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A NEW MECHANISM FOR THE OXIDATIVE POLYMERIZATION OF 4-HALOPHENOLATES TO POLYPHENYLENE OXIDES

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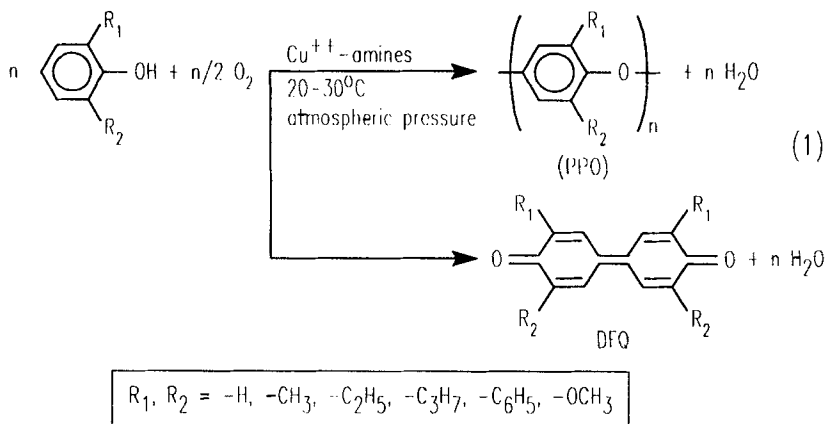
ABSTRACT

In order to elaborate a unitary theory and to explain many contradictory experimental results, a new and general mechanism for the polymerization of 4-halophenolates to polyphenylene oxides is proposed. In accordance with the proposed mechanism, the aromatic halogen atom in the para position, with very low reactivity, is transformed by “single electron transfer” from the phenolate anion to the catalyst [polycondensation activated by a “single electron transfer” (SET) mechanism] in an extremely reactive aliphatic halogen atom having an α -etheric and allylic structure. The “key” intermediate of this nonconventional polymerization reaction is assumed to be an intermediary quinol ether synthesized in situ by S_N2 a simple aliphatic nucleophilic substitution of the reactive halogen by monomeric phenolate anions. The intermediary quinol ethers creates chain extension of the polyphenylene oxide by rearrangement and redistribution reactions. This elaborate mechanism explains a great many of experimental results (including the anomalies sometimes observed in the polymerization of 4-halophenolates) in a unitary way.

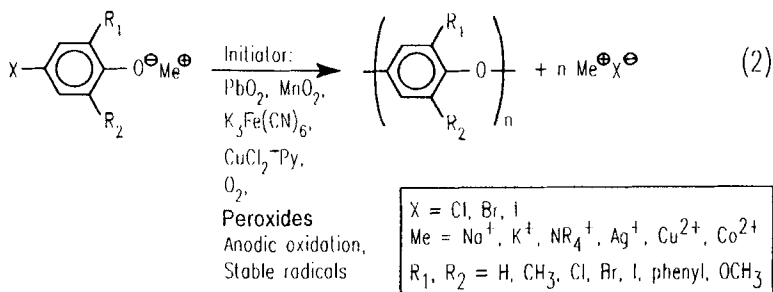
INTRODUCTION

It is well known that the most important method for polyphenylene oxide synthesis, especially poly(2,6-dimethyl-1,4-phenylene oxide), a high performance engineering thermoplastic, is the oxidative polymerization of phenols, an unconventional polymerization reaction discovered in 1959 by Hay [1] in the laboratories of General Electric (USA).

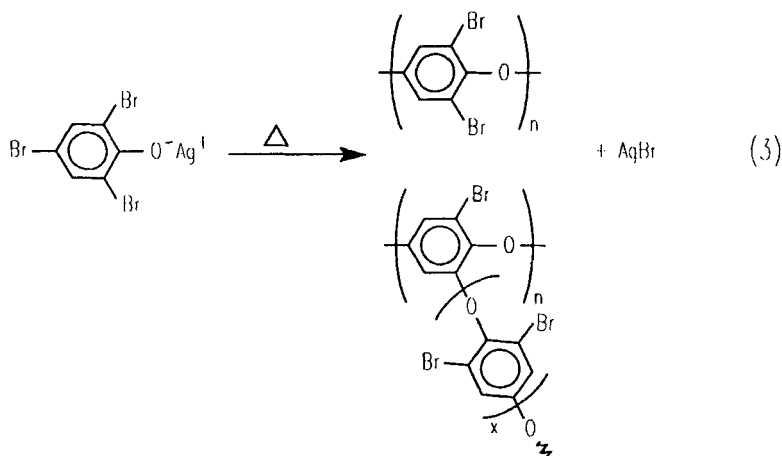
The reaction takes place in organic solvents between the monomeric phenol (2,6-xyleneol or 2,6-dimethylphenol) and molecular oxygen in the presence of a complex copper salt-amines catalyst under very mild reaction conditions, i.e., 20–30°C and atmospheric pressure. The oxidative polymerization products are polyphenylene oxide (PPO) in high yield (85–95%) and 3,3',5,5'-tetramethyl diphenylquinone (DPQ) as a by-product. The molecular oxygen is transformed directly in water:



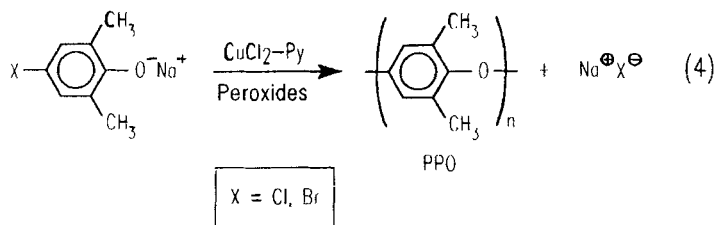
Another method for the synthesis of polyphenylene oxides is the oxidative polymerization of 4-halophenolates, a very old polymerization reaction studied by Hunter [2–4], Price [5–9], Heitz [10, 11], Harrod [12–15], Percec [25], and Kiskürek [15–19]. The products of this polycondensation reaction are polyphenylene oxide and an inorganic salt:



In 1919 Hunter [2–4] obtained branched polyphenylene oxides by the thermal polycondensation of 2,4,6-tribromo silver phenolate:

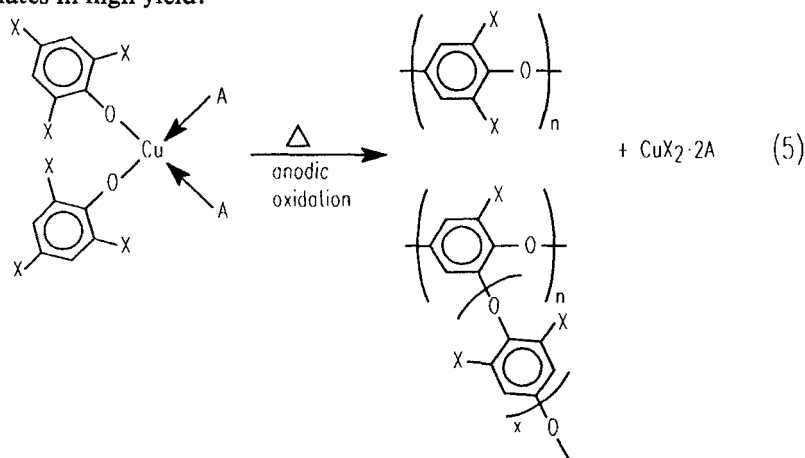


Price [5-9], W. Heitz [10, 11], and Percec [25] obtained poly(2,6-dimethyl-1,4-phenylene oxide) by polymerization of alkaline 2,6-dimethyl-4-halophenolates. The reaction is very fast, and the polymer obtained has practically the same structure as the polymer obtained by the oxidative polymerization of 2,6-xyleneol (Reaction 1), the only difference being the nature of the terminal groups:



It is very interesting that the polymerization reactions of alkali 2,6-disubstituted phenolates (Reactions 2 and 3) may be initiated by a large variety of such initiators as PbO_2 , MnO_2 [24], $\text{K}_3\text{Fe}(\text{CN})_6$ [5], $\text{CuCl}_2\text{-Py}$ [10, 11], O_2 [25], peroxides [28], anodic oxidation (electrochemical polymerization) [22, 23, 26, 27], and stable radicals (2,4,6-tritertbutylphenoxy radical) [8].

Harrod [12-14] and Kisakürek [15-23] obtained polyphenylene oxides by thermal (in solvent or in solid state) or electrochemical polymerization of copper or cobalt phenolates, in which the transitional metal (Cu^{2+} , Co^{2+}) is complexed with an amine. Branched polyphenylene oxides were obtained from 2,4,6-tris-halophenolates in high yield:



The present work elaborates a new and general polymerization mechanism of all 4-halophenolates in order to explain a great variety of accumulated experimental results in a unitary way.

EXPERIMENTAL PART

Raw Materials

4-Br-2,6-dimethylphenol, 99.6% purity, mp 77.7–78°C, was prepared by 2,6-dimethylphenol bromination in acetic acid as the reaction medium [29].

4-Br-2,6-dimethyl potassium phenolate was prepared in situ by 4-Br-2,6-dimethylphenol reaction with potassium tertiarybutoxide.

2,4,4,6-tris-brominephenolbromine was prepared by bromination of phenol in aqueous medium in the presence of sodium hydroxide [30].

Tetrahydrofuran (THF), dimethylsulfoxide (DMSO), pyridine (Py), and methanol (MeOH) (all p.a. Merck) were purified by conventional methods. The water content in all solvents was lower than 0.1%.

Bromine (Br₂) in its liquid state was used as the initiator. I₂ and CuCl₂ (anhydrous) were used as 0.1 M solutions in reaction solvents.

Polymerization Reaction (general procedure)

The solvents THF, DMSO, Py or MeOH, (20 mL), 4-Br-2,6-dimethylphenol (1.6 g, 8 mmol), and potassium tertiarybutoxide (0.9 g, 8 mmol) were charged in a 100-mL round-bottom flask with a reflux condenser, thermometer, and magnetic stirring. Then 0.8 mL of the initiator (Br₂, I₂, CuCl₂, etc.) was added under stirring. The reaction mass became opalescent from the beginning due to the insoluble KBr precipitate. A solution of HCl (50 mL, 0.1 M in a MeOH–water (1:1) mixture) was added to the reaction mass after a reaction time of 3–30 minutes at 25–30°C.

The precipitated polymer was filtered, washed with an aqueous methanol solution, and dried for 3 hours at 90–100°C.

The intrinsic viscosity was determined with an Ubbelohde viscometer in CHCl₃, at 30°C.

IR spectra were determined with a SPECORD 75 IR spectrophotometer.

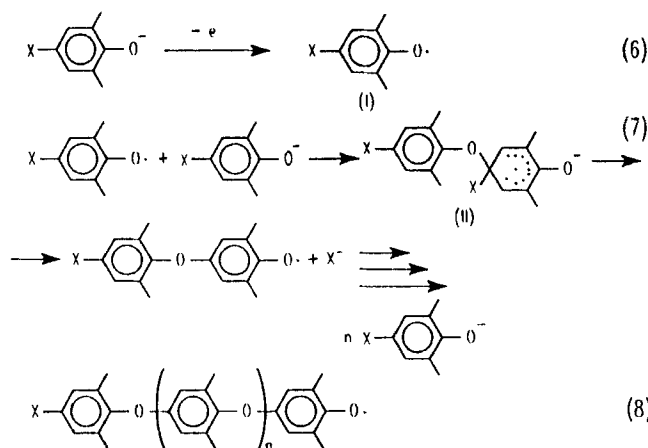
RESULTS AND DISCUSSION

The accepted mechanism of 4-halophenolates oxidative polymerization (sometimes named the “oxidative displacement of halogen”) was elaborated by Price [5] in 1960 and completed by Heitz [10, 11] in 1985.

The polymerization of 4-halophenolates, after Heitz, is a typical example of polycondensation activated by “single electron transfer” (SET mechanism). In this kind of reaction, the intermediates are more reactive than the monomers.

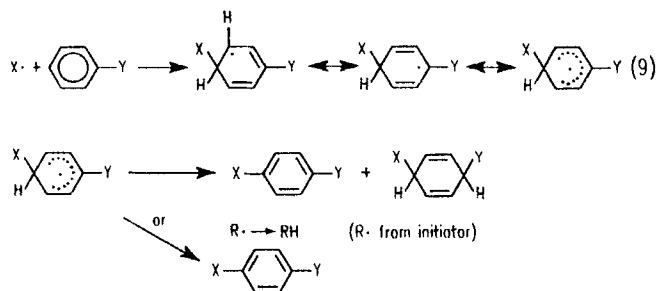
In the particular case of 4-halophenolates polymerization, the reactive intermediate of the reaction is postulated to be “radical-anion” (II).

The mechanism proposed by Price and Heitz is described by the following reactions:



In the first step, Reaction (6), the monomer anion is transformed into an aryloxy radical by a "single transfer electron." This aryloxy radical attacks the monomer anion and forms a radical anion, i.e., the reactive intermediate of this reaction. This intermediate liberates the halogen anion (X) and forms an aryloxy radical dimer which then attacks a new monomer molecule.

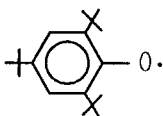
This mechanism, especially Reaction (7), is very similar to an aromatic homolytic substitution:



The mechanism proposed by Price and Heitz (Reactions 6, 7, and 8) contradicts some experimental data:

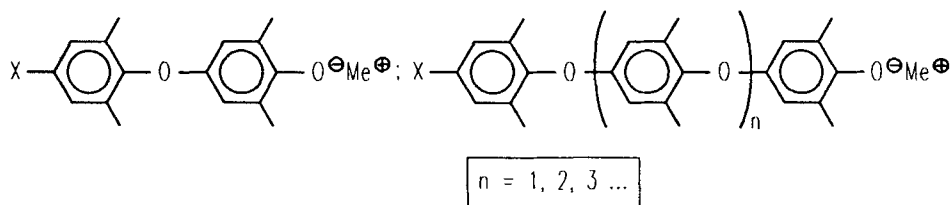
1. In aromatic homolytic substitution, the electron-withdrawing substituents (F, Cl, Br, I, $-\text{NO}_2$, $-\text{CN}$, etc.) have an activating effect and the electron-releasing substituents ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$, etc.) have a deactivating effect. On the other hand, in the oxidative polymerization of 4-halophenolates, alkyl substituents have a strong activating effect.
2. Aromatic homolytic substitution is a nonselective reaction. The ortho position is preferred, followed by the para and meta positions, with no significant differences. In the oxidative polymerization of 4-halophenolates, only the para position is attacked.
3. In aromatic homolytic substitution the relative substitution rates of the halogen atoms are $\text{F} > \text{Cl} > \text{Br} > \text{I}$. On the contrary, in the oxidative polymerization of 4-halophenolates, the relative rates of polymerization follow the order $\text{I} > \text{Br} > \text{Cl}$, which is very similar to aliphatic nucleophilic substitution.

- The existence of a radical anion (I) which has the same radical structure and anion character is assumed but was not proved experimentally.
- The proposed mechanism does not explain the great stability and low reactivity of such radicals as 2,4,6-tritertiarybutylphenoxy:



[with a half lifetime ($t_{1/2}$ of 2–3 weeks), may initiate the polymerization of 4-halophenolates by an attack on the monomer strong aromatic ring.

- As compared with the aryloxy radical derived from the monomer, which is very reactive ($t_{1/2} = 10^{-3}$ – 10^{-5} seconds) [33], the polyaryloxy radical has increased stability and low reactivity ($t_{1/2} = 150$ minutes). The mechanism does not explain the attack of a polyaryloxy radical with low reactivity on the stable aromatic ring of the monomer (Reaction 8) for the extension of the polymer chain.
- The mechanism of Price and Heitz doesn't explain why dimers and oligomers with the following structures:



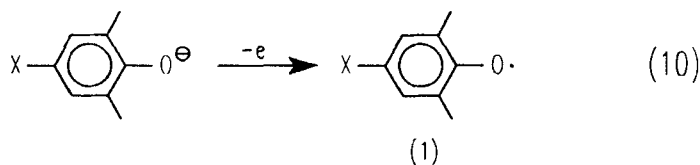
may be polymerized in the same way with the same catalysts, in spite of the fact that the halogen atom is not attached to the terminal phenolate aromatic ring.

- The fact that the formation of very high molecular weight polymers is favored by perfect anhydrous conditions is not very clearly explained.

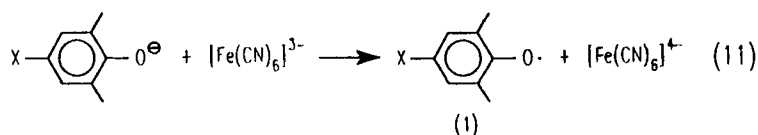
In order to explain all aspects of this unconventional polymerization reaction in a general way, including the above-mentioned contradictory experimental data, we propose a new polymerization mechanism.

INITIATION

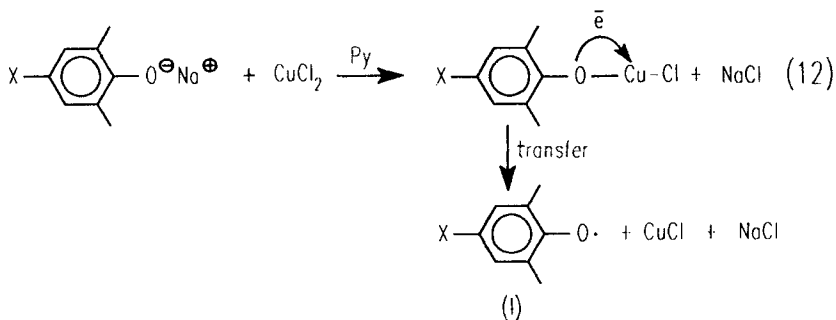
All the initiators (irrespective of their structure) transform the phenolate anions in the first step by "single electron transfer" from the anion to the initiator in very reactive aryloxy radicals:



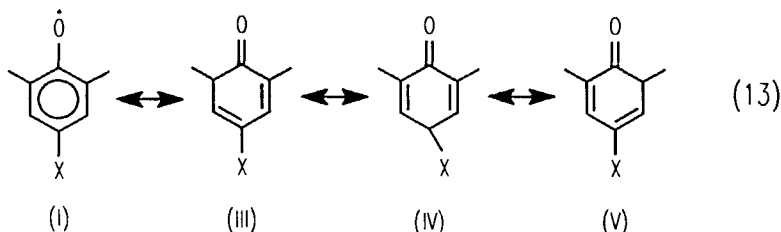
For example: in anodic oxidation (Reaction 10), the reaction with potassium ferriyanide:



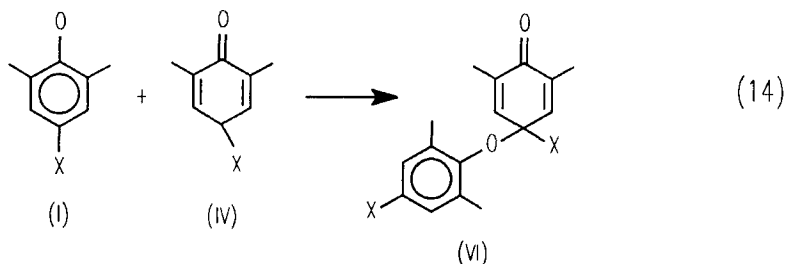
or the reaction with copper salts:



The aryloxy radicals (I) formed, identified by RES [1, 15, 32, 33], are resonance hybrids with the odd electron to the oxygen and the aromatic nucleus of monomer in the ortho and para positions:



Structures (I) and (IV) lead, by a classical C—O coupling reaction, to a cyclohexadienonic Structure (VI) where the aromatic halogen atom from the monomer of low reactivities is transformed into a very reactive halogen atom, having at the same time an allylic and α -etheric position:

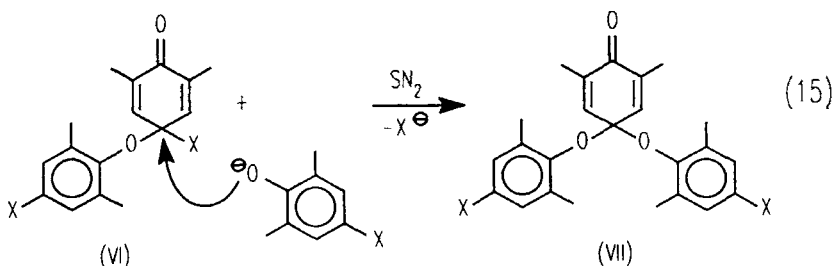


If there is an alkyl or an aryl group in the ortho position, the coupling between Structures (I) and (III) or (V) is suppressed by steric considerations. If the ortho position is occupied by halogen atoms (especially Cl and Br), C—O coupling in the ortho position is also possible.

Cyclohexadienonic Structure (VI) is an extremely important intermediate in 4-halophenolates oxidative polymerization.

PROPAGATION

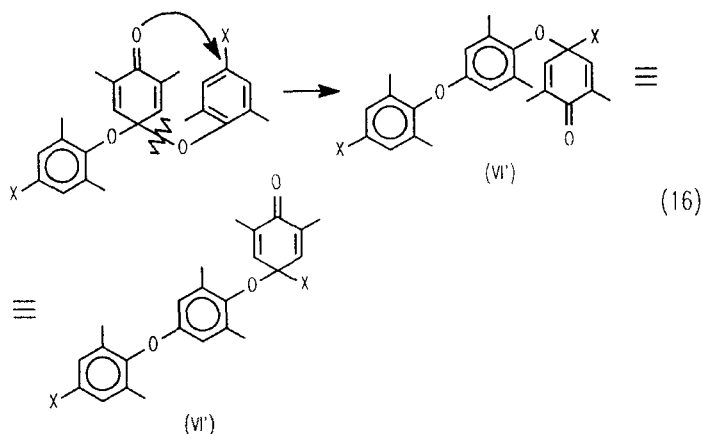
The main reaction of the proposed mechanism is the nucleophilic substitution of the very reactive halogen atom from cyclohexadienonic Structure (VI) by the phenolate anion of the monomer with the formation of the quinol ether (VII):



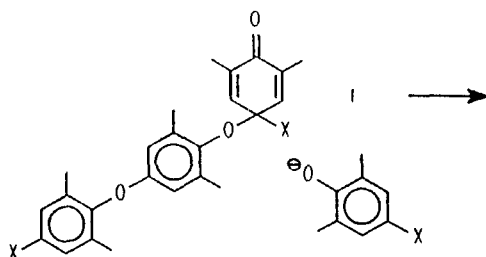
Quinol ether (VII) is the key intermediate of the reaction. The polymerizability of different kinds of 4-halophenolates is a function of the thermal stability of the intermediary quinol ethers and of the nucleophilicity of the monomer anion, depending on the nature of substituents in positions 2,6 of the monomers.

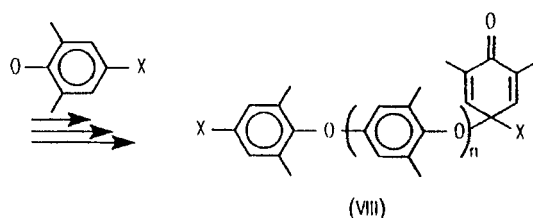
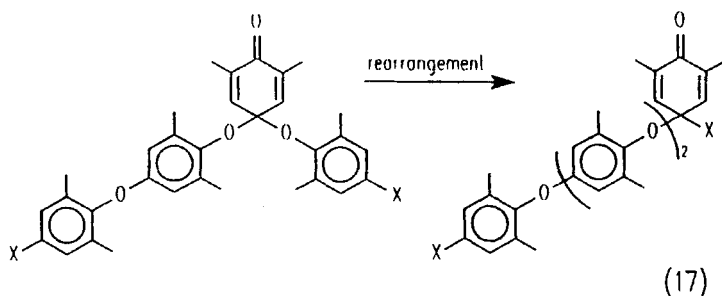
Quinol ether (VII) has two possibilities for the reorganization of its structure to regenerate the structure, similarly to cyclohexadienone (VI), with reactive halogen.

One possibility is quinol ether rearrangement (sigmatropic transposition [33]):



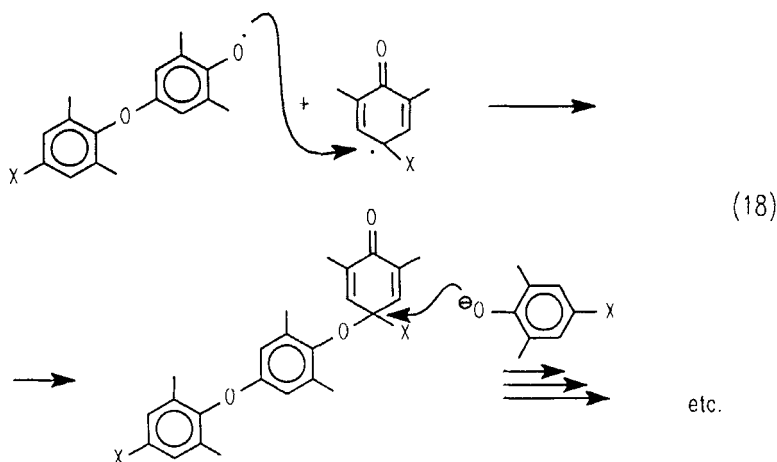
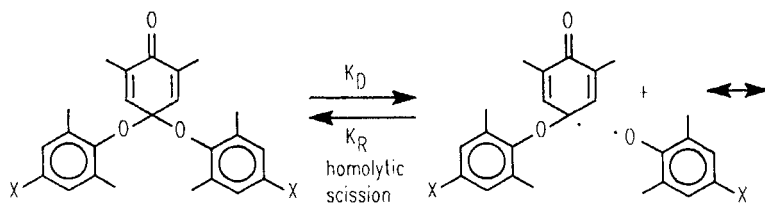
In fact, a terminal cyclohexadienonic structure is again obtained with reactive halogen which again develops a S_N2 reaction with the monomer anion for chain extension [31]:





In anhydrous conditions the polyphenylene oxide (VIII) which has two halogen atoms per molecule is obtained.

The second possibility is quinol ether redistribution in which the intermediary quinol ether first develops a homolytic scission to aryloxy radicals (an equilibrium reaction). The aryloxy radicals develop a coupling reaction between two resonance hybrids:

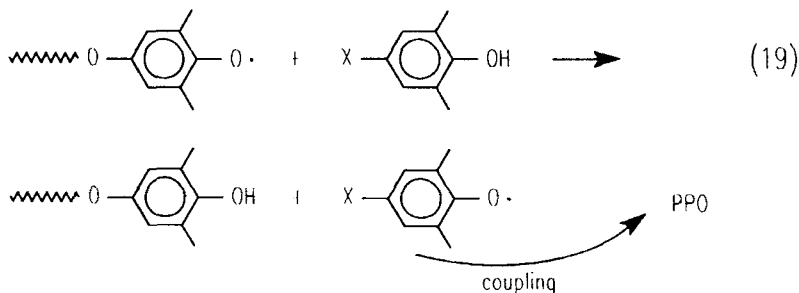


By analogy with the oxidative polymerization of 2,6-dialkylphenols [35], it is very probable that both reactions (quinol ether rearrangement and quinol ether

redistribution) should take place simultaneously. The importance of one or the other is given by the reaction conditions (i.e., the temperature of the reaction) and the nature of monomer.

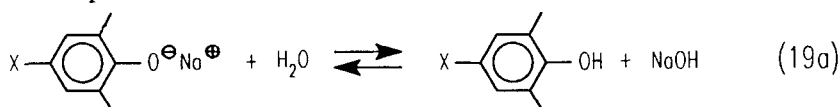
TERMINATION

1. By transfer with free phenol:



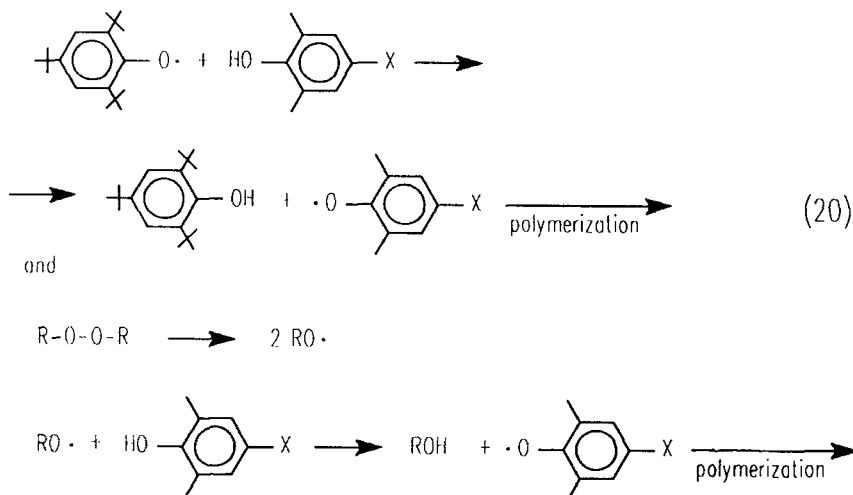
The presence of free phenols markedly decreases the molecular weight of the resulted polyphenylene oxide. The controlled addition of a free phenol is an excellent way to regulate the molecular weight [10, 11].

In the polymerization reaction developed in a two-phase system (water-organic solvents), the free phenol is always present because the equilibrium takes place when water is present:

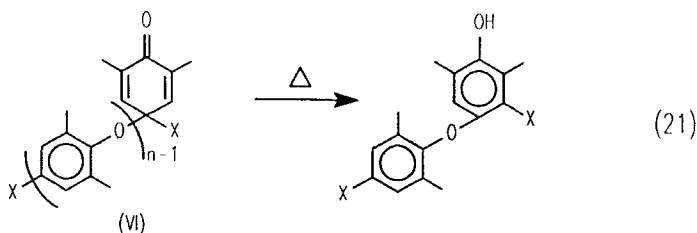


This explains why very high molecular weights are obtained in anhydrous systems.

The initiation of 4-halophenolates polymerization with the 2,4,6-tritertiary-butylphenoxy radical or peroxides (in two-phase systems) is explained by transfer with the free phenol:



By rearrangement of terminally cyclohexadienonic groups (restoration of aromaticity):



The reaction takes place rapidly at higher temperatures (100–150°C) but very, very slowly at room temperature.

The polymers obtained in anhydrous conditions usually have Structure (VI).

Summarizing, the proposed mechanism is presented in Scheme 1 as a cyclic process and has the following five steps.

I. Initiation reaction (electron transfer) (K_i)

II. Coupling of aryloxy radicals and generation of cyclohexadienonic structures with a very reactive halogen (having an allylic and α -etheric structure) (K_C)

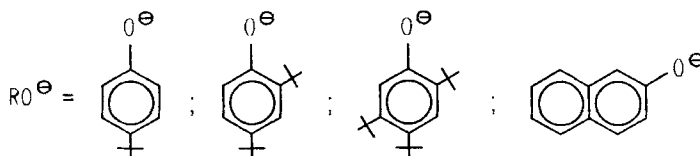
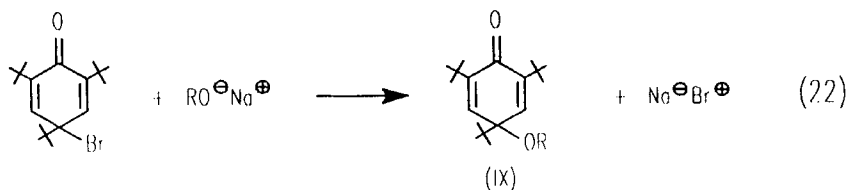
III. Synthesis of intermediary quinol ethers by aliphatic nucleophilic substitution of reactive halogen with monomeric phenolate anion (rate-determining step) (K_{SN_2})

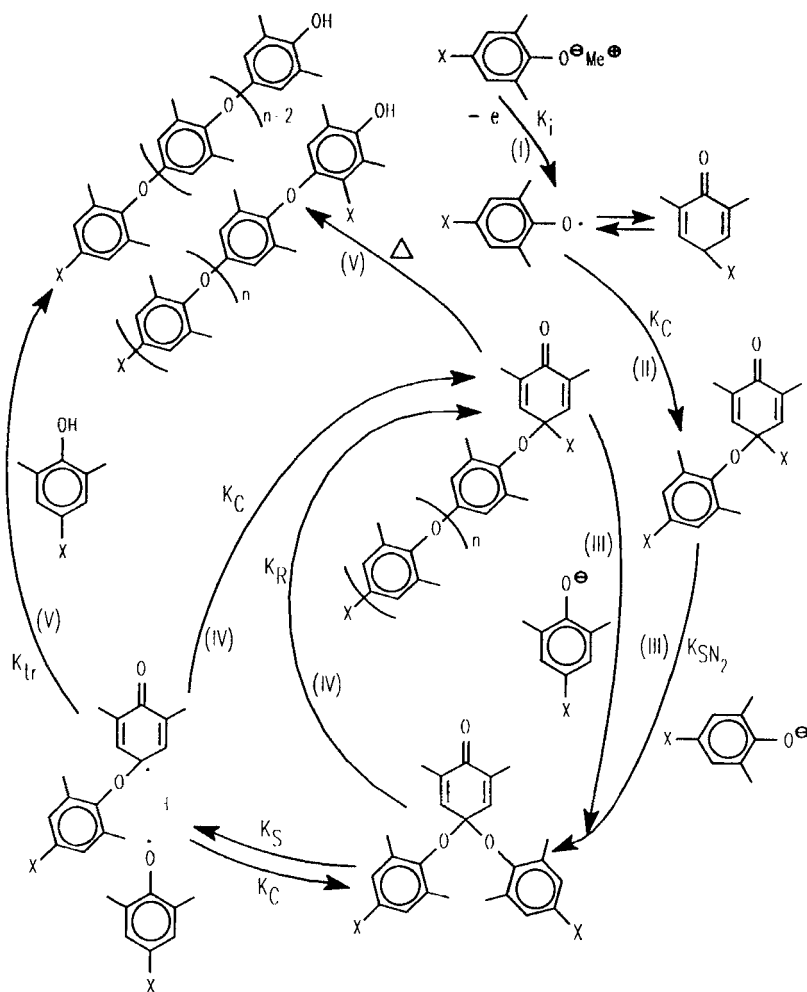
IV. Chain extension: (IV.1) By quinol ether rearrangement (K_R); (IV.2) by quinol ether redistribution ($K_S \rightleftharpoons K_C$) (homolytic scission of quinol ether). As a result of both reactions, the terminal cyclohexadienonic structure with reactive halogen is regenerated and the cycle II–III–IV–III is repeated.

V. Interruption of chain growth by transfer with free phenol or by rearrangement of the cyclohexadienonic to a halogenated terminal phenolic groups (K_{tr} , K_R).

ARGUMENTS FOR THE PROPOSED MECHANISM

1. The main reaction of the proposed mechanism, aliphatic nucleophilic substitution, is, in fact, the classical method for the synthesis of quinol ethers, intensively studied by Müller in 1957 [31] (before the discovery of phenol oxidative polymerization by Hay in 1959).



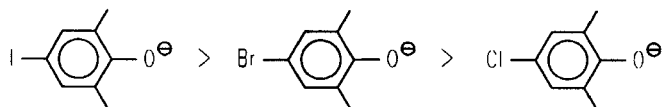


SCHEME 1.

The quinol ethers (IX) are obtained in high yield at room temperature and isolated as pure substances with characteristic melting points [31].

The reaction (22) is a very clear explanation for the liberation of free halogen anions X^- .

2. The relative order of the polymerization reaction (see Figs. 1 and 2)



is exactly the relative order in aliphatic S_N2 reactions.

In aromatic homolytic (or nucleophilic) substitution, the relative order is inverted: $F > \text{Cl} > \text{Br} > \text{I}$.

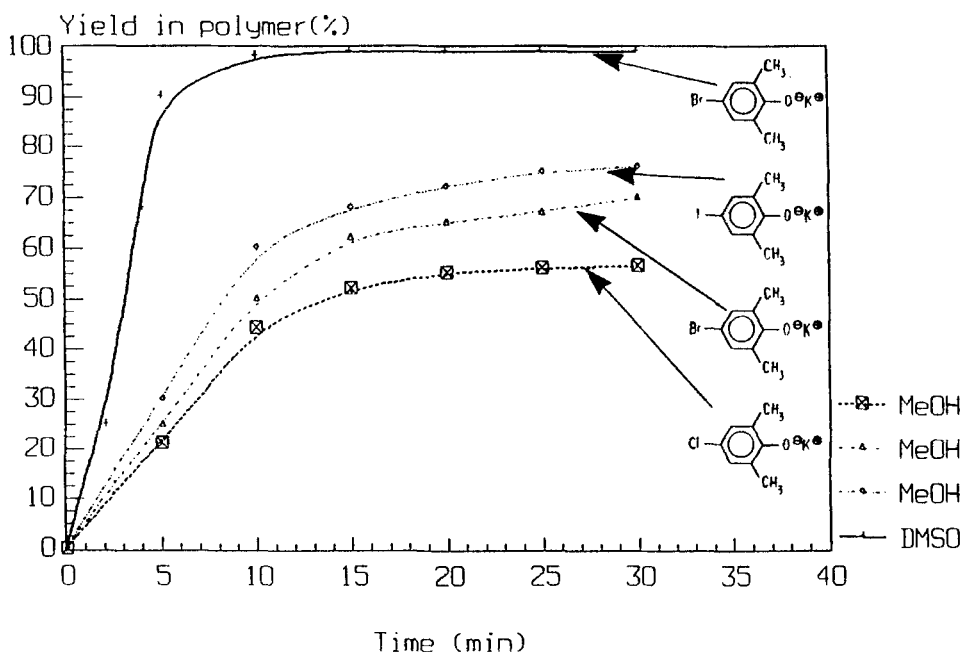
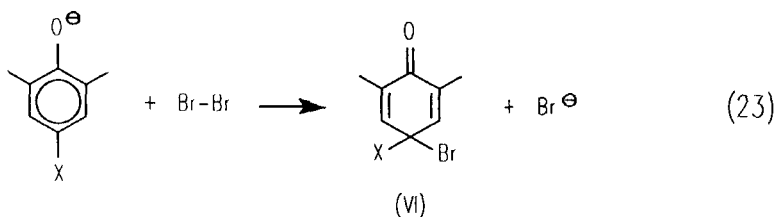


FIG. 1. The effect of the solvent and monomer nature on the yield in polymer. Temperature = 30°C, [monomer] = 0.16 mol/L, [initiator (Br_2)] = 0.006 mol/L.

3. The oxidative polymerization of 4-halophenolates takes place very easily in polar solvents ($\text{DMSO} > \text{DMF} \approx \text{HMPTA} > \text{THF}$), and protic solvents (such as alcohols) have a strong retarding effect. The same effects are observed in classical $\text{S}_{\text{N}}2$ aliphatic nucleophilic substitutions. In Fig. 1 we observe the solvent effect upon the polymer yield and in Fig. 2 the effect of the solvent upon the molecular weight of the polyphenylene oxides synthesized by the oxidative polymerization of 2,6-dimethylpotassium phenoxides.

In $\text{S}_{\text{N}}2$ aliphatic nucleophilic substitutions the accelerating effect of polar solvents is explained by the solvation of cations (Na^+ , K^+) and by the increase of the degree of dissociation (free anions are more reactive than undissociated ion pairs). The retarding effect of protic solvents is due to the solvation of anions (in our case, the phenolate anion) by hydrogen bonds of hydroxyl groups.

4. Free halogens (Br_2 , I_2) are very good initiators for 4-halophenolates oxidative polymerization. The first step in the reaction of phenolate with halogens is a cyclohexadienonic compound which may sometimes be isolated as a pure substance. In essence, this compound is similar to cyclohexadienone (VI) with very active allylic and α -etheric halogens.



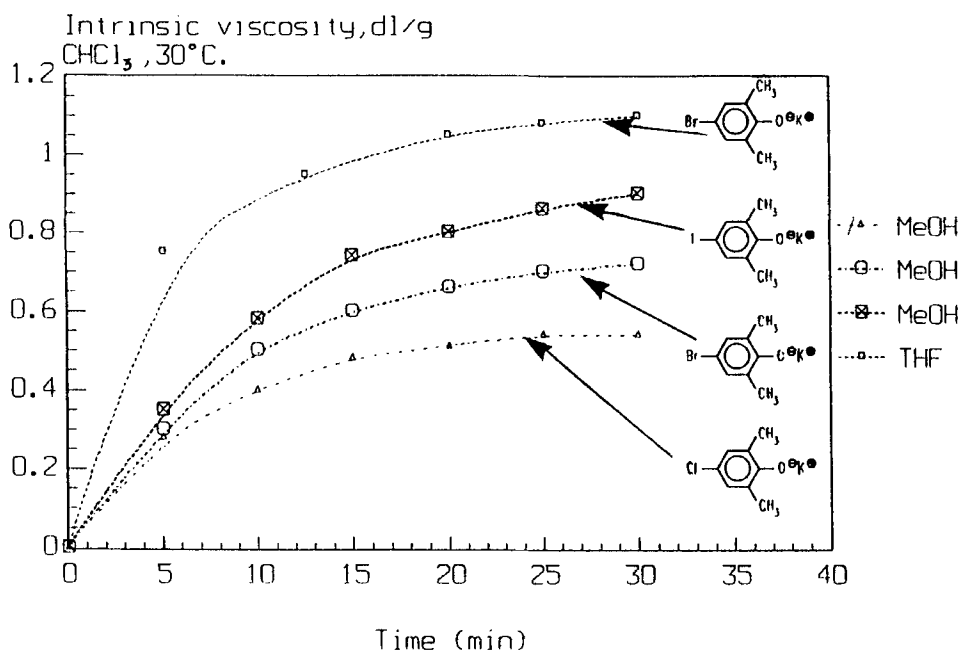
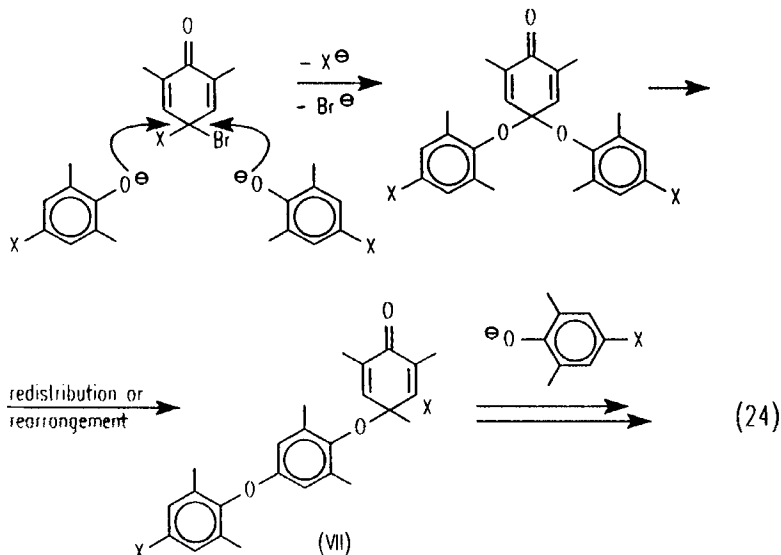
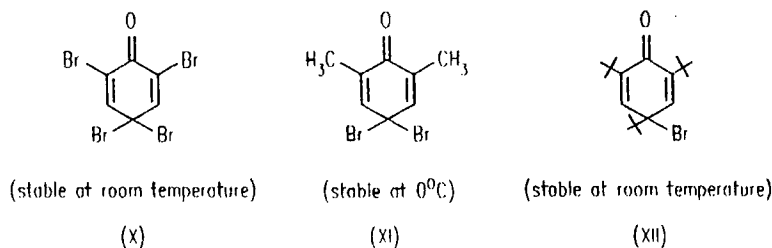


FIG. 2. The effect of the solvent and monomer nature on the molecular weight of polymer. Temperature = 30°C, [monomer] = 0.16 mol/L, [initiator (Br₂)] = 0.006 mol/L.

Cyclohexadienone (VI) reacts with two monomer anions by a simple S_N2 nucleophilic substitution reaction, and the quinol ether (VII) obtained develops chain extension by rearrangement or/and redistribution, regenerating, step by step, the cyclohexadienonic structure with reactive halogen as a terminal group:



5. Preformed cyclohexadienonic compounds are very efficient initiators.

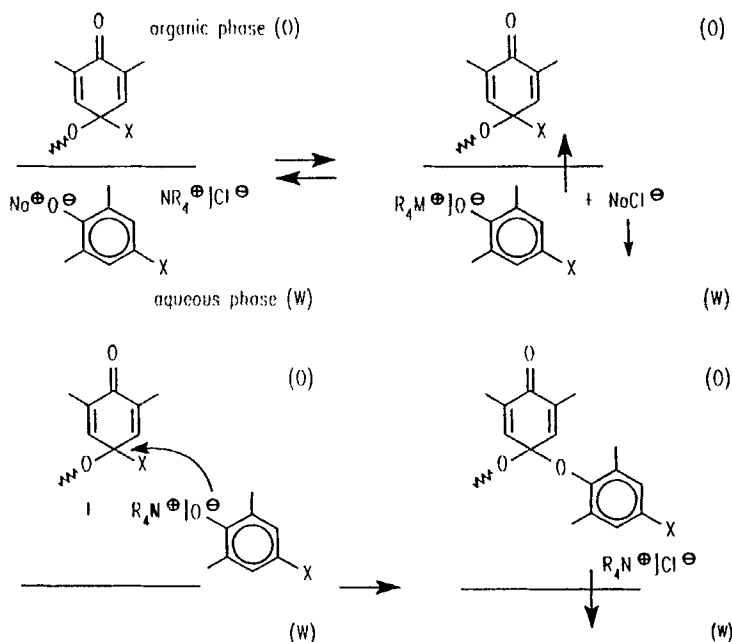


Cyclohexadienones (X, XI, XII), and similar compounds with an intermediary cyclohexadienone (VI), including reactive halogen, reacts with monomer anions to yield quinol ethers. Initiation with halogens or with preformed cyclohexadienones (X, XI, XII) is not an electron transfer reaction; it is a simple S_N2 reaction. With respect to this type of initiation, the polymerization of 4-halophenolates is not necessarily a SET mechanism.

The results of 4-Br-2,6-dimethylpotassium phenoxide polymerization with halogen and a cyclohexadienone compound are presented in Table 1.

6. Percec [25] developed a new process for 4-Br-2,6-dimethylphenol polymerization in two-phase systems (alkali water-organic solvents) in conditions of phase-transfer catalysis (quaternary ammonium salts) in the presence of molecular oxygen (air) and in the absence of initiators (in fact, oxygen acts as an initiator, transforming the phenolate into an aryloxy radical by a well-known succession of reactions).

The quaternary ammonium salt (phase-transfer catalyst TBAH, tetrabutylammonium hydrogen sulfate) catalyzes the S_N2 reaction between the phenolate anion (which exists in the water phase) and the halogen atom from cyclohexadienone (obtained by coupling two monomeric radicals) from the organic phase:



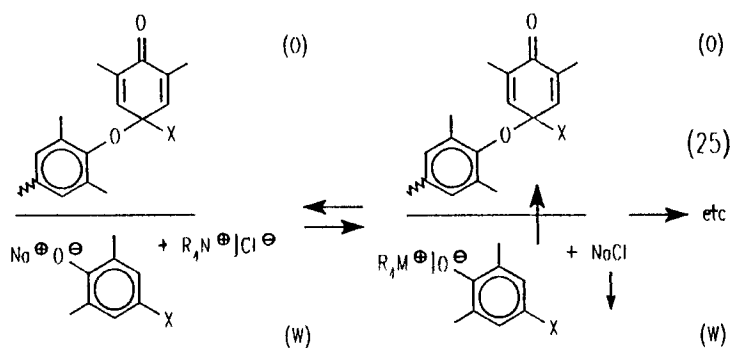


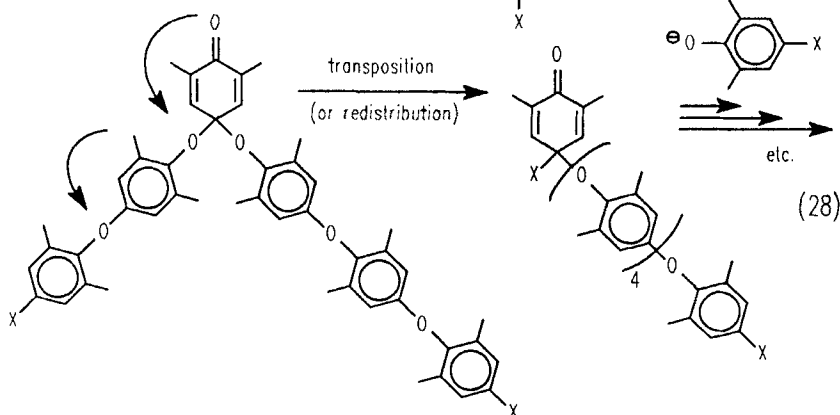
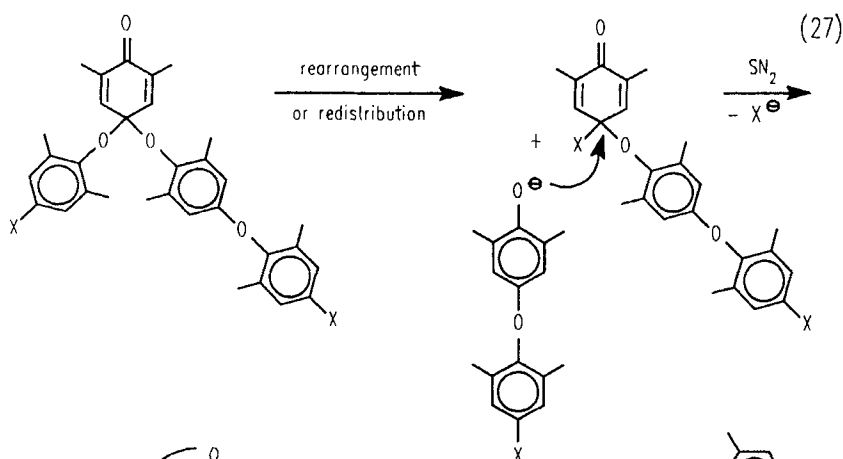
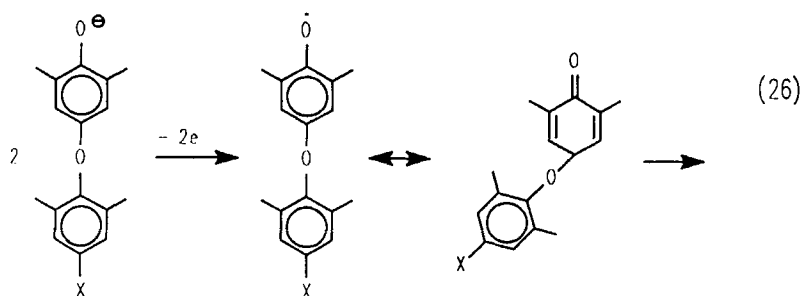
TABLE 1. Oxidative Polymerization of 4-Br-2,6-Dimethyl Potassium Phenolate^a

Initiator	Solvent	Reaction time, minutes	Polymer yield, %	Intrinsic viscosity, CHCl ₃ , 30°C, dL/g
Br ₂	THF	5	88	0.60
	THF	15	90	1.00
	DMSO	3	50	1.30
	DMSO	15	98	1.30
	MeOH	3	32	0.20
	MeOH	42	92	0.63
	MeOH	60	70	0.80
	MeOH	60	70	0.22
I ₂	THF	3	80	0.60
	THF	15	82	0.95
	DMSO	3	80	0.65
	DMSO	15	83	0.65
	MeOH	15	67	0.20
	MeOH	60	70	0.22
	THF	20	82	0.20
	THF	30	85	0.23
	THF	30	83	0.35
CuCl ₂	Py	20	88	0.40
	Py	30	93	0.43

^a[Monomer]: 0.16 mol/L; [initiator]: 0.006 mol/L; temperature: 30°C; inert atmosphere: N₂.

Thus, the new process of Percec for the oxidative polymerization of 4-Br-2,6-dimethylphenol in two-phase systems is explained perfectly by the proposed mechanism, including the redistribution reaction [36] and transfer with free phenolic groups [37]. The phase-transfer catalyst has an activating effect on the nucleophilic substitution reaction.

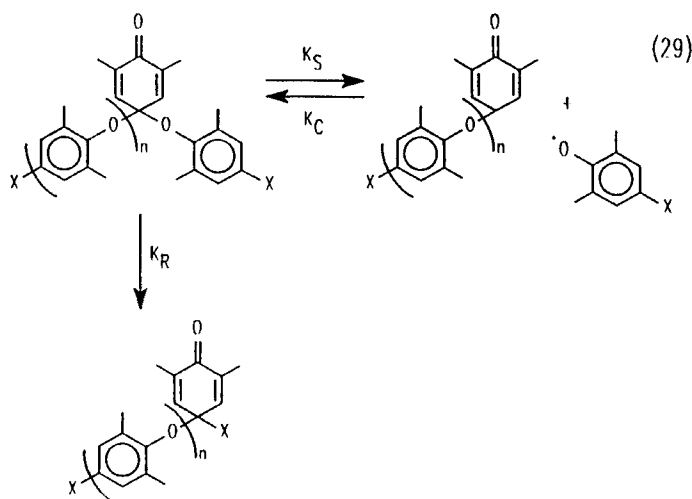
7. The polymerization of dimers and oligomers is explained by the same reactions involving quinol ethers as "key" intermediates (obtained by S_N2 aliphatic nucleophilic substitution reactions of very reactive halogen with dimer anions):



8. In anhydrous systems the quinonic group [from cyclohexadienone (VI)] is present in all reaction products (oligomers, polymers) during the polymerization reaction as a very characteristic doublet in the carbonyl region ($1550-1600\text{ cm}^{-1}$).

Naturally, the polymerizability of different kinds of 4-halophenolates depends on a number of complex factors.

One of the most important factors is the stability of the intermediary quinol ethers under the reaction conditions (especially the reaction temperature). As in the oxidative polymerization of 2,6-dialkylphenols, the quinol ether is able to develop two simultaneous reactions: homolytic scission, K_S (an equilibrium reaction), and rearrangement reaction, K_R (sigmatropic rearrangement).



The rearrangement reaction makes the main contribution to the increase of molecular weight. Because of the permanent equilibrium between polymeric chains with monomeric and polymeric radicals, the contribution to an increase in the molecular weight by this mechanism is lower in quinol ether redistribution (the average molecular weight of the system is conserved). The global increase of molecular weight is a result of contributions by both reactions. An increase of temperature favors the homolytic scission of the quinol ether and accelerates quinol ether rearrangement.

Another important factor affecting the polymerizability of 4-halophenolates is the nucleophilicity of the phenolate anions which is strongly influenced by the nature of the substituents located in the 2 and 6 positions.

As a rule, electron-releasing substituents (methyl, ethyl, propyl, methoxy groups) decrease the stability of the quinol ether and increase the polymerizability of 4-halophenolates because the S_N2 reaction is accelerated by an increase in the nucleophilicity of the monomeric anion and in the capability of quinol ether to develop a sigmatropic transposition. The polymerization of these monomers usually takes place at room temperature. Electron-withdrawing substituents ($-Cl$, $-Br$, $-COOR$, $-NO_2$) increase the stability of quinol ether and decrease its polymerizability. The S_N2 reaction is retarded by a decrease of nucleophilicity of monomers, and the capability to develop sigmatropic transpositions is decreased. This kind of monomer needs higher temperatures for polymerization (50 – $150^\circ C$). Phenolates with a free ortho position give more stable quinol ethers and decrease the polymerizability. Such 4-halophenolates (i.e., 4-chlorophenolate) need a very high temperature for conversion to polyphenylene oxides (150 – $180^\circ C$).

CONCLUSIONS

A new and general mechanism for the oxidative polymerization of 4-halophenolates to polyphenylene oxides is proposed.

In the first step, an aromatic halogen from the para position, with a lower reactivity, is transformed by a one-electron transfer (from the phenolate anion to the catalyst) into a very reactive halogen atom, with a simultaneous allylic and α -etheric structure. The main reaction of the proposed mechanism is aliphatic nucleophilic substitution of the above-mentioned very reactive halogen atom (situated in a cyclohexadienonic structure) with the phenolate anion of the monomer. The product of this reaction is an intermediary quinol ether which leads to an increased polymer molecular weight by two simultaneous reactions, i.e., quinol ether rearrangement and quinol ether redistribution.

The proposed mechanism explains most experimental data in a unitary way, including the anomalies observed in the oxidative polymerization of some 4-halophenolates.

REFERENCES

- [1] A. S. Hay, *Adv. Polym. Sci.*, **4**, 496 (1967).
- [2] W. H. Hunter, A. O. Olson, and E. A. Daniels, *J. Am. Chem. Soc.*, **38**, 1761 (1916).
- [3] W. H. Hunter and F. E. Joyce, *J. Am. Chem. Soc.*, **39**, 2646 (1919).
- [4] W. H. Hunter and R. B. Whitney, *Ibid.*, **54**, 1167 (1932).
- [5] G. D. Staffin and C. C. Price, *Ibid.*, **82**, 3632 (1960).
- [6] W. A. Butte, C. C. Price, and R. E. Hughes, *J. Polym. Sci.*, **61**, 528 (1962).
- [7] C. C. Price and N. S. Chu, *J. Polym. Sci.*, **61**, 135 (1962).
- [8] M. A. Semsarzadeh and C. C. Price, *Macromolecules*, **10**(2), 482 (1977).
- [9] C. C. Price, M. A. Semsarzadeh, and T. B. Nguyen, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **26**, 319 (1975).
- [10] W. Risse and W. Heitz, *Makromol. Chem.*, **186**, 1835 (1985).
- [11] W. Koch, W. Risse, and W. Heitz, *Makromol. Chem. Suppl.*, **12**, 105 (1985).
- [12] J. F. Harrod, *Can. J. Chem.*, **47**, 637 (1969).
- [13] B. G. Carr, J. F. Harrod, and P. Sheluwe, *Macromolecules*, **6**, 498 (1973).
- [14] B. G. Carr and J. F. Harrod, *J. Am. Chem. Soc.*, **95**, 5707 (1973).
- [15] J. F. Harrod, P. Sheluwe, D. Kisakürek, and A. Shaver, *Macromolecules*, **14**, 565 (1981).
- [16] D. Kisakürek and L. Türker, *Br. Polym. J.*, **21**, 367 (1989).
- [17] L. Türker and D. Kisakürek, *Ibid.*, **20**, 131 (1988).
- [18] M. Bastürkmen, H. Işçi, and D. Kisakürek, *Polym. Int.*, **30**, 387 (1993).
- [19] M. Bastürkmen and D. Kisakürek, *Polymer*, **34**(3), 625 (1993).
- [20] O. Sanli and D. Kisakürek, *Makromol. Chem.*, **193**, 619 (1992).
- [21] H. J. Ünal, O. Sanli, and D. Kisakürek, *Polymer*, **30**, 344 (1989).
- [22] M. Salak, U. Akbulut, D. Kisakürek, L. Türker, and L. Toppare, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1599 (1989).

- [23] U. Akbulut, M. Sakak, D. Kisakürek, and L. Toppare, *J. Macromol. Sci. – Chem.*, **A26**(12), 1623 (1989).
- [24] US Patent, 3,382,212 (CI 1,260-47) 1968; *Chem. Abstr.*, **69**, 1093b.
- [25] V. Percec and T. D. Schaffer, *J. Polym. Sci., Polym. Lett. Ed.*, **24**, 439 (1986).
- [26] E. Tsushida and H. Nishide, in *Reactive Oligomers*, Vol. 15 (F. W. Harris and H. J. Spinelli, Eds.), Washington, D.C., 1985, pp. 175–185.
- [27] K. Yamamoto, H. Nishide, and E. Tsushida, *Chem. Soc. Jpn.*, **2**, 152 (1986).
- [28] G. S. Stamatoff, US Patents 3,228,910 (1965), and 3,236,807 (1966).
- [29] S. Tsuruya and T. Yonezawa, *J. Catal.*, **36**, 48 (1975).
- [30] Houben-Weyl, *Methoden der Organische Chemie*, Band V/4, p. 261.
- [31] E. Müller, K. Ley, and G. Schlechte, *Chem. Ber.*, **90**, 2660 (1957).
- [32] S. Tsuruya, K. Okamoto, and T. Yoshimatsu, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 379 (1978).
- [33] W. G. Huysmans and W. A. Waters, *J. Chem. Soc., B*, 1047 (1966); *Ibid.*, 1163 (1967).
- [34] M. Ionescu, Unpublished Results.
- [35] G. D. Cooper and A. Katchman, *Adv. Polym. Sci.*, **91**, 660 (1969).
- [36] V. Percec and J. H. Wang, *Polym. Bull.*, **24**, 63 (1990).
- [37] V. Percec and J. H. Wang, *Polym. Bull.*, **24**, 4935 (1990).