The Radical and Ion-Radical Mechanism of Polymerization of 2,6-Xylenol. I. Formation of Polymer Radicals and Consecutive Products

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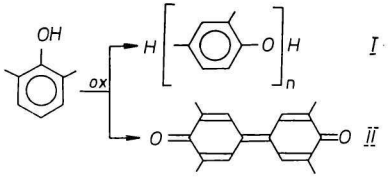
It was proved that on the surface of the crystalline copper(II) complexes $CuCl(OCH_3) \cdot 2$ pyridine and $CuCl_2 \cdot 2$ cyclohexylamine in a silicone paste, polymer phenoxy radicals were generated from 2,6-xylenol of the same type as those formed in a benzene solution in the presence of Ag_2O. The generated primary radicals with different spin density in the *para* position and on the oxygen atom can recombine in two ways. By recombination in the *para* position (C—C coupling) bisphenol (a derivative of 4,4-dihydroxydiphenyl) is formed and by recombination through the oxygen atom (C—O coupling) it is a dimer. In the beginning state of the reaction the formation of bisphenol is preferred and the product of its oxidation is diphenoquinone (DPQ). In course of the polymerization by recombination of the dimer radicals, polymer radicals with a sufficiently long life time are produced, so that their level constantly increases and a stationary concentration indicable by the EPR method is reached. In this condition, recombination of the primary radicals with the polymer radicals is statistically more favourable than the C—C coupling and the concentration of DPQ does not increase more.

In the oxidative polymerization of 2,6-xylenol [1] polyphenyl ether (*I*) and as final secondary product diphenoquinone (*II*—DPQ) originate:



I

II

Several papers [2, 3] deal with the mechanism of these reactions and their consecutive course was proved [4].

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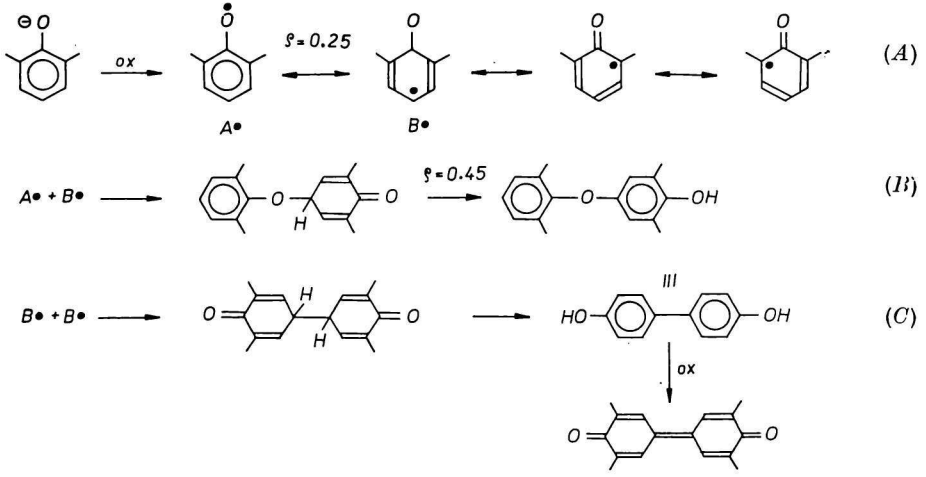
The initiation of the polymerization is connected with electron transfer (e^-) between the xylenol anion and the transition metal ion [2]. The formation of the primary (monomeric) and the secondary (polymeric) phenoxy radicals was proved by means of the EPR method in the oxidation of 2,6-xylenol with PbO_2 or Ag_2O [5].

The polymeric chain grows as a result of the consecutive reactions of the phenoxy radicals. For the propagation of the polymeric chain some mechanisms were proposed:

1. radical substitution [6],
2. mechanism of the „unpaired electron" [7, 8],
3. quinol ether equilibration [9—12] (redistribution—disproportionation),
4. quinol ether rearrangement [10, 13].

The impossibility of the hydrogen substitution in the *para* position by a radical was confirmed by the polymerization inactivity of methyl ethers of 2,6-xylenol and its dimers [6]. The shift of an electron on the chain supposed in the mechanism of the „unpaired electron" also is in contradiction with the EPR measurements of the substituted phenoxy radicals [14, 15]. The most probable mechanism seems to be the formation of quinol ethers [8, 13] by recombination of the phenoxy radicals. These products transform after rearrangement or redistribution to a polymer with different molecular weight. The formation of quinol ether during the radical reactions of substituted phenols is also known and many of them were already prepared as stable products [16].

While the part of the reaction mechanism dealing with the formation of the polymer chain was extensively discussed, relatively few papers were directed to elucidate the complex mechanism of the oxidation of 2,6-xylene. *McNelis* [17] suggested the following mechanism (*A*, *B*, *C*) of the formation of by-products (DPQ) through bisphenol (*III*):



The production of different quantities of DPQ in dependence on the composition of the $CuCl_2$ · pyridine catalyst is explained by *Finkbeiner* [18] with the existence of two catalytic complexes present in the polymerization system. The reaction in the dimeric system leads to the formation of DPQ, while the polymer production takes place in the monomeric one.

From the mechanism known till now, it is not possible satisfactorily to explain the considerable differences in the selectivity of catalysts with respect to the formation of both extreme types of units C—O and C—C. The aim of this series of papers is to provide understanding of the mechanism of formation of the oxidation products of 2,6-xylenol.

Experimental

Chemicals

2,6-Dimethylphenol (xylenol purified by zonal melting), impurities 0.01%, benzene p.a. without thiophene, pyridine trademark Lachema were used. Ag_2O was prepared from $AgNO_3$ and KOH, washed by ethanol, ether, dried in vacuum and stored in dark in argon atmosphere.

Preparation of polymer radicals

Ag_2O and a benzene solution of 2,6-xylenol were dosed into a double throat reaction vessel under argon atmosphere using electromagnetic mixing (at the temperature of 25°C, ultrathermostat). The samples were taken off for EPR measurements, and for determination of the conversion as well as for the quantity measurement of DPQ at different time intervals.

Determination of the conversion

The samples were taken off at different time intervals and placed into a centrifugal vessel. The reaction time was measured from the moment of putting the samples into the centrifuge. After centrifugation, the concentration of the unreacted OH groups were determined in the liquid phase by means of IR spectroscopy UR-10 (Zeiss, Jena) measuring the absorbance at the wave number 3590 cm^{-1}.

Determination of 2,2,2',2'-tetramethyl diphenoquinone

The diphenoquinones were ascertained in the reaction mixture spectrophotometrically (using a CF-4-R-Optica, Milano). Because of their low solubility, the diphenoquinones fall out from the solution during the reaction. The whole reaction mixture must be used for determination of diphenoquinone. The catalyst was centrifuged first and then DPQ was quantitatively extracted from the sediment with chloroform. Then, the liquid phase and the extract were mixed. The optical density of DPQ solutions was measured at 420 nm.

EPR technique

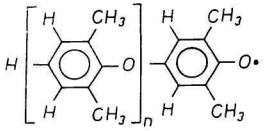
An EPR spectrometer Varian E-3 operating at 100 KHz modulation was used. The cells of 4 mm diameter were closed by a three-way stopcock. They were filled with the samples by means of a syringe in argon or highly purified nitrogen atmosphere. The direct generation of polymer radicals in absence of the solvent was carried out in silicone paste. The paste was prepared in inert atmosphere in silicone oil or vaseline from crystalline 2,6-xylenol, with which a quartz stick was covered. A similar paste was mixed on

the surface of the quartz stick from crystalline water-free $CuCl_2$ or from the catalytic $CuCl_2$ · amine complex with the xylenol layer. The stick was immediately put into the EPR cell and the signals were measured in different time intervals.

The calculation of the theoretical EPR spectra and their scanning were carried out with a spectrocomputer (Varian-Spectro-System 100) in the Varian Research-Center in Zürich.

Results and Discussion

Huysmans and *Waters* [5] observed by the EPR method the creation of free radicals in a benzene solution of xylenol in the absence of oxygen after their initiation with Ag_2O at laboratory temperature. The observed septet, the separate lines of which were still splitted, was interpreted as a polymer radical of the type (*D*):



(*D*)

supposing a steric unequivalency of both methyl groups neighbouring with the free electron on the oxygen.

The life time of the primary radicals of the order of fragments of seconds could be identified only by the flow technique (180 ml/min.) [5], while in the case of polymer radicals the half-life time of 150 minutes was determined. Our experiments concerning generation of a measurable level of polymer radicals in the system of Cu(II)-amine complexes and xylenol in a benzene solution failed. On the other hand, the lowering of mobility of the reacting substances in the system by direct contact of crystalline xylenol with the catalytic Cu(II) complex in the silicone paste provided an analogous EPR signal as obtained in the presence of Ag_2O in a benzene solution of xylenol.

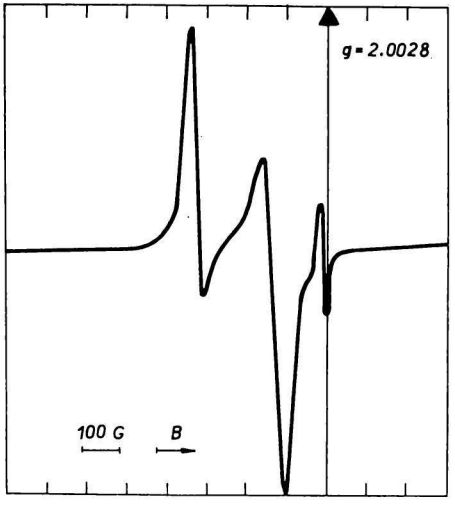


Fig. 1. EPR spectra generated by the contact of the crystalline catalyst $CuCl(OCH_3)$ · 2 pyridine with crystalline 2,6-xylenol in silicone paste.

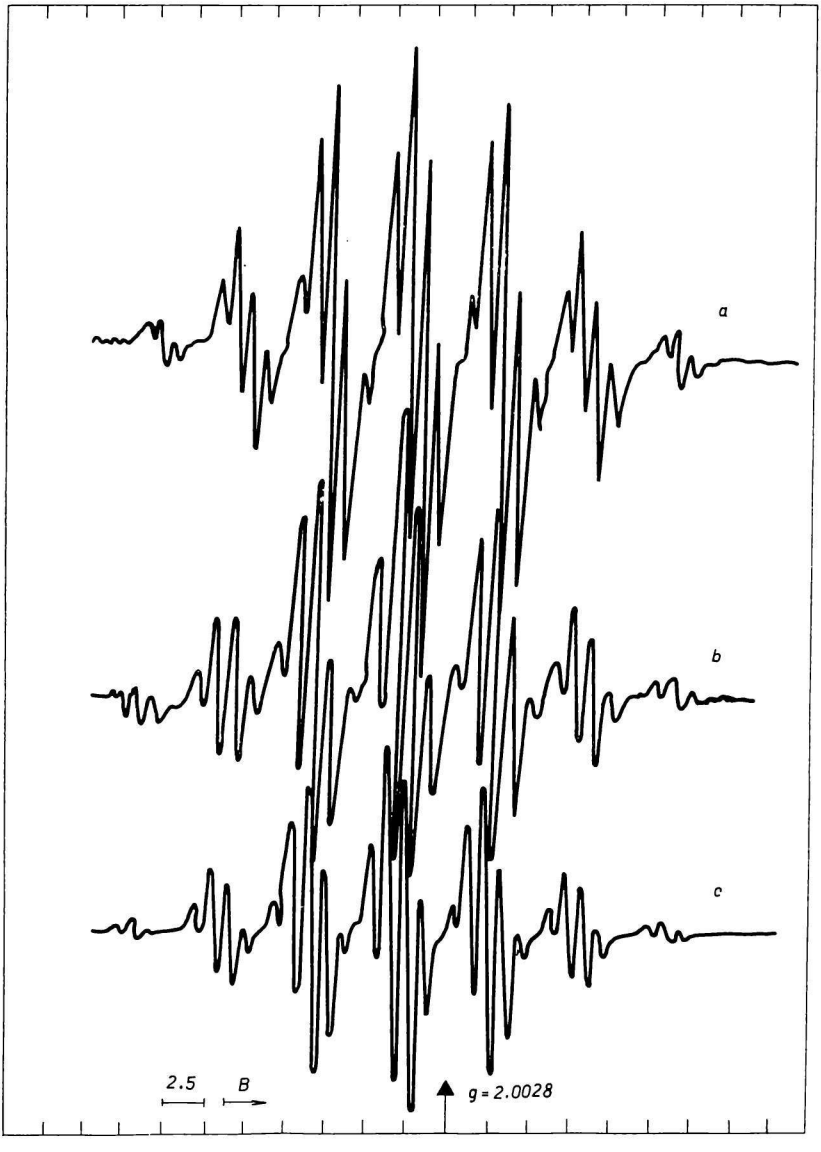


Fig. 2. EPR spectra of the polymer phenoxy radicals.
a) radical generated from 2,6-xylenol in silicone paste on the surface of the crystalline catalyst $CuCl_2(OCH_3) \cdot 2$ pyridine; *b*) radical generated from 2,6-xylenol in benzene solution in the presence of Ag_2O; *c*) simulated theoretical spectrum recorded by a spectrocomputer (Varian-Spectro-System 100).

Fig. 1 shows — besides two intensive lines with much higher g factors than 2 (connected with $3d^9$ unpaired electron of Cu(II)) belonging to the complex $CuCl(OCH_3) \cdot 2$ pyridine (total width 400 gauss) — also a less intensive unresolved signal of the free radical with $g = 2.006$. With properly chosen spectral parameters, there is possible to obtain splitting of the singlet to septet of a total line width of 37 gauss. The separate lines of the septet are further splitted to 3, 4, 5, 4, 5, 4, 3 lines. The nonuniform splitting may be explained in this case by the unequivalency of the two methyl groups. We suppose that the signal of the radical is superposition of three types of unequivalent protons with the splitting constants $a_H = 1$ gauss (two equivalent protons), $a^1_{CH_3} = 6$ gauss, $a^2_{CH_3} = 5$ gauss on the benzene ring. This conception was fully confirmed by the simulated EPR spectrum obtained with the spectrocomputer using the above splitting constants. They are in good agreement with the values of the splitting constants found at the generation of polymer radicals (that means, without an interacting third proton in *para* position on the benzene ring) in the presence of Ag_2O in benzene solution. Fig. 2 compares the spectrum of the radical formed on the surface of the crystalline catalyst $CuCl(OCH_3) \cdot 2$ pyridine in silicone paste with theoretically calculated spectrum of the polymer radical and with the spectra of the radicals generated by Ag_2O. The level of the radicals is of the order of about 10^{13} to 10^{14} spins, while one can ascertain an analogous signal but of a 20-times lower concentration at the generation of radicals on the surface of a crystalline catalyst of the type $CuCl_2 \cdot$ cyclohexylamine in silicone paste (Fig. 3). When crystalline $CuCl_2$ is mixed with crystalline xylenol in the absence of amine, a measurable level of free radicals is not observed, but redbrown diphenoquinone is immediately formed.

We suppose that the primary radicals are created in a redox process. The observed polymer radicals and DPQ are products of the consecutive reactions. The creation of both consecutive products takes place without two different catalytic centres. The parallel course of this reaction was studied on the system xylenol—Ag_2O by kinetic methods.

During the simultaneous generation of polymer radicals and creation of DPQ (Fig. 4*a*) at the constant molar ratio of Ag_2O : xylenol = 2.63 and at 25°C, there may be observed a significant lowering of the concentration of OH groups indicated

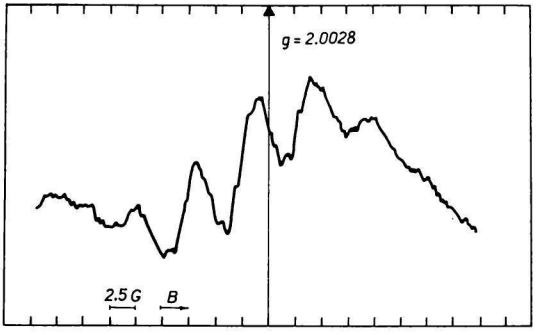


Fig. 3. EPR spectrum of the polymer phenoxy radical generated on the surface of a powder $CuCl_2 \cdot 2$ cyclohexylamine catalyst in the presence of crystalline 2,6-xylenol in silicone paste.

by IR spectroscopy (at 3580 cm^{-1}). The final quantity of DPQ is practically stabilized in the first period of polymerization and at the same time, it is possible to indicate by the EPR method the presence of the polymer radicals PO•. The highest level of radicals was observed in the first moment of the polymerization reaction (Fig. 4*b*).

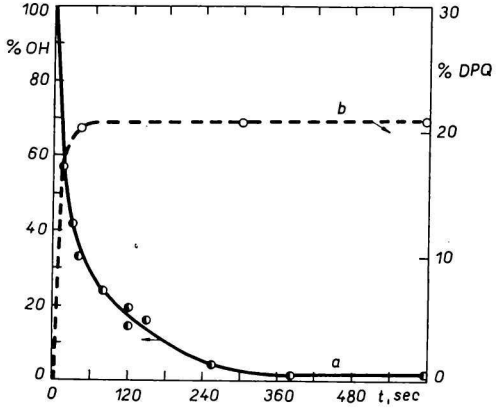


Fig. 4a. Change of the concentration of phenol OH groups in dependence of time. *a*) conversion curve (%), expressed by the rate of $I \cdot 100/I_0$ (OH groups in IR spectrum at 3580 cm^{-1}); *b*) creation of DPQ with time (percentage referred to the initial concentration of 2,6-xylenol).
[xyl] = 0.33 mole l^{-1}, T = 25°C, molar ratio of Ag_2O : [xyl] = 2.63, benzene solution.

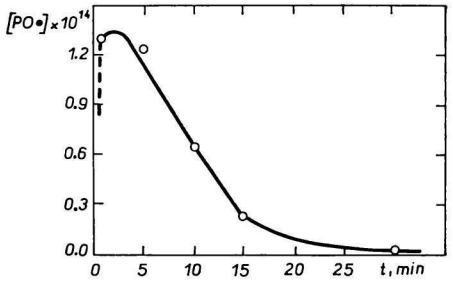


Fig. 4b. Change of the concentration of polymer phenoxy radicals (PO•) with time generated in the presence of Ag_2O under the same conditions as in Fig. 4*a*. The number of unpaired electrons calculated for 0.3 ml volume of benzene solution.

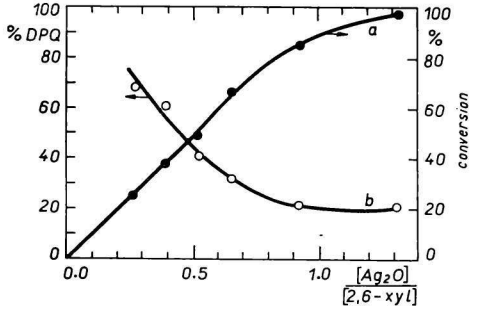


Fig. 5a. Dependence of the conversion (*a*) and formation of DPQ (*b*) upon the initial molar ratio of Ag_2O : [xyl].
[xyl] = 0.33 mole l^{-1}, τ = 10 minutes, T = 25°C, benzene solution, conversion related to the initial concentration of 2,6-xylenol.

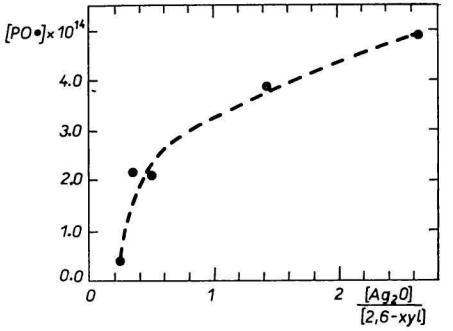
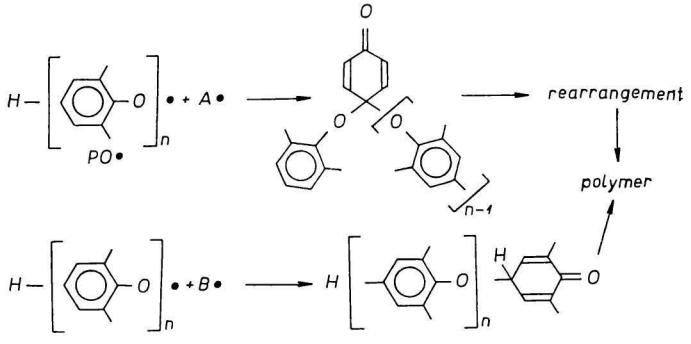


Fig. 5b. Dependence of the number of polymer phenoxy radicals upon the initial molar ratio of Ag_2O : [xyl].
The number of unpaired electrons calculated for 0.3 ml volume of benzene solution.

The faster the high level of polymer radicals is reached (a greater amount of catalyst with respect to the xylenol), the lower is the end-level of DPQ (Fig. 5*a*, *b*). This effect is due to the fact that the primary radicals have about two times higher spin density in the *para* position ($\varrho = 0.45$) than on the oxygen ($\varrho = 0.23$) [19] and an essentially shorter life time than the secondary polymer radicals. Owing to this fact the primary radicals immediately recombine to bisphenol and by further oxidation they change to DPQ according to the mechanism suggested by *McNelis* [17].

During the polymerization, however, as a consequence of the longer life time of the polymer (PO•) than of that of the primary radicals (A• and B•), the probability of an interaction of the primary radicals with the polymeric ones will increase instead of the recombination of two primary radicals (*E*):



The absolute concentration of the polymer radicals in the first minute immediately after their generation on the surface of the powder catalyst (1 g Ag_2O+0.2 g xylenol) is about 1.4×10^{14} spins in the volume of the sample (0.3 ml). This value is 10^3 times higher than the treshold sensitivity for the concentration of the unobservable primary radicals has to be.

The rate of reaching the stationary concentration of the polymer radicals varies with the type of amine used for the formation of the catalytic complex (Fig. 6).

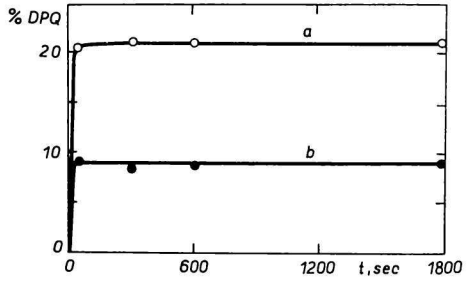


Fig. 6. Dependence of the formation of DPQ upon time.
a) polymerization in benzene; [xyl] = 0.33 mole l^{-1}, T = 25°C, molar ratio of Ag_2O : : [xyl] = 2.63; *b*) polymerization in the presence of pyridine [py] = mole l^{-1}; [xyl] = = 0.33 mole l^{-1}, molar ratio of Ag_2O : [xyl] = 2.63.

After adding pyridine into the reaction mixture (Ag_2O—xylenol) the concentration of DPQ decreased to one half of its value, while the level of polymer radicals remained unchanged. Lower reactivity in *para* position of the radical B• is not excluded in the presence of pyridine during recombination process.

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