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Vinyltetrazoles: synthesis and properties

V N Kizhnyaev, L I Vereshchagin

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Abstract. The published data on the synthesis of *C*- and *N*-vinyltetrazoles and their chemical transformations (homo- and copolymerisation) involving the heterocycle and the vinyl group are systematised and generalised. The areas of possible application of these compounds are considered. The bibliography includes 194 references.

I. Introduction

The first representatives of vinyltetrazoles were obtained 40 years ago by Finnegan and Henry[1,2] who proposed to use tetrazole-containing polymers as binding agents in the production of gunpowders and matches. A number of comprehensive reviews on the chemistry of tetrazoles have been published since then,[3–13] but the preparative procedures and properties of tetrazoles containing unsaturated substituents have not been detailed. At the same time, these compounds, particularly vinyl-substituted tetrazoles, can serve as a basis for new in principle polymeric materials possessing unusual and valuable properties. Thus one of the reasons for increased interest in vinyltetrazoles is the possibility of obtaining polymers with high energy characteristics as can be evidenced from numerous patents devoted to the construction of polymeric binding agents for jet engine fuels, gunpowders, explosives, *etc.*[2,14–20]

This paper is an overview of the published data and the first attempt to generalise the results of investigations into the synthesis, structures, physicochemical properties and polymerisability of vinyltetrazole derivatives.

V N Kizhnyaev, L I Vereshchagin Department of Chemistry, Irkutsk State University, 664003 Irkutsk, ul. K Marksa 1, Russian Federation. Fax (7-395) 224 22 38; Institute of Petroleum and Coal-Chemical Synthesis, Irkutsk State University, 664003 Irkutsk, ul. Lermontova 126, Russian Federation. Fax (7-395) 295 48 81. Tel. (7-395) 242 67 11. E-mail: kizhnyaev@chem.isu.ru (V N Kizhnyaev). Tel. (7-395) 242 63 21 (L I Vereshchagin)

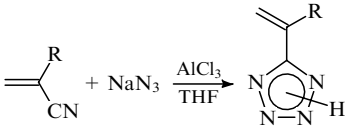
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II. Synthesis of vinyltetrazoles

The choice for a procedure for the synthesis of vinyltetrazole derivatives depends on the position of the vinyl group in the ring, but two main approaches stand apart among other methods. One of them consists of the formation of the tetrazole ring by cyclisation of open-chain compounds containing a vinyl group, while the second approach, which is more common, includes the formation of a double bond at the heterocycle.

1. Synthesis of *C*-vinyltetrazoles

Reaction of acrylonitrile with sodium azide in the presence of aluminium chloride occurs in one step and results in 5-vinyltetrazole (**1**) (conversion 55%). However, the yield is low and unstable due to polymerisation of the starting and target vinyl compounds. Using this approach, 5-isopropenyltetrazole (**2**) was prepared from methacrylonitrile in a somewhat better yield (conversion 71%, yield ~ 45%), since the C=C bonds in methacrylonitrile and isopropenyltetrazole are less prone to polymerisation.[21]

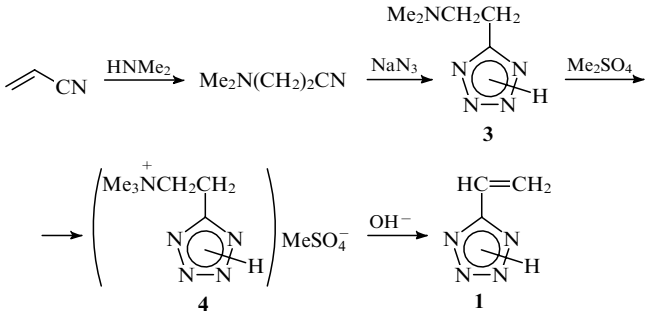


1, **2**

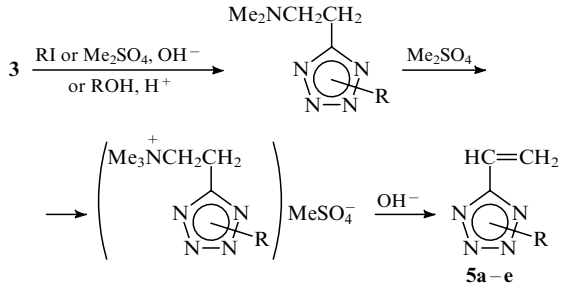
R = H (**1**), Me (**2**).

Cycloaddition of the azide ion to the C≡N bond of nitriles is significantly facilitated if the reaction is carried out in the presence of compounds able to form hydrazoic acid salts from sodium azide soluble in the solvent used. In addition, these salts increase the reactivity of the azide ion. They are prepared using ammonium chloride,[22,23] alkylamine hydrochlorides,[14,15] tetramethylguanidinium chloride,[24] boron trifluoride etherate[25] and aluminium chloride.[21]

Temporary protection of the double bond of acrylonitrile by addition of dimethylamine has made it possible to avoid polymerisation and resinification in the reaction of the azide ion with the nitrile group of 3-dimethylaminopropionitrile: 5-(2-dimethylaminoethyl)tetrazole (**3**) was prepared in high yield.[14,15] The Hoffmann deamination of the quaternary salt **4** gives 5-vinyltetrazole (**1**).



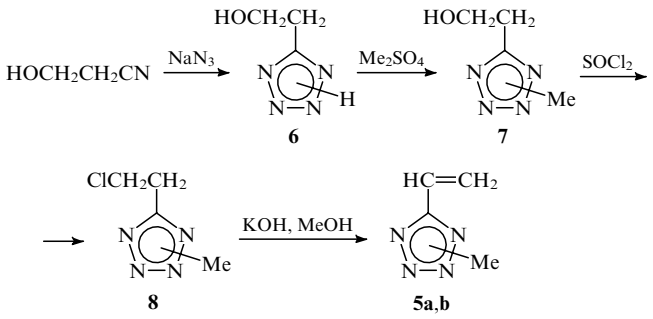
Preparation of *N*-alkyl-*C*-vinyltetrazoles **5a**–**e** is more difficult because of the impossibility of direct introduction of the alkyl substituent into 5-vinyltetrazole (**1**) due to spontaneous polymerisation under the reaction conditions. Therefore, the formation of the vinyl group by deamination of the quaternary ammonium salt is preceded by alkylation of the heterocycle in the tetrazole derivative **3**.[14, 15, 26–28]



R = 1-Me (**a**), 2-Me (**b**), 2-Et (**c**), 2-Pr^i (**d**), 2-Bu^t (**e**).

Hydrohalogenation of acrylonitrile resulting in 3-chloropropionitrile, its reaction with the azide ion and subsequent dehydrochlorination of the 5-(2-chloroethyl)tetrazole formed with potassium hydroxide in aqueous methanol is a more convenient approach to the synthesis of unsubstituted 5-vinyltetrazole (**1**).[21] In order to increase the yield of the vinyl compound and to suppress its spontaneous polymerisation, it was proposed to perform dehydrochlorination with a twofold excess of an alkali in the presence of ionol as the polymerisation inhibitor.[29]

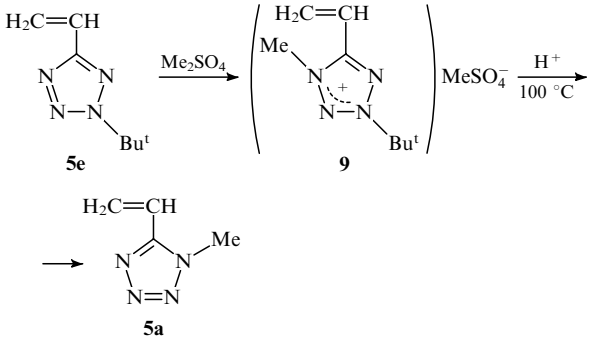
Ethylene cyanohydrin can be used as a starting material in the synthesis of vinyltetrazoles **5a**,**b**. Cycloaddition of the azide ion to the nitrile group results in 5-(2-hydroxyethyl)tetrazole (**6**),[16, 17] which is methylated with dimethyl sulfate and the hydroxyethyl group in compound **7** is further modified. Subsequent dehydrochlorination of the chloroethyl derivative **8** with methanolic KOH affords vinyltetrazoles **5a**,**b**.



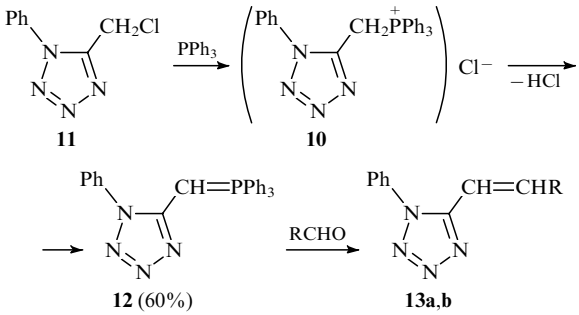
R = 1-Me (**a**), 2-Me (**b**).

The use of dehydrochlorination for the synthesis of vinyltetrazoles has a number of advantages. Deamination of the quaternary salts of 2-dimethylaminoethyltetrazoles proceeds upon heating, while dehydrochlorination of 2-chloroethyl compounds is usually carried out with potassium hydroxide solutions at low temperatures, which significantly decreases the risk of polymerisation of the target product. This method ensures reproducible and satisfactory yields of 5-vinyltetrazole (**1**) and its alkyl derivatives.[1, 2, 16–19, 21, 29–31]

A procedure for the synthesis of 5-vinyl-1-methyltetrazole (**5a**) starting from 2-*tert*-butyl-5-vinyltetrazole (**5e**) *via* the quaternary salt **9** has been proposed.[32]



The aforementioned methods cannot be extended to the synthesis of *N*-aryl-substituted *C*-vinyltetrazoles. The vinyl group was introduced into position 5 of the tetrazole ring containing a phenyl substituent at the nitrogen atom using the Wittig reaction.[31] Phosphonium salt **10** was prepared from 1-phenyl-5-chloromethyltetrazole (**11**); its dehydrochlorination gave the ylide **12**. The latter readily reacts with various aldehydes according to a common scheme to give compounds **13a**,**b**.



R = H (**a**), Ph (**b**).

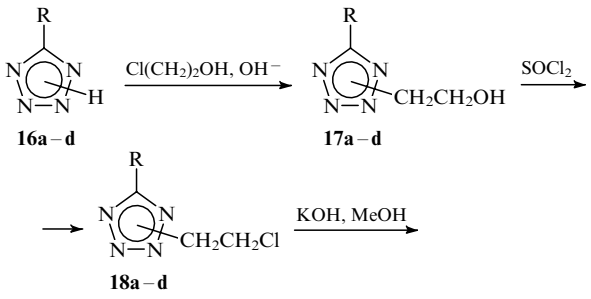
This reaction affords tetrazolyl-substituted alkenes in good yields.

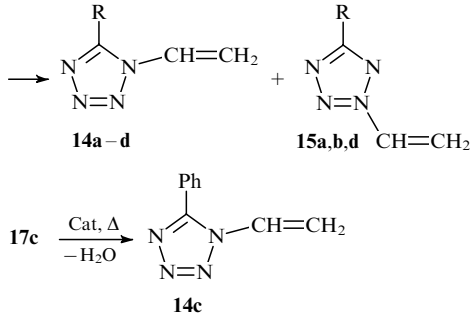
2. Synthesis of *N*-vinyltetrazoles

The major difference between the approaches used in the synthesis of *N*-vinyltetrazole derivatives and those described above is that the former makes use of compounds with preformed heterocycles as starting substrates.

N-Vinyltetrazoles **14** and **15** are synthesised from 2-chloroethyltetrazoles using three different approaches.

The first of them includes alkylation of tetrazoles **16a**–**d** with ethylene chlorohydrin with subsequent replacement of the hydroxy group in 2-hydroxyethyltetrazoles **17a**–**d** by chlorine under the action of thionyl chloride [1, 2, 17, 18] and dehydrochlorination of 2-chloroethyl derivatives **18a**–**d**. Vinyltetrazole **14c** can be prepared by dehydration of compound **17c**.[33]

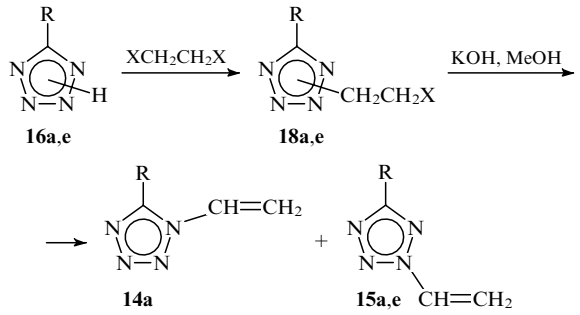




R = H (**a**), Me (**b**), Ph (**c**), NH_2 (**d**).

As in the case of *C*-vinyltetrazoles, dehydrochlorination is more preferable for the formation of the vinyl group.

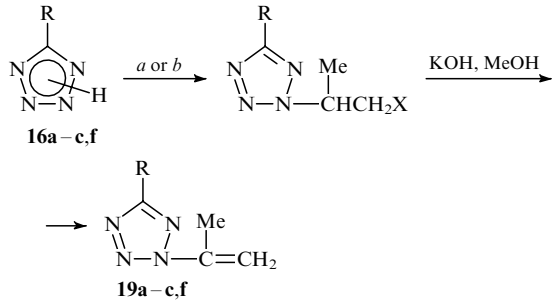
The second approach to the synthesis of *N*-vinyltetrazoles has been described in the studies,[34–36] where 1- and 2-(2-halogenoethyl)tetrazoles were synthesised by alkylation of tetrazole (**16a**) and 5-nitrotetrazole (**16e**) with 1,2-dichloro- or 1,2-dibromoethane under conditions of phase-transfer catalysis.



R = H (**14a**, **15a**, **16a**), NO_2 (**15e**, **16e**); X = Cl, Br.

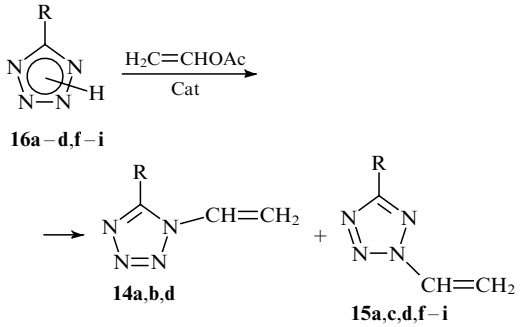
2-(2-Halogenoethyl)-5-nitrotetrazoles are prepared from the nitro derivative **16e**; their dehydrohalogenation was used for the synthesis of 2-vinyl-5-nitrotetrazole (**15e**).[36] It is of note that the alkylation yields a mixture of isomers in the majority of cases, the separation of which is often problematic.

The third approach to the synthesis of 2-(2-halogenoethyl)tetrazoles has recently been proposed.[37] This consists of selective alkylation of tetrazole and its 5-substituted derivatives with halo-substituted alcohols or allyl halides. Subsequent dehydrohalogenation of the intermediate compounds yields 2-isopropenyltetrazoles **19a–c**,**f**.



R = H (**a**), Me (**b**), Ph (**c**), CF_3 (**f**);
(*a*) $MeCH(OH)CH_2X$ (X = Cl, Br), H_2SO_4;
(*b*) $CH_2=CHCH_2Br$, H_2SO_4.

Reaction of vinyl acetate[31,38–43] or butyl vinyl ether[42] with tetrazoles **16a–d**,**f–i** is a convenient approach to the synthesis of *N*-vinyltetrazoles.



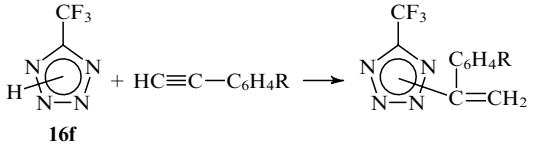
R = H (**a**), Me (**b**), Ph (**c**), NH_2 (**d**), CF_3 (**f**), NO_2Ph (**g**), CH_2Cl (**h**), $CH=CH_2$ (**i**).

The synthetic procedures proposed by different authors utilise different catalytic systems, but all of them make use of mercuric acetate in the presence of acetic[31,38–42] or sulfuric acids,[31] boron trifluoride etherate[41] and palladium–sodium acetate mixture as a catalyst.[42] The yields of the vinylation products and the position of the vinyl group in the substituted tetrazoles depend on the nature of the substituent at the carbon atom. Small-size or potent electron-withdrawing substituents direct the vinyl group to position 1 of the tetrazole ring predominantly. Electron-withdrawing substituents shielding the vicinal nitrogen atom favour the formation of 2-vinyltetrazoles **15**. In addition, such substituents decelerate or fully inhibit the reaction.

The catalytic system $Hg(OAc)_2–CF_3CO_2H$ was recommended for the preparation of 1-vinyltetrazole (**14a**).[43] The use of trifluoroacetic acid prevents secondary polymerisation. If the reaction time is small, the yield of the vinylation product is close to quantitative; the target product contains predominantly 1-vinyltetrazole (**14a**) and only a small amount (no more than 10%) of 2-vinyltetrazole (**15a**). Irrespective of the catalytic system used, vinylation of unsubstituted tetrazole gives two isomeric vinyltetrazoles **14a** and **15a** which are readily separated by vacuum distillation. A method for separation of 1- and 2-vinyl-substituted tetrazoles has been developed[40,44–46] which entails selective formation of $CuCl_2$ complexes; their subsequent degradation affords 1-vinyl-substituted tetrazoles.

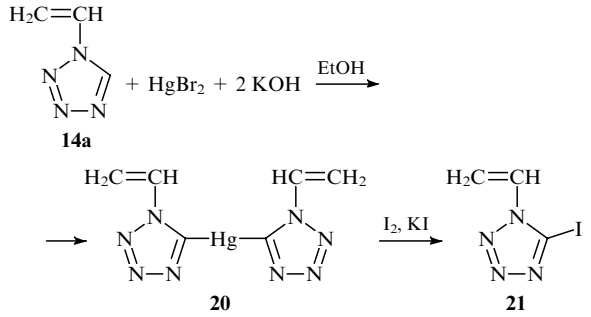
Vinylation of tetrazoles under the action of isopropenyl acetate was used in the synthesis of 1-isopropenyltetrazole in 30% yield.[43]

Some tetrazolyl-substituted alkenes were prepared by reaction of 5-trifluoromethyltetrazole **16f** with arylacetylenes. This reaction proceeds vigorously upon mixing of the reagents in the absence of the solvent and the catalyst.[47]



R = H, 4-Cl, 4-Me.

In contrast to the 5-vinyl derivative where the double bond must be protected, the synthesis of 1-vinyltetrazole allows the introduction of substituents into the heterocycle without preliminary protection of the vinyl group. Thus mercuration of 1-vinyltetrazole (**14a**) yields the mercury derivative **20**. Subsequent replacement of the mercury atom by iodine gives 1-vinyl-5-iodotetrazole (**21**).[48]



Several other approaches to the synthesis of vinyltetrazoles exist. These are based on reaction of vinyl isocyanide [49] or vinyloxazolones [50] with hydrazoic acid, reaction of *N*-methylacrylonitrile fluoroborate [25] with sodium azide, reactions of acrylonitrile with organotin azides [51] or cross-coupling of 1-benzyl-2-bromotetrazole with vinylboronic acid.[52] However, these methods have no preparative significance.

III. Electronic structures and geometry of vinyltetrazoles

Vinyl derivatives of five-membered nitrogen-containing heterocycles including vinyltetrazoles can be regarded as bifunctional compounds containing two unsaturated fragments, *viz*., the vinyl group and the azole ring. The intramolecular interactions in vinyltetrazoles and their effects on the electronic structure have been documented in numerous papers. [27, 53–59] In many of them, the authors did not restrict themselves to consideration of charge and energy characteristics of interacting molecules, but attempted to estimate their reactivities on the basis of calculations.

The distribution of the total charges ($\sigma + \pi$) calculated by the SNDO/S method based on the planar structure of vinyltetrazole molecules is shown in Figure 1.[43]

Calculations of total ($\sigma + \pi$) electron densities have shown [60, 61] that both carbon atoms in the vinyl group of *C*-vinyltetrazoles bear a negative charge, while the charge of the α-carbon atom of *N*-vinyltetrazoles is positive due to σ-electron-withdrawing properties of the nitrogen atom at the double bond. In both cases, the total electron density on the β-carbon atom of the vinyl group is higher than that on the α-atom. The π-electron distribution is characterised by reverse polarisation [60, 61] (the negative π-electron charge is concentrated on the α-carbon atom of the C=C bond), which testifies to the π-electron-withdrawing effect of the tetrazolyl substituent. Polarisation of the vinyl group ($\Delta q_{\beta\alpha}$) in *N*-vinyltetrazoles is more pronounced than in *C*-vinyltetrazoles. Introduction of electron-donor substituents, such as Me and NH_2, into position 5 of the tetrazole **14a** (compounds **14b**,**d**) reduces the electron-withdrawing effect of the tetrazolyl substituent on the vinyl group. Consequently, the total ($\sigma + \pi$) negative charge of the α-carbon atom and complete polarisation of the double bond of the vinyl group are increased. Similar changes in the distribution of electron density are induced by introduction of an alkyl substituent (compounds **5c** and **5b**) into position 2 of the tetrazole **1;** this effect does not depend on the size or structure of the alkyl group. [27]

Introduction of a methyl substituent into the vinyl group changes drastically the charge distribution pattern. The total ($\sigma + \pi$) negative charge of both 1-isopropenyl- (**22**) and 5-isopropenyltetrazole (**2**) is concentrated on the β-carbon atom, whereas the positive charge on the α-atom of the isopropenyl group. Special mention should be made of the much higher polarity ($\Delta q_{\beta\alpha}$) of the C=C-bond of isopropenyl derivatives in comparison with the corresponding vinyl compounds.

An analysis of distribution of the electron density in the heterocyclic fragment has shown that, in contrast to unsubstituted tetrazole, the vinyl group at C(5) has virtually no effect on the atomic charges in the ring.[55, 62] The carbon and the 'pyrrole' nitrogen atoms both bear positive charges, whereas 'pyridine' nitrogen atoms are charged negatively. The vinyl group at N(1) slightly changes the distribution of electron density in the tetrazole ring. As the 'pyrrole' nitrogen atom manifests σ-electron-withdrawing properties, the vinyl group localised in this position imparts a small negative charge to it. The positive charge of *N*-vinyltetrazole molecules is accumulated predominantly on the carbon atom, while in 1- (**14a**) and 5-vinyltetrazole (**1**) it is concentrated on the N(4) atom. Introduction of electron-donor substituents, such as Me and NH_2, into position 5 of 1-vinyltetrazole (**14a**) further increases the electron density at N(4). In contrast to 5-vinyltetrazole (**1**), the presence of a methyl substituent in position 2 of 5-vinyl-2-methyltetrazole (**5b**) slightly diminishes the negative charge on N(4), but increases it on N(1).

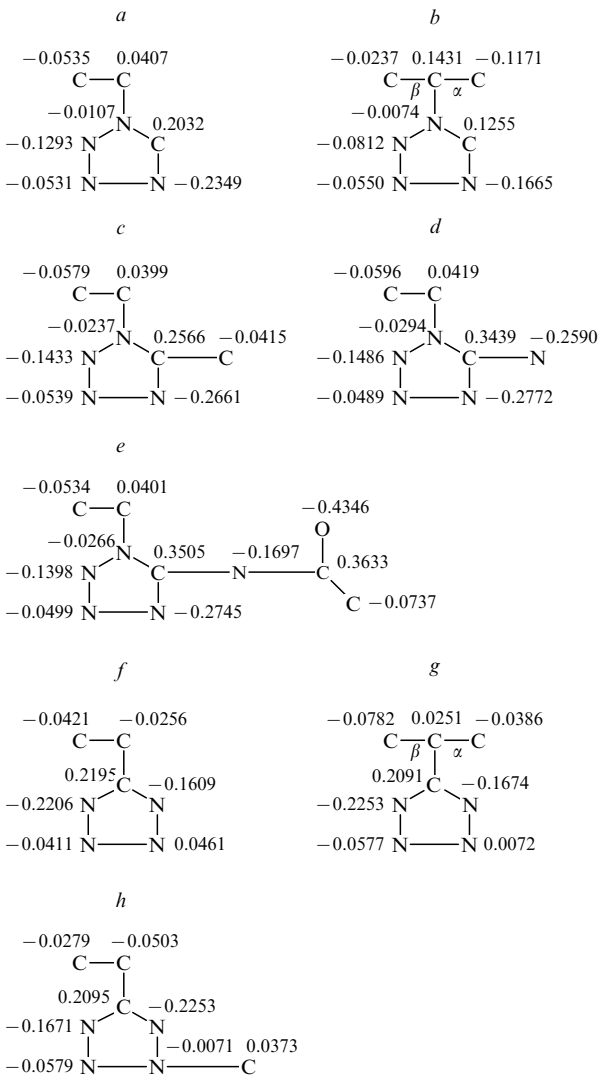
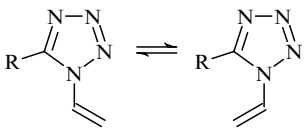


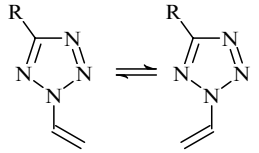
Figure 1. The distribution of total charges in vinyltetrazole molecules.[43] (*a*) 1-Vinyltetrazole (**14a**); (*b*) 1-isopropenyltetrazole (**22**); (*c*) 5-methyl-1-vinyltetrazole (**14b**); (*d*) 5-amino-1-vinyltetrazole (**14d**); (*e*) 5-acetylamino-1-vinyltetrazole (**14f**); (*f*) 5-vinyltetrazole (**1**); (*g*) 5-isopropenyltetrazole (**2**); (*h*) 2-methyl-5-vinyltetrazole (**5b**).

Studies of mutual effects of two unsaturated fragments in vinyltetrazole molecules should include an analysis of their spatial structures. According to quantum-chemical calculations, the optimised geometry of the monomers is planar. *s-cis*/*s-trans*-Isomerism is more characteristic of compounds in which the heteroaromatic nuclei are conjugated with the acyclic unsaturated fragment. Both conformers are typical of *C*- and *N*-vinyltetrazoles.[63–72]



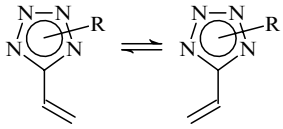
s-trans (R) *s-cis* (R)

R = H, Me, Bu^n, Bu^t, CF_3, Ph, NH_2, I, NO_2.



s-trans (N(1)) *s-cis* (N(1))

R = H, Me, Ph.



s-cis (N(1)) *s-trans* (N(1))

R = H, 1-Me, 1-Pr^i, 1-Bu^t, 2-Me, 2-Et, 2-Pr^i, 2-Bu^t.

A correlation dependence has been found between integral intensities of stretching vibrations of the C=C bond in the vinyl group of some unsubstituted *N*-vinylazoles and the difference in the electron charges on their carbon atoms.[64] This finding has allowed the authors to conclude that these compounds exist predominantly in the *s-trans*-conformation. At the same time, data from ^{13}C NMR spectroscopy do not exclude the *s-cis*-conformation.[65] More recent studies of stereochemical dependences of direct spin–spin coupling constants of $^{13}C-^{1}H$ in the vinyl group of vinylazoles revealed that the proportion of the *s-trans*-form in the conformer mixture increases with an increase in the number of nitrogen atoms in the heterocycle.[67,68] It may thus be concluded that 1-vinyltetrazole (**14a**) exists predominantly in the *s-trans*-conformation. Introduction of substituents into position 5 of the heterocycle results in stabilisation of the *s-trans*-conformation of *N*-vinyltetrazoles.[68,73] Both conformers of unsubstituted 5-vinyltetrazole (**1**) are equivalent as can be judged from the IR spectroscopic data.[72] The effect of the alkyl substituent in position 2 of *C*-vinyltetrazole on the conformer ratio is interpreted differently by different authors. According to study,[69] 5-vinyl-2-methyltetrazole (**5b**) represents a mixture of *s-cis* and *s-trans*-conformers whose ratio varies depending on the temperature and the nature of the solvent. According to electron-diffraction analysis data, 5-vinyl-2-methyltetrazole (**5b**) exists exclusively in the *s-cis*-conformation in the gas phase.[66] Quantum-chemical calculations have shown that the content of 5-vinyl-2-R-tetrazole rotamers has virtually no dependence on the substituent size, whereas the conformation equilibrium of 5-vinyl-1-R-tetrazoles is mainly determined by the steric effect of the substituent: the amount of the *s-trans*-conformer increases with an increase in the size of the alkyl substituent.[63]

IV. Physicochemical and spectroscopic properties of vinyltetrazoles

Recent advances in the synthesis of vinyltetrazole derivatives have stimulated studies into their physicochemical and spectroscopic properties. These studies and quantum-chemical methods may help establish a quantitative correlation between structural, physicochemical and spectroscopic properties and reactivities of vinyltetrazoles, including their radical polymerisation. It is from this standpoint that spectroscopic characteristics on vinyltetrazoles are considered in the overwhelming majority of published papers.[27,53,55,65,69,74,75]

1. Dipole moments of vinyltetrazoles

The experimental values of dipole moments of vinyltetrazoles (μ) (Table 1) significantly exceed those of vinylazole derivatives containing fewer nitrogen atoms in their rings. For example, the dipole moments of 1-vinylimidazole, 1-vinylpyrazole and 1-vinyl-1,2,4-triazole are equal to 3.2, 1.9 and 3.05 D, respectively.[76,77] These data point to a higher polarity of vinyltetrazole molecules in comparison with other vinylazoles. High values of dipole moments of unsubstituted tetrazoles are usually assigned to the polarising effect of unshared pairs of nitrogen atoms and the resulting nonuniform distribution of electron density in the tetrazole ring.[62] Introduction of a vinyl group further enhances the nonuniformity of the charge distribution. The values of dipole moments of unsaturated tetrazole derivatives (see Table 1) usually exceed those of the corresponding non-vinylated substituted tetrazole derivatives. Thus the μ values for tetrazole, 5-methyltetrazole and 5-aminotetrazole are equal to 5.14, 5.17 and 5.71 D, respectively.[4,5] Contrariwise, introduction of the isopropenyl group into position 5 decreases the polarity of a molecule in comparison with unsubstituted tetrazole. 2-Methyl-5-vinyltetrazole (**5b**) has a low dipole moment characteristic of tetrazole derivatives (including 2,5-disubstituted ones) with a substituent in position 2 of the heterocycle.[78] The hypothesis on the 1*H*-tautomeric conformation of unsubstituted tetrazole is based on the significant difference in the polarities of 1- and 2-substituted tetrazoles. A comparison of the experimental dipole moment of tetrazole (5.14 D) with theoretically calculated values of μ for the 1*H*- and 2*H*-tautomeric forms of tetrazole (4.8–5.23 and 1.63–2.35 D, respectively) corroborates this hypothesis.[5] Taking into account high values of μ for 5-vinyl- (**1**) and 5-isopropenyltetrazole (**2**) and their comparison with the corresponding value for unsubstituted tetrazole, one may conclude that both vinyltetrazoles exist predominantly in the 1*H*-conformation.

Table 1. Dipole moments (μ), polarographic reduction potentials ($E_{1/2}$) and characteristics of the absorption bands in the UV spectra of vinyltetrazoles (MeCN).[43]

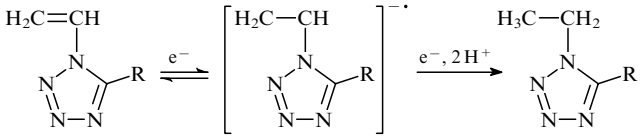
Compound	μ /D	$E_{1/2}$ /V	UV spectra	
			λ_{max} /nm	$10^{-3}\,\varepsilon$
1-Vinyltetrazole (**14a**)	5.34	−2.52	223 (224)[a]	7.30 (6.10)[a]
5-Methyl-1-vinyltetrazole (**14b**)	5.71	−2.59	218	6.45
5-Amino-1-vinyltetrazole (**14d**)	7.10	−2.70	242	6.0
5-Acetylamino-1-vinyltetrazole (**14f**)	4.05	−2.67	228, 196	8.78, 7.63
5-Phenyl-1-vinyltetrazole (**14c**)	–	–	239[a]	11.80[a]
1-Isopropenyltetrazole (**22**)	–	–	232.5	5.0
5-Vinyltetrazole (**1**)	5.21	−2.0	218	10.75
2-Methyl-5-vinyltetrazole (**5b**)	2.34	−2.42	218	10.30
5-Isopropenyltetrazole (**2**)	4.77	−2.03	223	8.60

[a] Data from Ref. 33.

2. Polarographic analysis of vinyltetrazoles

The mutual effect of two unsaturated fragments in the vinyltetrazole molecule is especially pronounced in their polarographic analysis.[43,60,79] Vinyltetrazoles are polarographically active, but the mechanisms of reduction of *N*- and unsubstituted *C*-vinyl derivatives are different.

The vinyl group in *N*-vinyltetrazoles, as in other alkenes,[80] in particular vinylazoles,[81] is completely reduced by a two-electron mechanism in the presence of proton donors.



R = H, Me, NH_2, NHAc.

Introduction of various groups, such as Me and NH_2, into position 5 of the tetrazole ring increases the electron density on the vinyl group and causes a shift of $E_{1/2}$ for the vinyl group towards more negative values in comparison with 1-vinyltetrazole (**14a**) (see Table 1). Under these conditions, the change in $E_{1/2}$ correlates with the electronic effects of the substituents present in the ring. Thus a satisfactory correlation was found between $E_{1/2}$ and the charge of the β-carbon atom (q_β), the difference of charges on the carbon atoms of the vinyl group ($\Delta q_{\beta\alpha}$)[43] and the values of induction constants (σ_I) (see Ref. 82) of the corresponding tetrazolyl substituents.

$$E_{1/2} = (-1.04 \pm 0.10) + (27.33 \pm 2.77)q_\beta \quad (r = 0.93, n = 3),$$

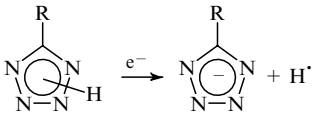
$$E_{1/2} = (-5.02 \pm 0.48) + (24.66 \pm 0.79)\Delta q_{\beta\alpha} \, (r = 0.99, n = 3),$$

$$E_{1/2} = (-4.32 \pm 0.43) + (2.71 \pm 0.51)\sigma_I \quad (r = 0.97, n = 3),$$

where r is the correlation coefficient and n is the number of compounds tested.

A quite unexpected [in comparison with 1-vinyltetrazole (**14a**)] shift of $E_{1/2}$ for 5-acetylamino-1-vinyltetrazole (**14f**) towards the negative region testifies to the electron-donor nature of the AcNH group.

A completely different reduction mechanism is observed in the case of 5-substituted tetrazoles, particularly 5-vinyltetrazole derivatives. In contrast to *N*-vinyltetrazoles, the double bond of the vinyl fragment in 5-vinyl- (**1**) and 5-isopropenyltetrazole (**2**) is not reduced. The polarographic activity of tetrazole ($E_{1/2} = -2.13$ V) and its 5-substituted derivatives is determined by their acidic properties; the polarographic wave is associated with proton reduction[79] which proceeds by a single-electron mechanism. Substitution of the methyl substituent for the acid proton favours reduction of the vinyl group in compound **5b**. It is of note that this process is characterised by a lower value of the negative potential in comparison with *N*-vinyltetrazoles (see Table 1).

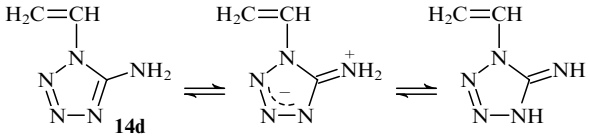


R = CH=CH$_2$, CMe=CH$_2$.

3. Ultraviolet spectra of vinyltetrazoles

The conjugation between the π-systems of the heterocycle and the vinyl group determines the presence of intense absorption bands of both *N*- and *C*-vinyltetrazoles in the near UV-region (see Table 1). Introduction of substituents into position 5 of 1-vinyltetrazole (**14a**) results in slight reduction of the extinction coefficient (ε), which can be attributed to the decrease in the conjugation between unsaturated fragments in compounds **14b**,**d** due to deviation of the vinyl group from the plane. A similar effect is observed after introduction of a methyl substituent into the α position of the vinyl group, the values of extinction coefficients ε of isopropenyltetrazoles being lower than those of vinyltetrazoles. Introduction of a methyl substituent into position 2 of tetrazole **1** has virtually no effect on the wavelength and intensity of the UV absorption band which testifies to the lack of conformational changes.

It is known that 5-dialkylamino-substituted tetrazoles undergo amine–imine rearrangements.[4,5] Evidence for the existence of the imine form can be derived from a more significant bathochromic shift of the UV absorption bands of these compounds in comparison with tetrazoles with unsubstituted amino groups which are thought to exist exclusively in the amino form. The absorption maximum in the UV spectrum of 5-amino-1-vinyltetrazole (**14d**) is noticeably shifted towards the longwave region relative to other vinyltetrazoles[43] and lies in the region close to the absorption band of the imino (rather than the amino) form (see Table 1). It may thus be concluded that in contrast to other tetrazole derivatives containing an unsubstituted amino group, 5-amino-1-vinyltetrazole (**14d**) undergoes amine–imine rearrangement.



14d

The parameters of UV absorption bands of *N*-vinyl- and substituted *C*-vinyltetrazoles do not depend on the nature of the solvent, the concentration and pH of the reaction medium. The dependence of spectroscopic characteristics on the aforementioned parameters was observed for 5-vinyltetrazole (**1**) which can be ionised: in aqueous solutions, a change in the concentration of a compound or an increase in pH caused a further shift of the absorption band towards the longwave region. In the ionised form, 5-vinyltetrazole (**1**) is absorbed at $\lambda = 226$ nm ($\varepsilon = 9900$).[43] In contrast to aqueous solutions, the position of the absorption band in acetonitrile and ethanol did not change with concentration. This finding suggests that 5-vinyltetrazole does not dissociate in these solvents.

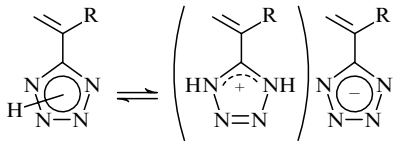
4. Infrared spectroscopy of vinyltetrazoles

There is little evidence on vibrational spectra of vinyltetrazoles. Among a variety of other studies, only two papers devoted to a detailed analysis of IR spectra of unsubstituted 1- and 5-vinyltetrazoles[71,72] and a few publications where spectral analysis of vinyltetrazole compounds was used to confirm the structures of the polymers prepared from them deserve mention.[79,83,84]

The IR spectra of vinyltetrazoles contain three main regions. The shapes and positions of low-frequency absorption bands around 600–1000 cm^{-1}, induced by extraplanar vibrations of C–H or by deformation and torsion vibrations of the tetrazole ring[85] change appreciably depending on the place of attachment of the vinyl group and the nature of the substituent in the heterocycle. Skeletal vibrations of the tetrazole rings are observed around 1000–1500 cm^{-1} and are characterised by several intense absorption bands around 1030–1090, 1125–1150, 1250–1270, 1320–1390 and 1430–1470 cm^{-1} irrespective of the vinyltetrazole structure. There is no unanimous opinion about the origin of the intense absorption band around 1560–1580 cm^{-1} in the IR spectra of tetrazole (**16a**) and its 5-vinyl derivative (**1**). Judging from quantum-chemical calculations,[72,85] this band has been assigned to the C=N vibrations of the ring. However, analysis of the IR spectra of vinyltetrazoles, model 1-, 2-, 1,5- and 2,5-substituted tetrazoles and 5-substituted tetrazolium salts revealed[83] that these spectra contain no band around 1560–1580 cm^{-1}. This finding led us to suggest that this band should be assigned to deformation vibrations of the tetrazole ring induced by the N–H bond characteristic exclusively of non-ionised forms of 5-substituted tetrazoles.

Vibrations of the double bond of the vinyl group in the IR spectra of all vinyltetrazoles under study are manifested as a narrow band around 1645–1655 cm^{-1}. The absorption intensity of various vinyl-substituted tetrazoles correlates with the previously observed dependence of integral intensities of stretching vibrations of the C=C bond on the polarity of the vinyl group.[64] Higher polarity of the vinyl fragments of *N*-vinyltetrazoles determines higher intensity of the absorption bands around 1645–1655 cm^{-1} in comparison with those in *C*-vinyltetrazole derivatives. A more detailed analysis of absorption spectra of 2-methyl-5-vinyltetrazole (**5b**) revealed two absorption bands in the region of C=C bond vibrations: a singlet band around 1656 cm^{-1} and a doublet band around 1648 and 1645 cm^{-1} (see Ref. 69). These bands were assigned to stretching vibrations of the vinyl groups of two different rotamers of compound **5b**. Deformation vibrations of the =CH-bond of the vinyl group are observed around 960–980 cm^{-1}.

The difference between the IR spectra of vinyltetrazoles is especially pronounced in high-frequency regions (2200–3700 cm^{-1}). The simultaneous presence of an acid proton and 'pyridine' nitrogen atoms in 5-vinyl- (**1**) and 5-isopropenyltetrazole (**2**) rings gives rise to intermolecular interactions typical of NH-unsubstituted azoles.[4,86] The IR spectra of *C*-vinyltetrazoles contain a broad absorption band around 3000–3500 cm^{-1} corresponding to stretching vibrations of NH···N and a band around 2300–2800 cm^{-1} assigned to the quaternary nitrogen atom, $\equiv N^+H$ (see Ref. 87). No such bands are observed in the IR spectra of *N*-vinyltetrazoles. This suggests that condensed forms of compounds **1** and **2** contain, along with molecular forms, two additional forms, one of which is bound by hydrogen bonds and the other one is ionised as a result of complete proton transfer.



The IR spectra of *N*-vinyltetrazoles and *N*-alkyl-5-vinyltetrazoles contain absorption bands around 2900–3200 cm^{-1} due to stretching vibrations ν(CH). The complex structure of the absorption band in this particular region of the IR spectrum of 1-vinyltetrazole (**14a**) is attributed to association of molecules *via* the $\geqslant$CH···N bond.[71]

The high-frequency region of the IR spectrum of 5-amino-1-vinyltetrazole (**14d**) contains absorption bands corresponding to the amino group (3150 and 3330 cm^{-1}). The existence of amine–imine rearrangement in compound **14d** is confirmed by IR (see Ref. 43) and UV spectral data: the presence of an absorption band in the IR spectrum around 1670–1680 cm^{-1} can be assigned to vibrations of the exocyclic C=N bond of its imino form.

5. NMR spectra of vinyltetrazoles

Structural studies of vinyltetrazole derivatives widely employ ^1H and ^{13}C NMR spectroscopy. Chemical shifts (δ) of the characteristic proton signals for the vinyl groups of all *N*-vinyltetrazoles studied lie in the range of δ 7.20–7.40 (H_A, q), 5.96–6.05 (H_B, d) and 5.30–5.50 (H_C, d), while signals for the carbon atoms lie around δ 126–128 (C_α) and 106–114 (C_β).[41,43,53,88,89] Greater shielding (relative to the carbon atom in ethylene) of the C_β atom [δ(C) = 123.3] testifies to effective conjugation of the vinyl group and the tetrazole ring.[67] Introduction of electron-donor substituents into the tetrazole ring induces a regular upfield shift of the C_β signal commensurate with an increase in the calculated total electron density on the β-carbon atom. The changes in $\delta(C_\beta)$ correlate with the values of the induction constants of σ_I of the tetrazolyl substituents.[43]

$$\delta(C_\beta) = (70.1 \pm 10.2) + (60.9 \pm 8.8)\sigma_I \quad (r = 0.999, n = 3).$$

Of special note are parallel changes in $E_{1/2}$ and $^{13}C_\beta$ chemical shifts in the ^{13}C NMR spectra. This dependence is described by equation:[60]

$$E_{1/2} = (0.044 \pm 0.016)\delta(C_\beta) - (7.360 \pm 1.780) \quad (r = 0.883, n = 4).$$

The effect of the tetrazolyl substituent on the chemical shifts of the vinyl group atoms is also determined by its position in the heterocycle. However, it is difficult to establish the difference between the δ values of the vinyl group in the ^1H and ^{13}C NMR spectra of 1- and 2-vinyltetrazoles.[41] An insignificant (1–3 ppm) upfield shift of the C_β signal was observed[67] for 2-vinyltetrazole (**15a**) and its derivatives in comparison with the corresponding 1-vinyl derivatives. In the presence of a vinyl group in position 5, the pattern of the ^{13}C NMR spectra of vinyltetrazoles changes considerably: the signal for the β-carbon atom of 5-vinyltetrazole (**1**) is more appreciably shifted downfield [$\delta(C_\alpha)$ = 119.99 and $\delta(C_\beta)$ = 124.70]. The polarity of the C=C bond in the vinyl group ($\Delta q_{\alpha\beta}$) of compound **1** is much lower than that of the 1-vinyl derivative **14a**;[60,61] as a result, the difference between the chemical shifts ($\Delta\delta_{\alpha\beta}$) diminishes correspondingly.[27,31,43,53] Introduction of an alkyl substituent into position 1 of 5-vinyltetrazole (**1**) has virtually no effect on the δ values of the vinyl group [$\delta(C_\alpha)$ = 118.87 and $\delta(C_\beta)$ = 126.85].[53,89] The signal of the C_α atom [$\delta(C_\alpha)$ = 122.49, $\delta(C_\beta)$ = 121.48] in the ^{13}C NMR spectra of 2-alkyl-5-vinyltetrazoles and 1-vinyltetrazoles is shifted downfield, but the difference in the chemical shifts $\Delta\delta_{\alpha\beta}$ is even less pronounced than in the case of unsubstituted 5-vinyltetrazole (**1**).[27] The methyl group in the α-position of the vinyl substituent strongly increases the polarity of the C=C bond in both *C*- and *N*-isopropenyl derivatives resulting in a drastic increase in $\Delta\delta_{\alpha\beta}$ (see Ref. 43).

The shapes of the proton signals in the ^1H NMR spectra of 5-vinyl- and 1-vinyltetrazoles are similar; the signals of 5-vinyltetrazoles lie in a narrower range (δ 5.62–6.91).[27,31,43,53] The H_B (δ 6.05 and 5.74, respectively) and H_C (δ 5.58 and 5.23, respectively) signals in the ^1H NMR spectra of isopropenyltetrazoles **2** and **22**, which represent a superposition of two quadruplets, are shifted upfield in comparison with the corresponding signals of the vinyl derivatives. The signals of the methyl group in the NMR spectra of compounds **2** and **22** are manifested as a superposition of two doublets (δ 2.24 and 2.40, respectively).[43]

The electronic effect of the vinyl group on the heterocycle is manifested in ^1H and ^{13}C NMR spectra of vinyltetrazoles. Thus the difference in the position of the vinyl group of 1- and 2-vinyltetrazoles determines the difference in the shielding of C(5), being by 12 ppm more protected in 1,5-disubstituted tetrazoles in comparison with 2,5-isomers. This effect was used for identification of isomeric vinyltetrazole derivatives.[41]

^{15}N NMR spectra of vinyltetrazole derivatives are less studied. A linear correlation was found[88] between δ and the electron density on nitrogen atoms, which allowed unambiguous interpretation of signals in the NMR spectra of vinyltetrazoles (Table 2). According to quantum-chemical calculations, the nuclei of 'pyrrole' nitrogen atoms of vinyltetrazoles resonate in a higher field in comparison with 'pyridine' nitrogen atoms.

Table 2. Chemical shifts in the ^{15}N NMR spectra of vinyltetrazoles ($MeNO_2$ as a standard).[88]

Compound	δ ^{15}N /ppm			
	N(1)	N(2)	N(3)	N(4)
1-Vinyltetrazole (**14a**)	−135.3	−19.1	10.1	−52.4
1-Methyl-5-vinyltetrazole (**5a**)	−157.6	−10.3	8.4	−56.6 [a]
2-Methyl-5-vinyltetrazole (**5b**)	−79.8	−103.7	0	−52.0 [a]

[a] In DMSO.

6. Acid–base properties of vinyltetrazoles

Acid–base properties of nitrogen-containing heterocyclic compounds are related to their most essential characteristics, which determine in many respects their reactivities and physiological activities. Unfortunately, vinylazoles fall out of this area of research. The values of basicity (pK_{BH^+}) and acidity (pK_a) constants of azoles and their vinyl derivatives are given in Table 3. Acidic properties of azole rings are increased with an increase in the number of nitrogen atoms, tetrazole being the strongest acid. As mentioned above, introduction of a vinyl group into position 5 of the tetrazole ring further increases the acidity of the heterocycle. Contrariwise, the basicity of azoles decreases with an increase in the number of nitrogen atoms in the ring, tetrazole being the weakest base among other azoles. An analysis of experimental data on basicities of various vinylazoles allows one to establish certain regularities in reactions between heterocyclic

Table 3. The values of pK_{BH^+} and pK_a for azoles and vinylazoles.[90–92]

Compound	pK_{BH^+}	pK_a
Imidazole	7.05	14.17
1-Vinylimidazole	7.32	–
1,2,4-Triazole	2.45	10.04
1-Vinyl-1,2,4-triazole	2.97	–
Tetrazole	−2.68	4.89
1-Vinyltetrazole (**14a**)	−3.43	–
5-Methyl-1-vinyltetrazole (**14b**)	−2.56	–
5-Vinyltetrazole (**1**)	−2.91 [a]	4.10 [a]
2-Methyl-5-vinyltetrazole (**5b**)	−2.77	–

[a] Data from Ref. 43.

and vinyl fragments. First, introduction of a vinyl group into imidazole and 1,2,4-triazole rings increases their basicities, while the vinyl group present in the tetrazole ring decreases it. This suggests that the mode of transfer of electronic effects changes on going from vinylimidazole and -triazole to vinyltetrazole derivatives. Second, like alkyl derivatives,[90] the corresponding *N*-vinyltetrazoles are weaker bases than *C*-vinyltetrazoles. On the whole, vinylazole derivatives are weaker bases in comparison with alkyl derivatives, which is confirmed by polarographic and NMR spectroscopic data. Third, introduction of a methyl substituent into 1- and 5-vinyltetrazoles enhances basic properties of the heterocycle, which is especially pronounced in the former case.

Numerous studies into protonation of various tetrazole derivatives provide support that the nitrogen atom in position 4 is the most basic site in the heterocycle.[90]

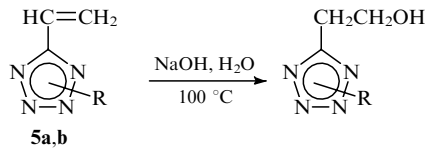
V. Reactions of vinyltetrazoles

The chemistry of vinyltetrazoles has not been studied in depth. One possible reason is that vinyltetrazole derivatives are used as monomers for preparation of high-energy polymeric products and are seldom used as starting compounds for other chemical reactions. Modification of the heterocycle is usually confined to reactions which have no appreciable influence on the energy characteristics of the tetrazole ring; reactions involving the vinyl group have not been sufficiently studied either. However, despite the obvious paucity of experimental data, certain conclusions can be made about the correlation between the structural and chemical properties and reactivities of vinyltetrazoles in order to compare them with those of vinyl derivatives of other five-membered nitrogen-containing heterocycles.

1. Reactions involving the vinyl group

As mentioned above, conjugation of the tetrazole ring with the vinyl group results in its pronounced polarisation. Taking into account the electron-withdrawing character of the heterocycle, it may be expected that the vinyl group will manifest higher (in comparison with alkenes) reactivity towards the nucleophilic reagents and lower reactivity in an electrophilic attack. However, it has been shown that the reactivity of the vinyl group is largely determined by its position in the ring. Whereas 5-vinyltetrazoles readily enter into addition reactions at the double C=C bond under the action of both nucleophilic and electrophilic reagents, the vinyl group of 1-vinyltetrazoles is virtually inert to both types of reagents.

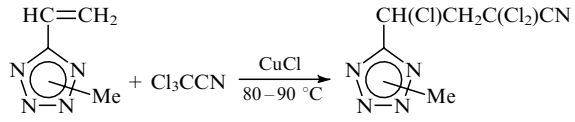
Hydration of the vinyl group of 1-methyl-5-vinyl- (**5a**) and 2-methyl-5-vinyltetrazoles (**5b**) resulting in the corresponding alcohols is an example of nucleophilic addition to the double bond.[19]



5a,**b**

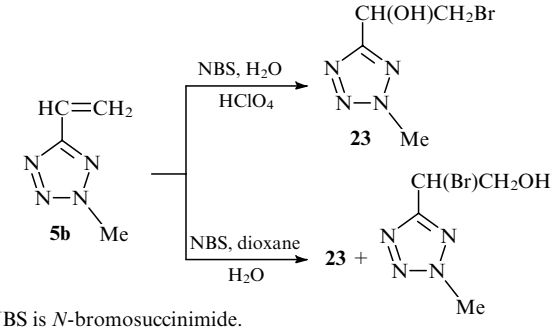
R = 1-Me (**a**), 2-Me (**b**).

In the presence of copper catalysts, compounds **5a**,**b** add trichloroacetonitrile surprisingly smoothly.[93]



5a,**b**

It is known that 2-methyl-5-vinyltetrazole (**5b**) reacts with hypobromous acid. Slow addition of an aqueous suspension of *N*-bromosuccinimide to compound **5b** in the presence of perchloric acid occurs regiospecifically and gives rise to 5-(2-bromo-1-hydroxyethyl)-2-methyltetrazole (**23**) in quantitative yield.[94]

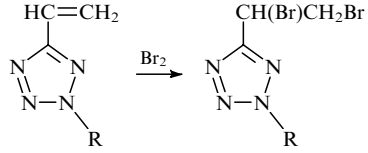


NBS is *N*-bromosuccinimide.

Reaction of vinyltetrazole **5b** with *N*-bromosuccinimide in aqueous dioxane yields an equimolar mixture of isomeric bromohydrins,[95] presumably as a result of stabilisation of the bromonium ion by dioxane as an electron donor.

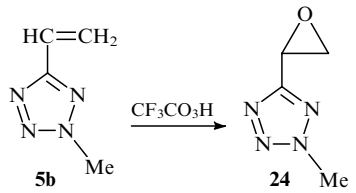
Reaction of 1-methyl-5-vinyltetrazole (**5a**) performed under analogous conditions yields polymerisation products, which is attributed [95] to higher ability of the isomer **5a** for radical polymerisation in comparison with compound **5b**.

Electrophilic addition of bromine to the vinyl group of 5-vinyltetrazole (**1**) and its homologues proceeds rather smoothly.[30]

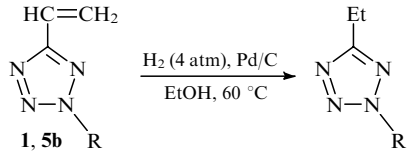


R = H, Me, Et.

Selective oxidation of the vinyl group in vinyltetrazoles has been studied with a view to obtaining epoxy derivatives of tetrazoles.[96,97] It was found that 2-methyl-5-vinyltetrazole (**5b**) is not oxidised by hydrogen peroxide, *tert*-butyl hydroperoxide or hydrogen peroxide in the presence of sodium tungstate as a catalyst or by sodium hypochlorite in alkaline media under conditions of phase-transfer catalysis. Compound **5b** is also inert with respect to hypochlorous acid. The C=C bond of vinyltetrazole **5b** could only be oxidised with trifluoroperacetic acid. Epoxide **24** was obtained in 25%–30% yield.



Selective hydrogenation of 5-vinyltetrazoles at the vinyl group occurs under relatively mild conditions.[43]



R = H (**1**), Me (**5b**).

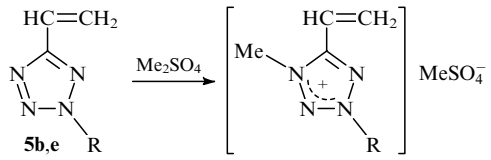
These few examples of chemical reactions of 5-vinyltetrazoles do not reveal any unusual behaviour of the vinyl group substituted by an aromatic heterocycle. The oxidation of the double bond resulting in epoxide **24** is the only exception.

2. Reactions involving the tetrazole ring

Reactions of vinyltetrazoles involving the heterocyclic fragment are more extensively documented in the literature. The tetrazole ring has several reaction centres, *viz*., the 'pyrrole' nitrogen atom (in unsubstituted 5-vinyltetrazoles), 'pyridine' nitrogen atoms, the carbon atom of unsubstituted 1- and 2-vinyltetrazoles manifesting CH-acidic properties. The diversity of reactions involving this heterocycle significantly expands the range of vinyltetrazole-containing monomers as starting materials for the synthesis of polymeric products. Therefore, reactions involving the heterocyclic fragment have attracted more attention than reactions involving the vinyl group.

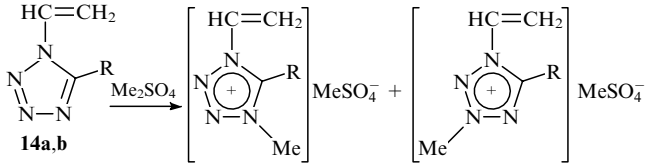
a. Reactions involving the nitrogen atom

Quaternisation reactions of tertiary nitrogen atoms of azole compounds and their vinyl derivatives by alkyl halides or dimethyl sulfate are well known.[98–100] It was found that the ability to undergo quaternisation reactions decreases with an increase in the number of nitrogen atoms in the heterocycle: quaternisation of tetrazole derivatives occurs under more drastic conditions than that of imidazoles or triazoles. Introduction of electron-donor substituents into the tetrazole ring increases slightly the reactivity of vinyltetrazoles in this reaction. Thus introduction of NH_2 or Me groups makes it possible to prepare quaternary salts of 5-amino-1-vinyl- (**14d**) and 2-methyl-5-vinyltetrazole (**5b**) by reaction with methyl iodide or dimethyl sulfate.[43, 88] At the same time, 1-vinyltetrazole (**14a**) can form salts exclusively under the action of dimethyl sulfate. A wide variety of quaternary salts of 5- and 1-vinyltetrazoles have been prepared by treatment with Me_2SO_4 in the presence or absence of solvents (20–80 °C).[88] Notably, 5-vinyl-2-R-tetrazoles are quaternised much more easily than 1-vinyl- and 5-vinyl-1-R-tetrazoles. ^{13}C and ^{15}N NMR spectroscopic studies revealed another interesting peculiarity, *viz*., selective formation of 1,3-dialkyl-5-vinyltetrazolium salts in reactions of 5-vinyl-2-R-tetrazoles with dimethyl sulfate.[88]

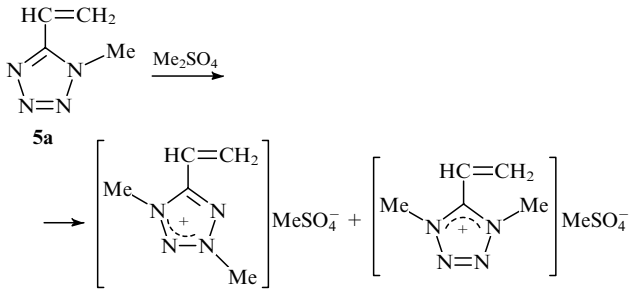


R = Me (**b**), Bu^t (**e**).

1-Vinyl- and 5-vinyl-1-R-tetrazoles yield a mixture of isomeric salts.[88]

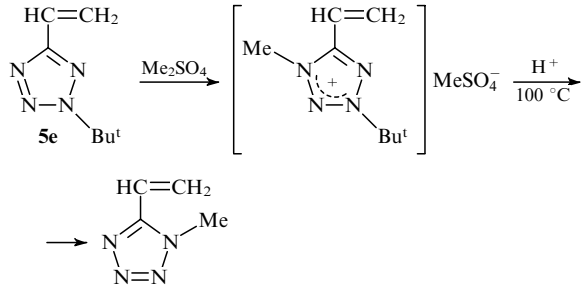


R = H (**a**), Me (**b**).



The isomeric ratio of the reaction product strongly depends on the structure of the starting vinyltetrazole.

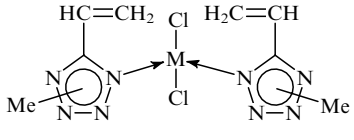
Quaternary salts of 2-*tert*-butyltetrazole derivatives, *e.g*., those prepared from compound **5e**, are readily transalkylated upon heating with the loss of the *tert*-butyl substituent. This reaction occurs regioselectively with intermediate formation of trisubstituted tetrazolium salts to give 1,5-disubstituted tetrazoles in 78%–96% yields.[32]



The salts prepared by reaction of vinyltetrazoles with Me_2SO_4 are prone to spontaneous polymerisation upon standing.[88] In contrast, the salts prepared by quaternisation of vinyltetrazoles with methyl iodide are not polymerised even under radical initiation conditions.

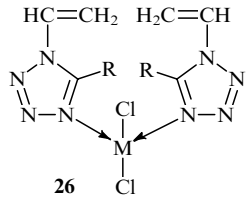
Vinyltetrazoles are as prone to complexation with metal ions as vinylazoles containing two or three nitrogen atoms in their rings. In most cases, such complexation occurs smoothly even at the stage of mixing of vinyltetrazole solutions with metal salts and does not require long-term heating. The structure and properties of the complexes formed depend on the nature of the ligand and the metal ion.

Reactions of 1-vinyl- (**14a**,**d**) and 5-vinyltetrazoles (**5a**,**b**) with Cu(II), Ni(II), Co(II) and Pd(II) chlorides yield donor–acceptor complexes (**25**, **26**) of the composition ML_2Cl_2 irrespective of the ratio of the starting reagents.



25

R	M	Ref.
1-Me	Ni(II)	103, 104
2-Me	Co(II)	103, 104
	Pd(II)	104–107

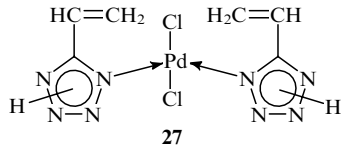


26

R	M	Ref.
H	Cu(II)	40, 46, 101, 102
	$Cu(SCN)_2$	40
	Ni(II)	101, 102
	Co(II)	102
	Pd(II)	101
NH_2	Cu(II)	101
	Ni(II)	101
	Pd(II)	101

A complex of the composition CrL_3Cl_3 was prepared using chromium(III) chloride.[103] Complex derivatives of 1-methyl- (**5a**) and 2-methyl-5-vinyltetrazoles (**5b**) with Rh(III), Ti(IV) and V(IV) ions have been prepared and characterised[104] using NMR and IR spectroscopy and X-ray diffraction analysis. It was found that in all cases studied coordination of the metal ion occurs to the nitrogen atom in position 4 of the heterocycle.[101, 105, 106] The vinyl group is not involved in the complexation: the positions of the signals for the carbon atoms of the C=C bond in the ^{13}C NMR spectra and the position of the absorption band in the IR spectra did not change upon complexation.[101, 103, 105, 106] The 1-methyl-5-vinyltetrazole (**5a**)$-PdCl_2$ complex in which the vibration frequency of the C=C bond of the vinyl group decreased from 1642 to 1625 cm^{-1} was the only exception (see Ref. 105).

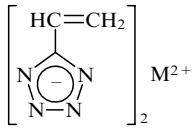
The behaviour of 5-vinyltetrazole (**1**) is similar to that of above-mentioned compounds. This forms complex **27** [PdL_2Cl_2 with palladium(II) chloride] due to a donor–acceptor interaction with the formation of an N–Pd bond.[101, 107]



27

The low-frequency region of the IR spectrum of the complex **27** contains an absorption band around 365 cm^{-1} which is characteristic of the Pd–Cl bond where the metal ion is coordinated to another atom (in our case, the nitrogen atom).[108]

A different situation is observed in reaction of 5-vinyltetrazole (**1**) with copper and nickel chlorides in water.[101] In this case, reaction products appear as salt-like complexes; the vinyltetrazolate anion plays the role of a ligand.



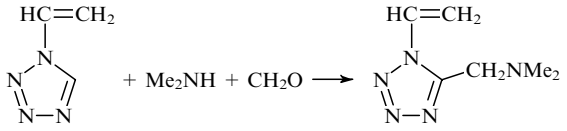
M = Cu, Ni.

An unusual effect was observed in reactions of 5-vinyltetrazole with $CuCl_2$ in organic solvents: complexation was accompanied by elimination of the vinyl group; the metal–unsubstituted tetrazole complex was formed as the final product.

Preservation of the vinyl group in the aforementioned complexes determines the interest in these compounds as candidate monomers for the synthesis of metal-containing polymers. Polymeric complexes prepared by polymerisation of $PbCl_2$ complexes with 2-methyl-5-vinyltetrazole have been studied.[107]

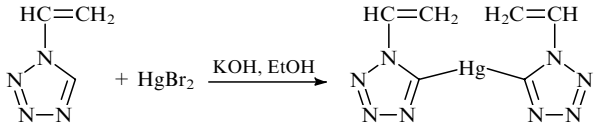
b. Reactions involving the carbon atom of the heterocycle

It has recently been shown that reactions of vinyltetrazoles involving the carbon atom of the heterocycle are possible. By virtue of their high CH-acidities (pK_a 23–25), 1-substituted tetrazoles enter into the Mannich reaction. Thus 1-vinyltetrazole (**14a**) is aminomethylated under mild conditions as a CH-acid to give 5-dimethylaminomethyl-1-vinyltetrazole (**28**).[63, 109]



14a **28**

Like other compounds with pronounced CH-acidities, 1-vinyltetrazole (**14a**) is mercurated by mercury(II) salts at the carbon atom of the tetrazole ring in the presence of bases to give symmetrical bistetrazolylmercurials (**20**).[48, 63]

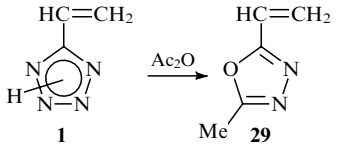


14a **20**

c. Recyclisation reactions

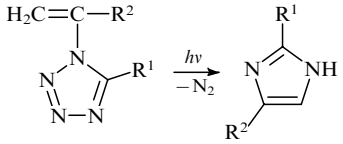
Some reactions of vinyltetrazole derivatives are accompanied by recyclisations; the heterocyclic products of these reactions contain fewer nitrogen atoms in their rings.

For the first time, such a reaction was described for 5-vinyltetrazole (**1**) by Arnold *et al.*[21] Reaction of compound **1** with acetic anhydride gives the corresponding 2,5-disubstituted 1,3,4-oxadiazole **29** in good yield.



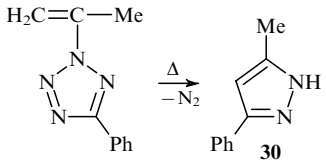
1 **29**

Some 1- and 2-vinyltetrazoles eliminate nitrogen upon photolysis or thermolysis to give diazole derivatives. 1-Vinyl-substituted tetrazoles afford imidazole derivatives.[33]



R^1, R^2 = H, Ph.

Heating of 2-isopropenyl-5-phenyltetrazole results in pyrazole **30**.[110]



30

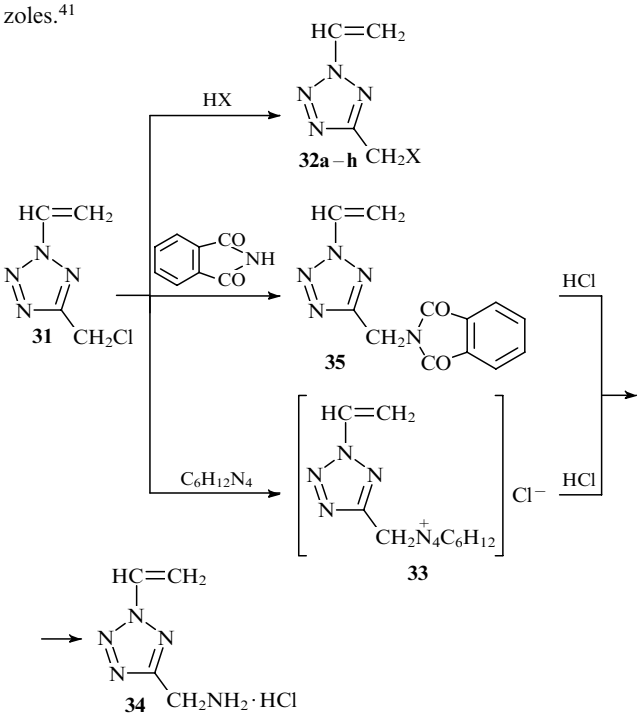
In certain cases, chemical transformations lead to destruction of the tetrazole ring. Several thermal degradation reactions of vinyltetrazoles are known. Kinetic parameters of monomolecular thermal degradation of a series of isomeric tetrazoles including 1-methyl-5-vinyl- (**5a**) and 2-methyl-5-vinyltetrazoles (**5b**) under isothermal conditions were studied using manometric methods.[111] It was found that the degradation of both isomers is characterised by high values of entropy of activation (on average, 33.5 J mol^{-1} K^{-1}). The activation energies of compounds **5a** and **5b** are equal to 180.0 and 198.9 kJ mol^{-1}, respectively. In the authors' opinion, monomolecular degradation occurs stepwise. For 1,5-disubstituted tetrazoles, reversible formation and subsequent degradation of intermediate azidoazomethines is the limit-

ing step, whereas the limiting step in the case of 2,5-disubstituted isomers is degradation of azodiazo compounds.

The rate of self-propagating high-temperature decomposition of 5-amino-1-vinyltetrazole (**14d**) was estimated to be equal to 0.5 mm s^{-1}, *i.e.*, virtually coincides with the combustion rate of unsubstituted tetrazole.[112]

3. Reactions of substituents in the ring

Substitution of the halogen in 5-chloromethyl-2-vinyltetrazole (**31**) by reactions with phthalimide, urotropin and other nucleophiles was used for the synthesis of functionalised 2-vinyltetrazoles.[41]

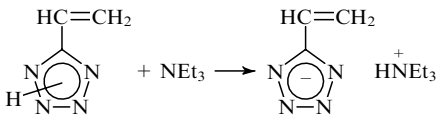


X = N⟨ ⟩ (**a**), NHPh (**b**), SH (**c**), N_3 (**d**), OEt (**e**), $OCH_2CH=CH_2$ (**f**), $OCH_2C{\equiv}CH$ (**g**), OAc (**h**).

Thus reactions of compound **31** with secondary amines and aniline afford 5-aminomethyl-2-vinyltetrazoles (**32a**,**b**) in good yields. 5-Mercaptomethyl-2-vinyltetrazole (**32c**) was prepared by reaction with thiourea with subsequent decomposition of the thiouronium salt. The chloromethyl derivative **31** readily forms salt **33** with urotropin; treatment of compound **33** with hydrochloric acid yields the primary amine hydrochloride **34**. Substitution of the primary amino group for chlorine in the Gabriel reaction proceeds successfully: treatment of chloromethyltetrazole **31** with sodium phthalimide gives 5-phthalimidomethyl-2-vinyltetrazole which is hydrolysed into amine **34** upon treatment with hydrochloric acid. Substitution of the azido group for the chlorine atom and the formation of the derivative **32d** occur under conditions of phase-transfer catalysis in the presence of benzyltriethylammonium chloride. Treatment of the chloromethyl derivative **31** with sodium alkoxides under conditions of phase-transfer catalysis yields ethers **32e–g**, while its reaction with sodium acetate affords an ester (**32h**).

4. Reactions of 5-vinyltetrazole with amines

Tetrazole and its 5-substituted derivatives manifest acidic properties and give salts upon reactions with bases including organic bases.[4,5] It was expected that 5-vinyltetrazole (**1**) would also react with bases to give monomeric salts. This reaction was studied in more detail with triethylamine as an example.[113] The formation of monomeric salts in the first step was confirmed by conductometric, UV spectroscopic and ^{1}H NMR data.



1

However, this reaction is accompanied by an increase in the viscosity of the reaction system and a drastic decrease in the relative intensities of signals for the protons of the vinyl group in ^{1}H NMR spectra. This suggests that polymerisation occurs in the system. Treatment of the reaction mixture with diethyl ether yields a viscous mass; its storage (and vacuum drying) leads to resinification or vitrification. Reactions of 5-vinyltetrazole (**1**) with ammonia, hydrazine, trimethylamine, diethylamine and pyridine proceed in a similar way.[114,115] Depending on the nature of the amine and reaction conditions, one can prepare polymeric 5-vinyltetrazole salts which are readily soluble or moderately swelling in water.

VI. Polymerisation of vinyltetrazoles

Vinyltetrazoles constitute a relatively novel class of monomers. The first vinyltetrazole derivatives were synthesised in the early 1960's in an attempt to construct promising polymeric materials. High polymerisability of these monomers and valuable properties of polymers prepared from them have stimulated further progress in the chemistry of vinyltetrazoles. Owing to high intrinsic energy and unique physicochemical and operation characteristics, polyvinyltetrazoles have attracted attention as promising to give impetus to organisation of large-scale production of some monomeric and polymeric tetrazole-containing products.[12,116,117]

Despite the high polymerisability of vinyltetrazoles reported in the very first publications, in-depth studies into polymerisation activities and properties of polymers prepared from them began in the 1980's. Both *N*- and *C*-vinyltetrazole derivatives manifest high polymerisability under conditions of radical initiation. Bulk polymerisation or polymerisation in solvents is carried out in the presence of thermally unstable initiators [*e.g.*, azobisisobutyronitrile (AIBN) and benzoyl peroxide (BP),[1,16,17] ammonium persulfate (AP),[79] H_2O_2,[118] transition metal acetylacetonates[42]] and redox systems [$H_2O_2-FeSO_4$,[118] $FeSO_4-(NH_4)_2S_2O_8-K_2S_2O_5$ (see Refs 1 and 17)]. Radical polymerisation of vinyltetrazoles induced by γ-irradiation[119] and electrochemically[120,121] has been described. The possibility of polymerisation of 5-vinyl-2-methyltetrazole under the action of cationic and anionic catalysts has been demonstrated.[122] A method for solid-phase polymerisation of 5-vinyltetrazole by exposure to high pressure has been developed.[123] Preparation of polymers from 1-methyl-5-vinyl- and 2-methyl-5-vinyltetrazoles grafted onto cellulose is also possible.[118]

The diversity of structural variants of vinyltetrazole derivatives and the vast body of evidence on quantitative aspects of their radical polymerisation have made it possible to study the effects of the structure of the vinyl monomer, the nature of the reaction medium and the initiator on the polymerisabilities of vinyltetrazoles.

1. Structures and activities of vinyltetrazoles in radical polymerisation

a. Effect of the position of the vinyl group on the activity of vinyltetrazoles in polymerisation

A comparative study of polymerisabilities of unsubstituted *C*- and *N*-vinyltetrazole derivatives has been carried out.[43,124] Acetonitrile was selected as a medium, since unsubstituted 5-vinyltetrazole behaves as a non-ionisable monomer in this solvent. In the presence of AIBN, polymerisation of 1- and 5-vinyltetrazoles proceeds as a steady-state reaction without an induction period with initial rates depending on the concentration of the reactants and the temperature. The orders of the reaction rates with respect

Table 4. Kinetic parameters of the polymerisation of vinyl-[43,124] and isopropenyltetrazoles[43,61] in MeCN (AIBN, 60 °C).

Monomer	E_{ef} (see [a])	$10^4 K_{ef}$ (see [b])	$10^5 K_{in}$ /s^{-1}	$K_p/K_t^{0.5}$ (see [c])	$E_p - 0.5 E_t$ (see [a])
5-Vinyltetrazole	74.5	22.42	1.12	0.67	16.7
1-Vinyltetrazole	80.4	12.5	1.33	0.34	20.6
5-Isopropenyl-tetrazole (**2**) [d]	85.6	3.4	0.35	0.18	–
1-Isopropenyl-tetrazole (**22**)	84.3	0.32	1.30	0.009	–

Note. E_{ef} is the effective activation energy of polymerisation; K_{ef} is the effective rate constant of polymerisation; K_{in} is the initiation rate constant; E_p and E_t are the activation energies for the propagation and termination of the polymeric chain.

[a] kJ mol^{-1}; [b] litre $mol^{-0.5}$ s^{-1}; [c] $litre^{0.5}$ $(mol\ s)^{-0.5}$.

[d] The polymerisation kinetics was studied in water in the presence of AP.

to the monomer and the initiator are 1 and 0.5, respectively, which suggests a bimolecular chain termination mechanism.

The reactivity criterion $K_p/K_t^{0.5}$ (where K_p and K_t are the rate constants for chain propagation and termination, respectively) (Table 4) suggest the higher activity of the *C*-vinyl monomer in the radical polymerisation; in addition, polymerisation of 5-vinyltetrazole is less energy-consuming.[124] A similar ratio of activities of *C*- and *N*-vinyltetrazole derivatives in the polymerisation reaction is consistent with the existing criteria for the estimation of polymerisation activities of vinyl monomers.[125–127] The electronic structure of 5-vinyltetrazole is characterised by a smaller charge, q_β, and a lower charge difference, $q_\alpha\ q_\beta$, in comparison with 1-vinyltetrazole.[60,61] Moreover, a small reduction of the acceptor induction effect of the substituent at the double bond of 5-vinyltetrazole is accompanied by a considerable decrease in the donor mesomeric effect in comparison with 1-vinyltetrazole. Thus, the tetrazolyl substituent in the *C*-vinyl monomer manifests stronger acceptor properties which accounts for higher activity of 5-vinyltetrazole.

The difference in the reactivities of *C*- and *N*-isopropenyltetrazoles is even more pronounced.[61] Polymerisation of 1- (**22**) and 5-isopropenyltetrazole derivatives (**2**) and their vinyl analogues occurs as a steady-state process without an induction period and is described by the kinetic equation:

$$W = K[M][I]^{0.5}.$$

The $K_p/K_t^{0.5}$ values (see Table 4) suggest that the activity of 5-isopropenyltetrazole (**2**) in radical polymerisation is 20 times higher than that of its isomer **22**.[61] As in the case of vinyltetrazoles, the polymerisation activity correlates with the smaller charge q_β and the smaller charge difference, $q_\alpha\ q_\beta$, of 5-isopropenyltetrazole (**2**) in comparison with 1-isopropenyltetrazole (**22**).

A comparison of kinetic and energetic characteristics of polymerisation of vinyl- and isopropenyltetrazole derivatives demonstrates a significant decrease in the activities of the latter in radical polymerisation. A 4–10-fold change in the polymerisation activity (*i.e.*, the $K_p/K_t^{0.5}$ ratio for the vinyl and isopropenyl derivatives[61]) of 5-vinyl- *vs.* 5-isopropenyltetrazole is, in general, typical of the transition from *C*-vinyl to *C*-isopropenyl compounds.[125] A change in the activity in the polymerisation of *N*-substituted vinyltetrazoles [1-vinyl- (**14a**) – 1-isopropenyltetrazole (**22**) pair] is more pronounced (see Table 4). These differences are attributed[61] to the regular changes in the electronic structures of the monomers on going from 1-vinyl- to 1-isopropenyltetrazole or from 5-vinyl- to 5-isopropenyltetrazole. Introduction of a methyl substituent into the α-position of the vinyl group both decreases the reactivities of both 5- and 1-isopropenyltetrazoles in comparison with vinyl monomers and reduces the molecular masses (MM) of the polymeric products.

b. Effect of substituents in the heterocycle on the polymerisation activities of vinyltetrazoles

Polymerisation of vinyltetrazole methyl derivatives differing in the position of the substituent in the heterocycle has been studied in the greatest detail.[43,124,128–130] Introduction of a methyl group into the tetrazole ring of 1- and 5-vinyltetrazoles does not change the character of the polymerisation of the monomers: as for unsubstituted vinyltetrazoles, the orders of the reaction with respect to the monomer and the initiator remain equal to 1 and 0.5, respectively.[43,124,128–130] However, the polymerisabilities of substituted vinyltetrazoles vary considerably. The methyl group in position 1 has virtually no effect on the activity of the monomer in comparison with unsubstituted 5-vinyltetrazole: the value of $K_p/K_t^{0.5}$ changes only insignificantly in the polymerisation in $CHCl_3$, whereas polymerisation in DMF is characterised by a slight increase in the activity despite the increase in the efficient polymerisation energies (Table 5). This does not contradict the results of quantum-chemical calculations of 5-vinyl- and 1-methyl-5-vinyltetrazole,[55] which points to the lack of the electron-donor effect of the methyl group in position 1. Moreover, the results of ^{13}C NMR studies and the values of induction and resonance constants[27,131] testify to a slight enhancement of the electron-withdrawing properties of the tetrazolyl substituent upon the introduction of the methyl group into position 1, which enhances the polymerisability of 1-methyl-5-vinyltetrazole in comparison with unsubstituted 5-vinyltetrazole.

Table 5. Kinetic parameters of the polymerisation of methyl-substituted *C*- and *N*-vinyltetrazoles (AIBN, 60 °C).

Monomer	Solvent	E_{ef} (see [a])	$K_p/K_t^{0.5}$ (see [b])	$E_p - 0.5 E_t$ (see [a])	Ref.
1-Methyl-5-vinyl-tetrazole (**5a**)	DMF	87.95	0.85	–	130
	without solvent	–	0.69	20	129
2-Methyl-5-vinyl-tetrazole (**5b**)	MeCN	81.3	0.31	19.9	43
	DMF	82.3	0.46	–	130
5-Methyl-1-vinyl-tetrazole (**14b**)	MeCN	81.8	0.21	21.3	43, 124

[a] kJ mol^{-1}; [b] $litre^{0.5}$ $(mol\ s)^{-0.5}$.

In contrast, the introduction of a methyl group into position 2 of *C*-vinyltetrazole or into position 5 of *N*-vinyltetrazole decreases the activities of methyl-substituted monomers in radical polymerisation (see Table 5). The difference in the $K_p/K_t^{0.5}$ values for the 5-vinyltetrazole – 2-methyl-5-vinyltetrazole pair is 2.2, while that for the 1-vinyltetrazole – 5-methyl-1-vinyltetrazole pair is 1.6.[43,124] Reduced activities of methyl-substituted monomers are also explicable in terms of the electronic effect of the methyl group, which being present in position 2 or 5, behaves as a potent electron donor. As a result, the electronic structures of 2- and 5-substituted monomers differ from those of unsubstituted vinyltetrazoles. This difference is more pronounced for the 5-vinyl- and 2-methyl-5-vinyltetrazole pair than for the 1-vinyl- and 5-methyl-1-vinyltetrazole pair, which probably determines the greater difference in the radical polymerisability of the former monomer pair.

The effects of substituents in the heterocycle on polymerisation activities of vinyltetrazoles have been clearly demonstrated for the polymerisation of *N*-vinyltetrazoles in water in the presence of AP.[60,84] According to kinetic data, polymerisation activities of *N*-vinyltetrazoles decrease in the following order: 1-vinyltetrazole (**14a**) > 5-methyl-1-vinyltetrazole (**14b**) > 5-amino-1-vinyltetrazole (**14d**) > 5-acetylamino-1-vinyltetrazole (**14f**) (Table 6). The changes in the activities of the first three compounds correlate with the decrease in the electron-withdrawing properties of the tetrazolyl substituent with respect to the

Table 6. Kinetic parameters of the polymerisation of *N*-vinyltetrazoles in water (AP, 60 °C).[43, 60, 84]

Monomer	E_{ef} /kJ mol^{-1}	$10^4 K_{ef}$ /litre$^{0.5}$ mol$^{-0.5}$ s^{-1}	$10^5 K_{in}$ /s^{-1}	$K_p/K_t^{0.5}$ /litre$^{0.5}$ (mol s)$^{-0.5}$	$E_p - 0.5\,E_t$ /kJ mol^{-1}	σ_I	σ_R
1-Vinyltetrazole (**14a**)	90.9	95.9	1.42	2.54	23.9	0.65	−0.33
5-Methyl-1-vinyltetrazole (**14b**)	84.3	73.3	1.29	2.09	22.2	0.64	−0.34
5-Amino-1-vinyltetrazole (**14d**)	75.2	48.0	1.46	1.46	19.0	0.59	−0.37
5-Acetylamino-1-vinyltetrazole (**14f**)	85.0	41.4	1.40	1.16	24.2	—	—

double bond (*i.e.*, σ_I and σ_R values), which results in regular changes in their electronic structures. 5-Acetylamino-1-vinyltetrazole (**14f**), the polymerisation activity of which would not differ from that of unsubstituted 1-vinyltetrazole, falls out of this series. Presumably, the presence of such a bulky substituent as NHCOMe in position 5 creates steric hindrance in the act of chain propagation. It should be noted that $K_p/K_t^{0.5}$ values depend not only on charge characteristics and σ_I and σ_R of substituents, but also on the values of polarographic reduction potentials ($E_{1/2}$) and chemical shifts of signals for β-carbon atoms of the vinyl group in ^{13}C NMR spectra.[57, 81] The dependences of $\log(K_p/K_t^{0.5})$ on σ_I, $E_{1/2}$ and $\delta(C_\beta)$ for 1-vinyl-, 5-methyl-1-vinyl- and 5-amino-1-vinyltetrazoles are linear.[84] The activity of 5-acetylamino-1-vinyltetrazole (**14f**) in polymerisation reactions is much lower than that expected based on these correlations. The reason is the aforementioned steric hindrance in the chain propagation step.

As regards their activities in radical polymerisation, vinyltetrazoles stand with methyl acrylate, acrylonitrile and acrylamide. Their high reactivities do not contradict the general concepts on the activating effect of electron-withdrawing substituents at the double bond. However, there exist other viewpoints as to high polymerisation activities of vinyltetrazoles. In terms of the chemical structures, 1-methyl-5-vinyl- and 2-methyl-5-vinyltetrazoles are considered to be similar to styrene,[128, 129] although at 40 °C $K_p/K_t^{0.5}$ values for 1-methyl-5-vinyltetrazole and 2-methyl-5-vinyltetrazole exceed that of styrene 25- (see Ref. 129) and 17.5-fold, respectively. This is explained[128] by either a significant decrease in the chain termination rate in the polymerisation of vinyltetrazoles or, alternatively,[69] by rotational isomerism of 2-methyl-5-vinyltetrazole which is absent in styrene and helps favourable orientation of the vinyl group in the chain propagation. However, the first assumption is not experimentally proved and the reason for the significant difference between the K_t values for styrene and vinyltetrazoles is unclear. The second assumption does not stand up to criticism, because despite hindered rotational isomerism of 1-methyl-5-vinyltetrazole, its reactivity is high. The most probable reason for the enhanced activity of vinyltetrazoles in comparison with styrene is higher electron-withdrawing activity of tetrazolyl substituents at the double bond compared to the phenyl group. As is known, electron-withdrawing substituents with the same degree of conjugation increase the activity of monomers in homopolymerisation.[125]

2. Effect of the nature of the solvent on radical polymerisation of vinyltetrazoles

Vinyltetrazole derivatives are related to polar (and, in the majority of cases, water-soluble) monomers. Heterocyclic substituents at the double bond contain nitrogen atoms of both 'pyrrole' and 'pyridine' types. Depending on the position of the vinyl group in the heterocycle, vinyltetrazoles manifest the properties of ionisable (unsubstituted *C*-vinyltetrazoles, such as 5-vinyl- and 5-isopropenyltetrazoles) or non-ionogenic monomers (protected *C*-vinyl- and *N*-vinyltetrazoles) because of their low basicities. However, even the latter compounds are not inert with respect to the reaction medium owing to the presence of unshared electron pairs of nitrogen atoms and an aromatic π-system of the heterocycle. This determines the existence of different interactions between the monomer and the solvent which is manifested in the polymerisation activities of vinyltetrazoles. There is evidence that self-association of 1-vinyltetrazole and 1-methyl-5-vinyltetrazole in various solvents affects the polymerisation activity of the monomers[86, 124] along with accelerating effects of water[124, 130, 132] and some low-molecular-weight additives[133] on polymerisation of vinyltetrazoles. The nature of the polymerisation medium also significantly affects the MM characteristics of the polymers synthesised. Thus MM of the polymeric products prepared in water-containing systems were found to be substantially increased.[79, 124, 130] Varying the nature of the solvent is the most efficient way to achieve control over polymerisation of vinyltetrazoles and of the effect on the structures and properties of the polymers obtained. The data listed in Table 7 confirm the important role of the solvent in the polymerisation of both the ionogenic (5-vinyltetrazole) and non-ionogenic (*C*- and *N*-vinyltetrazoles) monomers. A transition from the solvent-free polymerisation to the solution polymerisation favours, as a rule, higher yield of the polymeric product but differently affects the reactivities of the monomers. Thus the activities of 2-methyl-5-vinyltetrazole in solvent-free polymerisation and in polymerisation in chloroform were practically identical,[128] while characteristic viscosities of the polymers obtained significantly decreased with a decrease in the initial concentration of the monomer in the polymerisation system. Polymerisation in more polar solvents, especially in water, increases the activities of vinyltetrazoles and MM of the polymers formed.[43, 124] The activating effect of water is also manifested in the polymerisation in mixed solvents. The addition of water to DMF or acetonitrile causes a monotonic increase in the polymerisation rate and $K_p/K_t^{0.5}$ parameters for 5-vinyl-, 1-methyl-5-vinyl- and 2-methyl-5-vinyltetrazoles[43, 124, 130, 132] and increases the degree of polymerisation of the polymers obtained (Fig. 2). A sharp increase in $K_p/K_t^{0.5}$ was

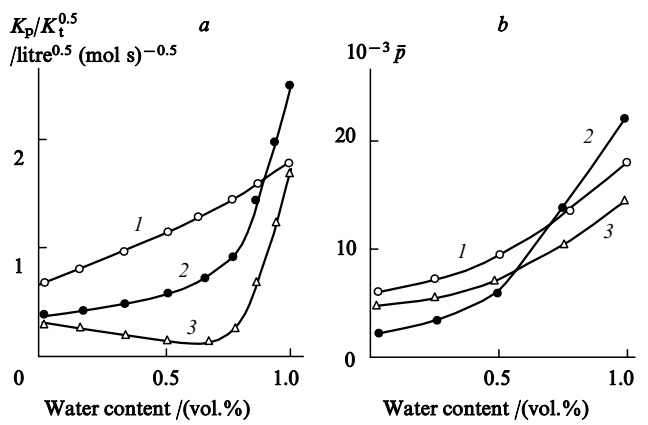


Figure 2. The dependence of the relative rate constant for chain propagation, $K_p/K_t^{0.5}$ (*a*) and the degree of polymerisation of the polymeric products ($\bar{p}$) obtained (*b*) by polymerisation of 5-vinyltetrazole (*1*), 1-vinyltetrazole (*2*) and 2-methyl-5-vinyltetrazole (*3*) on the composition of the MeCN–H_2O mixture (60 °C).[43, 124]

Table 7. The effect of the solvent on the kinetic parameters of the polymerisation of *C*- and *N*-vinyltetrazoles (60 °C).

Monomer	Solvent	E_{ef} /kJ mol^{-1}	$K_p/K_t^{0.5}$ /litre$^{0.5}$ (mol s)$^{-0.5}$	$E_p - 0.5\,E_t$ /kJ mol^{-1}	Ref.
5-Vinyltetrazole (**1**)	AcOH	–	0.65	–	43, 124
	MeCN	74.8	0.67	16.7	43, 124
	EtOH	83.3	0.90	19.4	43, 124
	H_2O	65.8	1.82	14.8	43, 124
1-Methyl-5-vinyl-tetrazole (**5a**)	without solvent	–	0.69	20.0	129
	DMF	87.95	0.85	–	130
	DMF – H_2O [a]	–	1.02	–	130
2-Methyl-5-vinyl-tetrazole (**5b**)	MeCN	81.3	0.31	19.9	43
	DMF	82.3	0.46	–	130
	DMF – H_2O [a]	85.1	0.75	–	130
	H_2O	77.6	1.86	–	43
1-Vinyltetrazole (**14a**)	MeCN	80.4	0.34	20.6	43, 124
	H_2O	90.9	2.54	23.9	43, 124
5-Methyl-1-vinyl-tetrazole (**14b**)	MeCN	81.8	0.21	21.3	43, 124
	H_2O	84.3	2.09	22.2	43, 124

Note. AIBN was used as the initiator in organic solvents; AP was used as the initiator in water. [a] Water content was 9.2 mol litre^{-1}.

observed in the AIBN-induced polymerisation of 1-vinyltetrazole and 2-methyl-5-vinyltetrazole in an H_2O – MeCN system with the water content > 0.8 vol.% (see Fig. 2 *a*).[43, 124] In aqueous solutions, the polymerisation activities of nonionogenic 2-methyl-5-vinyl-, 1-vinyl- and 5-methyl-1-vinyltetrazoles characterised by the parameter $K_p/K_t^{0.5}$ exceed those in acetonitrile 6-, 7.5- and 10-fold, respectively (see Table 7). In acetonitrile, the activities of the aforementioned monomers are lower than that of unsubstituted 5-vinyltetrazole, while the $K_p/K_t^{0.5}$ values of *N*-vinyltetrazoles in H_2O are higher than that of *C*-vinyltetrazole. Apparently, the most probable reason for enhanced polymerisation activity of non-ionogenic vinyltetrazoles in water is the increase in the concentration of the monomer in the microenvironment of the active centres of the growing macroradicals as a result of sorption of the hydrophobic monomer.[124] Selective sorption of organic monomers by polymeric coils and the resulting increase in polymerisation rates have repeatedly been observed for other water-soluble monomers.[134, 135] In water, the molecular masses of polyvinyltetrazoles formed increase severalfold (see Fig. 2 *b*).

Of special note is the effect of water on polymerisation of ionisable 5-vinyltetrazoles. The values of $K_{ef} = W[M_0]^{-1}$ and the initiation rate constant K_{in} for reactions performed in acetonitrile and water depend differently on the monomer concentration (Fig. 3).[124] The initial concentration of 5-vinyltetrazole does not affect K_{in} and K_{ef} in acetonitrile, but for polymerisation in water in the presence of AP, these constants depend on the monomer concentration. Moreover, the formal kinetic expression for the rate of polymerisation in water and the energy characteristics of the reaction depend on the monomer concentration. The classical equation $W = K[M][I]^{0.5}$ is observed only at the initial concentrations of 5-vinyltetrazole below 0.3 mol litre^{-1}. In this case, the effective activation energy, $E_{ef,}$ is equal to 65.8 kJ mol^{-1} (see Ref. 124). K_{in} and K_{ef} values increase with an increase in the initial concentration of the monomer from 0.5 to 2.0 mol litre^{-1}. The formal order of the reaction with respect to the monomer in the given concentration range is > 1, whereas the effective activation energy is 49.3 kJ mol^{-1} (see Refs 43 and 136). With these concentrations of the monomer, redox initiation involving 5-vinyltetrazole takes place.

5-Vinyltetrazole manifests the properties of a weak acid; therefore, its polymerisability, *e.g.*, expressed through the reduced polymerisation rate, depends on the pH of the reaction medium (Fig. 4).[124, 136] The maximum reaction rates and the molecular masses of the polymers formed are observed at pH values corresponding to self-dissociation of the monomer, whereas their minimum values are observed at pH close to the point of complete neutralisation of the NH-acid. Such a parallel dependence of the kinetic and molecular-mass characteristics on pH is also observed for unsaturated carboxylic acids and is determined by changes in the electronic structures of the polymerising monomers in the course of ionisation.[137]

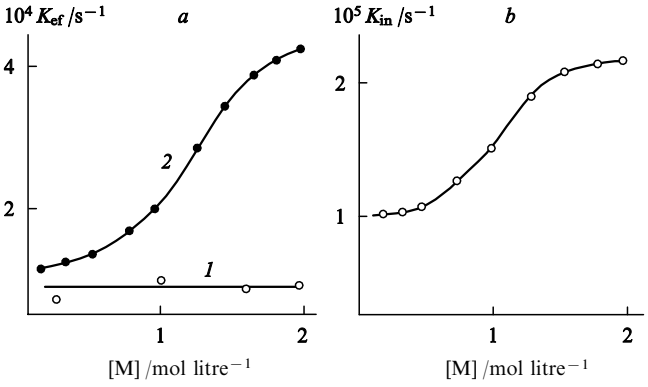


Figure 3. The dependences of the effective rate constant (K_{ef}) for the polymerisation of 5-vinyltetrazole (*a*) in acetonitrile (*1*) and water (*2*) and of the initiation rate constants (K_{in}) in water (*b*) on the concentration of the monomer (60 °C).

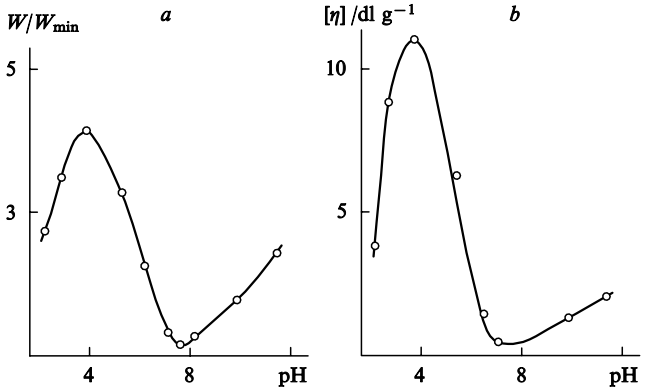


Figure 4. The pH dependence of the reduced rate constant (W/W_{min}) for the polymerisation of 5-vinyltetrazole (*a*) and the intrinsic viscosity [η] of the polymers formed (*b*) (H_2O, 60 °C).
$W_{min} = 0.13 \times 10^{-4}$ mol litre^{-1} s^{-1}. Concentrations: monomer, 0.25 mol litre^{-1}; AP, 10^{-3} mol litre^{-1}.

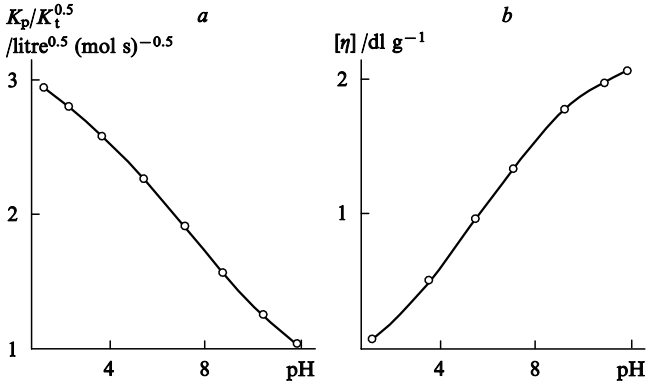
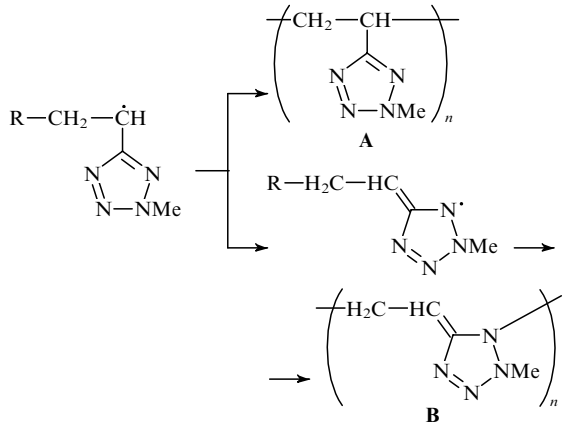


Figure 5. The effect of pH of the aqueous solution on the relative rate constant for chain propagation, $K_p/K_t^{0.5}$ (*a*) and the intrinsic viscosity [η] of the polymeric products obtained (*b*) upon polymerisation of 5-amino-1-vinyltetrazole (60 °C).

Among other *N*-vinyltetrazoles, 5-amino-1-vinyltetrazole is the most sensitive to pH changes in the course of polymerisation, which is probably related to the enhancement of the basic properties of the tetrazole ring and its ability to be protonated in acidic media. The $K_p/K_t^{0.5}$ values for this monomer increase with a decrease in pH (Fig. 5).[43] In contrast, the characteristic viscosities of the polymers formed increase with pH. The polymers synthesised at pH > 11 are insoluble.

Polymerisation of vinyltetrazoles is also affected by addition of some low-molecular-weight salts, *e.g.*, sodium thiocyanate.[133] In aqueous solutions of this salt, 1-vinyl-, 5-methyl-1-vinyl- and 2-methyl-5-vinyltetrazoles yield polymeric products of much higher molecular masses than in the absence of solvents or in organic media.

The structures of synthetic polymers also depend on the nature of the reaction medium. Under conditions of radical initiation, the polymerisation of 2-methyl-5-vinyltetrazole occurs by an isomerisation mechanism with simultaneous cleavage of the C=C bond of the vinyl group and the C=N bond of the tetrazole ring and formation of the C=C bond in the main polymeric chain.



An increase in the solvent polarity leads to the predominant formation of form **A,** while the proportion of form **B** in the final polymeric product increases in less polar solvents.

Thus, by varying the nature of the reaction medium one can gain reliable control over polymerisation of vinyltetrazoles and MM characteristics of the polymers synthesised.

3. Effect of the method of initiation on the polymerisation of vinyltetrazoles

The use of various methods of initiation for the polymerisation of vinyltetrazole derivatives allows control over polymerisation and modification of structural and molecular-mass characteristics of the polymeric products.

Polymerisation of 5-vinyl-2-methyltetrazole under conditions of anionic catalyst, BuONa, and cationic catalyst, $Ph_3C^+ClO_4^-$, initiation afforded a polymer with a high content of structures **B**.[122] The molecular masses of the polymers synthesised are $(5-50)\times10^3$, *i.e.*, by one order of magnitude lower than those of polymers prepared under the conditions of the radical initiation. In addition, ionic polymerisation leads to the opening of the tetrazole ring with cleavage of the C=N bond and formation of cross-linked structures. High-molecular-weight poly(5-vinyltetrazole) was prepared by electrochemical radical polymerisation of the monomer in water at 20 °C in the presence of potassium persulfate using a glass electrode.[121] A chelate-type polymeric complex of poly(5-vinyltetrazole) with Fe^{2+} (see Refs 138 and 139) was synthesised under analogous conditions using an iron electrode. γ-Radiation-induced polymerisation of 2-methyl-5-vinyltetrazole occurs by a radical mechanism: the reaction rate is proportional to the dose rate to the power 0.5.[119] All other factors being the same, the reactivity of the tetrazole-containing monomer in the radiation polymerisation exceeds those of styrene, acrylonitrile, methyl methacrylate and vinyl acetate.[119,140] Varying the irradiation conditions in the polymerisation of 2-methyl-5-vinyltetrazole allows preparation of polymeric products in a broad range of molecular masses $(2\times10^4-20\times10^5)$. Radiation polymerisation was accompanied by radiolytic degradation of the tetrazole ring with elimination of nitrogen.[119]

Radical polymerisation of vinyltetrazoles in the presence of initiators which enables a high degree of conversion and formation of high-molecular-weight products (MM ~ 10^6) is of particular practical interest. For the majority of monomers, the highest yields and MM were achieved by polymerisation in water in the presence of AP. In some cases, the use of redox systems permits one to increase the yields of the polymers with simultaneous reduction of the reaction time and the temperature. The increases in the reaction rates and conversion are especially pronounced in the case of 1-vinyl- and 5-methyl-1-vinyltetrazoles in the presence of redox systems in water: at 20 °C, polymerisation occurs virtually instantaneously with high self-heating and quantitative yields of the polymers.[79] In the presence of AP and BP, the polymerisation of 5-vinyltetrazole occurs even at 20 °C (where no thermolysis of the initiator occurs) and affords polymers of the highest MM.[141] The structures of tetrazole-containing monomers enable their donor–acceptor interactions with compounds containing a peroxide O—O fragment, which affects the polymerisation of vinyltetrazoles in the presence of peroxide initiators.

a. Polymerisation of 5-vinyltetrazole under the action of peroxide initiators

It was noted in one of the early papers [118] that the polymerisation of 1-methyl-5-vinyl- and 2-methyl-5-vinyltetrazoles with simultaneous grafting onto cellulose initiated by H_2O_2 is characterised by extraordinarily low values of activation energies (49.6 and 43.2 kJ mol^{-1}, respectively). This is also typical of polymerisation reactions occurring under redox initiation conditions. As mentioned above, the K_{in} and E_{ef} values for the polymerisation of 5-vinyltetrazole in water under the action of AP depend on the concentration of the monomer.[124] Obviously, the tetrazole-containing monomer is involved in the initiation step in the presence of peroxide initiators. As expected, 5-vinyltetrazole containing both nitrogen atoms with an unshared electron pair and a proton-donor NH bond interacts with the initiator the most actively.

The results of kinetic studies of the polymerisation of 5-vinyltetrazole induced by various initiators are presented in Table 8. Under conditions of thermolysis of BP, the reaction of the monomer with the initiator does not influence the polymerisation kinetics of 5-vinyltetrazole. As can be seen from Table 8, the polymerisation induced by BP under identical conditions is more energy-consuming and occurs at a lower rate than that in the presence of AIBN due to a much lower (*ca.* fivefold) initiation rate

Table 8. Kinetic parameters of the polymerisation of 5-vinyltetrazole in the presence of AIBN, BP and AP.[43, 141]

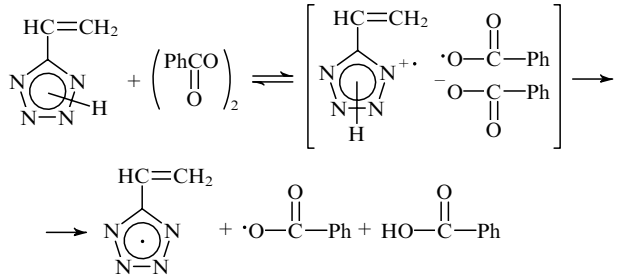
Initiator	Solvent	T /°C	Kinetic orders		E_{ef} /kJ mol^{-1}	$10^4 K_{ef}$ /litre (mol s)$^{-1}$	$10^5 K_{in}$ /s^{-1}
			[M]	[I]			
AIBN	EtOH	60	1.5	0.5	83.3	28.0	0.96
BP	EtOH	60	1.5	0.6	92.0	12.9	0.20
	EtOH	20	1.9	0.8	22.1	0.87	0.007
AP	H_2O	60	1.8	0.26	49.3	16.4	1.67
	H_2O	20	1.85	0.5	25.4	2.2	0.16

constant. Such a correlation of K_{in} for the polymerisation initiated by BP and AIBN is characteristic of vinyl monomers.[125]

A different situation is observed in the polymerisation of 5-vinyltetrazole in water at 50–70 °C in the presence of AP as the initiator. In addition to the concentration dependence of K_{in} and K_{ef} in the range of the monomer concentrations of 0.5–2 mol litre^{-1} (see Table 8), the kinetic order with respect to the monomer is increased, while the E_{ef} value is commensurate with the values of the activation energies for the reactions initiated by redox systems. In this case, K_{in} exceeds the corresponding value for the polymerisation in the presence of AIBN and BP (two- and eightfold, respectively), which ensures higher reaction rates. These data suggest the feasibility of an interaction of 5-vinyltetrazole with AP, which is manifested in the polymerisation kinetics.

Polymerisation of the vinyl monomer in the 5-vinyltetrazole–BP and 5-vinyltetrazole–AP systems occurs at the temperatures where no thermolysis of the initiators takes place.[141] The AP-induced low-temperature (10–30 °C) polymerisation of 5-vinyltetrazole in water proceeds at significantly higher rates than that in the presence of BP, which can be attributed to higher values of the initiation constant, K_{in}, for the 5-vinyltetrazole–AP system (see Table 8). This suggests that the donor–acceptor interaction of 5-vinyltetrazole with AP, which results in the formation of radicals initiating the polymerisation, proceeds more smoothly than with organic peroxides.

A mechanism of involvement of 5-vinyltetrazole in the generation of radicals initiating the polymerisation of the monomer in the presence of BP at reduced temperatures has been proposed.[43, 141]



Tetrazole derivatives are weaker electron donors than tertiary amines, therefore, 5-vinyltetrazole is less prone to donor–acceptor interactions with peroxide than, *e.g.*, alkylamines or *N*,*N*-dimethylaniline. However, the presence of an acid proton in the tetrazole ring favours decomposition of the charge-transfer complexes formed to yield radical species initiating the polymerisation. If a heterocycle contains no acid proton (*e.g.*, as in the cases of *N*-methyl- or *N*-vinyl derivatives), no polymerisation in the presence of AP or BP in aprotic solvents at 20 °C occurs. The addition of water to these systems induces polymerisation of both 2-methyl-5-vinyltetrazole and 1-vinyltetrazole. This fact points to the crucial role of the proton in reactions of tetrazole-containing compounds with AP or BP.

b. Spontaneous polymerisation of 5-vinyltetrazole

A characteristic feature of 5-vinyltetrazole is its spontaneous polymerisability in the absence of initiators at 20 °C and lower temperatures upon dissolution in water, ethanol, formamide, DMF and DMSO.[142] No spontaneous polymerisation of the monomer occurs in acetone or acetonitrile. The rate of spontaneous polymerisation of 5-vinyltetrazole and the polymer yields depend on the nature of the solvent and pH of the medium, reaching maximum values in water at pH 4.3. The logarithmic dependence of the polymerisation rate of 5-vinyltetrazole in water at 60 °C on the monomer concentration appears as:

$$\log W = (-5.79 \pm 0.05) + (1.90 \pm 0.11)\log[\mathrm{M}] .$$

The E_{ef} value for spontaneous polymerisation of 5-vinyltetrazole determined from the temperature dependence of K_{ef} [1.13×10^{-6} (at 50 °C), 1.49×10^{-6} (at 60 °C), 1.98×10^{-6} litre (mol s)$^{-1}$ (at 70 °C)] is 25.8 kJ mol^{-1} (see Refs 43 and 142), which accounts for the occurrence of this reaction at 20 °C and lower temperatures.

The molecular masses of the polymeric products synthesised by spontaneous polymerisation of 5-vinyltetrazole in water do not depend on the initial concentrations of the monomer and are commensurate with those of poly(5-vinyltetrazole) specimens prepared by initiator-induced polymerisation.

VII. Copolymerisation of vinyltetrazoles

Copolymerisation, like chemical modification, is used for changing physicochemical, physicomechanical, chemical and other properties of polymeric compounds as well as for conferring novel properties that are sometimes atypical of homopolymers. Vinyltetrazole derivatives are promising starting compounds for the synthesis of novel polymeric products by copolymerisation with other vinyl monomers. The activities of vinyltetrazoles in copolymerisation reactions allow easy variation of the composition, and, correspondingly, properties of the polymeric products obtained.

An analysis of results of copolymerisation studies involving vinyltetrazoles should be started from the consideration of reactivities of vinylazoles, which are thought to depend on the number of nitrogen atoms in the heterocycle.

An analysis of a vast body of experimental (often, contradictory) data on copolymerisation of vinylazoles[53, 54, 143–158] revealed that these compounds manifest lower activities in the copolymerisation with standard comonomers, such as styrene and methyl methacrylate (MMA). At the same time, an increase in the number of nitrogen atoms in the heterocycle of vinylazoles, which enhances the π-electron-withdrawing effect of the azolyl substituent on the double bond, is accompanied by enhancement of activities of vinylazoles in the reaction with a macroradical having a terminal styrene fragment.[53] In the copolymerisation with MMA, an opposite trend is observed.[158] In our opinion, the most correct approach to the study of structure–activity relationships of vinylazoles in copolymerisation was proposed by Smirnov *et al.*[54, 144] Thus for the *N*-vinylazole—diethyl maleate (DEM) and *N*-vinylazole–1-vinylpyrrolidone (VPD) systems, the activities of the monomers in the reaction of vinylazoles with the DEM radical are the higher the higher is the polarity of the C=C bond and the negative charge of the β-carbon atom of the vinyl group of the vinylazole. In contrast, the activities of vinylazoles in the reaction with the VPD radical increase with a decrease in polarity

Table 9. Constants of copolymerisation of vinyltetrazoles with other vinyl monomers in the presence of AIBN.

Vinyltetrazole	r_1	Comonomer	r_2	Solvent	Temperature /°C	Ref.
5-Vinyltetrazole (**1**)	0.29 ± 0.05	acrylic acid	0.67 ± 0.11	DMF	60	159
	2.93 ± 0.23	vinyl acetate	0.07 ± 0.03	DMF	60	160
	0.44 ± 0.03	*N*-vinylpyrrolidone	0.30 ± 0.07	DMF	60	150
	0.44 ± 0.09	maleic acid	0.21 ± 0.02	DMF	60	161
	0.61 ± 0.18	2-methyl-5-vinyltetrazole	0.52 ± 0.16	acetonitrile	60	162
	0.31 ± 0.02	styrene	0.78 ± 0.03	DMF	60	152
	0.36 ± 0.04	"	0.97 ± 0.03	DMF	–	63
5-Isopropenyltetrazole (**2**)	0.37 ± 0.02	*N*-vinylpyrrolidone	0.27 ± 0.05	DMF	60	154
	0.27 ± 0.01	"	0.10 ± 0.02	ethanol	60	154
	3.60 ± 0.50	"	0.25 ± 0.08	water (pH 2.3)	60	154
	0.70 ± 0.11	1-vinyltetrazole	1.78 ± 0.28	DMF	60	163
	0.90 ± 0.07	maleic acid	0.13 ± 0.06	DMF	60	161
	0.42 ± 0.02	styrene	0.45 ± 0.04	DMF	60	161
1-Methyl-5-vinyl-tetrazole (**5a**)	0.99 ± 0.04	acrylonitrile	0.068 ± 0.05	DMF	60	156
	2.12 ± 0.07	"	0.013 ± 0.01	DMF	60	164
	0.98 ± 0.06	methyl methacrylate	0.64 ± 0.06	DMF	60	53
	1.36 ± 0.06	2-methyl-5-vinyltetrazole	0.65 ± 0.05	DMF	65	165
	0.50 ± 0.07	"	0.49 ± 0.03	without solvent	65	164
	0.57 ± 0.07	styrene	0.28 ± 0.09	DMF	60	157
	0.86 ± 0.02	"	0.48 ± 0.04	DMF	65	164
	0.18 ± 0.03	chloroprene	2.94 ± 0.5	chloroform	60	155
2-Methyl-5-vinyl-tetrazole (**5b**)	0.22 ± 0.01	acrylonitrile	0.37 ± 0.07	DMF	60	156
	2.39 ± 0.20	"	0.07 ± 0.03	without solvent	65	153
	2.18 ± 0.18	"	0.02 ± 0.01	aqueous emulsion [a]	40	153
	1.49 ± 0.08	butyl methacrylate	0.51 ± 0.05	without solvent	–	166
	2.5	vinyl acetate	0.1	water [a, b]	–	167
	23.0	"	0.01	chloroform	65	86
	0.52 ± 0.16	5-vinyltetrazole	0.61 ± 0.18	acetonitrile	60	162
	0.76 ± 0.07	"	0.49 ± 0.03	DMF	65	63
	0.59 ± 0	hydroxyethyl methacrylate	0.54 ± 0.03	without solvent	65	153
	0.19 ± 0	glycidyl methacrylate	1.04 ± 0.06	chloroform	60	153
	0.60 ± 0	methacrylic acid	1.0 ± 0.12	acetone	60	153
	0.65 ± 0.05	1-methyl-5-vinyltetrazole	1.36 ± 0.06	DMF	65	165
	0.49 ± 0.03	"	0.50 ± 0.07	without solvent	65	164
	0.48	methyl methacrylate	1.0	chloroform	65	86
	0.51 ± 0.02	"	1.47 ± 0.07	without solvent	–	166
	0.77	styrene	1.18	chloroform	65	86
	0.64	"	1.07	without solvent	65	27
	0.08 ± 0.02	chloroprene	10.76 ± 0.8	chloroform	65	155
2-Ethyl-5-vinyl-tetrazole (**5c**)	0.83	styrene	1.04	without solvent	65	27
2-Isopropyl-5-vinyl-tetrazole (**5d**)	0.64	"	0.99	the same	65	27
	0.37	methyl methacrylate	1.01	"	65	27
2-*tert*-Butyl-5-vinyl-tetrazole (**5e**)	0.53	styrene	1.12	"	65	27
	0.43	methyl methacrylate	1.05	"	65	27
1-Vinyltetrazole (**14a**)	0.34 ± 0.01	acrylonitrile	0.57 ± 0.05	DMF	65	149
	0.23	*N*-vinylpyrrolidone	0.03	without solvent	60	54
	9.55	diethyl maleate	0.19	the same	60	54
	1.78 ± 0.28	5-isopropenyltetrazole	0.70 ± 0.11	ethanol	60	163
	0.29 ± 0.01	methyl methacrylate	6.68 ± 0.09	DMF	65	149
	0.20 ± 0.02	styrene	3.74 ± 0.09	DMF	65	149
5-Amino-1-vinyl-tetrazole (**14d**)	0.95	butyl methacrylate	1.04	DMF	–	168
	1.24 ± 0.10	vinyl acetate	0.55 ± 0.06	DMF	60	160
	0.15	*N*-vinylpyrrolidone	0.78	DMF	–	168
	0.69 ± 0.07	"	0.51 ± 0.05	DMF	60	150
	0.83 ± 0.05	maleic acid	0.27 ± 0.05	water [c]	60	161
	0.23	methacrylic acid	1.30	DMF	–	168
	0.42 ± 0.05	styrene	1.20 ± 0.05	DMF	60	151
2-Isopropenyl-5-methyltetrazole	0.72 ± 0.09	methyl methacrylate	1.19 ± 0.15	without solvent	65	63
	0.32 ± 0.01	styrene	1.19 ± 0.02	the same	65	63

[a] The redox system $Fe^{2+} - H_2O_2$. [b] Graft copolymerisation onto cellulose. [c] In the presence of AP.

and q_β. Thus, the activities of *N*-vinylazoles in reactions with electron-withdrawing radicals (DEM and MMA) decrease with an increase in the number of nitrogen atoms in the heterocycle, while those in reactions with donor radicals (VPD) increase. This

suggests that the activity of *N*-vinyltetrazole is the lowest (compared to those of other vinylazoles) in the copolymerisation with electron-withdrawing monomers and the highest in the copolymerisation with electron-donating monomers. However, the *N*-vinylazole – styrene system does not fit into this series. The activities of vinylazoles in the reaction with a macroradical containing a terminal styrene unit characterised by parameter $1/r_2$ (where r are effective relative activity constants) decrease in the following order: 1-vinylimidazole [0.1 (see Ref. 145)] < 1-vinyltetrazole [0.27 (see Ref. 149)] < 1-vinyl-1,2,4-triazole [0.67 (see Ref. 148)].

C-Vinyltetrazoles are more reactive in copolymerisation with styrene and MMA than *N*-vinyl derivatives (Table 9); their activities depend critically on the presence and positions of substituents in the molecule of the monomer. The presence of a methyl group in the vinyl fragment or in position 1 of *C*-vinyltetrazole changes the reaction pattern so that 5-isopropenyltetrazole is as active as styrene in the copolymerisation and the activity of 1-methyl-5-vinyltetrazole exceeds those of styrene and MMA (see Table 9). 2-Methyl-5-vinyltetrazole is less reactive towards the styrene radical ($1/r_2 = 0.84$)[86] than unsubstituted 5-vinyltetrazole ($1/r_2 = 1.28$).[152] In this case, the size of the alkyl substituent in position 2 does not affect the activities of the monomers in the copolymerisation.[27]

The interest of investigators in tetrazole-containing polymers has long been determined by the possibility of technological applications of these high-energy compounds. However, the properties of polymers based on tetrazole are very diverse owing to the presence of several reactive sites in the tetrazole ring. In some copolymers of vinyltetrazoles with other vinyl monomers, these properties are more pronounced. For this reason, copolymerisation reactions hold especially great promise in the synthesis of novel tetrazole-containing polymeric materials of practical importance.

VIII. Practical applications of vinyltetrazole derivatives

Despite diverse properties of vinyltetrazoles and their polymeric derivatives, their practical applications are not an issue of broad discussion. In this section we consider the prospects of practical applications of vinyltetrazoles.

Vinyltetrazoles present interest for organic synthesis as intermediates. They were used in the synthesis of tetrazole-containing bromohydrins,[94] epoxytetrazoles,[94] hydroxyethyltetrazole,[19] aziridine derivatives,[97] 2-(tetrazol-5-yl)bicyclo[2.1.2]hept-5-ene and 2-methyl-5-vinyl-1,3,4-oxadiazole.[21] The approaches to the synthesis of 5-iodo- and mercury-substituted vinyltetrazoles[48] have been outlined and the possibility of alkylation of 5-vinyltetrazole under electrophilic conditions has been demonstrated.[32] Various functionalised derivatives based on 5-chloromethyl-1-vinyltetrazole have been synthesised; for some of them biological activity is anticipated.[41] As vinyltetrazoles can easily form complexes with metal ions including Ni^{2+} and Pd^{2+}, it may be expected that these complexes will manifest catalytic activity in hydrogenation reactions.[101]

The construction of novel polymeric materials endowed with unique properties on the basis of tetrazole derivatives is the most promising line of research. High-energy characteristics of tetrazole polymers, their relatively low sensitivity to shock and friction, rather high thermal stability, low toxicity and evolution of a large volume of neutral gas upon decomposition make polymers and copolymers based on vinyltetrazoles promising components for gunpowders, explosives and propellants.[1, 14–20, 28] The majority of published papers confirm the fact that tetrazole-containing polymers used in various fuel systems differ favourably from analogous polymeric materials in enhanced intrinsic energy, good compatibility with other composition components and handling safety.

Meanwhile, other properties of vinyltetrazole-containing polymers are currently attracting the attention of investigators. Thus ternary copolymers of 2-methyl-5-vinyltetrazole with acrylic acid and its esters were recommended as components of rubber compositions possessing high mechanical characteristics.[169] Preparation of a film-forming substance for cosmetics based on hydroxyethylammonium salt of poly(5-vinyltetrazole) has recently been claimed.[170] A copolymer of 2-methyl-5-vinyltetrazole with 1-vinylpyrrolidone, methyl methacrylate and α,ω-hexamethacryloyl oligoacrylate has been recommended for the production of vision correcting lenses.[171] A cellulose acetate composition comprising polyvinyltetrazole can be used for the preparation of ultrafiltration membranes.[172] A copolymer of 2-methyl-5-vinyltetrazole with *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride has been patented as a film-forming substance possessing semiconducting and antistatic properties.[173] Graft copolymerisation of 2-methyl-5-vinyltetrazole was recommended to improve absorption properties of cotton and cellulose fibres.[174] A copolymer of butyl acrylate with acrylonitrile and 5-vinyltetrazole can be used as a polymeric binder of operating layers of magnetic storage media and an adhesive.[175] Taking into consideration high complex-forming ability of polyvinyltetrazoles with respect to heavy metal ions in aqueous media,[43, 176–178] it may be expected that these polymers will find use as efficient sorbents for the solution of various environmental problems or for the isolation of precious metals. Sodium salt of poly-5-vinyltetrazoles forms hydrogel compositions in the presence of Cr^{3+} ions; this polymer has been patented as a thickening agent in water-filled explosives.[179, 180]

The results of studies of physiological activities of tetrazole-containing polymers are promising, which opens new opportunities for the preparation of novel medicinal drugs based on them.

Unsubstituted poly-*C*-vinyltetrazoles manifest acidic properties and enter into interpolymeric reactions with natural high-molecular-weight compounds, which determines their anticoagulant properties.[181, 182] The anticoagulant activity can be varied significantly by combining structural fragments of vinyltetrazoles with other comonomers in the polymeric chain.[183, 184] Quaternary salts of polyvinyltetrazoles exert an opposite effect: they bind heparin in the circulating blood and thus favour blood coagulation.[185] The antiheparin activity of tetrazole-containing polycations compares favourably with that of currently employed medicinal drugs. Sodium salt of poly(5-vinyltetrazole), a polyelectrolyte endowed with pronounced antiinflammatory and aseptic properties, accelerates wound healing and suppresses cicatrisation.[43, 186, 187]

Tetrazole-containing polyelectrolytes manifest pronounced, sometimes extraordinarily high, immunoadjuvant activity towards a vast range of antigens.[183, 188–190] Homo- and copolymers of poly-5-vinyl- and poly-5-isopropenyltetrazoles were recommended for the construction of antigenic diagnostic preparations surpassing in activity those currently in practice.[191–194]

Thus, the broad spectrum of properties of vinyltetrazole-based polymers leaves hope that these compounds will soon find application in miscellaneous areas of human activity. In our opinion, studies aimed at the preparation of tetrazole-containing monomers and polymers will eventually lead to reduction of their production costs, which is undoubtedly important for the practical application of these novel products.

* * *

This review deals with generalisation of the known methods for the synthesis of *C*- and *N*-vinyltetrazole derivatives based on the formation of the tetrazole ring from open-chain compounds containing a vinyl group and formation of an unsaturated fragment in the preformed heterocycle. Some of these methods have been implemented in the flexible production system 'Tetrazoles' designed and launched at the pilot plant of St Petersburg State

Technological Institute (the Engineering and Design Department 'Tekhnolog', Russian Federation).

An analysis of structures and geometry of vinyltetrazole molecules, generalisation of their physicochemical and spectral properties and study of mutual effects of the two unsaturated fragments, *viz*., the vinyl group and the heterocycle, make it possible to predict chemical properties of these compounds in addition reactions involving the vinyl group as well as in alkylation, quaternisation, complexation, *etc*.

The radical polymerisability of vinyltetrazoles is one of their most essential features. A detailed analysis of effects of various factors (monomer structure, reaction medium, initiation procedure, *etc*.) on the polymerisation of vinyltetrazoles allows development of novel polymeric materials. Pilot-plant production of polyvinyltetrazoles has been started in two enterprises in Russia. A broad spectrum of valuable properties of vinyltetrazoles and their polymers leaves hope that this class of compounds will find application in various branches of science and technology.

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