Polyacroleinoximes: synthesis and structure

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Dedicated to Boris A. Trofimov on the occasion of his 65th birthday with heartiest wishes

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Abstract

Quantitative and qualitative estimations have been performed of the compositions of chain fragments from polyacroleinoxime macromolecules. Polyacroleinoximes, obtained by a polyacrolein condensation reaction with hydroxylamine, are polymers having about 90% of oxime groups; the latter can exist both in the free state and in the cyclic form **III**. N-Hydroxypiperidine rings were formed by the interaction of neighboring oxime groups, which were oxidized to radicals **V**, identified by EPR spectroscopy. The composition of structure **III** is explained by the involvement of radicals **V** in the process. The polyacroleinoxime phosphorylation reaction with phosphorus pentoxide occurs quantitatively to form phosphate groups **IV** in the macromolecules. The molar ratio of nitrogen:phosphorus involved approaches 2:1, which allows the number of N-hydroxypiperidine cycles and free oxime groups in the polymer to be estimated (Table 1).

Keywords: Polyacroleinoximes, N-hydroxypiperidine cycles, nitroxyl radicals

Introduction

In recent years, the syntheses of pyrroles and their N-vinyl derivatives by the reaction of oximes with acetylenes (the Trofimov reaction)[1] have aroused considerable interest. Much experimental evidence on the structure and physical properties of the obtained products has been accumulated. Fields for their practical application have also been found. The involvement of polymeric oximes into the reaction, however, has not been well understood up to now. This can be explained by scarce data on preparation methods, as well as on the structure and properties of polymeric oximes. The cation polymerization of acroleinoxime leading to polymers with molecular mass (*M*) no greater than 500 have been reported.[2] High molecular polyacroleinoximes (PAO) have not been described previously. For their synthesis, we used a polymer-analogous transformation, the interaction of hydroxylamine with high molecular weight polyacrolein (PA).

Results and Discussion

The aim of this work is to determine a qualitative and quantitative content of structural fragments constituting a macromolecular chain of polyacroleinoximes. The PA needed for this was obtained by radical polymerization of monomer acrolein using oxidation–reduction initiators (Table 2). PA with molecular mass up to 80,000 was used in experimental work on polymer-analogous transformations. The starting PA macromolecules contain 10–20 % of oxyvinyl groups formed due to 1,4-addition.[3–5] In the main, up to 90% of the aldehyde groups exist in their proper aldehyde structures as well as in hydrated and cyclic structures (**I**). The hydrated and cyclic structures are able to open in alkaline solutions. The absence of a band at 1640 cm^{-1} in the IR spectra of brominated PA (Figure 1) proves the presence of the -C=C- bond in the initial polymers.

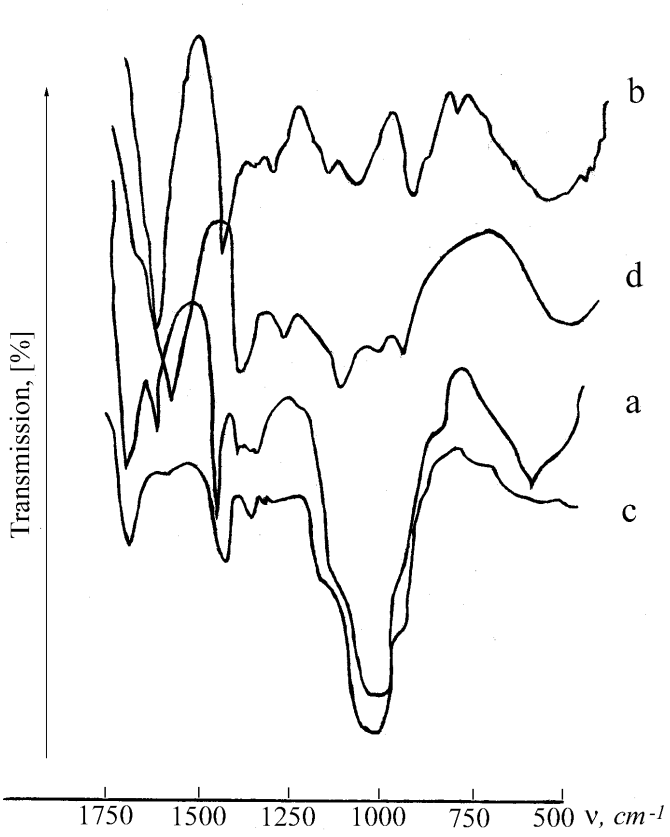
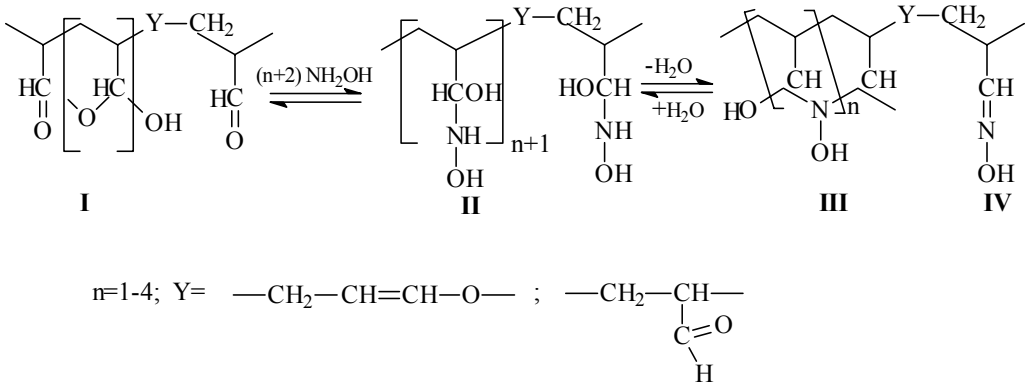


Figure 1. The IR spectra of polymers: polyacrolein-**a**, polyacroleinoxime-**b**; brominated polyacrolein-**c**, polyacroleinoxime-**d**.

The condensation reaction proceeds by the known two-step mechanism (Scheme 1) including the formation of a tetrahedral intermediate carbonylhydroxylamine **II**.[6]



n=1-4; Y= —CH_2—CH=CH—O— ; —CH_2—CH(C=O)H

Scheme 1

In spite of the fact that this reaction is hydrolytically reversible it has been used for the determination of functional aldehyde groups.[5] The content of these units and their cyclic forms is no more than 7 mol %, whereas the general number of oxime groups is 75–90% (Table 1).

Table 1. The quantitative content of structural fragments of polyacroleinoximes, mol

No	-C=C-	HC=O, non-opened rings	-HC=NOH, total number	N-hydroxypiperidine rings	HC=NOH, free groups
1	20	10	70	65	5
2	19	6	75	70	5
3	16	7	77	72	5
4	8	3	89	83	6

In the IR spectra of the polymers (Fig. 1), there are absorption bands in the 3416 (-OH), 2926 and 2859 (-CH_2-), 937 cm^{-1} (-N-O-) regions. A wide absorption band at 1642 cm^{-1} is caused by mutual absorption of -C=N oxime groups and -C=C- bonds. When PAO is brominated the band intensity is decreased, and its maximum is at 1630 cm^{-1} proving the presence of free oxime groups. The number of double bonds varies from 8 to 20% (Table 1). A band at 1000–1500 cm^{-1} does not occur in the PAO IR spectra, which indicates the involvement of cyclic forms of aldehyde groups in the condensation reaction with hydroxylamines. The PAO obtained are pale yellow powders, insoluble in organic solvents but well soluble in alkaline solutions. In the EPR spectrum of solid PAO there is an anisotropic signal with g_1=2.03, g_2=2.01, g_3=1.98, which corresponds to a concentration of paramagnetic centers of 9.8×10^{19} sp/g (Figure 2).

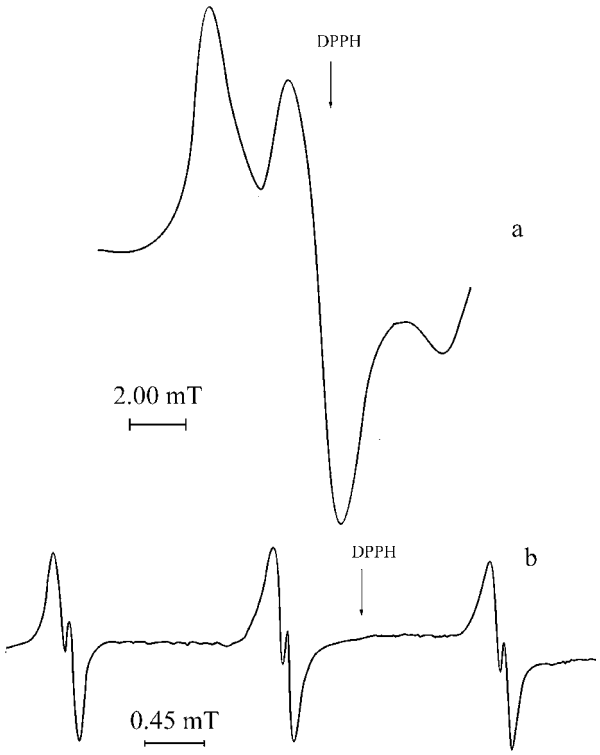
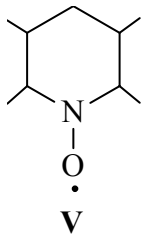


Figure 2. EPR polyacroleinoxime spectra: **a** solid state, **b** sodium hydroxide solution under high-resolution conditions.

The EPR signal of polymers in 2*M* alkaline solution is quite stable. It consists of the main triplet with a constant of superfine structure a_N=1.73 mT, and additional splitting resulting from the interaction of an unpaired electron with a nucleus of spin 1/2. The obtained data prove the presence of stable nitroxyl radicals in PAO. The identity of the PAO EPR spectrum to that of a model compound, 2,2,6,6-tetrahydroxypiperidinoxyl, and the additional splitting on the proton [doublet with a constant of 0.11 mT (Figure 2)] under high resolution conditions, provide evidence for the presence of radicals **V** in macromolecules formed owing to the oxidation of N-hydroxypiperidine rings.

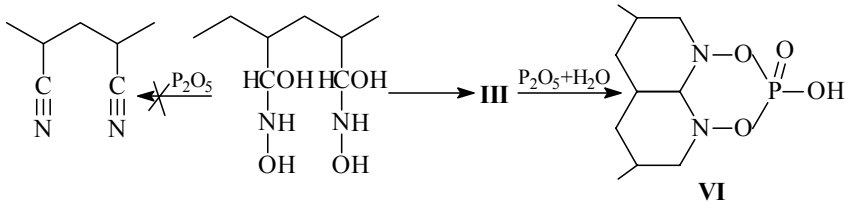


V

N-hydroxypiperidine cyclic units in the polymer are formed as a result of intermolecular interaction of oxime groups in the process of PAO preparation according to Scheme 1. The

typical band of the >C-N bond is observed in the IR spectra of oximated polymers at 1156–1160 cm^{-1} (Figure 1). The calculations show that one nitroxyl radical is contained in approximately 100 units of the macromolecule at a concentration of paramagnetic centers of 10^{20} sp/g.

There is a labile equilibrium between free and hydrated oximes in alkaline solutions. Its shift to the right (Scheme 1) leads to N-hydroxypiperidine cycles and free oxime groups **IV**. This is why the reaction of PAO in aqueous alkaline media with epichlorohydrin, for example, behaves analogously to that of low molecular-weight oximes to form glycidyl units in the macromolecules; the formation of chlorohydrin groups[7] is observed under heterogeneous conditions when the N-hydroxypiperidine rings are not open. However, this reaction is complicated by hydrolytic processes, and cannot be applied for the calculation of the quantitative ratio of N-hydroxypiperidine cycles to free oxime groups. In the reaction of PAO with phosphorus pentoxide in DMFA solution the phosphate groups are formed under an equilibrium shift to the right, according to Scheme 2. This process is more preferable than that of the formation of nitrile groups not observed in the macromolecule.[8]



VI

Scheme 2

The interaction of PAO with phosphorus pentoxide proceeds quantitatively, forming structures with an N:P ratio of 2:1 in the polymer. The maximum phosphorus content in macromolecules is 11–13%, which corresponds to the content of 70–83% of structures **VI** (Table 1). The content of free oxime groups in the polymer is no more than 6 %.

Conclusions

Polyacroleinoxime molecules obtained by condensation of polyacroleins with hydroxylamines contain from 70 to 90% of general oxime groups. The number of oxime groups depends on the initial polymer structure. It has been established that N-hydroxypiperidine rings are formed in macromolecules due to neighboring oxime groups, as a result of intermolecular interaction. The numbers of N-hydroxypiperidine rings are up to 65–83 mol%, whereas a free oxime groups' content is only 6%. The oxyvinyl fragment contents in macromolecules of polyacroleinoximes are from 8 to 20 mol%. The numbers of aldehyde groups are in the range of 3–10 mol%. The presence of aldehyde groups in the polymer is determined by an inverse condensation process.

Experimental Section

The polyacroleins were obtained in the presence of oxidation–reduction systems (Table 2) by the published methods.[2,8]

Table 2. The analysis results of the starting polyacroleins

No.	Initiator, Molar ratio	Concentration, %	-HC=O, total, %	Found, * %		-C=C- mol, %	*M*
				C	H		
1	$Fe^{+2}/K_2S_2O_8$=1.4:1	2.4	80	64.01	7.13	20	75000
2	$Ag^{+}/K_2S_2O_8$=1:1	1.0	81	64.09	6.89	19	72000
3	Co^{+2}Acetylacetonate	0.5	84	64.11	7.05	16	60000
4	$Fe^{+2}/K_2S_2O_8$=1:1	0.6	92	64.31	7.17	8	80000

* Calculated, %: C 64.50; H 7.14.

Molecular mass (*M*) found in sulfuric acid solution. The number of oxyvinyl bonds was found by the published method.[9]

Polyacroleinoximes were obtained by the condensation of polyacroleins with hydroxylamines by the published method[3] (Table 3).

Table 3. The analysis results of polyacroleinoximes

No.	Found, %			Calculated, %		
	C	H	N*	C	H	N
1	53.83	7.61	14.58	54.03	7.20	14.78
2	53.29	7.01	15.11	53.70	6.77	15.68
3	52.89	7.45.	15.55	53.27	7.15	15.92
4	52.23	7.37	18.30	51.91	7.04	18.00

* The nitrogen content corresponds to the general number of oxime groups.

The numbers of aldehyde groups and non-opened cycles in the polyacroleinoximes (*y*) were determined according to the following formula:

$$a\text{-}c=y,$$

where *a* is the general number of aldehyde groups; *c* is the general number of oxime groups (mol %).

Phosphorus-containing polyacroleinoximes. PAO (1.0 g) (N=14.7%), in 10 ml dimethylformamide containing 0.1% water is added to 1.49 g of P_2O_5 in 10 ml of the solvent. The mixture is heated for 4h at 100 °C. The polymer is washed with water, then ethanol, and

dried in vacuum. The polymer (1.1 g) is isolated. The analysis data of the polymers obtained analogously are presented in Table 4.

Table 4. Analysis results of phosphorus-containing polyacroleinoximes

No.	Found, %				N/P,	Calculated *, %			
	C	H	N	P	mol.	C	H	N	P
1	50.13	5.42	10.31	11.52	1.98	41.95	5.03	10.58	11.70
2	41.25	5.16	10.89	12.38	1.95	40.91	4.93	11.09	12.27
3	40.33	5.07	10.78	11.92	2.00	40.09	4.91	11.99	12.40
4	36.81	4.62	12.37	13.48	2.03	36.44	4.44	12.62	13.05

* Taking into account the structure of Table 1.

The free oxime groups (*x*) were determined according to the formula: *c*-*b*=*x*, where *b* is the number of N-hydroxypiperidine rings.

Additional Information

The IR spectra of phosphonylated polyacroleinoximes contain absorption bands in the 2870 (P-OH), 1250 (P=O), 1158 (C-N), 1050 (P-O) cm^{-1} region. There is no band typical of a nitrile group in the 2200–2300 cm^{-1} region.

In the ^{31}P- NMR spectra of solid phosphorus-containing polymers a single signal with δ_P 0.4 ppm (relative to 85% H_3PO_4) was observed. The signal is typical for phosphorus(V) surrounded by oxygen atoms. Potentiometric titration data for the polymers with 0.1*M* NaOH solution[8] indicate the monobasicity of the acids obtained.

References

1. Trofimov, B. A.; Mikhaleva, A. I. *N-Vinylpyrroles*; Nauka: Novosibirsk; 1984.
2. Masuda S.; Ota T.; Tanaka H.; Asahi J. *Polym. J.* **1978**, *10,* 1.
3. Schulz, R. C. *Angew. Chem. Sect. B* **1957,** *69,* 153.
4. Andreeva, I. V.; Koton, M.M.; Artem'eva, V.N.; Sazanov, Yu. N.; Fedorova, G. N. *Vysokomolekular Soed.* **1976,** *18A,* 1707.
5. Schulz, R. C.; Fauth, H.; Kern, W. *Macromolec. Chem., Sect. B* **1956,** *20,* 161.
6. Barton, D.H.R.; Ollis, D.W. *General Organic Chemistry;* Khimiya: Moscow, 1983 *Vol.5*, p 717.
7. Khabibulina, A. G.; Antonik, L. M.; Vakul'skaya, T.I.; Voronkov, M. G. *Doklady Russ. Ac. Sci.* **2002,** *385*. 641.
8. Khabibulina, A. G. *PhD Thesis,* ISU, Irkutsk, 2002.
9. Losev, I. P., Fedotova, O. Ya. *Laboratory Manual on the Chemistry of High-Molecular Compounds*; Goskomizdat: Moscow, 1962, p 82.

