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Phenoxazine polymers: synthesis and structure

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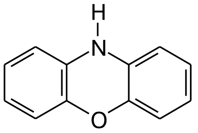
Phenoxazine polymers were obtained for the first time under conditions of chemical oxidative polymerization in aqueous alcohols and in an interphase process. The interphase process gave products with the higher molecular weight. Dependencies of the yields and degree of polymerization of phenoxazine from polymerization method, concentration of reactants, their ratio, reaction temperature and time, as well as chemical structures of the obtained polymers depending on the synthesis conditions, were studied. The polyphenoxazine chain growth is accomplished by the C—C-addition at the *para*-position of the phenyl rings with respect to nitrogen. Even when an excess of oxidant was used, the polyphenoxazine structure has only phenyleneamine units. The polymers obtained are amorphous and thermally stable.

Key words: polyphenoxazine, interphase oxidative polymerization, UV and IR spectroscopy, differential scanning calorimetry.

Interest of researches to the synthesis of electroactive polymers with the system of polyconjugation is due to the fact that, because of the development of modern technologies, these polymers possessing a combination of unique properties can find their application in the new fields of studies.[1—4] Polyaniline is the most demanded polymer from this class, that is explained by simplicity of its synthesis under conditions of oxidative polymerization and its stability under operating conditions. However, the search for new electroactive polymers is restrained by limited solubilities of new monomers under standard conditions of oxidative polymerization (in aqueous acids). This prompted the authors to develop methods for the synthesis of new electroactive polymers.

In the present work, polymers of phenoxazine, a heterocyclic compound having in its structure a nitrogen atom and an oxygen atom binding two phenyl rings, were obtained for the first time.



The processes of oxidative polymerization of phenoxazine were studied in aqueous alcohols and under interphase conditions. For the polymers, their chemical structure was established and thermal stability was studied.

Experimental

Ammonium persulfate (pure for analysis grade) was purified by recrystallization according to the known procedure.[5] Phenoxazine, 97% (Acros organics), hydrochloric acid (chemically pure grade), DMF (Acros organics), as well as methanol (JT Baker), ethanol (pure for analysis grade), isopropanol (specially pure grade) and *tert*-butanol (pure for analysis grade) were used as purchased. Toluene (pure for analysis grade) was purified by fractional distillation.[6] Aqueous solutions of reactants were prepared using DI water.

For the oxidative polymerization of phenoxazine in aqueous alcohols (isopropanol, methanol, ethanol, and *tert*-butanol), a required amount of the monomer was dissolved in alcohol, the oxidant (ammonium persulfate) was dissolved in water or aq. hydrochloric acid. The ratio of alcohol and water was 1 : 1 (v/v). The aq. solution of ammonium persulfate was added dropwise to the alcoholic solution of monomer incubated at 0 °C with constant stirring. The temperature of the reaction was kept below 0 °C and the polymerization was carried out with constant, vigorous stirring. After the synthesis was completed, the product that obtained was filtered off, repeatedly washed with DI water to remove the reactant residues, and dried *in vacuo* until the weight was constant (the yield was determined by thermogravimetry). Found (%): C, 77.1; N, 7.5; O, 10.9; H, 4.5. $C_{12}H_9NO$. Calculated (%): C, 78.7; N, 7.7; O, 8.7; H, 4.9.

Interphase oxidative polymerization of phenoxazine. A required amount of monomer was dissolved in a mixture of organic solvents, toluene and isopropanol in the ratio 1.5 : 1.0 (v/v), the oxidant (ammonium persulfate) was dissolved in water or aq. hydrochloric acid. The ratio of the aqueous and organic phases was 1 : 2 (v/v). The changes in the indicated ratios lead to a sharp decrease in the solubility of phenoxazine. Since the oxidation reaction proceeds on the interface, the organic and aqueous phases were mixed at once without gradual addition of the reactants, which was the case in the synthesis of polyaniline. The process was carried out with vigorous stirring using an electronic stirrer with a RW 16 Basic upper drive (Ika Werke) in a narrow cylinder-shaped round-bottom two-neck flask (for increasing efficiency of stirring) at 0 °C. After the synthesis was completed, the reaction solution was precipitated first into a five-fold excess of the methanol—DI water mixture in the ratio 1.5 : 1.0 (v/v),

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then into isopropanol. The product that obtained was filtered off and repeatedly washed with DI water to remove the reactant residues and dried *in vacuo* until the weight was constant (the yield was determined by thermogravimetry). Found (%): C, 79.1; N, 7.2; O, 9.7; H, 4.0. $C_{12}H_9NO$. Calculated (%): C, 78.7; N, 7.7; O, 8.7; H, 4.9.

Molecular weight of polyphenoxazine was measured by GPC on a Milton Roy instrument equipped with a Milton Roy RI-detector and a PLgel 5um MIXED-C column using *N*-methylpyrrolidone as an eluent at 60 °C. The eluent flow rate was 1 mL $\min^{-1}$. The volume of injected sample was 150 μL. Polystyrene was used for the calibration. The accuracy of MW determination was ~5%.

IR spectra of the polyphenoxazine samples were recorded on a Specord M-82 spectrophotometer in the region 4000—400 cm^{-1} and processed using the Soft-Spectra program. The samples were prepared in KBr pellets.

Electron absorption spectra of polyphenoxazine solutions in DMF were recorded on a UV-1700 registration spectrophotometer (Shimadzu) in the region 190—1100 nm.

^{13}C NMR spectra were recorded on a Varian VXR-500 spectrometer in deuterated DMSO.

Analysis of polyphenoxazine samples by X-ray photoelectron spectroscopy was performed in a XSAM-800 two-chamber apparatus (Kratos Analytical Ltd.) using a characteristic line MgK_α ($h\nu = 1253.6$ eV) as an exiting radiation.

Potentiometric measurements were carried out on a Solartron 1286 electrochemical analyzer (Schlumberger, UK) in 0.1 *M* HCl at the potential scanning rate 5 and 10 mV s^{-1}. A solution of polyphenoxazine (4 μL) was deposited on the printed electrodes and dried in air.

X-ray diffraction studies were carried out at room temperature on a DRON-2 computerized diffractometer (CuKα radiation, $\lambda = 0.154$ nm) with a modernized collimation allowing us to record reflection with 0.5°θ and considerably decreasing parasitic background and fluctuations. We used an X-ray reflection technique, placing samples in a special metallic cuvette with the operating volume $17\times17\times1.5$ mm^3.

Thermal analysis of phenoxazine polymers was performed on a TGA Netzsch TG 209 F1 instrument in the dynamic mode of heating in the range 30—1000 °C in air and in the flow of nitrogen. The samples were preliminary incubated at 30 °C for 15 min, and then, after the polymer was heated to 1000 °C, for another 30 min. A weighted amount of polymers (100 mg) was used, the rate of heating was 10 deg $\min^{-1}$, the rate of nitrogen flow was 50 mL $\min^{-1}$. Calcined aluminum oxide was used as a standard. Analysis samples was carried out in an Al_2O_3 crucible.

Calorimetric studies of phenoxazine polymers was performed on a Mettler TA-4000 differential scanning calorimeter with a DSC-30 heating cell in the range from room temperature to 350 °C at the rate 10 deg $\min^{-1}$ under nitrogen atmosphere.

Results and Discussion

Methods for the synthesis of polyphenoxazine

Phenoxazine is insoluble in acids, therefore, its oxidative polymerization cannot be carried out under standard conditions, *i.e.*, in dilute aqueous acids. The oxidative polymerization of phenoxazine was for the first time successfully accomplished in aqueous alcohols (isopropanol, methanol, ethanol, and *tert*-butanol). The data on how the yield of polyphenoxazine depends from the concentration of monomer, oxidant, acid, medium, temperature, and the reaction time are given in Table 1.

The dependence of how the yield of polyphenoxazine from the reaction conditions showed the following: the yield of polymer increases with the increase in the concentration of monomer. It is desirable to carry out polymerization of phenoxazine at the stoichiometric or somewhat higher ratio [oxidant] : [monomer] = 1.25—1.50. Like in polymerization of phenothiazine,[7] the temperature of the reaction mixture should be maintained between −10 and +15 °C. Under such conditions, molecular weight of the oxidation products reaches $M_w = 2.4\cdot10^4$, degree of polymerization is more than 130, index of polydispersity is 1.2.

Polymerization of phenoxazine was also for the first time successfully accomplished in the interphase process developed by us earlier for the oxidative polymerization of diphenylamine[3,8,9] and phenothiazine[7,10]. In the interfacial polymerization, the reactants (monomer and oxidant)

Table 1. Polymerization of phenoxazine in aqueous alcohols

C /mol L^{-1}	[Ox] : [M]	[HCl] : [M]	*T*/°C	τ/h	Yield (%)
	mol/mol				
0.02	1.25	0	0	3	91
0.05	1.25	0	0	3	93
0.10	1.25	0	0	3	95
0.15	1.25	0	0	3	85
0.20	1.25	0	0	3	—[a]
0.05	0.66	0	0	3	57
	1.00	0	0	3	71
	1.50	0	0	3	96
	5.00	0	0	3	68
	1.25	5	0	3	90
	1.25	10	0	3	86
	1.25	20	0	3	79
	1.25	30	0	3	79
	1.25	0	−10	3	86
	1.25	0	15	3	93
	1.25	0	40	3	71
	1.25	0	60	3	64
	1.25	0	0	1	96
	1.25	0	0	6	89
	1.25	0	0	24	86
	1.25	0	0	3	90[b]
	1.25	0	0	3	90[c]
	1.25	0	0	3	93[d]

Note. C is the concentration of phenoxazine, Ox is the oxidant, M is the monomer. Isopropanol was the reaction medium.

[a] Is not soluble in isopropanol.

[b] Methanol was the reaction medium.

[c] Ethanol was the reaction medium.

[d] *tert*-Butanol was the reaction medium.

are distributed between two immiscible phases: the unionized form of monomer is in the organic medium, whereas the oxidant is in the aqueous phase; the growth of polymer occurs on the interface. Variations in the organic solvents allow one to use a great number of earlier unavailable monomers, which are insoluble in aqueous acids, whereas the presence of oxidant and acid in a separate phase gives one an opportunity to vary their type and concentration keeping unstable oxidation products intact. Since the oxidation proceeds on the interface, there is no necessity in a gradual addition of reactants, like it is desired in the synthesis of polyaniline.

The following system has proved the most suitable medium for the interfacial polymerization of phenoxazine: a solution of monomer in the toluene—isopropanol solvent mixture (1.5 : 1.0, v/v) and an aqueous solution of oxidant ($(NH_4)_2S_2O_8$) in the ratio 2 : 1 (v/v). The changes in the indicated ratios leads to a sharp decrease of the phenoxazine solubility. The data on how the yield of polyphenoxazine depends from the concentration of monomer, oxidant, acid, temperature, and the reaction time are given in Table 2.

As in the case of interphase oxidative polymerization of phenothiazine,[7] the presence of an acid in the reaction medium leads to the drop in the yield of polyphenoxazine. The interphase process is better to carry out in the absence of an acid and at high enough concentrations of the monomer (0.1—0.2 mol L^{-1}), as well as at stoichiometric or somewhat higher ratio [oxidant] : [monomer] = 1.25—1.50 in the range −10 —+15 °C. For the best results, the interfacial polymerization of phenoxazine should be carried out for 3—6 h. The molecular weight of the oxidation products (M_w) reached $3.7 \cdot 10^4$, degree of polymerization was higher than 200, index of polydispersity, 1.1.

Table 2. Interfacial polymerization of phenoxazine

C /mol L^{-1}	[Ox] : [M]	[HCl] : [M]	*T*/°C	τ/h	Yield (%)
	mol/mol				
0.05	1.25	0	0	3	39
0.10	1.25	0	0	3	85
0.20	1.25	0	0	3	89
0.10	0.66	0	0	3	35
	1.00	0	0	3	35
	1.50	0	0	3	64
	5.00	0	0	3	88
	1.25	1	0	3	93
	1.25	3	0	3	73
	1.25	5	0	3	67
	1.25	10	0	3	47
	1.25	0	−10	3	25
	1.25	0	15	3	71
	1.25	0	40	3	80
	1.25	0	60	3	76
	1.25	0	0	1	76
	1.25	0	0	6	82
	1.25	0	0	24	75

Note. C is the concentration of phenoxazine, Ox is the oxidant, M is the monomer.

The product of phenoxazine oxidation is a blue powder, completely soluble in *N*-methylpyrrolidone, DMF, DMSO, dioxane, acetone, THF, chloroform.

Chemical structure of polyphenoxazine

The structure of phenoxazine polymers obtained by two methods, *i.e.*, polymerization in aqueous alcohols and in the interphase process, was studied by IR and UV spectroscopy.

The IR spectra of all the polyphenoxazine samples exhibit an absorption band at 3380 cm^{-1} corresponding to the stretching vibrations of the ν_{N-H} bonds in the phenylenamine structures. The band around 3055 cm^{-1} in the polymer is related to the stretching vibrations of the ν_{C-H} bonds in the benzene ring.

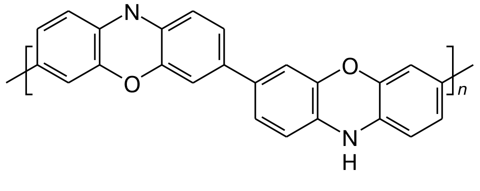
In the IR spectra of polyphenoxazine, the strong bands at 1587 and 1483 cm^{-1} are observed, which correspond to the stretching vibrations of the ν_{C-C} bonds in the aromatic rings (Figs 1 and 2).

The absorption bands at 1330, 1290, and 1270 cm^{-1} are related to the stretching vibrations of the ν_{C-N} bonds (see Refs 11—13). The IR spectra of polyphenoxazine have no absorption band in the region 1650 cm^{-1} corresponding to the stretching vibrations of the $\nu_{C=N}$ bonds in the quinodiimine structures.

The bands in the region 869 and 836 cm^{-1} are due to the out-of-plane deformation vibrations of the δ_{C-H} bonds in the 1,2,4-trisubstituted benzene ring. This indicates that, as in the case of polyphenothiazine,[7,10] polymerization of phenoxazine proceeds by the type of C—C-addition at *para*-position of the phenyl ring with respect to nitrogen.

The band at 739 cm^{-1} is related to the out-of-plane deformation vibrations of the δ_{C-H} bonds in the 1,2-disubstituted benzene ring of the terminal groups. Intensity of this band depends on the method of polymerization. In the IR spectra of phenoxazine polymers obtained under the interphase conditions, the intensity of the band at 739 cm^{-1} is lower (Fig. 2), *i.e.* degree of polymerization is higher.

Analysis of the results of spectroscopic studies allows us to suggest a chemical structure of polyphenoxazine as the following form:



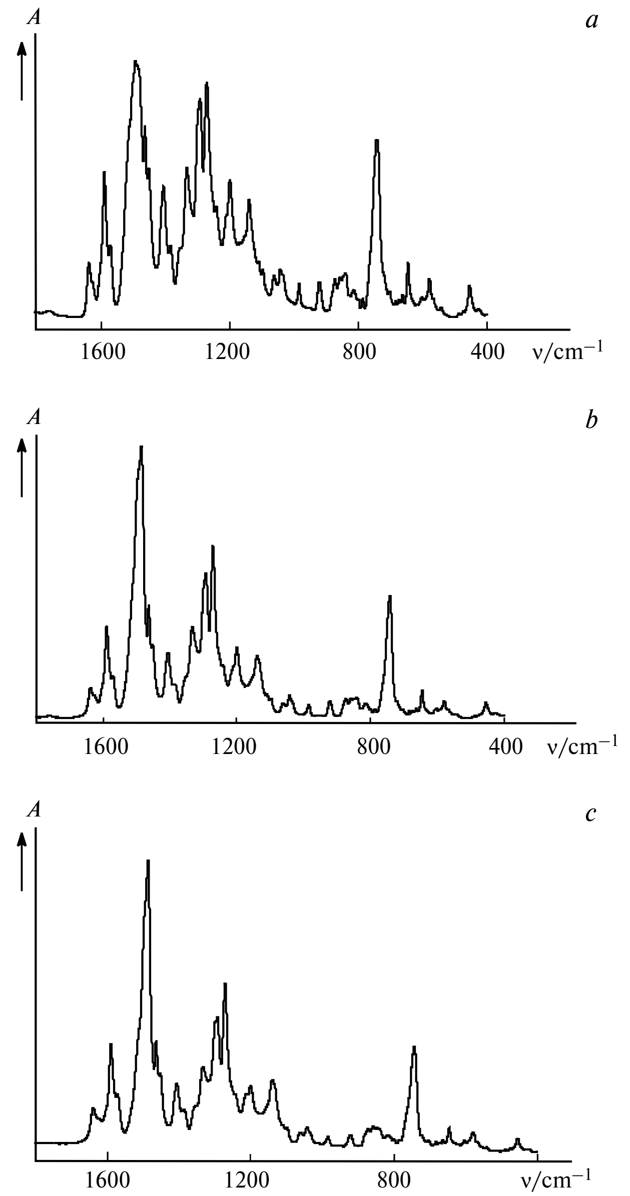


Fig. 1. The IR spectra of polyphenoxazine obtained by polymerization in isopropanol in the presence of 0.0625 (*a*), 0.075 (*b*), and 0.250 mol L^{-1} of $(NH_4)_2S_2O_8$ (*c*). [Monomer] = 0.05 mol L^{-1}, T = 0 °C, the reaction time was 3 h.

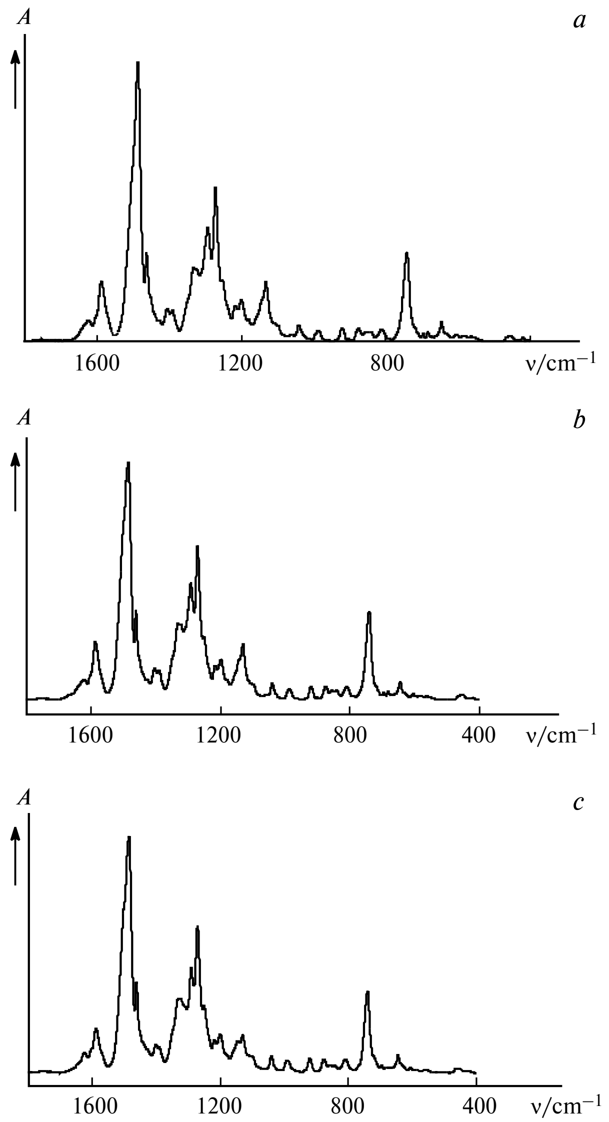


Fig. 2. The IR spectra of polyphenoxazine obtained by the interfacial polymerization in the presence of 0.1 (*a*), 0.15 (*b*), and 0.5 mol L^{-1} of $(NH_4)_2S_2O_8$ (*c*). [Monomer] = 0.1 mol L^{-1}, T = 0 °C, the reaction time was 3 h.

Thus, polyphenoxazine is a half-staircase heterocyclic polymer containing, together with nitrogen atoms, atoms of oxygen, which are involved into the general system of polyconjugation. The polymeric structure contains no quinodiimine units, that was confirmed by the X-ray photoelectron spectroscopic data. These data show that only phenyleneamine units are present in the structure of polyphenoxazine independent on the method of polymerization. The peak corresponding to the bond energy 400.5 eV is related to the C—N bond (see Ref. 14). The UV spectroscopic data confirm these observations. Figure 3 shows examples of the electron absorption spectra of polyphenoxazine obtained by the interfacial polymerization. The band at λ_{max} = 329 nm characterizes a reduced amine form (the π—π^*-transition) of the polymer. There is no absorption band in the long-wave region at 620 nm corresponding to the oxidized quinonoid form, even in the cases when the stoichiometry of the molar ratio oxidant : monomer is exceeded. The absence of the quinodiimine units in the structure of polyphenoxazine was also confirmed by the ^{13}C NMR data. The ^{13}C NMR spectrum of the polymer contains no signal corresponding to the carbon atoms of the C=N groups δ_C = 148 (see Refs 7 and 13).

We also studied how concentration of the oxidant affects the structure of polyphenoxazine formed. When phen-

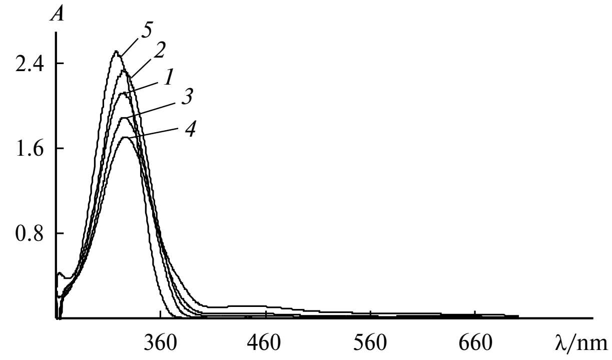


Fig. 3. The electron absorption spectra in DMF of polyphenoxazine obtained by the interfacial polymerization in the presence of 0.10 (*1*), 0.125 (*2*), 0.15 (*3*), and 0.50 mol L^{-1} of $(NH_4)_2S_2O_8$ (*4*); *5* is the spectrum of monomer. [Monomer] = = 0.1 mol L^{-1}, $T = 0$ °C, the reaction time was 3 h.

oxazine is polymerized in isopropanol, an increase in the concentration of the oxidant leads to a decrease in intensity of the band at 739 cm^{-1} corresponding to the out-of-plane deformation vibrations of the δ_{C-H} bonds in the 1,2-disubstituted benzene ring of the terminal groups (see Fig. 1), whereas under the interphase conditions, the growth in the ratio [oxidant] : [monomer] in the order 1.0, 1.5, 5.0 produces no significant changes in the structure of the polymer (see Fig. 2).

Electroactivity of phenoxazine polymers

The phenoxazine polymers obtained are electroactive, that was confirmed by cyclic voltammetry. The polymer immersed in the electrolyte is capable of reversible oxidation-reduction when the sign of applied potential changes. Figure 4 shows an example of cyclic voltammogram of polyphenothiazine obtained under conditions of interfacial polymerization. The redox-peaks can be clearly identified on the cyclic voltammogram, whose intensities increase with the increase in the rate of potential scanning.

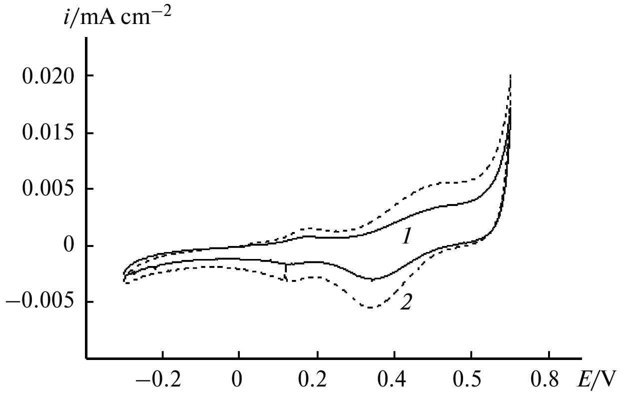


Fig. 4. The cyclic voltammograms of polyphenoxazine in 0.1 *M* HCl at the rate of potential scanning 5 (*1*) and 10 mV s^{-1} (*2*).

Thermal stability of polyphenoxazine

Thermal stability of phenoxazine polymers was studied by TGA and DSC. Figure 5 shows the temperature dependence of the polyphenoxazine loss in weight upon heating to 1000 °C in the flow of nitrogen and in air.

The loss in weight in polyphenoxazine at low temperatures is related to the removal of moisture.[15—18] In the polymer obtained in isopropanol, the loss in weight at 230 °C is due to the decomposition of the low-molecular-weight oligomers, whose presence was shown by GPC. Polyphenothiazine obtained by the interfacial polymerization contains no low-molecular-weight oligomers, and the TGA integral curves show no loss in weight in the indicated temperature range. This is confirmed by the DSC data (Fig. 6, curve *a*). The DSC thermogram of polyphenoxazine obtained in isopropanol has an endothermic peak at 285 °C related to decomposition.[19—25] On the re-heating, this peak is absent (Fig. 6, curve *b*). The X-ray crystallographic data show that polyphenoxazine is an amorphous polymer regardless of the polymerization conditions.

In the inert medium above 580 °C, the loss in weight is gradual. At 1000 °C depending on the polymerization method, the residue is 35—51%. Polyphenoxazine obtained by the interfacial polymerization possesses higher thermal stability.

Processes of thermooxidative destruction of polyphenoxazine begin at 430—520 °C depending on the polymerization method. For polyphenoxazine obtained by polymerization in isopropanol and in the interphase process, the 5% loss in weight is observed at 250 and 190 °C, whereas the 50% loss in weight, at 630 and 580 °C, respectively.

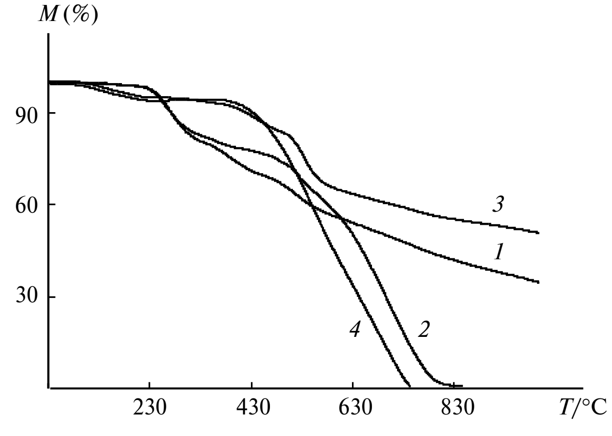


Fig. 5. The loss in weight of the phenoxazine polymers upon heating to 1000 °C at the rate 10 deg min^{-1} in the flow of argon (*1*, *3*) and in air (*2*, *4*). Polyphenoxazine was obtained by polymerization in isopropanol (*1*, *2*) and by the interfacial polymerization (*3*, *4*). [Monomer] = 0.05 (*1*, *2*) and 0.1 mol L^{-1} (*3*, *4*), [oxidant] = 0.0625 (*1*, *2*) and 0.125 mol L^{-1} (*3*, *4*), $T = 0$ °C, the reaction time was 3 h.

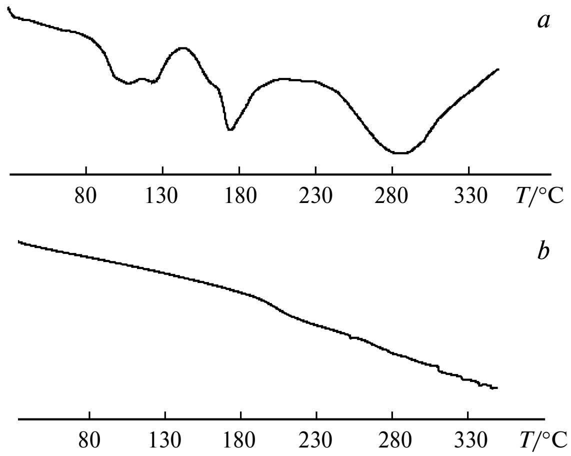


Fig. 6. The DSC thermograms of polyphenoxazine, obtained by polymerization in isopropanol, upon heating in the flow of argon to 350 °C at the rate 20.0 deg min^{-1} (*a*) and upon re-heating (*b*).

It is known[14,15,18,19] that polyaniline loses a half of its initial weight at 450 °C.

In conclusion, the processes of chemical oxidative polymerization of phenoxazine under homogeneous and heterophase conditions were accomplished for the first time to obtain new heterocyclic polymer containing, together with nitrogen atoms, atoms of oxygen involving into the chain of polyconjugation. It was studied how the polymerization method and reaction conditions affect the product structures.

The IR spectroscopic data showed that the chemical oxidative polymerization of phenoxazine proceeds as a C—C-addition at *para*-position of the phenyl rings with respect to nitrogen. It was shown that regardless of the polymerization conditions, only phenyleneamine units are present in the structure of polyphenoxazine. Phenoxazine polymers are amorphous.

Heterocyclic phenoxazine polymers are electroactive and possess high thermal stability. Processes of thermo-oxidative destruction of polyphenoxazine start at 430—520 °C. In the inert medium at 1000 °C depending on the reaction conditions, the residue is 35—51%.

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