Copolymerization of *C*-Vinyltriazoles and *C*-Vinyltetrazole with Vinyl Monomers

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SUMMARY:
The copolymerizations of 4(5)-vinyl-1,2,3-triazole, 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole and 2-methyl-5-vinyltetrazole with styrene, methyl methacrylate and vinyl acetate have been examined and the corresponding copolymerization parameters r_1, r_2 were evaluated. The reactivities Q of these monomers are lower than that of styrene contrarily to other *C*-vinylheterocyclic monomers; it is assumed that it results from a limited stabilization of the corresponding radicals. In the case of 4(5)-vinyl-1,2,3-triazole, copolymerizations carried out at different temperatures and varied monomer concentrations show that intermolecular monomer association (as evidenced by NMR and IR measurements) does neither affect the copolymer composition nor the internal monomer triad structure of the copolymer.

The free radical copolymerization of two *C*-vinyltriazoles, namely 4(5)-vinyl-1,2,3-triazole (**1**) and 1-*p*-bromophenyl-4-vinyl-1,2,3-triazole (**2**) and of 2-methyl-5-vinyl-tetrazole (**3**) has been examined with styrene, methyl methacrylate and vinyl acetate in order to study the influence of several ring-nitrogen atoms on the reactivity of the *C*-vinyl group.

For monomer **1** with an hydrogen substituted nitrogen atom the influence of molecular association upon its copolymerization behaviour has also been examined[1-3].

1	**2**	**3**
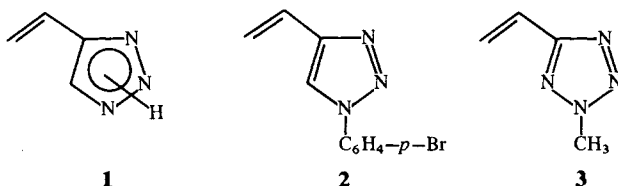
Experimental Part

4(5)-Vinyl-1,2,3-triazole (**1**) was obtained by the Wittig reaction of methylenetriphenylphosphorane with 4(5)-formyl-1,2,3-triazole[4] which itself resulted from the cycloaddition of hydrogen azide[5] with 2-propynal (propargyl aldehyde)[6]: To a fresh solution of methylenetriphenylphosphorane (0,2 mol) in dimethyl sulfoxide[7] a saturated solution of 4(5)-formyl-1,2,3-triazole (0,1 mol) in dimethyl sulfoxide is added under stirring. The addition is exothermic, and the solution is further heated at 85 °C for 17 h. After cooling, the solution is poured onto crushed ice. The precipitated triphenylphosphine oxide is filtered off, and the

filtrate is neutralised with 2 M HCl, extracted several times with diethyl ether; the extracts are dried over anhydrous magnesium sulfate. After evaporation of the ether the oily residue was distilled under reduced pressure of nitrogen in the presence of hydroquinone; yield 28% of **1**; b.p. 64 – 66 °C/0,05 mmHg.

$C_4H_5N_3$ (95,04)	Calc.	C 50,52	H 5,30	N 44,18
	Found	C 49,96	H 5,32	N 43,60

IR (KBr): 3 155 (C—H triazole ring), 1 645 cm^{-1} (C=C vinyl bond).

^{1}H NMR (CDCl$_3$, TMS, 100 MHz): δ = 5,38 (1 vinyl H, dxd, ^3J = 11 Hz, ^2J = 2 Hz); 5,85 (1 vinyl H, dxd, ^3J = 18 Hz, ^3J = 2 Hz); 6,74 (1 vinyl H, dxd, ^3J = 18 Hz, ^2J = 11 Hz); 7,80 (1 triazole H, s); 14,90 (NH, broad signal).

1-p-Bromophenyl-4-vinyl-1,2,3-triazole (**2**) was prepared by condensation of p-bromophenyl azide[8] with *trans*-1-diethylamino-1,3-butadiene[9], followed by diethylamine elimination from vinyltriazoline in alkaline medium[10].

2-Methyl-5-vinyl-tetrazole (**3**) was prepared following the method of Finnegan et al.[11] by dehydrohalogenation of 5-(2-chloroethyl)-N-methyltetrazole.

Solvents: N,N-dimethylformamide was dried over polyphosphoric acid and distilled under reduced pressure of nitrogen. Chloroform was dried over calcium chloride and distilled twice.

Comonomers were purified by repeated distillation.

Copolymerizations were carried out at 65 °C in presence of azodiisobutyronitrile (AIBN) (10^{-2} mol·l^{-1}) as initiator; the total concentration of monomers was 2 mol·l^{-1}. For copolymer solubility reasons, copolymerizations of **1** and **2** with styrene and methyl methacrylate were carried out in dimethylformamide; the other experiments were carried out in chloroform.

Copolymer compositions were determined by elemental analysis for nitrogen or bromine.

Experimental results are given in Tab. 1. Reactivity ratios r_1 and r_2 were calculated by the Fineman-Ross method[12] as illustrated in Fig. 1 using the following relation:

$$\frac{F_1(f_1 - 1)}{f_1} = \frac{F_1^2}{f_1} r_1 - r_2$$

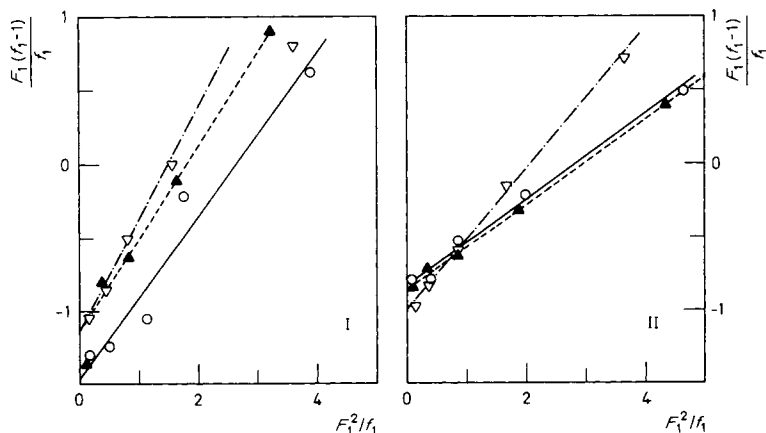where F_1 and f_1 are the mole ratios [M$_1$]/[M$_2$] and [m$_1$]/[m$_2$], respectively.

Fig. 1.   Fineman-Ross diagrams for radical copolymerization of C-vinylazoles with I: styrene, II: methyl methacrylate; (○): 4(5)-vinyl-1,2,3-triazole (———), (▲): 1-p-bromophenyl-4-vinyl-1,2,3-triazole (– – –), (▽): 2-methyl-5-vinyl-tetrazole (– · – · –)

Homopolymerization of **1** was carried out in dimethylformamide at 65 °C in the presence of AIBN as initiator and absence of oxygen (repeated thawing/freezing cycles). The rate of polymerization was followed dilatometrically; the data are represented in Fig. 2.

Fig. 2. Rate of polymerization R_p of 4(5)-vinyl-1,2,3-triazole. Influence of the initiator ($\bullet$) and monomer ($\circ$) concentration; $T = 65\,°C$; solvent: dimethylformamide
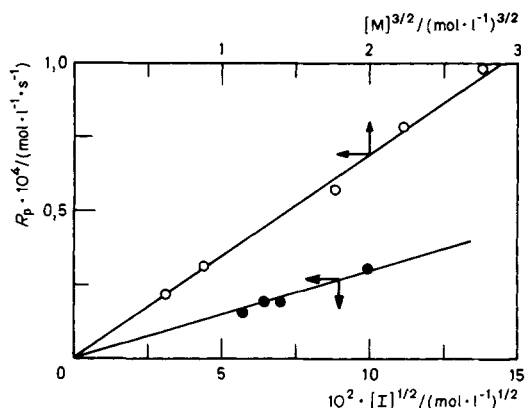
Discussion

Fig. 3 represents the copolymerization diagrams; the curves indicate the copolymer compositions as calculated from the r_1 and r_2 reactivity ratios. The values of r_1 and r_2 as well as the e and Q Alfrey-Price parameters[13] are given in Tab. 2.

From these data it is evident that both C-vinyltriazoles **1** and **2** and C-vinyltetrazole **3** behave similarly in copolymerization towards styrene and methyl methacrylate. With this latter, the tendency of **3** for monomer alternation is, however, less pronounced than for **1** and **2**. Towards vinyl acetate, monomers **2** and **3** behave also similarly, and the incorporation of vinylacetate is very limited. The significance of the calculated high Q-values on the basis of these copolymerizations is very questionable.

N-substitution in C-vinyltriazoles and introduction of an additional nitrogen atom in the ring (tetrazole) has very little effect, if any, on vinyl group reactivity. From the point of view of Q values, the monomers are less reactive than styrene, on the contrary with several other C-vinyl hetero-aromatic monomers, where the presence of the heteroatom increases the reactivity of the vinyl bond. These monomers are often characterized by Q values higher than unity (styrene), and introduction of a second ring-heteroatom further increases monomer polymerisability[14-16].

Reactivity is, however, strongly affected by ring structure and vinyl group position, as shown by the values of Tab. 3, and must be correlated with the resonance stabilisation of the corresponding radicals, and more quantitatively with the localisation energy or resonance stabilisation energy between attacking radical and the monomer, as shown by some authors[14,17].

In the case of 4-vinyl-1,2,3-triazoles and 2-methyl-5-vinyltetrazole, the resonance stabilisation of the corresponding radicals is indeed limited and comparable to 4-vinylthiazole and isopropenylisoxazole reported in Tab. 3. On this basis, higher

Tab. 1. Copolymerization of C-vinylazoles (M_1) with styrene (ST), methyl methacrylate (MMA), and vinyl acetate (VOAc)[a]
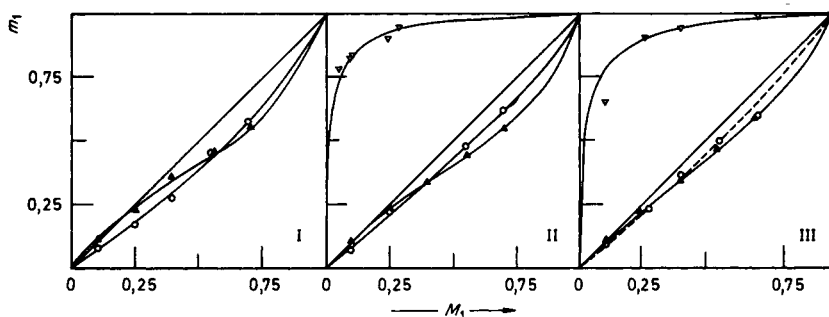
| Comonomer M_2 | Monomer M_1 | | | | | | | | | | | |
| | 4(5)-vinyl-1,2,3-triazole (1) | | | | 1-p-bromophenyl-4-vinyl-1,2,3-triazole (2) | | | | 2-methyl-5-vinyl-tetrazole (3) | | | |
	M_1	yield in %	% N	m_1	M_1	yield in %	% Br	m_1	M_1	yield in %	% N	m_1
ST	0,11	15,8	3,27	0,08	0,099	4,54	4,94	0,071	0,112	5,6	5,12	0,096
ST	0,25	8,62	7,19	0,175	0,250	5,3	13,19	0,226	0,270	6,7	12,3	0,232
ST	0,399	7,40	11,55	0,279	0,398	15,0	17,66	0,339	0,402	7,00	19,11	0,363
ST	0,549	5,20	19,24	0,458	0,551	7,4	22,00	0,479	0,555	9,1	26,14	0,50
ST	0,698	13,8	24,56	0,578	0,697	10,9	25,51	0,622	0,700	9,1	31,36	0,603
MMA	0,108	7,7	4,92	0,116	0,099	3,2	7,29	0,106	0,109	8,5	5,56	0,10
MMA	0,259	7,03	9,94	0,234	0,248	8,1	14,16	0,241	0,249	9,0	12,34	0,226
MMA	0,401	12,1	15,42	0,361	0,398	8,5	17,95	0,339	0,402	7,4	18,74	0,347
MMA	0,566	12,5	19,8	0,461	0,552	7,3	21,35	0,446	0,547	10,5	25,08	0,47
MMA	0,707	12,8	23,98	0,551	0,697	7,5	24,04	0,548	0,697	10,5	31,28	0,592
VOAc					0,049	7,0	15,33[b]	0,781	0,109	13,6	35,78	0,65
VOAc					0,097	19,0	15,69[b]	0,829	0,259	9,7	46,9	0,903
VOAc					0,102	11,2	15,72[b]	0,833	0,407	6,1	48,67	0,946
VOAc					0,196	16,2	16,17[b]	0,898	0,60	12,8	46,43	0,892
VOAc					0,284	16,5	16,48[b]	0,946	0,703	8,9	50,78	1,00

a) M_1, m_1: mole fractions of C-vinylazoles in the monomer mixtures and in the copolymer, resp.
b) Nitrogen content.

Tab. 2.   Reactivity ratios and e-Q parameters of C-vinyltriazoles and C-vinyltetrazole

M_1	M_2	r_1	r_2	$r_1 r_2$	e_1	Q_1
4(5)-Vinyl-1,2,3-triazole	ST	0,55	1,44	0,79	− 0,32	0,47
(1)	MMA	0,29	0,83	0,24	− 0,8	0,55
1-p-Bromophenyl-4-	ST	0,67	1,24	0,84	− 0,38	0,57
vinyl-1,2,3-triazole	MMA	0,29	0,84	0,24	− 0,79	0,54
(2)	VOAc	≈ 39,0	0,07	0,27	− 1,34	4,6
2-Methyl-5-vinyltetrazole	ST	0,77	1,18	0,91	− 0,49	0,66
(3)	MMA	0,48	1,00	0,48	− 0,46	0,53
	VOAc	≈ 23,0	0,01	0,23	− 1,4	3,2

Fig. 3.   Copolymerization of 4(5)-vinyl-1,2,3-triazole (1), 1-p-bromophenyl-4-vinyl-1,2,3-triazole (2), and 2-methyl-5-vinyltetrazole (3) with styrene (○), methyl methacrylate (▲), and vinyl acetate (▽); M_1, m_1: mole fractions of C-vinylazoles in feed and in copolymer, resp.

Tab. 3.   Reactivity of C-vinyl-heteroaromatic monomers. Influence of vinyl structure and vinyl group position

Monomer[a]	Q-value	Ref.
2-Isopropenyl-4,5-dimethyloxazole	2,86	[18]
4-Isobutyl-2-isopropenyl-5-methyloxazole	4,36	[14]
2-Isopropenyl-5-methylisoxazole	0,89	[14]
2-Vinylthiazole	3,53	[15]
4-Vinylthiazole	0,81	[15]

[a]   Comonomer is styrene.

reactivities might be expected for other isomers of C-vinylazoles studied here, i. e.: 5-vinyl-1,2,3-triazole and 1-methyl-5-vinyltetrazole.
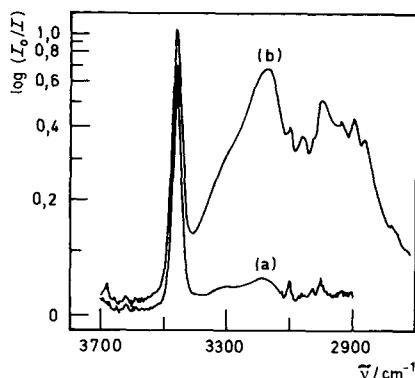
Fig. 4. IR absorption of 4(5)-vinyl-1,2,3-triazole (1) in carbon tetrachloride; $T = 30\,°C$; conc. $= 0,0065$ mol $\cdot$ l^{-1} (a) and 0,031 mol $\cdot$ l^{-1} (b)
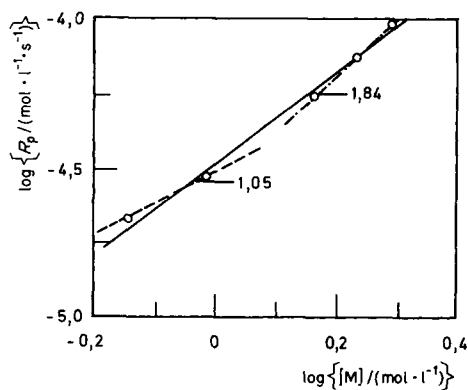

Fig. 5. Dependence of the logarithm of the rate of polymerization of 4(5)-vinyl-1,2,3-triazole (1) on monomer concentration (numbers give slopes of dashed lines)

Monomer association vs. copolymerization

Special attention was devoted to the eventual influence of molecular association of 4(5)-vinyltriazole (1) on the copolymer composition. IR spectrometry of 1 in carbon tetrachloride solution shows indeed a fine absorption band at $3\,465$ cm^{-1} ($\varepsilon_0 = 380$ l $\cdot$ mol^{-1} $\cdot$ cm^{-1}), attributed to the free N—H vibration, as it is also the case for imidazole and pyrazole. The broader absorptions between $2\,700$ and $3\,400$ cm^{-1} correspond to the associated N—H—N vibrations of the oligomers (Fig. 4) and decrease strongly on dilution. Using the classical method of Mecke-Kempter[19] or the more accurate one of Coggeshall and Saier[20] one finds an average association constant of 35 and 39 l $\cdot$ mol^{-1}, respectively, for cyclic aggregates. If one assumes linear or branched oligomers, the method of Lassettre[21] permits to evaluate a K_2 association constant of 62 l $\cdot$ mol^{-1} against 60 for unsubstituted triazole[3].

This intermolecular association persists even in dimethylformamide solution as described previously on the basis of ^{1}H NMR and ^{13}C NMR measurements[22,23]. Moreover, polymerization kinetics of 1 obey following rate equation

$$R_P = \text{const} \cdot [\text{Init}]^{0,5} \cdot [M]^a$$

in which the exponent a increases noticeably with increasing monomer concentration (averaging to about 1,5) and also points to molecular association of the monomer (Fig. 5).

Due to molecular association, incorporation of monomer **1** in a growing polymer chain could be affected as suggested below, since close proximity of vinyl groups in a dimer of **1** might cause rapid reaction of the second monomer once the first has reacted.
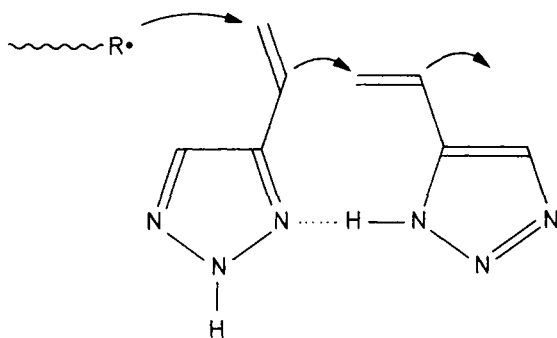
C-vinyl-1,2,3-triazole (**1**) dimer

If this assumption was correct, variations of monomer concentration and temperature would affect incorporation of **1** in a copolymer, together with comonomers sequence distribution.

However, it was found experimentally that copolymers of **1** with either styrene or methyl methacrylate do not differ in their analytical compositions, neither in their triad monomer distribution (as followed by ^{1}H NMR) by increasing copolymerization temperature (50 – 65 – 75 °C) or by varying the total monomer concentration (1, 2 and 3 mol $\cdot$ l^{-1}) at same mole ratio $M_1/M_2 = 2/3$ ($M_1 = 1$).

Copolymers of **1** with methyl methacrylate at various total monomer concentration and same mole ratio did not show the presence of monomer **1** triads that could have been formed by monomer **1**-dimer addition to a monomer **1**-radical terminated copolymer chain. Furthermore, overall triads distribution (both monomer **1** and methyl methacrylate centered) was found to be independent on monomer concentrations.

Therefore, it must be concluded that molecular association of *H*-triazole rings does not affect the copolymerization of monomer **1**, at least in our experimental conditions.

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