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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

The Reactivity of 1-Vinyl-1,2,4-triazole in the Radical Copolymerization with Crotonic Aldehyde

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Abstract—Copolymerization of 1-vinyl-1,2,4-triazole with crotonic aldehyde under the conditions of free-radical initiation has been studied. 1-Vinyl-1,2,4-triazole was found to be more reactive than crotonic aldehyde. The composition and structure of copolymers were determined by the elemental analysis, IR and quantitative ^{13}C NMR spectroscopy. New polyfunctional water-soluble copolymers possessing thermostability up to 300°C were obtained.

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Designing of multifunctional polymer materials with a complex of valuable properties is a promising and state-of-the-art direction of scientific research, which is governed by the necessity of the development of high technologies [1, 2]. When designing biologically active compounds and materials for high technologies, a great attention is paid to vinylazoles and (co)polymers on their basis [3, 4]. An example of polyvinylazoles with a complex of valuable properties is poly-(1-vinyl-1,2,4-triazole) possessing good solubility in water and polar organic solvents, readily regulated molecular mass, chemical and thermal stability, ability to complex formation, biocompatibility [5]. Copolymers of 1-vinyl-1,2,4-triazole also possess valuable properties [5]. Homo- and copolymers of 1-vinyl-1,2,4-triazole show a high stabilizing ability upon the formation of water-soluble nanocomposites with metal nanoparticles [6–9].

The attention of researchers is drawn to polymers containing various functional groups (carboxylic, ketone, aldehyde, etc.), which are promising for elaboration of medical and biological materials [2, 10–15]. However, the data on copolymerization of vinyl azoles with unsaturated aldehydes are lacking.

In the present study we have investigated the radical copolymerization of 1-vinyl-1,2,4-triazole with crotonic aldehyde and established the structure and properties of new water-soluble copolymers. Free-radical copolymerization of 1-vinyl-1,2,4-triazole with crotonic aldehyde proceeds with the opening of the double bonds of the monomers and the formation of copolymers of various composition.

Copolymers were obtained in 7–46% yield (Table 1); they are white powders with intrinsic viscosity of 0.04–0.50 dl g^{-1}, readily soluble in water and DMF. The yield of copolymers **I, II, IV, V** increases with time. The copolymers are enriched with the units of 1-vinyl-1,2,4-triazole regardless of the conditions of the reaction. The increase in the content of crotonic aldehyde in the starting mixture notably decreases the yield of the copolymer and drastically decreases its viscosity, which is due to a low reactivity of the aldehyde. The increase in the time of copolymerization increases the number of the units of crotonic aldehyde in copolymers.

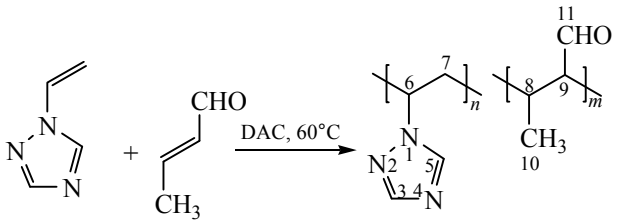


Table 1. Parameters of free-radical copolymerization of 1-vinyl-1,2,4-triazole (M_1) with crotonic aldehyde (M_2), yields, composition, and intrinsic viscosity of copolymers **I–VIII**

Co-polymer	Ratio of the monomers in the reaction mixture $[M_1]$:$[M_2]$, mol%	Time, h	Composition of copolymer $[m_1]$:$[m_2]$,[a] mol%	[η], dl g^{-1}	Yield, %
I	80:20	16	82:18	0.50	46
II	80:20	4	93:7	0.46	32
III	65:35	60	88:12	0.21	39
IV	50:50	80	82:18	0.13	32
V	50:50	20	87:13	0.11	24
VI	35:65	80	81:19	0.08	10
VII	20:80	80	56:44	0.05	8
VIII	20:80	20	72:28	0.04	7

[a] From the data of elemental analysis.

The composition and chemical structure of the obtained copolymers were determined by the IR, ^{13}C NMR spectroscopy, and elemental analysis. In the IR spectra of the copolymers of 1-vinyl-1,2,4-triazole with crotonic aldehyde the band of the double bond stretching vibrations at 1654 cm^{-1} is lacking; the bands appear corresponding to the stretching and bending vibrations of the triazole cycle (3110, 1505, 1434, 1275, 1139, 1003, 662 cm^{-1}) and the units with the aldehyde group at 1716 cm^{-1}.

In the ^{13}C NMR spectra the intense signals of the carbon atoms of the triazole ring [144.8–140.8 ppm (C^3), 153.4–151.5 ppm (C^5)], methine [59.5–51.0 ppm (C^6)] and methylene groups [43.0–40.9 ppm (C^7)] are observed. The atoms of comonomer (crotonic aldehyde) resonate at (δ_C, ppm): 205–201 (C^{11}), 37.5–33.5 (C^8), 50.0–46.5 (C^9), 12.6–10.0 (C^{10}) [16, 17]. The reaction of copolymerization is proved by strongly broadened overlapping signals of the carbon atoms of the CH groups in the α-position with respect to the nitrogen atom of the triazole ring (~57.8 ppm). The integral intensity of these signals is equal to the integral intensity of the carbon atoms of the aldehyde and methylene groups of the crotonic aldehyde which entered the reaction of copolymerization (δ_C 205–201 and 50.0–46.5 ppm, respectively).

Table 2. The content of the elements and composition of copolymers calculated by quantitative analysis of the ^{13}C NMR spectra

Co-polymer	Content of the elements, wt %			Composition of copolymer $[m_1]$:$[m_2]$, mol %
	N	C	H	
I	39.08	52.75	6.73	85:15
III	40.98	51.19	6.43	90:10
IV	39.56	51.96	6.55	86:14
VI	38.20	51.89	6.41	82:18

The composition of the obtained copolymers was calculated from the data of elemental analysis (Table 1) and by the use of the method of quantitative ^{13}C NMR spectroscopy [18] (Table 2). The results obtained by the two methods are in good agreement and suggest that all the synthesized copolymers are enriched by the units of 1-vinyl-1,2,4-triazole.

To estimate the relative reactivity of the monomers of 1-vinyl-1,2,4-triazole and crotonic aldehyde in the free-radical copolymerization we have calculated the copolymerization constants at low conversions using the least square method and the Fineman–Ross [19] and the Kelen–Tudos equations [20]. To this end we have additionally performed the reactions with the conversion of the comonomers not exceeding 8% (Table 3). The calculated values of the constants of copolymerization are r_1 2.05±0.23 for 1-vinyl-1,2,4-triazole and r_2 0.001 for crotonic aldehyde and are indicative of a higher reactivity of 1-vinyl-1,2,4-triazole with respect to crotonic aldehyde. That is why the copolymers obtained under different conditions (the ratio of the monomers, the time of the reaction), are enriched with the units of 1-vinyl-1,2,4-triazole (Table 2). The observed lowering of viscosity of copolymers and the decrease in their yield (Table 1) with the increase of the content of the aldehyde in the starting mixture of the monomers, apparently, results from the low activity of crotonic aldehyde due to the termination of the chain by degradational transfer of the chain to the monomer. As in the case of polymerization of allyl monomers, the labile H atoms of crotonic aldehyde at the α-position to the double bond result in the formation of the resonance-stabilized unreactive macroradical, which inhibits the free-radical

copolymerization of 1-vinyl-1,2,4-triazole and crotonic aldehyde. A similar effect was observed when studying copolymerization of crotonic aldehyde with vinylpyrrolidone [15].

The behavior of the obtained copolymers upon heating was studied by the method of thermogravimetric analysis using the quadruple mass-spectrometer (see the figure). In the course of thermal decomposition of copolymers three successive stages of thermooxidative destruction are observed. The first stage (100–215°C) is followed by the loss of 24% of the mass of the sample and the endothermic effect caused by elimination of the physically bound water, as indicated by the peak with *m*/*z* 18 in the mass spectrum. The second stage is realized in the interval 215–475°C and is followed by an exothermic effect with the loss of 52.8% of the mass of the sample due to the elimination and oxidation of the aldehyde and methyl groups from the units of crotonic aldehyde, as well as decomposition of the triazole ring to fragments with subsequent oxidation to H_2O, CO_2, and NO_2. This is confirmed by the presence of the peaks of ions with *m*/*z* 18, 44, 46 in the mass spectrum. The third stage is characterized by two overlapping exothermic peaks. The first peak (475–630°C) is followed by the loss of 36.9% of mass due to the deep decomposition of the sample with the predominant formation of CO_2, NO_2, H_2O, as indicated by the peaks with *m/z* 44, 46, 18 in the mass spectrum. The second less intense peak (630–650°C) is followed by the loss of 6.2% of the mass of the sample and is due to the burning out of the carbon backbone with the predominant formation of CO_2 with mass 44.

Therefore, new functionalized copolymers containing the triazole and aldehyde groups with a wide range of the compositions and intrinsic viscosity were obtained by free-radical polymeriztion of 1-vinyl-1,2,4-triazole with crotonic aldehyde. According to the data of elemental analysis and quantitative ^{13}C NMR spectroscopy in the macromolecules of copolymers prevail the units of vinyltriazole (56–93 mol %), which demonstrates a higher reactivity as compared with crotonic aldehyde. The obtained copolymers are soluble in water, possess high thermal stability, and are promising for the development of new materials for medical use.

EXPERIMENTAL

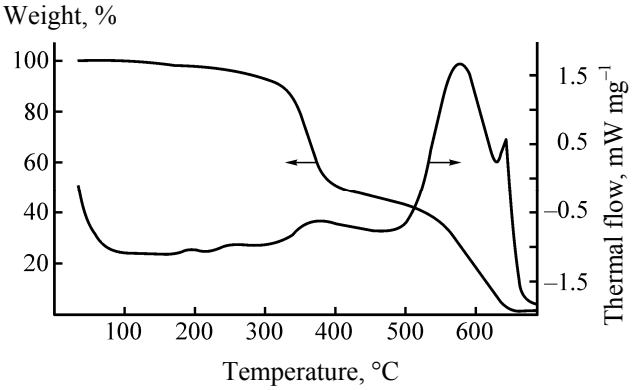
IR spectra were recorded on a Bruker IFS 25 spectrometer in KBr pellets in the range 400–4000 cm^{-1}.

Table 3. Parameters of free-radical copolymerization of 1-vinyl-1,2,4-triazole (M_1) with crotonic aldehyde (M_2) for calculation of the constants of relative activity of the monomers

Ratio of the monomers in the reaction mixture $[M_1]$:$[M_2]$, mol%	Yield, %	*N*, wt %	Composition of copolymer $[m_1]$:$[m_2]$,[a] mol%
80:20	7.5	40.96	91:9
65:35	6.3	39.11	85:15
50:50	5.5	37.18	80:20
35:65	4.0	34.27	72:28
20:80	3.4	33.98	71:29

[a] From the data of elemental analysis.

The ^{13}C NMR spectra were registered on a Bruker DPX 400 spectrometer at working frequency of 100.4 MHz in DMSO-d_6 solution. Chromium trisacetylacetonate (0.02 M) was used as a relaxant. Quantitative calculations were performed as described in [18]. Elemental analysis was performed on a Thermo Finnigan gas analyzer. The intrinsic viscosity of copolymers was measured using the Ubbelohde viscometer at 25°C in 0.1 M aqueous solution of NaCl by the method of dilution. Thermograms of the samples were taken on a Netzsch STA 449 Jupiter derivatograph with the rate of heating of 10 deg min^{-1} in the flow of air to 700°C, mass of the sample 5 mg. The copolymerization constants were calculated by the methods of Fineman–Ross [19], Kelen–Tudos [20] and the data of the



TG and DTA curves of the copolymer of 1-vinyl-1,2,4-triazole and crotonic aldehyde.

composition of copolymers determined from the mass fraction of nitrogen (conversion of the monomers did not exceed 8%).

1-Vinyl-1,2,4-triazole was obtained by the method described in [21]; fraction with bp 41–42°C (2 mm Hg), n_D^{20} 1.5100 was used. Crotonic aldehyde was purified by double distillation, bp 104°C, n_D^{20} 1.4366. Radical initiator, azoisobutyronitrile (AIBN), and the solvents were purified by the known procedures [22].

Synthesis of copolymers of 1-vinyl-1,2,4-triazole with crotonic aldehyde I–VIII. The copolymerization of vinyltriazole with crotonic aldehyde was carried out in bulk under the conditions of free-radical initiation with 3 wt % of AIBN in sealed tubes in an argon atmosphere at 60°C during 80 h. The ratio of the monomers in the reaction mixture was varied from 0.80:0.20 to 0.20:0.80 mol. fractions. Copolymers were isolated by double reprecipitation from the DMF solution into the mixture of ethanol with acetone (1:2), dried in vacuum to constant mass at 50°C.

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