Copolymerization of 1-Vinyltetrazole with Vinyl Monomers

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INTRODUCTION

Recently, there has been ever increasing interest in the reactivity and features of polymerization of vinyltetrazoles as intermediate products in the synthesis of polymer materials having complex useful properties.[1-3] The polymerization of *N*-vinyltetrazoles has not been studied. It is only reported that 1-vinyltetrazole derivatives give insoluble and nonfusible homopolymers.[4]

For the first time, the free radical copolymerization of 1-vinyltetrazole (VT) with styrene, methyl methacrylate, and acrylonitrile has been studied in the present paper.

EXPERIMENTAL

VT was synthesized by interaction of tetrazole with vinylacetate[5] and purified by distillation *in vacuo* (bp 94–95°C 1 mm Hg, n_D^{20} 1.5003).

^{1}H-NMR (CDCl$_3$, TMS, 100 MHz), δ = 5.46 (1 vinyl H, CH$_2$-*cis*, J_1 = 15.0 Hz, J_2 = 2.2 Hz); 6.09 (1 vinyl H, CH$_2$-*trans*, J_1 = 8.8 Hz, J_2 = 2.2 Hz); 7.50 (1 vinyl H, —CH=, J_1 = 8.8 Hz, J_2 = 15.0 Hz); 9.42 (1 H, CH-rings).

^{13}C-NMR (CD$_3$OD, TMS, 90.56 MHz), δ = 109.86 (CH$_2$=), 127.86 (—CH=), 142.72 (C rings).

IR (thin layer) cm^{-1}; 1085 (ν, δ-rings), 1639 ($\nu_{C=C}$), 3125 ($\nu_{CH\ rings}$).

The commercially obtained styrene, methyl methacrylate and acrylonitrile were purified by usual methods and their purity was checked by thin-layer chromatography.

The copolymerization was carried out in glass ampoules under argon atmosphere at 65 ± 0.1°C in the presence of azodiisobutyronitrile (10^{-2} mol L^{-1}), purified by crystallization from ethanol (mp 102°C). For copolymer solubility reasons, copolymerization were carried out in dimethylformamide, purified by distillation with benzene and water.[6] The total concentration of monomers amounted to 2 mol L^{-1}. The polymerization was stopped by chilling the solution and pouring it into a large amount of methanol. Copolymers were collected by filtration, washed with methanol, and dried to constant weight at 50°C/1 mm Hg.

Copolymer compositions were determined from the data of an elemental analysis for nitrogen. Experimental results are given in Table I. The reactivity ratios of copolymerization were calculated by the Fineman–Ross method[7] according to the equation

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

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TABLE I
Copolymerization of 1–Vinyltetrazole (M_1) with Styrene (ST), Methyl Methacrylate (MMA), and Acrylonitrile (AN)

Comonomer M_2	M_1	% N	m_1	Yield (%)	$F_1 = M_1/M_2$	$f_1 = m_1/m_2$	$f_1 = (F_1/f_1)(f_1 - 1)$	F_1^2/f_1	Correlation coefficient
ST	0.209	3.81	0.065	7.6	0.264	0.070	−3.51	1.00	0.988
	0.304	6.00	0.103	11.1	0.438	0.115	−3.37	1.67	
	0.395	8.52	0.146	5.4	0.652	0.171	−3.16	2.49	
	0.493	11.35	0.195	2.1	0.972	0.242	−3.05	3.90	
	0.589	14.88	0.255	4.2	1.431	0.343	−2.74	5.97	
	0.696	21.01	0.360	5.9	2.285	0.563	−1.77	9.27	
MMA	0.197	2.15	0.037	14.3	0.246	0.038	−6.22	1.59	0.999
	0.395	5.49	0.094	8.5	0.652	0.104	−5.62	4.09	
	0.595	11.98	0.206	7.2	1.467	0.259	−4.20	8.31	
	0.692	17.06	0.293	9.1	2.250	0.414	−3.19	12.23	
	0.794	25.26	0.433	5.3	3.854	0.765	−1.18	19.42	
AN	0.197	34.51	0.254	17.2	0.245	0.340	−0.48	0.18	0.996
	0.288	36.81	0.326	12.5	0.404	0.483	−0.43	0.34	
	0.386	38.30	0.373	16.1	0.627	0.594	−0.43	0.66	
	0.491	41.36	0.468	11.6	0.965	0.881	−0.13	1.06	
	0.581	42.24	0.496	8.3	1.387	0.985	−0.02	1.95	
	0.692	45.40	0.595	12.0	2.248	1.470	0.72	3.44	
	0.795	47.78	0.670	11.1	3.833	2.028	1.97	7.44	

The calculations of electronic and molecular structure of VT were done with a semiempirical SCF method in MNDO approximation[8] using the QCPE program.

RESULTS AND DISCUSSION

According to the calculations, the VT molecule has practically a planar preferential geometric structure (Fig. 1) and is characterized by the carbon vinyl α-atom having no steric hindrance. The distribution of charges in the cycle is such that the first and the fourth nitrogen atoms have a maximum electron density, the effective nitrogen atom charge in position 1 being somewhat higher. It is evidently influenced by the vinyl bond polarization under the effect of the electron cycle system. Thus, the 1-tetrazolyl radical exhibits strong electron-acceptor property. It is evidenced by the Hammett induction constant σ_I value for the 1-tetrazolyl group, calculated from the data on acidity of the 1-tetrazolylacetic acid that amounts to 0.65.[9]

Alternately, due to the aromaticity of a tetrazole ring[10] the 1-tetrazolyl group can behave as an electron donor at the expense of a conjugation effect. To evaluate the conjugation effect on the vinyl group reactivity, the Taft resonance constant, σ_R, expressing the conjugation effect contribution into the Hammett constant, has been estimated. In calculations, a correlation relation was applied. It correlates the difference in the values of chemical shifts of a terminal carbon atom in vinyl monomer and ethylene groups with induction and resonance constants of a substituent linked to the vinyl group:[11]

$$\Delta\delta C_\beta = 11.9\sigma_I + 63.5\sigma_R$$

The value calculated from the ^{13}C-NMR spectroscopic data for the 1-tetrazolyl group amounts to -0.33. The value obtained is close to σ_R found for
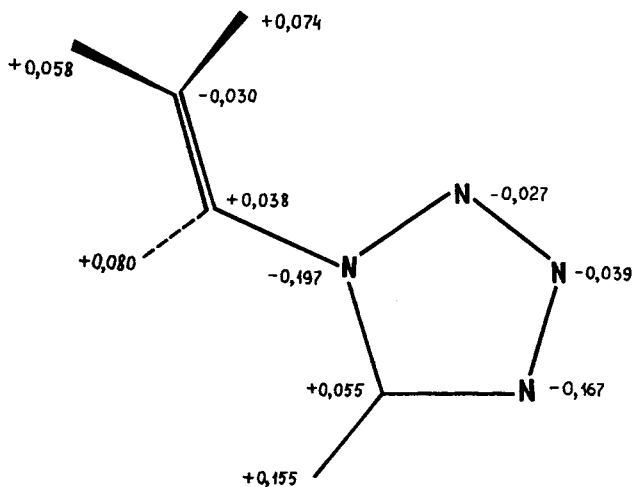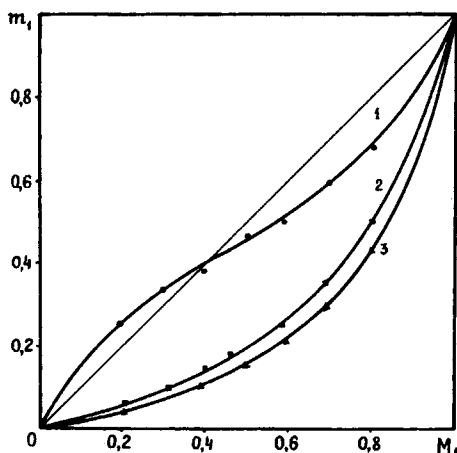

Fig. 1. Electron structure of 1-vinyltetrazole.

Fig. 2. Copolymer composition of 1-vinyltetrazole (M_1) with acrylonitrile (1), styrene (2), and methyl methacrylate (3) vs. the monomer mixture composition.

other N-azolyl groups, the 1,2,4-triazolyl group, in particular.[12] This suggests that in radical copolymerization the 1-vinyltetrazole will behave like other N-vinylazoles that are characterized by a lower activity in copolymerization with styrene and methyl methacrylate. So, the value of $r_1 = 0.1 \pm 0.02$; $r_2 = 10 \pm 0.2$ and $r_1 = 0.03 \pm 0.1$, $r_2 = 4.1 \pm 0.02$[13] are founded for the pairs of 1-vinylimidazole–styrene and 1-vinylimidazole–methyl methacrylate at 60°C; and for the system 1-vinyl-1,2,4-triazole–styrene and 1-vinyl-1,2,4-triazole–methyl methacrylate at 60°C, the reactivity ratios are $r_1 = 0.62 \pm 0.02$, $r_2 = 1.48 \pm 0.08$ and $r_1 = 0.32 \pm 0.08$, $r_2 = 1.43 \pm 0.1$ correspondingly.[12]

Figure 2 presents the composition of VT copolymers with styrene, methyl methacrylate, and acrylonitrile versus the starting monomer mixture. The reactivity ratios of the comonomer pairs studied are given in Table II. The Alfrey–Price parameters for VT are calculated from the data obtained. The results confirm the above suggestions of a lower VT activity in copolymerization with styrene, methyl methacrylate, and acrylonitrile.

In addition, the electron density distribution in the neighborhood of carbon atoms of the vinyl group (Fig. 1) shows that the VT has to exhibit a sufficiently high activity in polymerization by the cationic mechanism.

TABLE II

Copolymerization Constants and the Alfrey–Price Parameters for Copolymerization of VT with Styrene, Acrylonitrile, and Methyl Methacrylate

M_1	M_2	r_1	r_2	Q	e
1-Vinyl	ST	0.20 ± 0.02	3.74 ± 0.09	0.17	-0.26
tetrazole	AN	0.34 ± 0.01	0.57 ± 0.05	0.23	-0.08
	MMA	0.29 ± 0.01	6.68 ± 0.09		

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