_2 = 1.44$; **3**/MMA, $r_1 = 0.29$, $r_2 = 0.83$; **7**/St, $r_1 = 0.67$, $r_2 = 1.24$; **7**/MMA, $r_1 = 0.29$, $r_2 = 0.84$) whereas only limited incorporation of VOAc was observed for the copolymerization with **7** (**7**/VOAc, $r_1 = 39$, $r_2 = 0.007$). Importantly, no influence of the association between *H*-bonding triazole groups was pointed out. Finally, it was shown that *N*-substitution of the 1,2,3-triazole ring has very little effect, if any, on vinyl group reactivity.

Recently, Coughlin and co-workers reported the preparation of thermally and electrochemically stable 1,2,3-triazole-based proton-conducting materials for applications in polymer electrolyte membrane fuel cells by hydrosilylation coupling of 4VT **30** and polymethylhydrosiloxane.[18] In order to investigate the influence of the chemical structure on the conductivity and thermal properties of the resulting materials, the authors also synthesized homopolymer **74** using AIBN in THF at 70 °C (Scheme 19). The resulting methyl pivalate protected P4VT ($M_n = 21.0$ kDa, PDI = 2.5, $T_g = 48$ °C) was then deprotected by reaction with sodium methoxide to afford P4VT **75**. Interestingly, optimal proton conductivities were observed for 1,2,3-triazole-based materials.

RAFT polymerization of 4-vinyl-1,2,3-triazoles

Unexplored for several decades due to delicate preparation and narrow range of available structures, this class of 4VT monomers that possess numerous desirable features such as thermal and chemical stability, aromaticity, a large dipole moment and access to structural diversity through substitution at the *N*-position, lately experienced a renaissance under the impetus of the Hawker's group and the rise of CuAAC.[6,8] In the frame of their work on the development of materials with original structures and performances, they initially examined in detail the RAFT polymerization of a large spectrum of functional 4VT monomers with pendent substituents such as alkyl, aryl, alcohol or ester groups, and the properties of the resulting well-defined P4VT materials



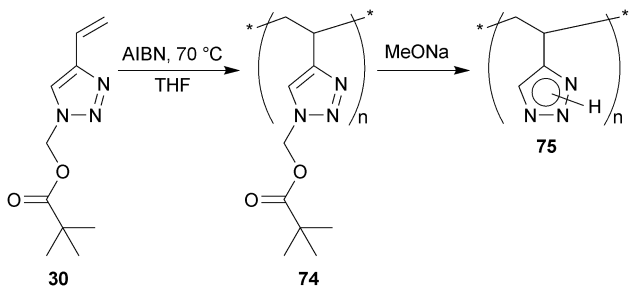
Scheme 18 Conventional radical copolymerization of 4(5)-vinyl-1,2,3-triazole **3** or 1-bromophenyl-4-vinyl-1,2,3-triazole **7** with styrene, methyl methacrylate and vinyl acetate.[4]

77–84 (Scheme 20). The use of *S*-methoxycarbonylphenylmethyl dithiobenzoate **76** as chain transfer agent (CTA) and AIBN as a source of radicals ([M] : [CTA] : [AIBN] = 500 : 1 : 0.2; in bulk at 70 °C) allowed for an excellent control of the polymerizations affording polymers having molar mass in good agreement with theoretical values and exhibiting narrow molar mass distributions (PDI < 1.3). This was for instance illustrated by the multigram scale preparation of poly(1-octyl-4-vinyl-1,2,3-triazole) **78** ($M_{n(exp)} = 44.9$ kDa; $M_{n(theor)} = 44.0$ kDa; PDI = 1.08).

Aiming to further extend the P4VT-based library and produce materials with a wide range of functionality and physical properties, the same group subsequently prepared a series of random and block copolymers by RAFT polymerization (Scheme 21). For instance, styrene was copolymerized with adamantyl-, alcohol- and carboxylic acid-functionalized 4VTs **17**,**22**,**23** and **28** to afford P4VT random copolymers **85–89** (7–9 mol% of triazole incorporation for copolymers **86–89** and 32 mol% for the adamantyl functionalized copolymer **85**). P4VT homopolymers and copolymers **77–89** exhibited glass transition temperatures (T_gs) ranging from 3 °C for polymer **84** to 148 °C for **80** depending on the nature of the *N*-substituent (Table 1).

RAFT polymerization of 5-vinyl-1,2,3-triazoles

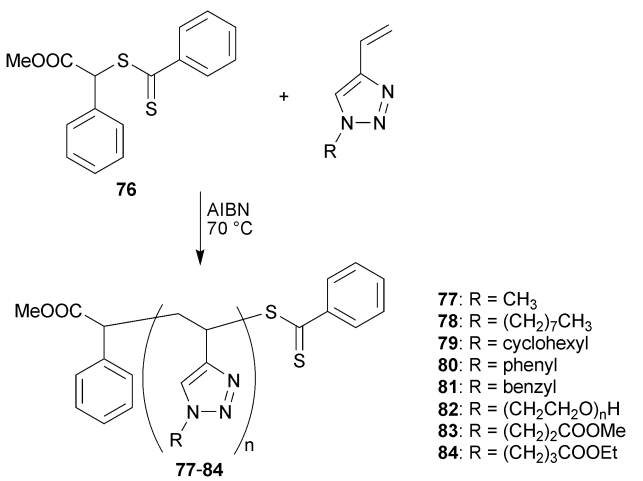
Poly(5-vinyl-1,2,3-triazole)s (P5VTs) derived from 5VTs **48–51** were obtained by RAFT polymerization at 70 °C in DMF using **76** as CTA and AIBN as initiator (Scheme 22).[8] The polymerization kinetics and the properties of the resulting materials were strictly compared to the parent polymers issued from 4VT monomers **13**,**16**,**19**,**22**. A first interesting observation was the strong influence of the monomer regiochemistry on the rate of



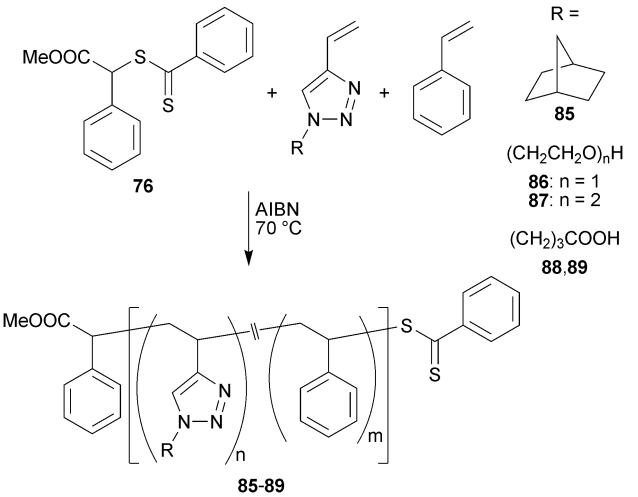
Scheme 19 Conventional radical polymerization of methyl pivalate functionalized 4-vinyl-1,2,3-triazole monomer **30**.[18]

polymerization of the different regioisomers. Indeed, 5VT monomers polymerized significantly faster than their 4VT counterparts in spite of more prominent steric hindrance issues. As previously suggested by Smets and co-workers,[4] these disparate reactivities can be attributed to different electronic environments of the vinyl groups. This was corroborated by ^{13}C NMR data which pointed out a much lower electron density for 5-vinyl groups than for 4-vinyl groups (vinyl β-carbon resonances for 1-octyl-4-vinyl-1,2,3-triazole **13** and 1-octyl-5-vinyl-1,2,3-triazole **47** at 120.29 and 127.39 ppm, respectively) which eases electron transfer from propagating radicals to monomers in the case of the 1,5-regioisomers.

Comparison of the solubility and thermal properties of the isomeric 4VT- and 5VT-based polymers gave clear evidence of the impact of the triazole ring regiochemistry and the nature of the substituent at the *N*-position on the properties of the macromolecular materials. Whereas comparable thermal resistances (onsets of weight loss around 320 °C) were disclosed by TGA for the different P4VTs and P5VTs, DSC analyses highlighted dramatic differences in T_g values (Fig. 1). Interestingly it was shown that the presence of the polar aromatic triazole ring promotes a dramatic increase of T_g. Indeed, in contrast to poly (*n*-octyl acrylate) and poly(4-octyl styrene) which display very low T_gs (respectively −65 and −45 °C), poly(1-octyl-4-vinyl-1,2,3-triazole) **78** and poly(1-octyl-5-vinyl-1,2,3-triazole) **90** exhibit relatively increased T_g values (7 and 95 °C, respectively). The T_g values are also significantly influenced by the nature of the substituent at the *N*-position and range from 7 to 220 °C. For example, poly(1-cyclohexyl-4-vinyl-1,2,3-triazole) **79** has a T_g of 105 °C *vs.* 7 °C for poly(1-octyl-4-vinyl-1,2,3-triazole) **78** whereas poly(1-cyclohexyl-5-vinyl-1,2,3-triazole) **91** shows a remarkably high T_g of 220 °C. It is worth noting that owing to restricted mobility of the 1,5 structures, P5VT materials always display considerably higher T_g than their 1,4-regioisomers ($T_{g(1,5)} \sim T_{g(1,4)}$ + 70 to 100 °C). Solubility tests also underlined the strong impact of the polar 1,2,3-triazole moiety on the solubility behavior of 1,4-isomers (octyl-substituted species) which in sharp contrast to the corresponding polymers based on styrene, acrylate or vinyl pyridine motives are fully soluble in methanol. Finally it was shown that solubility was strongly affected by regiochemistry as 1,5-regioisomers were soluble in a more limited range of solvents than 1,4-regioisomers.[8]



Scheme 20 Dithioester mediated RAFT polymerization of 4-vinyl-1,2,3-triazoles **8**,**13**,**16**,**18**,**19**,**22**,**25** and **27**.[6,8]



Scheme 21 Dithioester mediated RAFT copolymerization of 4-vinyl-1,2,3-triazoles **17**,**22**,**23** and **28** with styrene.[6]

Macroalkoxyamine mediated radical polymerization of 4-vinyl-1,2,3-triazoles

Whereas P4VT homopolymers have been exclusively prepared under conventional free radical or RAFT polymerization methods, P4VT-based diblock copolymers have been synthesized using an alkoxyamine-terminated polystyrene macroinitiator (M_n = 12.4 kDa, PDI = 1.12). Chain extension with 1-octyl-4-vinyl-1,2,3-triazole **13** and 1-octyl-5-vinyl-1,2,3-triazole **48** afforded low-polydispersity diblock copolymers (M_n = 18.8 kDa, PDI = 1.13 and M_n = 16.4 kDa, PDI = 1.10, respectively).[8]

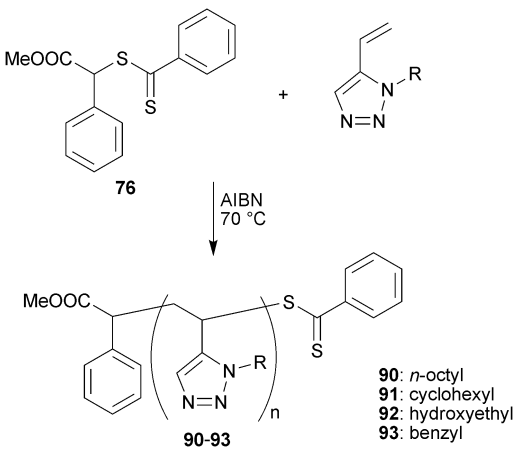
4-Vinyl-1,2,3-triazole-based glycopolymers obtained by RAFT polymerization

Aiming to design well-defined hydrolytically stable glycopolymers, Stenzel and co-workers recently reported the preparation of mannose-functionalized polymers from 1-(ethyl-*O*-α-D-mannopyranoside)-4-vinyl-1,2,3-triazole **34** (Scheme 23).[9] The aqueous polymerization of **34** at 60 °C in the presence of 3-benzylsulfanylthiocarbonylsulfanyl propionic acid **94** trithiocarbonate and 4,4′-azobis(4-cyanovaleric acid) (ACPA) initiator was observed to be a living process that afforded water-soluble P4VT-based glycopolymer **95** with excellent control over molar mass and polydispersity (M_n = 51.5 kDa, PDI = 1.16). Subsequent chain extension of a glycopolymer macroRAFT CTA (**95**, M_n = 25.8 kDa, PDI = 1.24) with *N*-isopropyl acrylamide afforded a low-polydispersity thermosensitive diblock copolymer, poly(1-(ethyl-*O*-α-D-mannopyranoside)-4-vinyl-1,2,3-triazole)$_{129}$-*b*-poly(*N*-isopropyl acrylamide)$_{93}$ (**96**, M_n = 32.4 kDa, PDI = 1.12) capable to undergo reversible micelle formation in water (D_h = 22.5 nm in water at 40 °C). Turbidity measurements revealed strong binding abilities of the resulting glycomaterials to Concanavalin A and enhanced activity was observed at 40 °C for the diblock copolymer micellar structures.

Table 1 Properties of poly(4-vinyl-1,2,3-triazoles) and poly(5-vinyl-1,2,3-triazoles) **77–95** synthesized by RAFT polymerization

Polymer	Monomer	R group	Regioisomer	CTA	M_n (kDa)	PDI	T_g (°C)	mol%[a]
77	**8**	methyl	1,4-	**76**	14.1	1.18	124	—
78	**13**	n-octyl	1,4-	**76**	44.9	1.08	7	—
79	**16**	cyclohexyl	1,4-	**76**	~20	< 1.2	105	—
80	**18**	phenyl	1,4-	**76**	41.0	1.29	148	—
81	**19**	benzyl	1,4-	**76**	~20	< 1.2	76	—
82	**22**	CH_2CH_2OH	1,4-	**76**	28.0	1.20	140	—
83	**25**	$(CH_2)_2COOMe$	1,4-	**76**	9.4	1.06	29	—
84	**27**	$(CH_2)_3COOEt$	1,4-	**76**	21.5	1.07	3	—
85	**17**	norbornyl	1,4-	**76**	21.8	1.03	109	75
86	**22**	CH_2CH_2OH	1,4-	**76**	15.1	1.25	98	90
87	**23**	$(CH_2CH_2O)_2H$	1,4-	**76**	17.5	1.07	107	90
88	**28**	$(CH_2)_3COOH$	1,4-	**76**	18.3	1.04	112	90
89	**28**	$(CH_2)_3COOH$	1,4-	**76**	20.4	1.06	107	95
90	**47**	n-octyl	1,5-	**76**	~20	<1.2	95	—
91	**48**	cyclohexyl	1,5-	**76**	~20	<1.2	220	—
92	**50**	CH_2CH_2OH	1,5-	**76**	~20	<1.2	163	—
94	**49**	benzyl	1,5-	**76**	~20	<1.2	162	—
95	**34**	ethoxy-mannose	1,4-	**94**	25.8	1.24	N.A.	—
95	**34**	ethoxy-mannose	1,4-	**94**	58.5	1.16	N.A.	—

[a] Molar ratio of 4VT monomers for random copolymerizations with styrene.



Scheme 22 Dithioester mediated RAFT polymerization of 5-vinyl-1,2,3-triazole monomers **48–51**.[8]

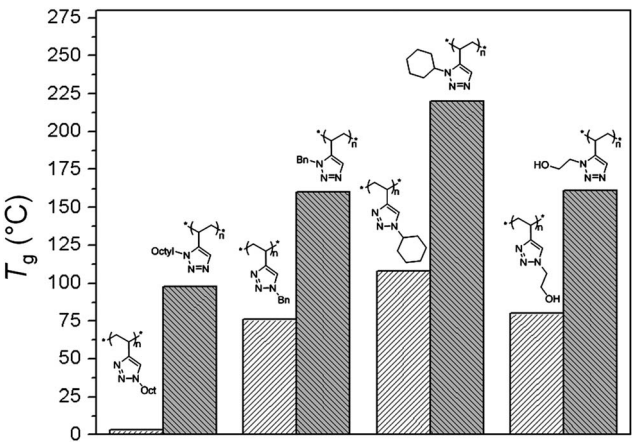


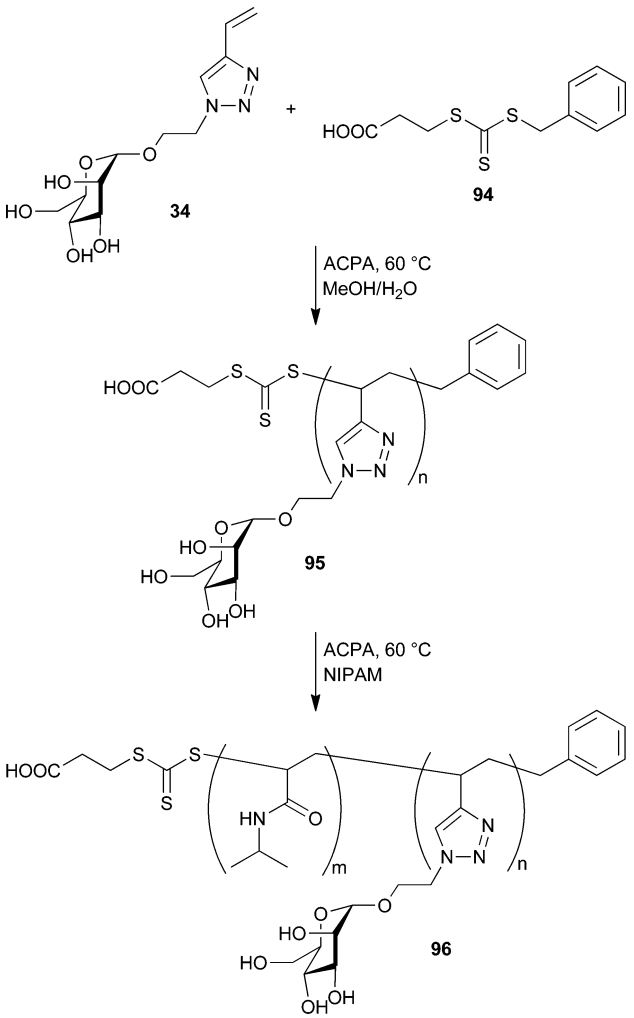
Fig. 1 Glass transition temperatures for isomeric poly(1,4-vinyl-1,2,3-triazole) and poly(1,5-vinyl-1,2,3-triazole) derivatives (M_n = 20.0 kDa and PDI < 1.2 in all cases). Reproduced with permission from ref. 8. Copyright 2009, American Chemical Society.

E Synthesis and properties of poly(*N*-vinyl triazole)s

Conventional free radical (co)polymerization of 1-vinyl-1,2,3-triazoles

The free radical (co)polymerization of *N*-vinyl derivatives of 1,2,3-triazoles has been investigated in detail in the past decade. Encouraged by the industrial development of poly(*N*-methyl-5-vinyl-tetrazole) for application as solid jet-engine fuel component in the early nineties,[19] Kizhnyaev and co-workers have explored the polymerization behaviour of a large range of vinylazoles, *i.e.* diazoles, triazoles and tetrazoles (Scheme 24), under free radical conditions. A review on this topic has been recently published,[20] but its content is fundamentally different from the present review since 1-vinyl-1,2,3-triazole-based monomers and polymers represent only a small fraction of considered structures and mainly result from non-substituted 1-vinyl-1,2,3-triazole **52**. However, the discussed properties of the different azole-based materials made by polymerization or chemical modification of existing polymers and their relative comparison represent a strong basis for the potential development of novel P1VT materials.

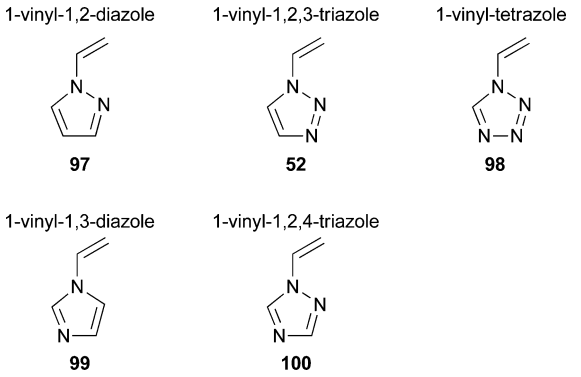
In the course of their studies, Kizhnyaev and co-workers notably showed that the polymerization behaviour of the *N*-vinyl derivatives strongly differs from the corresponding *C*-vinyl analogues due to the very dissimilar electronic environments of the vinyl group.[21] The rate of polymerization of 1-vinyl-1,2,3-triazole **52** was found to be one order of magnitude higher than for 4(5)-vinyl-1,2,3-triazole **3** under similar conditions at 60 °C pointing out that the radical species generated from *N*-vinyl monomers exhibit enhanced reactivity. The authors also highlighted very disparate polymerization behaviours among the *N*-vinyl class of vinylazole monomers. A close comparison of the kinetics of isomeric 1-vinyl-triazoles polymerizations gave clear evidence of the higher reactivity of 1-vinyl-1,2,3-triazole **52** over 1-vinyl-1,2,4-triazole **100** ($k_p/k_t^{0.5}$ respectively equal to 0.54 and 0.37 (l/(mol s))$^{0.5}$ at 60 °C in acetonitrile) demonstrating the crucial impact of the nitrogen atoms



Scheme 23 Trithioester mediated RAFT polymerization of mannose-based 4-vinyl-1,2,3-triazole monomer **34**.

arrangement among the different azole heterocycles on the C=C double bond electronic environment and on the monomer polymerizability. In contrast, the number of nitrogen atoms in the heterocycle (2 to 4) does not appear to play a predominant role on the monomer reactivity since 1-vinyl-1,2-diazole **97** and 1-vinyl-tetrazole **99** exhibit very similar kinetic parameters ($k_p/k_t^{0.5}$ respectively equal to 0.37 and 0.34 (l/(mol s))$^{0.5}$ at 60 °C in acetonitrile) but significantly lower than 1-vinyl-1,2,3-triazole **52** ($k_p/k_t^{0.5}$ equal to 0.54 (l/(mol s))$^{0.5}$ at 60 °C in acetonitrile).

Relying on the propensity of the triazole cycles to generate diverse weak interactions (such as *H*-bonding), the same research group further investigated the influence of the polymerization medium on the kinetics of 1-vinyl-1,2,3-triazole **52** polymerization.[22] The influence of water, acetic acid and their mixtures with acetonitrile was carefully examined. It was shown that the addition of protic species has a substantial acceleration effect on the polymerization process as confirmed by the significant rise of $k_p/k_t^{0.5}$ from 0.54 at 60 °C in acetonitrile to 2.25 and 1.94 (l/(mol s))$^{0.5}$ respectively in water and acetic acid. This behaviour was rationalized on the basis of vinyl electronic environment modifications upon shifting from pure acetonitrile to aqueous solutions. Indeed, using ^{13}C NMR measurements, the authors



Scheme 24 Different vinylazole monomers investigated for the preparation of carbochain polymers with azole side groups.[20]

underlined that the electronic density of the vinyl group β-carbon was decreasing owing to the electron-withdrawing effect enhancement generated by the triazole cycle interacting with water or acetic acid through *H*-bonding. Interestingly, the nature of the polymerization medium also strongly impacted the molar masses of poly(1-vinyl-1,2,3-triazole)s that tended to raise with increasing content of water or acetic acid in mixtures with acetonitrile. The polymerization kinetics of **52** were also proven to strongly depend on the pH of the polymerization solution. Plotting the evolution of the polymerization rate *vs.* the pH of the polymerization medium, Kizhnyaev underlined a drastic polymerization acceleration effect under acidic conditions, especially at low pH values (pH = 3), resulting from the protonation of the triazole moiety and the increase of the electron-withdrawing effect of the pendent group. Surprisingly, basic conditions also promoted an acceleration of the polymerization for pH values ranging from 7 to 10. It was suggested that this increase was due to the ability of triazole rings to promote donor–acceptor interactions with alkali-metal cations.

Shatalov and co-workers reported the preparation of copolymers of 1-vinyl-1,2,3-triazole **52** with *N*-vinylcaprolactam by means of free-radical copolymerization.[23] The reactivity ratios of the comonomers were proven to be quite comparable and inferior to 1 (respectively $r_1 = 0.55$, $r_2 = 0.76$) illustrating a tendency toward alternation during copolymerization. Because poly(*N*-vinylcaprolactam) is a water-soluble biocompatible thermosensitive polymer (LCST ~35 °C in water), the temperature-responsive behaviour of the copolymers in aqueous solutions was further investigated by turbidity measurements at different temperatures. It was shown that increasing the content of **52** in the copolymer enables to shift the LCST value toward higher temperatures. The authors also pointed out the possibility of dramatically tuning the LCST of the copolymers upon incorporation of inorganic salts in the aqueous solution. This was clearly illustrated by a copolymer exhibiting a molar fraction of **52** equal to 0.59 which LCST varies from 8 °C in the presence of Na_2SO_4 (at 0.4 M) to 82 °C in the presence of NaCNS (at 1 M).

Conventional and controlled radical polymerizations of 1-vinyl-1,2,3-triazoles

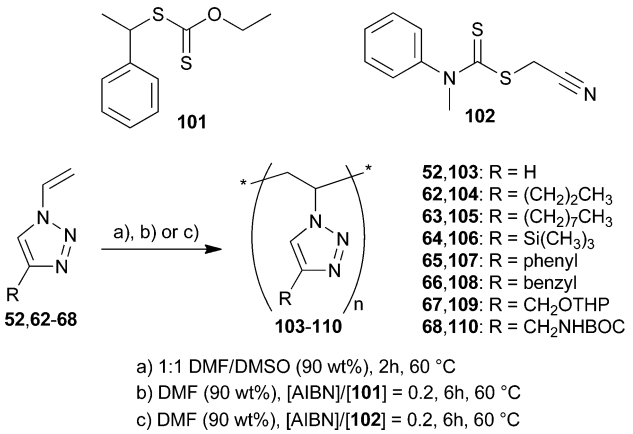
In parallel to the development of a library of 4VT- and 5VT-based polymer materials, Hawker and co-workers have recently explored the preparation of original macromolecules based on

the conventional and RAFT polymerizations of functional 1VT monomers **52**,**62–68** (Scheme 25).[15] Because propagating *N*-vinyl triazole radicals display very high reactivities and rapidly add to activated C=S bonds to generate macroRAFT radicals exhibiting very poor tendency to fragmentation, it is crucial to employ CTAs that increase the likelihood of fragmentation through destabilization of these intermediate radical centers.[24] In this context, Hawker and co-workers screened different polymerization conditions using CTAs classically suitable for *N*-vinyl monomers, *i.e.* xanthate **101** and dithiocarbamate **102**. In contrast to the conventional free radical process that resulted in the preparation of poorly defined high molar mass materials (M_n > 60.0 kDa, PDI > 2.1), xanthate-mediated RAFT polymerization using **101** afforded well-defined polymers. However, this strategy was somewhat limited by the exclusive preparation of low molar mass polymers and slow polymerization kinetics (30% of conversion after 6 h at 60 °C for [**101**]/[AIBN] = 5). Further improvement of the polymerization process was obtained by substituting *O*-ethyl-*S*-(1-phenylethyl) dithiocarbonate **101** for commercially available cyanomethyl *N*-methyl-*N*-phenyl dithiocarbamate **102**. Under these conditions, the polymerization kinetics were much faster (80% of the monomer being consumed after 6 h at 60 °C) and higher molar mass polymers exhibiting low PDI were achieved.

Alkoxyamines were also explored as mediating agents. Whereas 1-phenylethyl TIPNO-based alkoxyamine was unable to mediate efficiently the homopolymerization of *N*-vinyl triazoles, well-defined random copolymers of styrene and *N*-vinyl triazoles were obtained up to 20 mol% triazole feed ratio (for instance, [M]/[alkoxyamine] = 500, [St]/[**66**] = 9 : 1, M_n = 42.0 kDa, PDI = 1.17, 9.5 mol% of *N*-vinyl triazole units). The same random copolymerization of **66** with styrene was applied to the synthesis of diblock copolymers using TIPNO-based poly (ethylene glycol) and polystyrene macroalkoxyamines to afford a P(1VT-*r*-St) second block.

The authors finally investigated the structure/properties relationship for the different synthesized 1VT-based polymers **103–110**. Evaluation of the polymers' thermal resistance by ATG (similar onsets of weight loss around 350 °C for polymers **104–110**, 400 °C for poly(1-vinyl-1,2,3-triazole) **103**) underlined the predominant impact of the aromatic triazole ring over the chemical nature of the group located at the 4-position. Dramatic discrepancies in the properties stemming from the nature of the pendent group were however pointed out for this library of polymers by DSC measurements. For example, T_g values ranging from 70 °C (R = $(CH_2)_7CH_3$) to 183 °C (R = phenyl) were observed. Comparison with previously reported P4VT and P5VT structural isomers showed for instance that P1VT having *n*-octyl substituents display intermediate T_g values higher than 4VT-based polymers but lower than 5VT-based analogues (T_g = 7, 95 and 70 °C for P4VT **78**, P5VT **90** and P1VT **105**, respectively).

As expected, the solubility behavior of the 1VT-based polymers was intimately related to the substitution pattern. After deprotection of P1VT **109** and **110**, the corresponding hydroxymethyl- and aminomethyl-functionalized P1VT analogues were indeed readily dissolved in water. In agreement with Kizhnyaev's reports, RAFT-made poly(1-vinyl-1,2,3-triazole) **103** was soluble in polar solvents such as DMF or DMSO and in acidic or NaCl



Scheme 25 Conventional free radical polymerization and xanthate or dithiocarbamate mediated RAFT polymerization of the 1-vinyl-1,2,3-triazoles library developed by Hawker and co-workers.[15]

(5 wt%) aqueous solutions suggesting potential applications in proton exchange membranes and biomaterials. The other polymers with less polar pendent groups were soluble in the most common organic solvents, except for **105** which exhibited poor solubility in ethanol and DMSO.

Conclusions and perspectives

The synthesis of *C*-vinyl- and *N*-vinyl-1,2,3-triazoles and resulting polymer materials is at present a well-established field of research. The recent advent of the "click" chemistry philosophy has paved the way to the preparation of an extensive library of interesting 1,2,3-triazole-based monomers and related polymers with a wide range of chemical and physical properties. However, the potential applications of these polymers are still far from having been exhaustively assessed. While the influence of the monomer structural parameters, *i.e.* regiochemistry of the triazole ring, the chemical nature of the substituents on the heterocycle or the position at which the vinyl group is anchored to the triazole ring, on the properties of the resulting polymers has been investigated in detail (polymerization kinetics, thermal properties, solubility…), major efforts now need to focus on the transition to materials development. For instance, as suggested by the promising work of Coughlin and co-workers reporting outstanding proton conductivities for 1,2,3-triazole-based materials (up to 0.1 mS cm^{-1} below 80 °C),[18] it is evident that more interest should be sparked by the preparation of vinyl-1,2,3-triazole-based polymers for water-free polymer electrolyte membrane fuel cells. Other fields that obviously deserve more attention deal with the generation of original biomaterials, drug delivery systems, metallo-polymers and materials with tunable complexation abilities for depollution and metal recovery. Functional, bio-sourced or pH sensitive water-soluble poly (vinyl-1,2,3-triazole)s could indeed constitute credible alternatives to polymers typically used in this research area. Finally, a more detailed study of the polymerization kinetics of such interesting monomers should impact the level of complexity of the macromolecular materials that could be produced in the future.

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