Investigation of Regularities and Products of Oxidative Polycondensation of 1,3-Benzenediol

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**ABSTRACT**

In the presence of H$_2$O$_2$, H$_2$O$_2$ + Fe$^{3+}$, NaOCl, OH + O$_2$ oxidants, 1,3-benzenediol (BD) enters into reaction of oxidative polycondensation and forms the oligomer product, including dihydroxyphenylene links. The kinetic regularities of BD oxidative polycondensation with oxygen in the alkaline medium have been studied by volumetric and EPR methods. It has been established that the reaction follows a first order both in monomer and alkali. In the reaction course the quintuplet EPR signals have been registered, each line of which is faintly split into a triplet, that has been assigned to the dimeric radical. It has been established that BD oligomer oxidation with oxygen in the alkaline medium proceeds without an induction period and has a first order in relation to the concentration of dihydroxy-phenylene-linked anions. At the same time, the accumulation of relatively stable macroaroxylic radicals has been observed. The mechanism of 1,3-BD oxidative polycondensation has been suggested, including the stages of single-electron oxidation of BD anion into oxyphenoxyl radicals and recombination of their resonance forms.

**INTRODUCTION**

Phenol [1], hydroquinone [2] and naphthols [3, 4] enter into the oxidative polycondensation reaction in the presence of such oxidants as H$_2$O$_2$, NaOCl and O$_2$ + OH with formation of oligomer products, including the corresponding phenol links through C-C links of the aromatic ring. By means of polymerization of naphthoquinone [5], copolymerization of quinones with vinyl monomers [6-8], oxidative polycondensation of 8-oxyquinoline [9] and aminophenols [10] the other oligomers including in
macromolecules links with reactive phenol hydroxyl groups have been also prepared and investigated. These oligomers possess heat, thermal and radiation stability, semiconductivities, paramagnetism and ability to solution and melting [5].

The products of their oxidation display high electric conductivity and paramagnetic properties [11,12]. Such oligomers and macroaroxyl radicals have the prospect of being used as thermoresistant non-subliming stabilizers of radical-chain processes, and also as an initial component for production of heat and thermostable polyepoxides, epoxy resins, and materials on their base [13].

In this connection, the study of regularities and products of 1,3-BD oxidative polycondensation and the synthesis of a new reactive oligomer, including dihydroxyphenylene links in the chain of aromatic polyconjugation, is of some interest. These studies investigate how the position of hydroxyl groups of di-atomic phenols has influence up on their reaction capacity in oxidative polycondensation, which is important for obtaining binding agents in glass-reinforced plastics production [8,10].

EXPERIMENTAL

The oxidative polycondensation of BD was carried out in the presence of H2O2 in a three-necked flask of volume 0.1 provided with a mixer, cooler and a dropping funnel. The flask was loaded with 0.05 mole of BD, to which 0.0218 mole H2O2 was added in the form of 14% or 30% aqueous solution while stirring. The reaction was carried out within a temperature range of 343-373K during 1.0-1.5 h. At the end of the reaction, the reaction mass was evaporated on a water bath and then dried in vacuum (10-1 mm.Hg) at 353-373K up to the constant mass.

The oxidative polycondensation of BD in the presence of NaOCl as well as drying and cleaning of resulting oligomers was carried out in the same way. In this instance 30% NaOCl aqueous solution was used as an oxidant.

The reaction of BD oxidative polycondensation in the presence of NaOH and air oxygen (or pure oxygen) was carried out in a reactor of 0.25 L volume, provided with a mechanical mixer, an inverse cooler and an air bubbler. The amount 11 g BD, 4.0 g NaOH, 30 mL of water were loaded into the reactor and heated on an oil bath. To achieve a temperature of 371K, air with the rate of 8 L/h freed from carbonic gas and heated to 368–371K, was let through the reacting mass. After completing the reaction in order to trap the ions of sodium or potassium, the reaction mass was treated by cationic exchange resin KU-2 and separated on a glass filler. Then the water was distilled off, the oligomer was purified by removal of the monomer and dried in vacuum (13.3 Pa) to constant mass.

The study of the kinetics of BD oxidative polycondensation with oxygen in the alkaline medium was studied by means of differentiating automatic gas volumeter DATV-70-2M on oxygen at a constant pressure equal to 9.8 × 10^4 Pa. The reaction was carried out in a glass reactor, having a magnetic agitator, the ultrathermostat U-10 and a device, which permitted the introduction of alkali into the reaction medium, upon attaining the given temperature without breaking the leak-proofness of the BD system. BD and a part of the solvent were loaded into the reactor, connected to the volumeter. Ethyl alcohol and distilled water were used as solvent. NaOH was dissolved and loaded into the device. The system was blown through and filled with oxygen. After the thermostating and checking of leak-proofness of the system the NaOH solution was added to the reaction mixture through the device. The volume of oxygen consumed and its amount were determined from volumeter data. Assuming that each oxygen molecule can react with four BD molecules, the content of the reacted BD was calculated [9], the kinetics of oligomer of 1,3-benzenediol (OBD) oxidation with oxygen in the alkaline medium was studied by the oxygen consumption in the same way.

To study the kinetics of radical processes in oxidative polycondensation of BD and oxidation of OBD, the reactions were conducted at 298 K in a tube, placed into the cavity of the radiospectrometer PE-1306. Methyl alcohol was used as the solvent. The monocystal CuSO4.5H2O with non-paired spins equal to 7×10^17 spin was used as a standard sample. Paramagnetic centers concentration was determined by comparing the twice integrated EPR spectra of the studied and the standard sample.

Molar masses and the molar-mass distribution of the products of BD oxidative polycondensation were
determined by the method of gel-permeation chromatography on a Waters chromatograph (refractometric detector) [14]. By means of polymerization of naphthoquinone [18], copolymerization of quinines with vinyl monomers [19, 20], oxidative polycondensation of 8-oxyquinoline [11] and aminophenols [21] the other oligomers including in macromolecules links with reactive phenol hydroxyl groups have been also prepared and investigated. Three Styrogel columns with 200, 500 and 1000 Å of porosity were used. Tetrahydrofuran was used as an eluent, with the supply rate about 0.001-0.0011 L/min. The samples were introduced into the column in a form of 0.1-0.2% solution during one minute. The tests were performed at temperature of 297.2 K.

Calibration of the device was performed by low-molecular fractions of OBD, determined by preparative chromatography. The measured dependence of the molecular mass (M) and the volume of retention (V_R) for OBD in the linear region is described by the equation:

\[ V_R = C_1 - C_2 \times \lg M \]

where \( C_1 = 30.8 \) and \( C_2 = 4.0 \)

\( M_w \) and \( M_n \) values were calculated according to the formula:

\[
\bar{M}_w = \sum W_i M_i \quad \text{and} \quad \bar{M}_n = \frac{1}{\sum M_i / W_i}
\]

where \( W_i \) is the weight fraction of \( i \) with molecular mass \( M_i \) was specified by the ratio of the i-part area of the chromatogram along the total area. The correction was determined according to the device broadening by [15].

\[
\bar{M}_n^u = 1.02 \bar{M}_n \quad \text{and} \quad \bar{M}_w^u = 0.98 \bar{M}_w
\]

where \( \bar{M}_n^u \) and \( \bar{M}_w^u \) are real values of molar masses.

IR-spectra of OBD were read on the Specord-80 spectrometer in (500-4000 cm\(^{-1}\)) area. Thin films of OBD applied over NaCl monocrystals, were used. Electronic spectra were recorded on the Specord UV-Vis spectrometer in an ethanol.

**RESULTS AND DISCUSSION**

**Regularities of BD Oxidative Polycondensation**

It has been established that in contrast to 1,2-benzene-diol [4], which reacts with H\(_2\)O\(_2\) with intense heat release at ambient temperature, BD oxidative polycondensation in the presence of H\(_2\)O\(_2\) proceeds by heating over 343K only. An efficient interaction of BD with H\(_2\)O\(_2\) occurs over 373 K. In this case the yield of oligomer product achieves 90–98%. The activity and the conversion degree of BD in the given reaction exceed considerably those of phenol [4], which when interacting with H\(_2\)O\(_2\) in identical conditions is transformed into oligomer products with 30–35% yield.

When carrying out the reaction of the BD with H\(_2\)O\(_2\) at relatively large amounts of H\(_2\)O\(_2\) (0.044 mole per 0.05 mole of BD) even at 343–353K the oligomers are formed with quantitative yield (90–98%). A concentration change in H\(_2\)O\(_2\) does not affect much the oligomerization course in the range of 14–30%. Fe\(_2\)(SO\(_4\))\(_3\) introduction in trace amounts into the reaction medium causes sharp acceleration of BD polycondensation and the reaction temperature can be decreased to 313–328K. This fact is due to catalysts of H\(_2\)O\(_2\) decomposition into active species in the presence of Fe\(^{3+}\)[16]. It has been discovered that 30% aqueous solution of NaOCl also demonstrates high efficiency in BD oxidative polycondensation at 373–388K. With equimolar ratios of BD and NaOCl, the oligomer products yield reaches 96% within 1 h.

BD Oxidative polycondensation can be carried out in an alkaline medium with air oxygen at temperatures 333–363K. In this case, alkali content increases from 0.023 to 0.057 mole of BD, the temperature and the reaction time increases from 1 to 8 h leads to the growth of oligomer product output, and also to the growth of their molar masses.

Oligomer output achieves ~80-90%, depending on the reaction course conditions. Furthermore, NaOH substitution for KOH leads to an increase in the oligomer product output, and the application of pure oxygen as an oxidant decreases the reaction time to 3–5 h.

The study of kinetic laws of BD oxidative polycondensation in the presence of NaOH+O\(_2\) shows that the process is of autocatalytic character (Figure 1), as was found to occur monophenol oxidative polycondensation under the same conditions [1, 3, 9, 10]. The induction period time decreases with temperature increase and high reagent concentration. It means that the appearance of induction period has been connected with accumulation of active centres in the reaction.
medium. Reaction in an alkaline medium proceeds with a fairly high rate both in ethanol and in water.

An BD concentration increase from 0.024 to 0.152 mol/L in water and from 0.03 to 0.12 mol/L in ethanol is accompanied by a maximal reaction rate W increase at 313K of about 7 and 4 times, respectively. An increase in w is observed also at alkali concentration change from 0.03 to 0.179 mol/L, where W grows in the range of \((1.26\sim 9.3)\times 10^{-4} \text{ mol L}^{-1}\text{.min}^{-1}\). The process temperature has great influences on its rate (Table 1).

From Figure 2 it follows that the reaction of BD oxidative polycondensation is of the first order in BD and alkali both in aqueous and alcohol-alkaline media. At constant pressure of oxygen \((9.8\times 10^4 \text{ Pa})\) and constant excess concentration of alkali, according to the first order reaction equation, the values of efficient reaction rates constants \(k\) were calculated, and from temperature dependencies of the latter ones, efficient values of activation energy \(E\) were calculated. As seen from Table 1, \(k\) values in the alkaline medium are rather high. They exceed those of phenols considerably \([(1,2-8.14)\times 10^{-6}\text{s}^{-1} \text{ at } 322-348 \text{ K}]\), but are noticeably inferior to those of 1,2-BD \((7.17-15.7)\times 10^{-3}\text{s}^{-1} \text{ at } 303-321 \text{ K}\).

The reaction capacity increase in the reaction of oxidative polycondensation with oxygen in an alkaline
medium in the commercial phenols 1,3 BD-1,4 BD is also confirmed by $E$ value of these processes in the aqueous medium: 134.1; 80.7 and 34.3 kJ/mol, respectively. Such dependence is connected with the second hydroxyl group inductive effect upon electron density distribution in 1,3-BD and 1,4-BD molecules, and also with resonance stabilization of the intermediate radical state in 1,4-BD oxidation process.

From the data of Table 1 and Figure 1 it is seen that BD oxidative polycondensation in water proceeds less rapidly in comparison with that in ethanol. The same effect was also found in 1,4-BD oxidative polycondensation study [2], and with oligooxyarylene oxidation [3]. The rise of the $k$ values and decrease of the reaction $E$ is observed in passing from water to methanol.

The study of BD oxidative polycondensation with oxygen in the alcohol-alkaline medium by the EPR method has shown that with the initial monomer concentration 0.067-0.302 mol/L and temperature 298K a quintiplet signal appears, each line of which is faintly split into a triplet. The appearance of EPR signals is preceded by the induction period which decreases with increased concentration of BD and alkali.

The kinetic curves of radical process are given in Figure 3. The dependencies of radical centre accumulation rates and the initial concentration of BD and alkali NaOH are linear and pass through the zero point of the coordinates; i.e. the process has a first order both on monomer and alkali (Figure 4). The rate constant value discovered from the first order equation (at $[\text{NaOH}]_0$/

<table>
<thead>
<tr>
<th>N</th>
<th>Solvent</th>
<th>[m]$_0$ x 10$^2$ (mol/L)</th>
<th>[NaON]$_0$ x 10$^2$ (mol/L)</th>
<th>T</th>
<th>W or W$_0$ x 10$^4$ (mol.L$^{-1}$.min$^{-1}$)</th>
<th>$K_{ef}$ x 10$^3$ (min$^{-1}$)</th>
<th>$E_{ef}$ (kJ/mol)</th>
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<tbody>
<tr>
<td>1</td>
<td>CH$_3$OH</td>
<td>9.10</td>
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<td>21.0</td>
<td>23.5</td>
<td>73.3</td>
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<td>9.10</td>
<td>17.9</td>
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<td>10.1</td>
<td>11.1</td>
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<td>308</td>
<td>5.52</td>
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<td>17.9</td>
<td>303</td>
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<td>4.5</td>
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<td>17.9</td>
<td>323</td>
<td>11.4</td>
<td>4.26</td>
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<td>9.10</td>
<td>17.9</td>
<td>313</td>
<td>3.84</td>
<td>4.26</td>
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<td>17.9</td>
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<td>18.0</td>
<td>323</td>
<td>15.0</td>
<td>4.26</td>
<td></td>
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<tr>
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<td>18.0</td>
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<td>7.32</td>
<td>4.26</td>
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<td>4.26</td>
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<td>11</td>
<td>CH$_3$OH</td>
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<td>18.0</td>
<td>303</td>
<td>3.24</td>
<td>4.26</td>
<td></td>
</tr>
</tbody>
</table>

(*) $W$ values for BD (1-7), $W_0$ values for OBD (8-11) are presented.
[BD]_0 \geq 2) is equal to (2.4\pm0.13) \times 10^{-4}\text{ s}^{-1} at 298K.

The autocatalytic character of the kinetic curves, observed in BD oxidative polycondensation by the oxygen consumption and by the EPR method, is probably connected with active centres accumulation in the reaction medium, which is typical of oxidative polycondensation of single-atomic phenols [1, 3, 4], but it is not observed for 1,2-BD and 1,4-BD [2].

In this connection, in order to find the kinetic dependence of BD oxidative polycondensation at advanced stages of the conversion, a study of OBD oxidation (M_n = 350, M_w =340, and the content of hydroxyl groups = 30.3%) with oxygen in the alkaline medium was carried out.

The kinetic curves of OBD oxidation with the oxygen in alkaline medium at 303-323K are shown in Figure 3. It is noticed that the reaction of OBD oxidation proceeds without an induction period at high rate at initial stages, both in water and in ethanol. From the dependencies of the initial rate W_0 on the components initial concentrations, it is clear that OBD oxidation is of the first order on each component. Kinetic curves at [NaOH]_0 [OBD]_0 \geq 2 are adequately linear in the corresponding coordinates; the calculated values of the effective rate constants are shown in Table 1. It is observed that W and k values of BD and OBD oxidation from monomer to oligomer do not vary considerably, but some decrease of E_{ef} values is observed. It should be noted that methanol is a more "efficient" solvent than water for OBD oxidation.

The EPR study of OBD oxidation has shown that in the given case a narrow singlet signal with 2.0027 g - factor with \Delta H=0.521-0.633 is observed. This is an indication of the absence of hyperfine splitting in protons of benzene ring due to the presence of the polyconjugated bonds system. In Figure 4 the kinetic curves of processes proceeding with OBD oxidation are shown. A radical centre accumulation occurs without any induction period. After some time, a stationary concentration of radical centres, i.e. stable macroaroxyl radicals, is achieved. Radical centres accumulation rate depends on the concentration of OBD and alkali and is of the first order. The value of the reaction rate constant is \( (0.87\pm0.015) \times 10^{-7}\text{ s}^{-1} \) at 298K.

The Study of Products of 1,3-BD Oxidative Polycondensation

The products of BD oxidative polycondensation are resin-type or solid substances of dark-brown colour, easily-soluble in water, alcohols, acetone, dioxane and other polar organic solvents. The GPC method showed that they are oligomers with \( \overline{M}_n = 560-690 \) and \( \overline{M}_w =

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**Table 2. Compositions and some properties of OBD.**

<table>
<thead>
<tr>
<th>OBD prepared condition</th>
<th>Elemental composition (%)</th>
<th>OH- group (%)</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>( M_w/M_n )</th>
<th>Absorption O_2 (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>66.10</td>
<td>4.11</td>
<td>30.3</td>
<td>890</td>
<td>560</td>
<td>1.53</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}_2 + \text{Fe}^{3+} )</td>
<td>66.30</td>
<td>4.25</td>
<td>30.6</td>
<td>960</td>
<td>580</td>
<td>1.56</td>
</tr>
<tr>
<td>( \text{NaOCl} )</td>
<td>66.05</td>
<td>3.93</td>
<td>30.2</td>
<td>1040</td>
<td>620</td>
<td>1.68</td>
</tr>
<tr>
<td>( \text{NaOH} + \text{O}_2 )</td>
<td>66.18</td>
<td>4.02</td>
<td>29.7</td>
<td>1190</td>
<td>690</td>
<td>1.72</td>
</tr>
</tbody>
</table>

In the table the experimental results of element analysis and content of hydroxyl groups have been presented, their calculation values of these parameters for benzenediol links are: C - 66.67 (%), H - 3.70, O - 29.65 (%), and OH - 31.48.
Narrow molecular weight distribution (MWD) is typical for them. On the MWD curves two maxima are observed at values $V_R=107.5$ mL and $V_R=100$ mL, the former corresponds to di- and trimeric fractions and the latter corresponds to tetra- and heptameric fractions. The results of elemental analysis and determination of hydroxyl groups confirm that oligomer products of resorcinol oxidative polycondensation consist of resorcinol structural units.

In IR-spectra of OBD the adsorption bands of associated phenol hydroxyl groups (3260 and 1200 cm$^{-1}$) and aromatic nuclei (1470, 1500, 1600 and 1640 cm$^{-1}$) are observed. The adsorption bands in out-of-plane deformation vibrations of non-substituted aromatic C-H bonds at 690, 730 and 840-850 cm$^{-1}$ are indicative of the fact that benzenediol links in macromolecules are connected with each other mainly in positions 1 and 4 of the aromatic ring, i.e. polycombination takes place through C-C bonds of aromatic nuclei.

The adsorption band at 730 cm$^{-1}$ refers, probably, to vibrations concerning three neighbouring C-H groups of aromatic nuclei of the end resorcinol links.

There is a broad and intense peak at 208-232 nm with a maximum at 215 nm in electronic spectra of OBD obtained in the presence of oxygen and NaOH. Two maxima also occur at 280 and 335 nm. The former is an E-band, corresponding to $\pi\rightarrow\pi^*$ excitation, and the adsorption band at 280 nm probably characterizes $n\rightarrow\pi^*$ transition in which a non-binding electron pair of oxygen- OH group takes place. The last peak indicates the presence of a polyconjugation system. OBD demonstrates electro-exchange properties and consumes molecular oxygen from alkaline solutions. In the presence of basic catalysts, OBD easily enters into reactions with epichlorohydrin and epoxy resins, forming infusible and insoluble polymer materials.

**On the 1,3-Benzenediol Oxidative Polycondensation Mechanism**

On the basis of the results obtained from the study of the kinetic regularities, of the content and structure of the BD oxidative polycondensation products together with literature data on phenols oxidation [17, 18], it is possible to reach the conclusion that the original act of this process is the generation of phenoxy-type radical centre.

890-1190 (Table 2). Narrow molecular weight distribution (MWD) is typical for them. On the MWD curves two maxima are observed at values $V_R=107.5$ mL and $V_R=100$ mL, the former corresponds to di- and trimeric fractions and the latter corresponds to tetra- and heptameric fractions. The results of elemental analysis and determination of hydroxyl groups confirm that oligomer products of resorcinol oxidative polycondensation consist of resorcinol structural units.

In IR-spectra of OBD the adsorption bands of associated phenol hydroxyl groups (3260 and 1200 cm$^{-1}$)
At first, an acid-base equilibrium is established in the alkaline medium in the presence of oxygen, then BD anion oxidation with oxygen occurs, as BD in neutral media in normal conditions does not practically react with oxygen.

The further course of the process, obviously is connected with isomerization of BD anion-radical into dioxiphenylene radicals and their recombinations.

As a result of the recombination of these radicals with further proton migration and their conversion into the aromatic structure, the following type of the dimer formation is possible:

These dimers can oxidize into their corresponding radicals and recombination of these radicals resonance forms followed by the migration of a proton leads to the oligomer products formation.

In BD oxidation with oxygen in the alcohol-alkaline medium the observed EPR spectra of the radicals (Figure 6) do not correspond to 1,3-BD anion-radicals as its proton density differs greatly [17]. Besides, the lifetime of 1,3-BD anion-radicals is very short; the second hydroxyl group in the meta position exerts only inductive influence upon redistribution of aromatic nucleus electron density, but does not take part in resonance stabilization of the unpaired electron.

The observed quinplet signals with faint splitting of each component to a triplet, relate probably to the radical of dimer I.

In these structures there are approximately 4 equivalent protons in 5,6,5', 6' for positions, and faint splitting of each component to a triplet occurs on two protons in 2,2' positions. Induction period occurrence and
the radical process kinetic curves plot in BD oxidative polycondensation can be explained by these interconversions.

OBD oxidation with oxygen in the alkaline medium proceeds in the same way; as evidenced by the first order on dihydroxyphenylene links and alkali. At the same time, stable macroaroyl radicals accumulate in the system upon OBD oxidation. This is connected with the fact that the unpaired electron is delocalized by the system of polyconjugate bonds, and the stiff-chain structure of the OBD molecule creates a certain steric hindrance for recombination of these radicals.

It should be emphasized that both BD and OBD oxidation with oxygen in the alkaline medium are limited by a single-electron transition from BD dianion to the oxygen molecule, i.e. by reaction (3), that correlates well with experimentally found value of the reaction order.

CONCLUSION

It is shown that BD enters into the reaction of oxidative polycondensation in the presence of such oxidants as H₂O₂; H₂O+Fe³⁺, NaOCl, NaOH+O₂ and forms an oligomer product, including benzenediol links in the chain of aromatic polyconjugation. Polycombination of dihydroxyphenylene links proceeds through C-C links of the aromatic ring mainly in 2 and 4 positions. The study of kinetics showed the BD oxidative polycondensation with oxygen in alkaline medium. The reaction proceeds with an induction period, which decreases with increase of temperature and BD anions concentration in the reaction medium. It has a first order both in BD concentration and in alkali concentration.

Radical centre formation is registered by the EPR method in the BD oxidative polycondensation. The EPR spectra are a quintet, each line of which is faintly split into a triplet, and was assigned to a dimer radical. Rate values and rate constant, determined from oxygen consumption, greatly exceed those for radical centres accumulation, i.e. not all the generated radicals are stable in the BD oxidative polycondensation.

The reaction of OBD oxidation with oxygen in the alkaline medium proceeds without an induction period. The EPR spectra registered from OBD oxidation are of narrow singlets. After 15-20 min the radical centres concentration at OBD oxidation does not practically change, i.e. stable macroaroyl radicals are formed. Radical centres accumulation at the OBD oxidation shows a dependence upon oligomer and alkali concentrations on first order. It has been suggested that the BD oxidative polycondensation includes stages of a single-electron oxidation of BD anion to oxyphenoxy radicals and recombination of their resonance forms. It has been discovered that both the BD and OBD oxidations with oxygen in the presence of alkali in methanol proceed more rapidly than in water.

REFERENCES


