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Synthesis and Properties of Carbon-Chain Polymers with Pendant 1,3,4-Oxadiazole Rings

V. N. Kizhnyaev, A. F. Pokatilov, L. I. Vereshchagin, L. V. Adamova, A. P. Safronov, and A. I. Smirnov

Irkutsk State University, Irkutsk, Russia
Ural State University, Yekaterinburg, Russia

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Abstract—Carbon-chain polymers with 1,3,4-oxadiazole rings were prepared by radical polymerization and polymer-analogous transformations. The kinetic relationships of the polymerization of vinyl-1,3,4-oxadiazole monomers and some properties of the resulting polymers were studied. The thermodynamics of interaction of poly-2-vinyl-5-methyl-1,3,4-oxadiazole, a nonionic water-soluble polymer, with water was examined.

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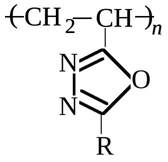
Macromolecular compounds containing 1,3,4-oxadiazole rings in the backbone are widely used as chemically stable and heat-resistant, semiconducting, fiber-forming, and gas-separating materials [1, 2]. The main routes to these polymers, including commercial procedures, involve polycondensation of bifunctional heterocyclic compounds or formation of the 1,3,4-oxadiazole ring in a macromolecule of a polymeric precursor. At the same time, available data on vinyl derivatives of oxadiazoles, on their polymerization, and on the properties of carbon-chain polymers with pendant 1,3,4-oxadiazole rings are scarce and concern the synthesis of vinyl-1,3,4- and vinyl-1,2,4-oxadiazoles, and also the use of polyvinyl-1,2,4-oxadiazoles for preparing heat-resistant fibers [1, 3–5]. Recently we studied the polymerization of vinyl monomers with 1,3,4-oxadiazole rings [6].

This paper deals with the synthesis of poly-2-vinyl-5-R-1,3,4-oxadiazoles



[R = CH_3 (**I**), Ph (**II**), CF_3 (**III**), C_9H_{19} (**IV**)] by radical polymerization of the corresponding vinyl monomers and by polymer-analogous transformations of the macromolecular precursor, poly-5-vinyltetrazole (PVT), and with the properties of the resulting carbon-chain polymers containing pendant 1,3,4-oxadiazole rings.

EXPERIMENTAL

2-Vinyl-5-methyl-1,3,4-oxadiazole was prepared in one step from 5-vinyltetrazole as described in [4]; yield ~80%. 2-Vinyl-5-phenyl-1,3,4-oxadiazole was prepared in two steps. First 5-vinyltetrazole was acylated with benzoyl chloride in the water–toluene system at room temperature in the presence of a phase-transfer catalyst. Then the organic phase was separated and heated to 368–373 K to decompose the benzoyl derivative of vinyltetrazole. After the gas evolution ceased, the solvent was removed and the residue was subjected to fractional distillation. Yield of the target product ~70%. 2-Vinyl-5-trifluoromethyl-1,3,4-oxadiazole was prepared by mixing equimolar amounts of 5-vinyltetrazole and trifluoroacetic anhydride in methylene chloride at room temperature. After the reaction completion, the solvent was removed and the product was isolated by vacuum distillation (yield ~95%). The constants of the synthesized vinyl monomers purified by column chromatography on alumina are given in Table 1. The purity of the compounds was checked by NMR, IR, and UV spectroscopy. The kinetic relationships of the polymerization of the vinyl monomers were studied by the procedure described in [6].

The synthesis of poly-2-vinyl-5-R-1,3,4-oxadiazoles **I**–**IV** by polymer-analogous transformations

Table 1. Characteristics of 2-vinyl-5-R-1,3,4-oxadiazoles

R	bp, K (*P*, kPa)	n_D^{20}	*d*, g cm^{-3}
CH_3	314 (1.33)	1.4905	1.12
CF_3	313 (20.0)	1.3945	1.32
Ph	395 (1.33)	1.5885	1.17

involved the reaction of PVT with acetic anhydride, trifluoroacetic anhydride, benzoyl chloride, and decanoyl chloride, respectively, in pyridine or dimethylformamide (DMF) on heating. As in the case of the monomers, the reaction completion was judged from the cessation of evolution of gaseous nitrogen from the reaction mixture. The resulting polyvinyloxadiazoles were precipitated with diethyl ether, washed with the precipitant, and vacuum-dried to constant weight. The degree of conversion of the tetrazole fragments into oxadiazole fragments was calculated from elemental analysis data (Table 2).

The reaction of polyvinyloxadiazole **I** with formamide was performed by heating a solution of the polymer in excess formamide at 348 K in an argon flow for 5 h with continuous stirring. The resulting poly-3-vinyl-5-methyl-1,2,4-triazole was precipitated by pouring the reaction mixture into a mixture of acetone and diethyl ether, washed with the precipitant, and vacuum-dried to constant weight. The degree of conversion of the oxadiazole fragments into triazole fragments was about 97% according to ^{13}C NMR and elemental analysis of the resulting polymer.

The reaction of **I** with aniline was performed in polyphosphoric acid at 358–363 K in an argon flow for 7–8 h with continuous stirring. The resulting poly-3-vinyl-4-phenyl-5-methyl-1,2,4-triazole was precipitated by pouring the reaction mixture into water, reprecipitated from DMF into diethyl ether, and vacuum-dried to constant weight. The degree of conversion of oxadiazole fragments into triazole fragments was 95% according to ^{13}C NMR and elemental analysis of the resulting polymer.

Complexes of polyvinyloxadiazole **I** with metal salts were prepared by combining the solutions of the polymer and salt in appropriate solvent at room temperature with stirring. The precipitates of the metal complexes were washed with water, filtered off, and vacuum-dried to constant weight. The compositions of the products were determined by elemental analysis.

For thermodynamic studies of the interaction with water, we used nonfractionated, thoroughly dried in a vacuum, samples of polymer **I** prepared both by radical polymerization ($M = 6 \times 10^5$) and by polymer-analogous transformations ($M = 1.7 \times 10^5$). The isothermal sorption of water vapor with the polymer samples at 298 K was studied gravimetrically using highly sensitive quartz spirals [7]. The sorption isotherms were expressed in the coordinates $x/m = f(p/p_s)$, where x is the amount of water vapor absorbed by the polymer sample of weight m, and p/p_s is the relative water pressure. The Gibbs energies of mixing Δg_m were calculated from the sorption isotherms of water vapor [8]. The integral heat of solution of the polymers in water and the integral heat of dilution of polymer solutions of given concentration in a large amount of the solvent were determined with a DAK-1-1-A microcalorimeter. The mean specific enthalpies of mixing Δh_m and the mean entropies of mixing Δs_m were calculated by the procedure suggested in [9].

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-500 spectrometer, and the IR spectra, on a Specord M80 spectrometer. The molecular weights of the polymer samples were determined by small-angle light scattering with an FSR laser photometer (Russia). The thermograms of the polymers were recorded on an MOM derivatograph (Hungary) in the dynamic mode at a heating rate of 5 deg min^{-1}. The

Table 2. Conditions and results of the synthesis of poly-2-vinyl-5-R-1,3,4-oxadiazoles **I**–**IV** by the modification of poly-5-vinyltetrazole (PVT). Molar ratio PVT : acylating agent = 1 : 5

Polyvinyl-oxadiazole	Acylating agent	Solvent	τ, h	*T*, K	Nitrogen content in reaction product, %		Conversion, %
					calculated	found	
I	$(CH_3CO)_2O$	Pyridine	2	373	28.07	25.45	91
II	PhC(O)Cl	″	2	393	17.01	16.28	97
III	$C_9H_{19}C(O)Cl$	″	1	373	13.42	12.61	96
IV	$(CF_3CO)_2O$*	DMF	0.5	318	18.81	17.07	93

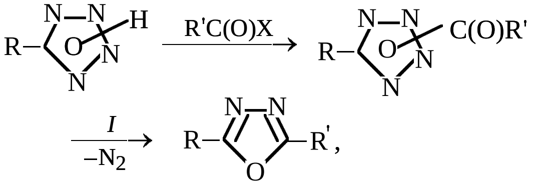
* Molar ratio PVT : acylating agent = 1 : 1.5.

Table 3. Kinetic parameters of the polymerization of 1-vinyl-5-R-1,3,4-oxadiazoles (acetonitrile, AIBN, 333 K)

R	E_{app}	$E_p - 0.5E_0$	$k_{app} \times 10^5$, $l^{0.5}$ $mol^{-0.5}$ s^{-1}	$K_i \times 10^5$, s^{-1}	$k_p/k_0^{0.5} \times 10^2$, $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$
	kJ mol^{-1}				
CH_3	95.1	29.7	25.4	1.4	0.068
CF_3	88.5	21.0	76.5	1.3	0.21
Ph	109.3	35.2	1.8	1.1	0.0055

viscosities of polymer solutions were measured with an Ubbelohde viscometer at 273 K.

The synthesis of the monomeric and polymeric compounds containing 1,3,4-oxadiazole rings is based on the recyclization at elevated temperatures of unstable acylated derivatives of tetrazole into the oxadiazole ring with the release of gaseous nitrogen:



where R = CH_2=CH–, –(CH_2–CH–)$_n$–; X = Cl, O(O)CR'.

The starting compound can be 5-vinyltetrazole or its polymer. In the first case, the reaction yields monomeric vinyl derivatives of substituted 1,3,4-oxadiazoles, and in the second case, carbon-chain polymers with pendant 1,3,4-oxadiazole rings. A distinctive feature of the reaction with trifluoroacetic anhydride as acylating agent is that the transformation of the tetrazole ring into the 1,3,4-oxadiazole ring occurs virtually quantitatively at room temperature in the case of the synthesis of the vinyl monomer and at 313–318 K in the case of the modification of the polymeric precursor. In all the other cases, the similar transformation of the azole ring requires heating to 373–393 K.

As shown in [6], vinyl derivatives of 1,3,4-oxadiazole are very active in radical polymerization and form polymeric products of high molecular weights in high yields. The kinetic relationships of the radical polymerization of 2-vinyl-5-methyl-, 2-vinyl-5-phenyl-, and 2-vinyl-5-trifluoromethyl-1,3,4-oxadiazoles do not differ from those found previously for vinyl derivatives of azoles containing only nitrogen heteroatoms in the ring [10–13]. In the polymerization of all the three monomers in acetonitrile under the action of AIBN, the reaction order with respect to the initiator concentration is 0.5, and with respect to the monomer concentration, 1.0. As expected, the highest activity in the radical polymerization is exhibited by the monomer containing in the 1,3,4-oxadiazole ring an acceptor trifluoromethyl group. For 2-vinyl-5-trifluoromethyl-1,3,4-oxadiazole, the parameter $k_p/k_0^{0.5}$ used as a criterion of the monomer activity in radical polymerization is by a factor of 3 higher than for 2-vinyl-5-methyl-1,3,4-oxadiazole (Table 3). In turn, the latter monomer is by an order of magnitude more active than the vinyloxadiazole with the phenyl substituent in the ring. The energy consumption in the chain propagation step (the quantity $E_p - 0.5E_0$) regularly increases with a decrease in the monomer activity parameter. The fact that 2-vinyl-5-trifluoromethyl-1,3,4-oxadiazole is the most active in the polymerization among the compounds studied is well consistent with the typical trend noted previously for vinylazoles [14]: an increase in the activity of monomers in radical polymerization with an increease in the electron-withdrawing power of the heterocyclic substituent at the vinyl group.

The lower reactivity in polymerization of phenyl-substituted vinyloxadiazole compared to the methyl-substituted monomer is attributable to the steric effect of the bulky phenyl substituent or to the lower reactivity of the radical center due to additional delocalization of the unpaired electron. Comparison of the kinetic parameters of the polymerization of vinyl 1,3,4-oxadiazole derivatives (Table 3) with those reported for another *C*-vinylazole, 2-methyl-5-vinyltetrazole ($k_p/k_0^{0.5} = 0.31$ $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$ [14]), shows that the oxadiazole monomers are less reactive in the polymerization, which is consistent with the stronger electron-withdrawing power of the tetrazolyl substituent compared to the oxadiazolyl substituent. 2-Vinyl-5-methyl-1,3,4-oxadiazole is a water-soluble monomer, and water exerts a strong accelerating effect on its polymerization. In aqueous solution, the activity parameter of the monomer increases by a factor of 18 ($k_p/k_0^{0.5} = 1.24$ $l^{0.5}$ $mol^{-0.5}$ $s^{-0.5}$ [6]) compared to the polymerization in acetonitrile (Table 3), and the

Table 4. Solubiity and decomposition points of polyvinyloxadiazoles

Polymer	Solvent	Softening point, K	Decomposition onset point, K
I	DMF, DMSO, acetone, acetonitrile, ethanol, acetic acid, 1,2-dichloroethane, water	478	622
II	DMF, DMSO, CH_2Cl_2	483	603
III	DMF, DMSO, acetonitrile, acetic acid	460	585
IV	1,2-Dichloroethane, benzene, dioxane	–	579

molecular weights of the resulting polymers increase. Whereas the molecular weight of samples of polyvinyloxadiazole **I** prepared in acetonitrile is within $(1–7) \times 10^5$, in an aqueous solution it is possible to prepare polymer samples with M as high as 4×10^6.

Spectroscopic studies of the polymers show that the polymer backbone is formed exclusively by opening of the vinyl double bonds, without involvement of the heterocyclic fragments. Polyvinyloxadiazoles **I**–**V** prepared by the polymer-analogous transformation from PVT have a similar structure. The absorption bands of the 1,3,4-oxadiazole ring at 1250, 1350, 1530, and 1580 cm^{-1} remain unchanged in the spectrum of the polymers prepared by various procedures. A minor distinctive feature of the spectra of the polymers prepared by the modification to a conversion less than 95% is the presence of a broad absorption band at 2250–3700 cm^{-1} corresponding to the vibrations of the residual N–H groups in the unsubstituted tetrazole rings [15]. The ^1H NMR spectra of polyvinyloxadiazoles **I** and **II** prepared by various procedures are similar in the shape and position of signals of the methyl (δ 2.4 ppm) and phenyl (δ 7.2–7.6 ppm) groups. Protons of the nonyl substituent in the spectra of **IV** give four signals at δ 0.9 (CH_3), 1.32, 2.02, and 3.25 ppm (CH_2). The CF_3 groups in the ^{13}C NMR spectra of samples of **III** prepared by different procedures give a quartet at 113.0–119.5 ppm.

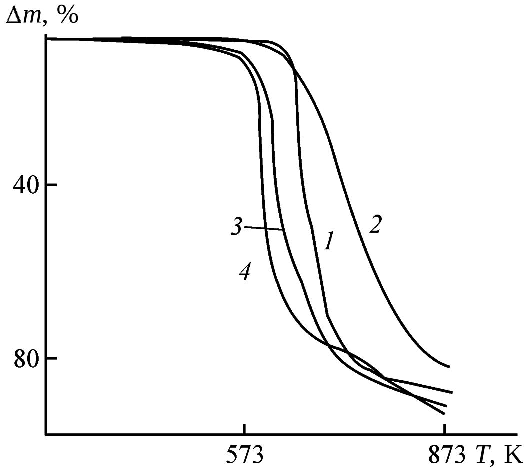


Fig. 1. Dynamic thermogravimetric analysis of polyvinyloxadiazoles (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**. (Δm) Weight loss and (T) temperature.

Polyvinyloxadiazoles **I**–**III**, irrespective of the synthesis procedure, are amorphous colorless powders (polymer **IV** is rubber-like) with the softening and decomposition points depending on the substituent in the heteroring (Table 4, Fig. 1). On the whole, carbon-chain polyvinyloxadiazoles can be regarded as relatively heat-resistant polymers, despite the fact that they are inferior to the known heterochain oxadiazole-containing polymers by approximately 100°C [2].

The solubility of polyvinyloxadiazoles is characterized by the same trends as the solubility of vinylazole polymers containing only the nitrogen heteroatoms in the heterorings [16]. Polyvinyloxadiazole **I** whose heterocyclic fragments contain a small alkyl substituent, CH_3 group (Table 4), dissolve in the widest set of solvents. An increase in the size of the alkyl group (passing to nonyl-substituted polyvinyloxadiazole **IV**) results in the loss of the solubility in polar solvents, but makes the polymer more readily soluble in low-polarity liquids such as benzene and dioxane. Polyvinyloxadiazoles are not polyelectrolytes; therefore, solutions of polymers prepared by polymerization show a linear concentration dependence of the reduced viscosity (Fig. 2). However, the polymers prepared by the modification and containing residual N–H-unsubstituted tetrazole fragments (>5 mol %) behave in solutions as typical polyelectrolytes: Their reduced viscosity increases with the dilution.

In contrast to hydrophobized polyvinyloxadiazoles with phenyl, nonyl, and trifluoromethyl substituents, polymer **I**, similarly to polymers with the 1,2,4-triazole ring, is a nonionic water-soluble macromolecular compound. Comparison of 1,2,4-oxadiazole- and 1,2,4-triazole-containing polymers is interesting from the viewpoint of the effect of the ring-forming heteroatoms (at their equal number) on the compatibility with water. However, it was noted previously [16] that polyvinylazoles containing sequences of two and more nitrogen atoms in the ring are insoluble in water (e.g., poly-1-vinyl-1,2,3-triazole, poly-1-vinyl-1,3,4-triazole, poly-1-vinyltetrazole). Polyvinylazoles containing an isolated “pyridine” nirogen atom in the heteroring are water-soluble (poly-1-vinylimidazole, poly-1-vinyl-1,2,4-triazole). In the structure of the 1,3,4-oxadiazole ring, there are two vicinal “pyridine” nitrogen atoms which, by analogy with poly-1-vinyl-1,3,4-triazole, is unfavorable for the affinity of the polymer for water, and an isolated oxygen atom of the furan ring. Apparently, this oxygen atom is responsible for the solubility of **I** in water.

The thermodynamic parameters of the interaction with water of polymer **I** prepared by polymerization and modification were estimated from the sorption and calorimetric data. For both samples of **I**, the isotherms of water vapor sorption asymptotically increase at $p/p_s \to 1$ (Fig. 3), which is typical of polymers infinitely miscible with water. The concentration dependences of the Gibbs energy of mixing (Δg_m) of the polymers with water, calculated from the sorption isotherms, are negative, and the second derivative $\partial^2\Delta g_m/\partial W_2^2 > 0$, i.e., the systems are thermodynamically stable in the entire composition range. Polyvinyloxadiazole **I** prepared by the modification exhibits somewhat lower affinity for water because of the presence of residual tetrazole fragments. Comparison with the Δg_m values obtained for mixing of poly-1-vinyl-1,2,4-triazole with water shows that the oxadiazolyl substituent is substantially less hydrophilic than the triazolyl substituent. This fact cannot be attributed to the presence of the methyl substituent in the heteroring of **I**, since the previous studies showed that electron-donor methyl substituents in azolyl fragments of polyvinylazoles, as a rule, enhance the affinity of the polymer for water [16].

The weaker, compared to the 1,2,4-triazole-containing polymer, interaction of polyvinyloxadiazole **I** with water also follows from the substantially smaller negative enthalpies of mixing (Δh_m) of **I** with water (Fig. 4b). The stronger exothermic effect of the donor–acceptor interaction with water and the shape of the dependence $\Delta h_m = f(W_2)$ for the sample of **I** prepared by the polymer-analogous transformation are attributable to the presence of the residual monomeric units with N–H-unsubstituted tetrazole rings [17].

The difference in the water affinity of oxadiazole- and triazole-containing polymers is also manifested in variation of the entropy parameters at formation of the aqueous systems. Dissolution of oxadiazole polymers is characterized by substantially smaller negative entropies of mixing $T\Delta s$ (Fig. 4c), which indicates that these polymers show a weaker tendency to form joint ordered polymer–water structures, compared to the triazole-containing polymer. Thus, the difference between the triazole and oxadiazole derivatives in the kind of one of the three heteroatoms does not result in the loss of the capability of the polymer with the 1,3,4-oxadiazole pendant group to dissolve in water but appreciably decreases its thermodynamic affinity for water.

As noted above, poly-2-vinyl-1,3,4-oxadiazoles can be prepared by modification of PVT. In turn, oxadiazole polymers can act as precursors for preparing

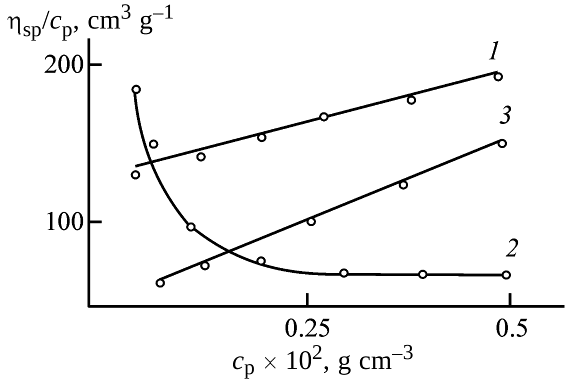


Fig. 2. Reduced viscosity η_{sp}/c_p of aqueous solutions as a function of polymer concentration c_p: polyvinyloxadiazole **I** prepared by (*1*) polymerization and (*2*) polymer-analogous transformation; (*3*) poly-3-vinyl-5-methyl-1,2,4-triazole.

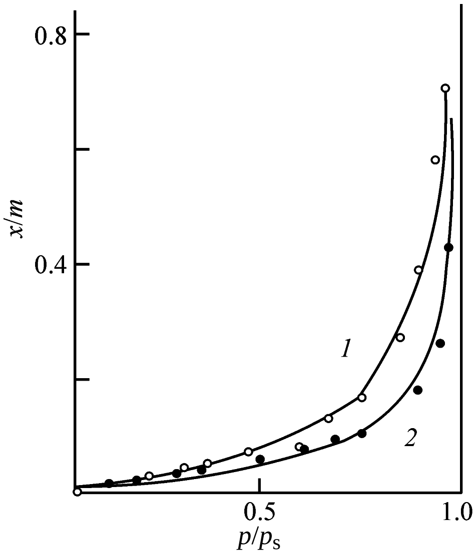


Fig. 3. Isotherms of water vapor sorption at 298 K for polyvinyloxadiazole **I** prepared by (*1*) polymerization and (*2*) polymer-analogous transformation. (*x*/*m*) Weight ratio of water and the polymer; (p/p_s) relative vapor pressure.

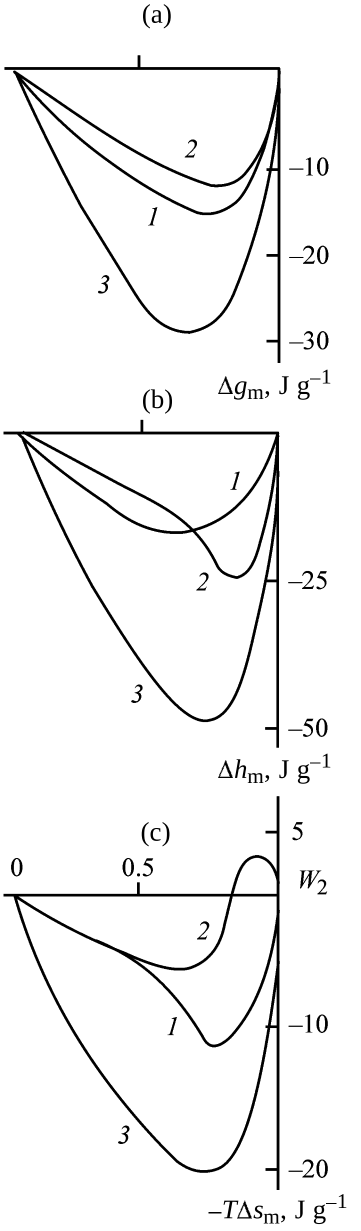
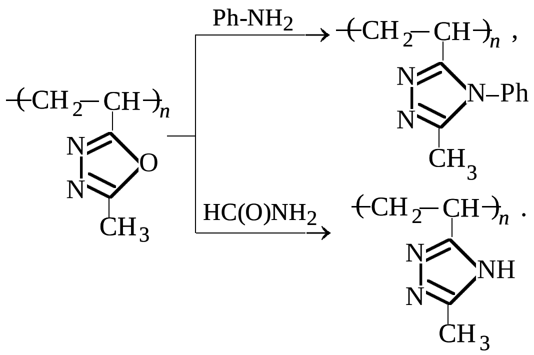


Fig. 4. Mean specific thermodynamic quantities of mixing with water at 298 K of polymer **I** prepared by (*1*) polymerization and (*2*) polymer-analogous transformation, and (*3*) of poly-1-vinyl-1,2,4-triazole [9]: (a) Gibbs energy Δg_m, (b) enthalpy Δh_m, and (c) $T\Delta s$. (W_2) Weight fraction of the polymer.

macromolecular compounds with other heterocyclic fragments. Similarly to the known transformations of heterochain polymers containing the 1,3,4-oxadiazole ring into those containing the 1,2,4-triazole ring [2], polyviyloxadiazole **I** reacts with formamide or aniline to form the corresponding poly-*C*-vinyl-1,2,4-triazoles, which are extremely difficult to prepare by polymerization:



The reaction with formamide gave poly-3-vinyl-5-methyl-1,2,4-triazole with a high conversion (up to 97%); this was confirmed by the ^{13}C NMR spectrum of the final product. The ^{13}C NMR spectrum of the starting polymer **I** consists of the following signals (ppm): 11.7 ($-CH_3$), 32.3–39.5 ($-CH-CH_2-$ of polymer chain), 167.5 (C^2 of ring), and 169.5 (C^5 of ring). The chemical shifts in the spectrum of the triazole-containing polymer are somewhat different (ppm): 12.9 ($-CH_3$), 35.4–44.7 ($-CH-CH_2-$ of polymer chain), 158.2 (C^3 of ring), and 172.7 (C^5 of ring). Assignment of the latter two signals to the triazole ring was based on the NMR data for model 3,5-disubstituted 1,2,4-triazoles. In contrast to the starting polyvinyloxadiazole, the triazole-containing polymer is insoluble in organic solvents but remains soluble in water. Because of weak acid properties of the 1,2,4-triazole ring, poly-3-vinyl-5-methyl-1,2,4-triazole in aqueous solutions exhibits no polyelectrolyte properties (linear concentration dependence of the reduced viscosity, Table 2), in contrast to tetrazole-containing polymeric NH acids [17].

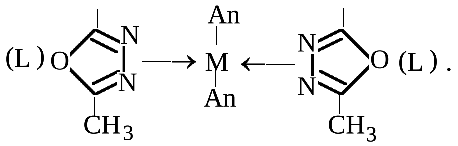
The reaction of polyvinyloxadiazole **I** with aniline in polyphosphoric acid yields poly-3-vinyl-4-phenyl-5-methyl-1,2,4-triazole with a high degree of conversion (up to 95%). The ^{13}C NMR data confirm that the final product contains the phenyl fragment (a set of signals in the range 126.1–130.8 ppm). The resulting triazole-containing polymer is soluble in DMF and DMSO but, in contrast to the starting polymer, insoluble in water.

Similarly to other known polyvinylazoles [18], polyvinyloxazole **I** forms complexes with metal ions. Complexes with Cu^{2+}, Ni^{2+}, Pd^{2+}, and Ag^+ salts are formed just when solutions of the polymer and salt are mixed at room temperature. The resulting complexes of the composition L : MAn_n = 2 : 1 (Table 5) are soluble neither in organic solvents nor in water and separate out from the reaction mixtures as finely dispersed precipitates. In the IR spectra of the reaction products, the absorption bands of the bending vibra-

Table 5. Complexation of poly-2-vinyl-5-methyl-1,3,4-oxadiazole with metal salts MAn_n. L : MA_n = 2 : 1 (base mole : g-equiv)

MAn_n	Solvent	Yield, %	Found, %		
			C	N	Cl
$CuCl_2$	Ethanol	80	32.6	14.5	15.9
$NiCl_2$	"	73	27.5	11.8	16.0
$AgNO_3$	H_2O	91	34.4	9.8	
$Pd(CH_3COO)_2$	DMF	55	27.4	11.4	

tions of the heteroring are shifted toward higher frequencies by approximately 10–20 cm^{-1}. In accordance with the generally accepted views on the structure of metal azole complexes, it can be suggested that the complexation with polyvinyloxadiazole is due to the donor–acceptor interaction of the ring nitrogen atoms with the metal ion:



Participation of the oxygen atom in the coordination is not confirmed.

CONCLUSION

Previously unknown carbon-chain polymers with pendant 1,3,4-oxadiazole fragments can be successfully prepared from low- and high-molecular-weight precursors. The synthesized vinyl-1,3,4-oxadiazole monomers are somewhat less active in radical polymerization than vinylazoles containing only nitrogen heteroatoms in the ring. Polyvinyl-1,3,4-oxadiazoles are nonionic, relatively heat-resistant polymers and can act as starting compounds for further chemical modification.

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