The Radical and Ion-Radical Mechanism of Polymerization of 2,6-Xylenol. IV.
Reaction Catalyzed by Copper(II)-amine Complexes

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The reaction scheme of the radical and ion-radical mechanism of the oxidative polymerization of 2,6-xylenol conditioned by the type of the actually used catalyst (Ag$_2$O; CuCl$_2$ · 2 cyclohexylamine) is described. An equilibrium state between complexes of copper(II) coordinated in various degrees with cyclohexylamine as a function of the molar ratio of Cu(II) : amine was ascertained. The catalytic activity passes through a maximum, indicating that only the copper(II) complex uncompletely coordinated with amine is effective for polymerization. In inert atmosphere during the polymerization the concentration of the Cu(II) ions decreases, the reaction approaches the equilibrium state, while in the presence of oxygen the catalyst is regenerated. If the momentary surplus of monomer in the beginning of the polymerization is very high, the concentration of Cu(II) ions will decrease in such a degree that the consecutive reaction of phenoxy radicals with the Cu(II) complexes cannot effectively take place. Due to this circumstance the recombination of the primary radicals takes place with precedence forming bisphenol and finally undesirable diphenoquinone. After reaching a steady state concentration of the Cu(II) ions diphenoquinone is not formed any more because the reaction of phenoxy radicals with Cu(II) ions is preferred. This state observed only later in the stationary region of polymerization can be established already in the beginning of the polymerization suppressing the local monomer surplus with respect to the catalyst to the lowest degree.

In the previous papers the experimental parameters of the formation of aryloxy radicals [1] and their reactivity with copper(II) ions [2] were discussed. It was possible to prove an electron transfer from the phenoxy radical to Cu(II) leading to positive phenoxonium ions [3]. In this paper the experimental study is also extended to the reaction of 2,6-xylenol with Cu(II)-amine complexes and the kinetic data of the catalytic activity are presented.

On the basis of these studies the reaction mechanism of the polymerization of 2,6-xylenol with Cu(II)-amine complexes and the formation of secondary products s explained.

Generally it is supposed that the initiation of polymerization is connected with an electron transfer from the xylenol anion to the Cu(II) ion bonded in a complex [4]. *Blanchard* and co-workers [5] suggest in complexes with pyridine two active centres of monomeric (*I*) or dimeric (*II*) type
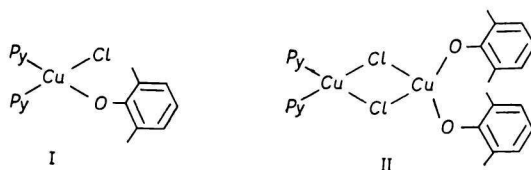
These different active centres lead to two different final products of the reaction, namely to polyether and diphenoquinone (DPQ). A study of the electron transfer in Cu(II)-pyridine complexes by means of the EPR method has been given by *Ochiai* [6]. The study of the redox mechanism of CuCl-pyridine complexes in the presence of oxygen leads the author to the conception of a free radical mechanism. In the presence of pyridine the oxidation Cu(I) $\rightarrow$ Cu(II) takes place forming a complex with a quartet signal with lines of different intensity. The quartet is caused by interaction of an unpaired 3 d^9 electron of the Cu(II) ions with the magnetic moment of the copper nucleus ($I = 3/2$). After adding dibutylphenol the intensity of the signal gradually decreases with time in consequence of the electron transfer. The unstable singlet of low intensity at $g = 2.00$ is assigned by the author to (*tert*-butyl)$_2$C$_6$H$_3$O· radicals. In this mechanism an important function of the O^{2-} ions is supposed, lying in the transient participation in the formation of the complex.

Experimental

Reagents, the method of polymerization, the analysis of the reaction products, the preparation of Cu(II)-amine complexes and the EPR technique were discussed in previous papers [1—3]. An EPR spectrometer of the type Varian E-3 with 100 kHz modulation was used.

Results and Discussion

EPR signals of Cu(II)-amine complexes and the activity of the catalytic complex

A catalytic activity of CuCl$_2$ in the absence of oxygen as well as its reactivity with respect to the generated free radicals in the polymerization products was not supposed [4—7]. But the experiments of the present work have shown that the presence of strong basic amines (for instance: cyclohexylamine, morpholine) lead to the formation of complexes active also in the absence of oxygen. Under these conditions in benzene—ethanol solutions EPR signals similar to those published by *Ochiai* [6] were observed. Interaction of the unpaired electron with the donor nitrogen in the ligand at laboratory temperature does not lead to further splitting of the spectra. Such a distinction of complexes can take place only in the glassy state at −177°C [7].

Equilibrium state was established between the soluble and solid form of copper(II) complexes as a function of the molar ratio Cu(II) : cyclohexylamine in the catalytic system. It was shown that while the EPR signal in the soluble form of the complex from the ratio 1 : 5 does not change with further surplus of amine, in the sedimenting solid blue complex the signal changes with number of coordinated amines (Fig. 1a). The separation of the complex from the solution in the form of solid phase is a function of the absolute concentration of $CuCl_2$. At the concentration of 0.25 mole l^{-1} precipitation of the blue sediment has been observed. In the twice diluted solutions a sedimenting solid complex has been formed at the ratio 1 : 200. By gradual increasing of the amine with respect to Cu(II) the relative intensities of the quartet lines of the EPR signal vary in that way that the line closer to the position on the free electron $(g = 2.00)$ grows stronger (Fig. 1b). It is known that the compounds of
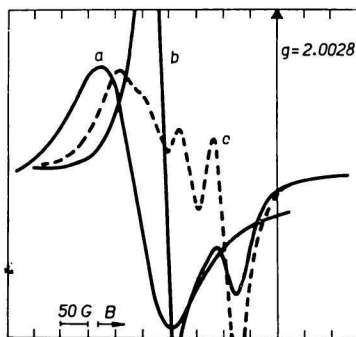

Fig. 1a. EPR spectra of $CuCl_2$-cyclohexylamine complexes in ethanol solution. Molar ratio of Cu(II) : amine (a) 1 : 1; (b) 1 : 3; (c) 1 : 5.
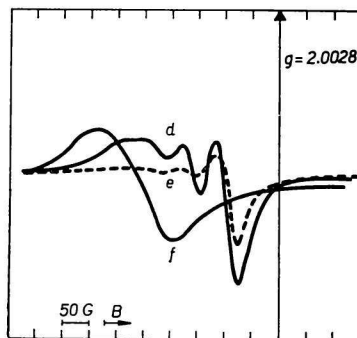

Fig. 1b. Molar ratio of Cu(II) : amine (d) 1 : 150; (e) 1 : 200. EPR signal of 0.025 mole l^{-1} solution of $CuCl_2$ in waterless ethanol (f).
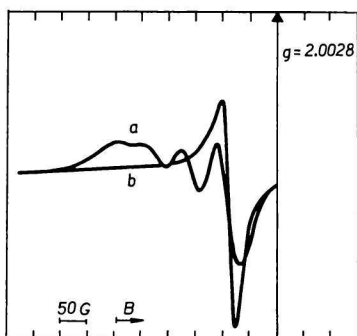

Fig. 2. EPR spectrum of $CuCl_2$-cyclohexylamine complexes in the molar ratio Cu(II) : amine 1 : 10 in different phases of the heterogeneous system. Liquid phase (a); precipitated solid phase (b).
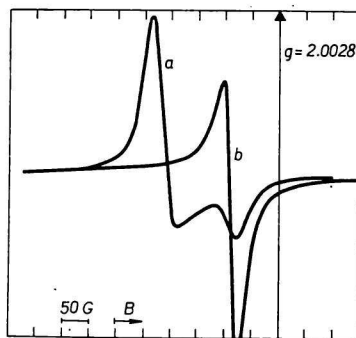

Fig. 3. EPR spectrum of sedimented solid $CuCl_2$-cyclohexylamine complexes at different molar ratios of Cu(II) : amine (a) 1 : 5; (b) 1 : 10.

Cu(II) in crystalline form have asymmetric EPR signal with two g values: $g_{||} \sim$ ~ 2.00 and $g_{\perp} \sim 2.2$. A hyperfine interaction of $g_{||}$ with the Cu nucleus ($I = 3/2$) was not observed whereat $g_{\perp}$ produces a quartet. The shifts in the g values by changing the molar ratio of Cu(II)-amine are observed in the interval of the two $g_{||}$ and $g_{\perp}$ values mentioned. In Fig. 2 the EPR signal of Cu(II)-amine complex measured in solution is compared with the signal of the precipitate at the molar ratio 1 : 10. The sedimented complex of the bivalent copper
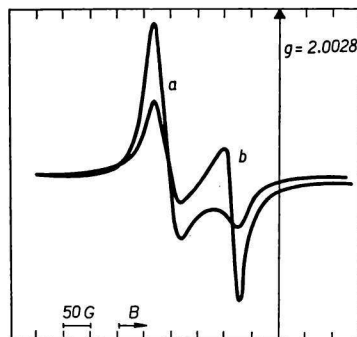

Fig. 4. EPR spectra of powder complexes of CuCl₂-cyclohexylamine prepared in the stoichiometric ratio (a) 1 : 2; (b) 1 : 4.

coordinated by cyclohexylamine to the highest degree has the g value expressively shifted in the direction of the free electron up to $g = 2.07$ compared with a complex, separated from the solution at the molar ratio Cu(II) : amine = 1 : 5. In this case a doublet was observed in which the strongest line had its g value very near to the g value of the Cu(II) ions in ethanol solution of CuCl₂ (2.16) (Fig. 3). Also complexes of exactly defined compositions of Cu(II)-cyclohexylamine, namely with the ratio of 1 : 2 and 1 : 4 were prepared (Fig. 4). Complexes higher coordinated with cyclohexylamine, e.g. with the ratio 1 : 6, indicated on the basis of EPR signals
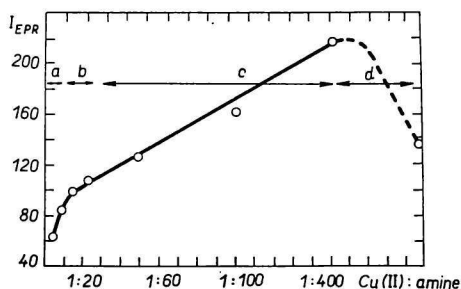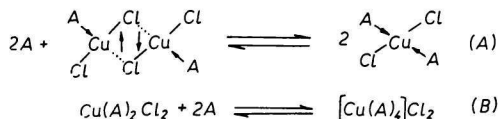

Fig. 5. Change of intensity of the EPR signal of CuCl₂-cyclohexylamine complexes in dependence on the ratio of Cu(II) : amine.

In region (a) the complex is diamagnetic, in region (b), where the complex of the composition CuCl₂ · 2 cyclohexylamine is formed, the system is catalytically active. In region (c) the system is catalytically inactive. In region (d) dark blue complexes, coordinated to the highest degree with cyclohexylamine, and not active any more, are formed.

in the blue precipitate could not be prepared in crystalline form. It follows from the comparison of the EPR signals of model complexes of known composition with signals of the sedimented complexes that with increasing content of cyclohexyl-amine in the reaction mixture higher with amine coordinated complexes are for-med with restricted solubility. In the presence of xylenol the solubility of these complexes rises and complexes with lower coordination of amine are formed. By adding only a small amount of amine to the $CuCl_2$ solution a three times lower number of $3\,d^9$ unpaired electrons than it would be expected from the original amount of the present Cu(II) ions was observed. By further increase of the amine concentration the total area of EPR signals of the complex becomes greater and at the molar ratio Cu(II) : amine = 1 : 150 the area of the signal proportional to the original number of free spins of the Cu(II) ions is renewed (Fig. 5). The observed effect of the decrease of the original unpaired electrons of Cu(II) ions at very small concentration of the amine can be explained by mutual compensation of the spins forming a dimeric complex being in equilibrium with the monomeric one; the dime-ric complex, however, in contrast to the monomeric is not paramagnetic (A). At sur-plus of amine a higher number of coordinated amines was observed (B)

$$2A + \begin{matrix} A \\ \diagdown \\ Cu \\ \diagup \\ Cl \end{matrix} \begin{matrix} Cl \\ \diagup \\ \end{matrix} \begin{matrix} Cl \\ Cu \\ \diagdown \\ A \end{matrix} \rightleftharpoons 2 \begin{matrix} A \\ \diagdown \\ Cu \\ \diagup \\ Cl \end{matrix} \begin{matrix} Cl \\ \diagdown \\ A \end{matrix} \quad (A)$$

$$Cu(A)_2 Cl_2 + 2A \rightleftharpoons [Cu(A)_4]Cl_2 \quad (B)$$

The different degree of coordinated amine is effectively expressed in the catalytic process of the polymerization of 2,6-xylenol; $CuCl_2$ and similarly also the complexes fully coordinated with cyclohexylamine e.g. $[Cu(A)_4]Cl_2$ are catalytically inactive. The condition for catalytic activity is given by a low number of coordinated cyclo-hexylamine molecules, namely 2.
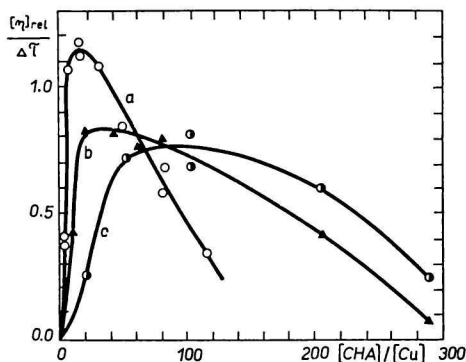

Fig. 6. Dependence of the average polymerization rate of 2,6-xylenol expressed by the relative viscosity after the time τ, upon the molar ratio of cyclohexylamine : Cu(II) for different absolute concentrations (mole l^{-1}) of $CuCl_2$ (*a*) 0.025; (*b*) 0.01; (*c*) 0.004. Temperature 30°C; $\tau = 30$ minutes.
$[xy] = 1$ mole l^{-1}; $[\eta]_{rel}^{25}$ in chloroform; $c_{polymer} = 0.3$ g/100 ml.

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Dependence of the catalytic activity upon the molar ratio of cyclohexyl-amine : Cu(II) at different initial concentrations of $CuCl_2$ (in the range of 0.025 to 0.004 mole l^{-1}) indicates the existence of equilibrium state between the complexes coordinated to different degrees. The appropriate curves (Fig. 6) pass through a maximum which is for decreasing concentration of the copper shifted to the higher ratio of cyclohexylamine : Cu(II). The measure of the activity is the viscosity number $[\eta]$ reached after 30 minute polymerization of the 2,6-xylenol.

Interaction of Cu(II)-amine complexes with 2,6-xylenol

In inert atmosphere and at laboratory temperature immediately after the contact of 2,6-xylenol benzene solution with an ethanol solution of $CuCl_2$—cyclohexylamine complex an effective reaction takes place, the kinetics of which can be followed on the basis of decrease of the EPR signal intensity of the respective complex with time (Fig. 7). In the absence of oxygen (capable to regenerate the catalytic complex)
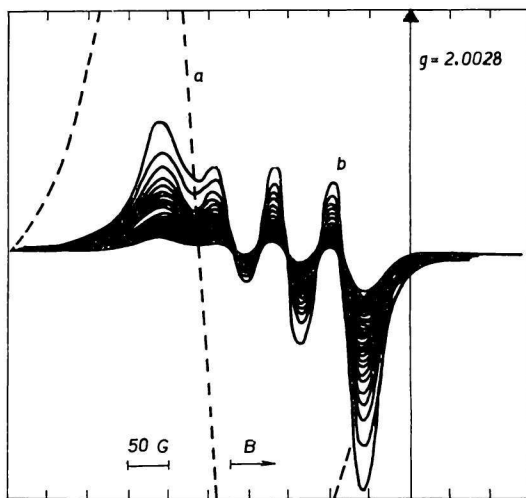

Fig. 7. Changes of the EPR signal of the catalytic complex $CuCl_2$-cyclohexylamine (molar ratio Cu(II) : amine = 1 : 25) with time, after adding 2,6-xylenol.
a) methanol solution of $CuCl_2$ (0.025 mole l^{-1}) before mixing with cyclohexylamine;
b) after adding cyclohexylamine and starting the polymerization — spectral readings every minute.

an exponential decrease of the catalytic complex takes place (Fig. 8). The reaction gradually reaches the equilibrium state, in consequence of which the disappearance of the total Cu(II) bound in a complex cannot be observed even at 8-times higher surplus of xylenol. The most probable factor determining the equilibrium is the cyclohexylamine hydrochloride formed in the reaction process which can be analytically proved (C)
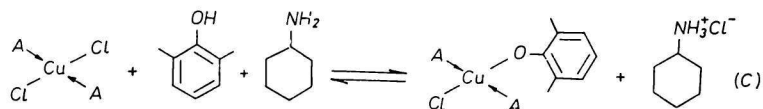
In the presence of oxygen in the reaction mixture, Cu(II) is continuously regenerated and the EPR signal does not change with time.

Under the same conditions the simultaneously followed amount of the formed polymer and the undesirable DPQ points at the origin of the diphenoquinone in the first minute of polymerization. At laboratory temperature after 1 or 2 minutes a steady state concentration about 3% is reached (Fig. 9). After this time the conversion is about 10% (Fig. 10). The polymerization passes namely from its beginning nonstationarily in consequence of the surplus of xylenol in comparison with the amount of Cu(II) bonded in the complex. Since the reaction connected with the electron transfer from the negative xylenol ion to the copper ion takes place faster than the oxidation of the reduced catalyst, a nonstationary state occurs, whereby the recombination of the primary generated radicals to bisphenol and then to diphenoquinone prevails. In case that in the reaction system an equilibrium concentration of the Cu(II) ions is established, an interaction of the radicals with Cu(II) is statistically more favourable than the recombination of the phenoxy radicals. The logical consequence of this fact is that an appropriate dosing of xylenol into a catalyst solution must lead to a decrease of the diphenoquinone formation.
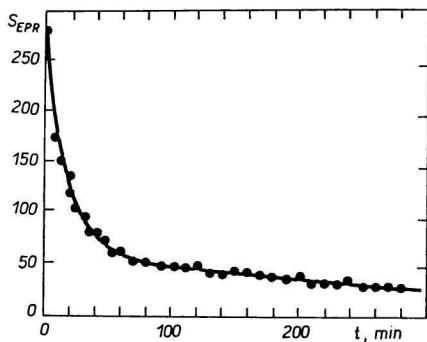

Fig. 8. Oxidation kinetics of 2,6-xylenol followed according to changes of the total area of the EPR signal of the $CuCl_2$-amine complex 1 : 25 with time, in ethanol—benzene solution at laboratory temperature.
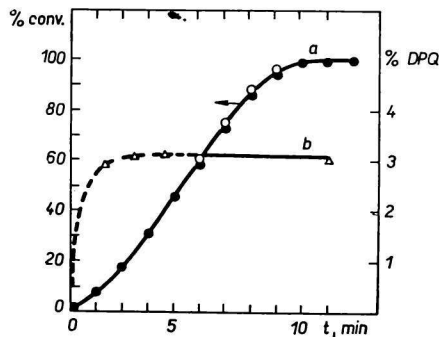

Fig. 9. Dependence of the formation of DPQ and conversion of 2,6-xylenol with time.

a) curve of conversion expressed in % of the reacted oxygen; b) increase of DPQ (weight % calculated for the original concentration of xylenol).

$[xy] = 0.75$ mole l^{-1}; Cu(II) $= 0.01$ mole l^{-1}; cyclohexylamine : $CuCl_2 = 43$, temperature 30°C; solvent benzene——ethanol in the molar ratio 75 : 25.

This assumption has been fully confirmed as it is demonstrated in Fig. 11. With permanent excess of Cu(II) in the polymerization process it is possible to lower the concentration of the undesirable DPQ to 0.6%. These experiments show that at the formulation of the reaction mechanism it is necessary to take into account the
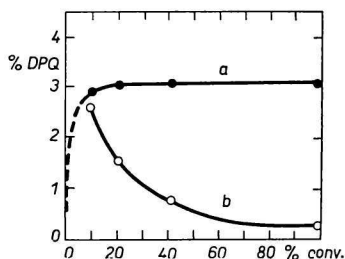

Fig. 10. Dependence of the concentration of DPQ on the conversion of 2,6-xylenol. *a*) percentage of DPQ related to the beginning concentration of xylenol; *b*) percentage of DPQ related to the concentration of the reacted xylenol. The other parameters are the same as in Fig. 9.
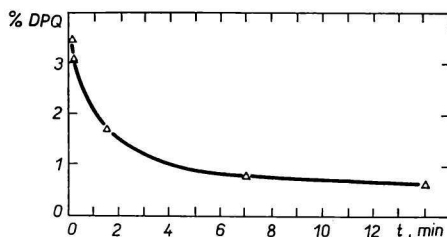
*Fig. 11.* Dependence of the concentration of DPQ on the time of dosing. The same amount of 2,6-xylenol added into the solution of CuCl$_2$-cyclohexylamine catalyst (3.75 ml of xylenol for 0.25 ml solution of the catalyst). The other conditions are the same as in Fig. 9 and 10.

reaction of the phenoxy radicals with Cu(II)-amine complexes as it was shown in our previous papers [2, 3]. Under these conditions neither the level of the primary nor that of the polymeric radicals reaches a high value making thus possible to follow the kinetics by means of the EPR technique. Only in the first moment it is possible to catch a very weak signal in the noise at the $g = 2.00$ disappearing during the reaction.

Conclusions

On the basis of the experimental results discussed in previous papers [1—3] it is possible to suggest a reaction scheme of the polymerization of 2,6-xylenol to polyphenylethers, satisfactorily explaining the formation of by-products.

In principle there are two different mechanisms of the polymerization of xylenol. In the first case, the level of the free polymeric radicals is so high that it is possible to measure it by means of the EPR technique, but a relatively high amount of undesirable DPQ is formed. This mechanism has an evidently radical character and it is possible to initiate it by metal oxides, namely by Ag$_2$O and PbO$_2$. For the second type the level of polymeric radicals is not measurable by means of normal EPR technique, whereby at the same conversion the concentration of DPQ is one order lower. This type of polymerization shows a radical-ion character catalyzed by complexes of bivalent copper uncompletely coordinated with amine. The high selectivity of these systems leading to the formation of polymer has been assigned to the rise of concentration of phenoxonium ion, which fastly reacts with 2,6-xylenol anions according to the equation (*D*)

$$+ A(HCl) \longrightarrow \quad (D)$$
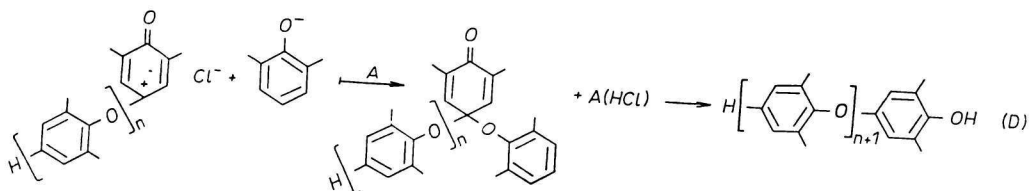
A similar reaction of stable phenoxonium ions with nucleophils by means of IR spectroscopy was studied by *Dimroth* and co-workers [8]. Dichlorodicyanobenzoquinone was used as oxidation agent of phenol by *Becker* [9], who also suggested for this case a radical-ion mechanism.

The two different possible ways of polymerization can be expressed by the radical-ion scheme.
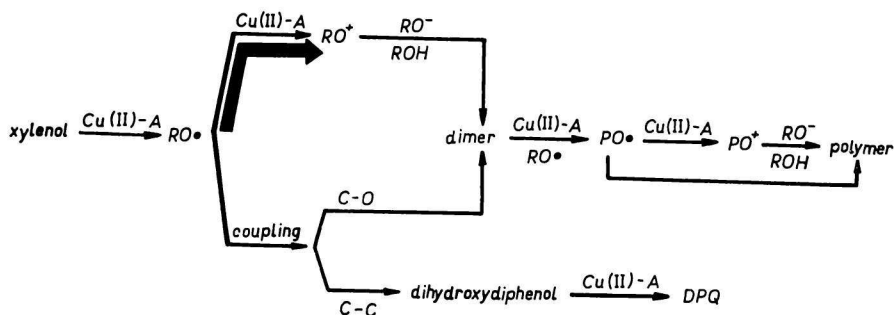
The radical scheme.

RO· = primary phenoxy radical, PO· = polymeric radical.
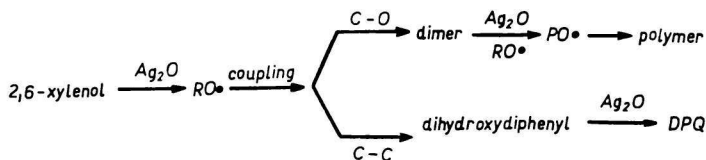
The radical-ion scheme.

Cu(II)-A = catalytic complex, RO⁺ = phenoxonium ion, PO⁺ = polymeric cation.

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