Polymerization by Oxidative Coupling. II. Co-Redistribution of Poly(2,6-diphenyl-1,4-phenylene Ether) with Phenols
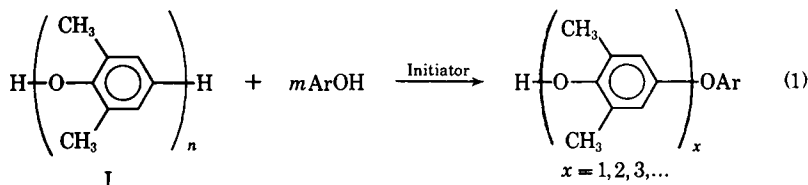
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Synopsis

Poly(2,6-diphenyl-1,4-phenylene ether) reacts with phenols in the presence of an initiator to form a mixture of low molecular weight hydroxyarylene ethers.   Although the reaction is similar to the equilibration of poly(2,6-dimethyl-1,4-phenylene ether) with phenols, higher reaction temperatures and larger initiator concentrations are required.   Compounds as 3,3′,5,5′-tetraphenyl-4,4′-diphenoquinone, *tert*-butyl perbenzoate, and benzoyl peroxide are active initiators.   The structure of the polymer affects the extent to which the polymer equilibrates.
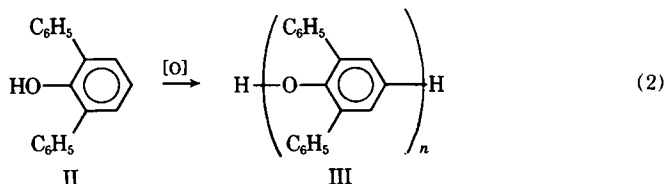
INTRODUCTION

Many phenols co-redistribute with poly(2,6-dimethyl-1,4-phenylene ether) I, to form a mixture of low molecular weight hydroxyarylene ethers

$$H \left(O - \underset{CH_3}{\overset{CH_3}{\bigcirc}} \right)_n H \quad + \quad m\,ArOH \quad \xrightarrow{\text{Initiator}} \quad H \left(O - \underset{CH_3}{\overset{CH_3}{\bigcirc}} \right)_x OAr \quad (1)$$

$$\text{I} \qquad\qquad\qquad\qquad\qquad\qquad x = 1, 2, 3, \ldots$$

[reaction (1)].[1]   The series of equilibration reactions which occurs in the co-redistribution is related to the redistribution mechanism for the oxidative coupling of 2,6-dimethylphenol to form polymer I.[2]
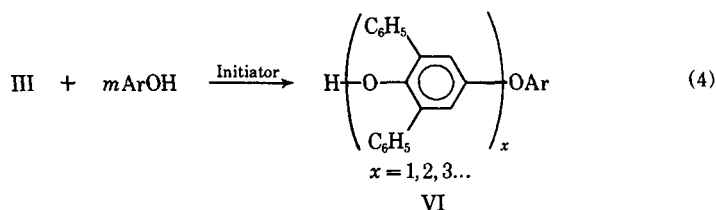
Poly(2,6-diphenyl-1,4-phenylene ether) (III) has been prepared by the oxidative coupling polymerization of 2,6-diphenylphenol, (II) [reaction (2)][3,4] and, by analogy to the synthesis of I, proceeds by a redistribution mechanism.   Support for the redistribution mechanism has been presented

$$HO - \underset{C_6H_5}{\overset{C_6H_5}{\bigcirc}} \quad \xrightarrow{[O]} \quad H \left(O - \underset{C_6H_5}{\overset{C_6H_5}{\bigcirc}} \right)_n H \quad (2)$$

$$\text{II} \qquad\qquad\qquad \text{III}$$

by Bolon,[4] who showed that the dimer (IV) could redistribute to form a mixture of oligomers [reaction (3)] and could be oxidized to form (III).[4] Evidence for a co-redistribution of III with phenols [reaction (4)] would aid

$$x = 1, 2, 3, \ldots$$

(3)

IV   V
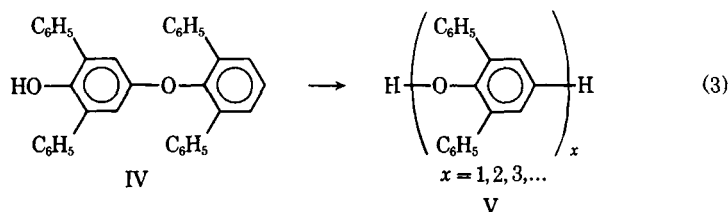
in the determination of structural details of polymer III (e.g., the nature of the head endgroups), would further elucidate the mechanism of the polymerization reaction and could provide a synthetic route to 4-aryloxy-2,6-diarylphenols. This report describes the reaction of III with four phenols, the reaction conditions and materials required for extensive reaction, and the isolation of one of the co-redistribution products.

$$III \; + \; m\mathrm{ArOH} \;\xrightarrow{\;\text{Initiator}\;}\;$$

$$x = 1, 2, 3 \ldots$$

(4)

VI

EXPERIMENTAL

Small-Scale Equilibration Reactions

Poly(2,6-diphenyl-1,4-phenylene ether[5] (III, 0.500 g; intrinsic viscosity in chloroform at 30°C, 0.32 dl/g), 2,6-diphenylphenol[6] (II, 0.500 g; 2.30 mmole) and 3,3',5,5'-tetraphenyl-4,4'-diphenoquinone[6,7] (VII, 0.050 g; 0.103 mmole) in 25 ml chlorobenzene were heated at reflux for 2 hr. The solution was cooled to 25°C and added dropwise to vigorously stirred methanol (250 ml). After standing for several hours, the polymer was collected on a preweighed fritted (fine) filter funnel, washed with methanol, dried at 50°C/10 mm Hg overnight, and weighed. Recovered polymer yields were used as a measure of extent of reaction and are presented in the tables. A 5-ml aliquot of the filtrate was concentrated on a rotary evaporator, and the phenolic components were converted into trimethylsilyl ether derivatives by adding 2 drops of bis(trimethylsilyl)acetamide[8] and analyzed by gas chromatography on a 2-ft silicone rubber column with a program from 100 to 300°C at 10°C/min. The unsilylated concentrated solution was analyzed by two-dimensional thin-layer chromatography on 8 × 8 ft silica gel plates with trans-1,2-dichloroethylene and benzene as developing solvents. Approximate R_f values for various values of x in V are listed in Table I for the two thin-layer solvents.

TABLE I

	R_f	
x	Benzene	trans-Dichloroethylene
1	0.8	0.8
2	0.8	0.6
3	0.8	0.5
4	0.83	0.45
5	0.85	0.4
6	0.87	0.35
<6	0.9	0.3

A second series of weaker spots on the thin layer chromatograms is attributed to compounds with the general structure:
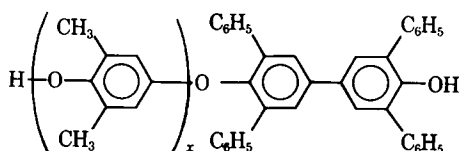
which were derived from the equilibration of X with the polymer. R_f values for this series are given in Table II.
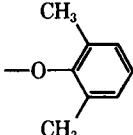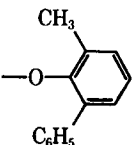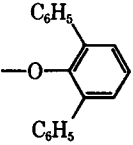
The spots were detected by spraying with a solution of 10% phosphomolybdic acid in 90% ethanol.

The equilibration procedure described above was used to determine effects of reaction variables. In these cases, the only change in the procedure was the specific variable (or variables) described in the text. For studies on various polymers, the polymers were materials described previously.[5] For reactions with various phenols, the phenols were purified by recrystallization or distillation (in the case of 2-methyl-6-phenylphenol). Gas chromatograph retention times with the program described above for the volatile products with structure VI ($x = 1$; trimethylsilyl ether derivative) from equilibration of III with various phenols are listed in Table III.

Side products which were trapped from gas chromatographs and were identical to authentic samples had the following retention times: X, 38 min; 4-benzoyloxy-2,6-diphenylphenol, 21 min; 4,4″-dihydroxy-3,3′,5,5′-tetramethylbiphenyl, 17 min; 4,4′-dihydroxy-3,3′-dimethyl-5,5′-diphenylbiphenyl, 23 min. An increase in the maximum temperature of the gas chromatograph program to 350°C permitted elution of the trimethylsilylether of V ($x = 3$) at 36 min.

TABLE II

x	Benzene	trans-Dichloroethylene
0 (compound X)	0.6	0.4
1	0.55	0.3
>1	0.5	0.2

TABLE III

—OAr	Retention time, min
—OC$_6$H$_5$	19
CH$_3$ —O—[ring] CH$_3$	20
CH$_3$ —O—[ring] C$_6$H$_5$	21
C$_6$H$_5$ —O—[ring] C$_6$H$_5$	25

To determine the approximate molecular weight at which equilibrated polymer was insoluble in methanol, a low molecular weight sample of III prepared with a CuCl-tetramethylethylenediamine catalyst[5] was stirred with methanol (250 ml/g polymer). The methanol-insoluble fraction corresponded to 20% of the total weight. The intrinsic viscosity was 0.05 dl/g (CHCl$_3$, 30°C) and the number-average molecular weight (Mechrolab osmometer) was 1500 (or $\overline{DP}_n \sim 6$).

4-Phenoxy-2,6-diphenylphenyl Acetate VIII

Poly(2,6-diphenyl-1,4-phenylene ether[5] (III, 2.44 g, 10 mmole monomeric units; intrinsic viscosity in chloroform at 30°C, 0.1 dl/g), phenol (1.88 g, 20 mmole) and 3,3',5,5'-tetraphenyl-4,4'-diphenoquinone (VII, 0.244 g, 0.5 mmole) in 50 ml chlorobenzene were heated at reflux 1 hr. Acetic anhydride (10 ml) and 5 ml pyridine were added, and the solution was heated at reflux 1 hr. The solvent was removed at reduced pressure with a rotary evaporator and the white solid residue was triturated two times with boiling n-hexane (100 ml) leaving a residue (ca. 1.5 g). The n-hexane extracts were cooled to 0°C and the crystals that formed were isolated by filtration. The crystalline product was identified as compound IX by NMR, infrared spectra, and mixed melting point with the diacetate of an authentic sample of X.[9] The yields were 0.20 g (mp 206–210°C) from the first crop and 0.05 g (mp 203–204°C) from the second crop. The NMR spectrum (in deuteriochloroform, TMS reference) showed singlet peaks at 1.78 and 7.65 ppm and a poorly resolved grouping at 7.45 and 7.48 ppm in the relative intensity ratio 6:4:20. Characteristic bands in the infrared (KBr pellet)

occurred at 1750 (carbonyl), 870 (isolated aryl hydrogen), and 745 and 695 cm^{-1} (phenyl).

The solvent was evaporated from the filtrates which left oily residues weighing 2.6 g and 0.55 g.   The oil was chromatographed on a preparative scale gas chromatograph (2 ft silicone column, heated from 100°C to 300°C at 10°C/min), and the fraction eluted at 20 min was collected.   The liquid sample solidified on standing.   Recrystallization from n-pentane at −10°C gave VIII, 0.45 g, mp 102–103°C.   The NMR spectrum (in deuteriochloroform, TMS reference) of IX showed peaks at 1.77, 7.05, 7.18, 7.27, and 7.38 and 7.40 ppm in the relative intensity ratio 3:3:2:2:10   Characteristic bands in the infrared (thin film of pure liquid) occurred at 1760 (carbonyl), 1215, and 1185 (C—O—C), 900 (isolated aryl hydrogen), and 750 and 695 cm^{-1} (phenyl).

ANAL.   Calcd for $C_{26}H_{20}O_2$:   C, 82.1%; H, 5.3%;   Found: C, 82.0%; H, 5.3%.

Acetylation of the Terminal Phenolic Hydroxyl Group in III

A solution of poly(2,6-diphenyl-1,4-phenylene ether) (4.0 g, intrinsic viscosity 0.32 dl/g in chloroform at 30°C) in 48 ml pyridine and 48 ml toluene was heated to reflux under a nitrogen atmosphere.   Acetic anhydride (3.0 ml) was added, the reaction temperature was maintained at reflux for 3 hr, then allowed to cool and left at 25°C for 3 days.   The solution was filtered and the polymer was precipitated by adding the solution dropwise to 600 ml methanol.   The polymer was washed twice in acetone and dried overnight at 45°C/12 mm.   The product weighed 3.96 g, [η]0.30 dl/g.   The sharp infrared absorption at 3550 cm^{-1} for the starting material in carbon disulfide (2.5% solution in a 1.0 cm cell, absorbance 0.137) disappeared completely in the acetylated product.

Equilibration of Acetylated III

The acetylated polymer was heated with 2,6-diphenylphenol and 3,3',-5,5'-tetraphenyl-4,4'-diphenoquinone in chlorobenzene by the small-scale equilibration procedure described above.   No low oligomers (e.g., IV) were detected by chromatography, and a 100% yield of polymer resulted.   The polymer which had not been acetylated was equilibrated in an identical manner and was recovered in a 35% yield.

RESULTS

Reaction Products

A chlorobenzene solution of 2,6-diphenylphenol (II) and an equal weight of polymer III in the presence of a catalytic quantity of the initiator, 3,3',-5,5'-tetraphenyl-4,4'-diphenoquinone (VII) was heated at 132°C for 2 hr. A mixture of oligomers ranging from monomer II to methanol-insoluble polymer (VI, $x >$ ca. 5) was produced.   The lower molecular weight components (monomer through tetramer) were resolved with two-dimensional thin layer
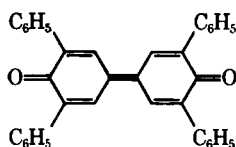
VII

chromatography. The dimer from the equilibration reaction had R_f values which were identical to the values for an authentic sample of IV. Furthermore, the redistribution products from reaction (3) and the initial oxidation products from reaction (2) displayed chromatographic behavior which was identical to that of the products of the monomer–polymer equilibration. The monomer, dimer, and trimer could also be detected by gas chromatography. The retention times were identical to the oligomers from reactions (2) and (3). The similarity that was found between dimer equilibration and monomer–polymer equilibration supports reaction (5) as an overall description of the monomer–polymer reaction. This was supported further by the similarity of product concentrations for the two reactions when II and III were present in equal weights in the monomer–polymer equilibration:
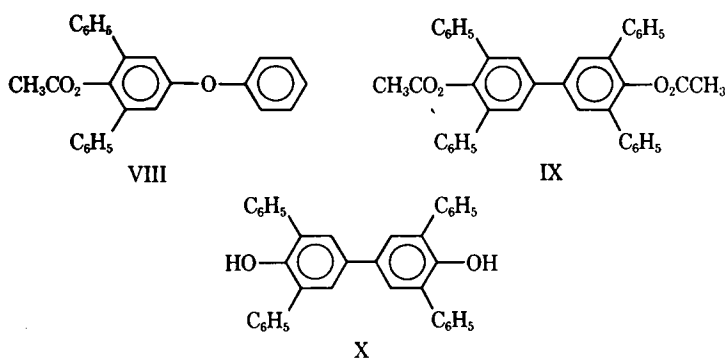

(5)
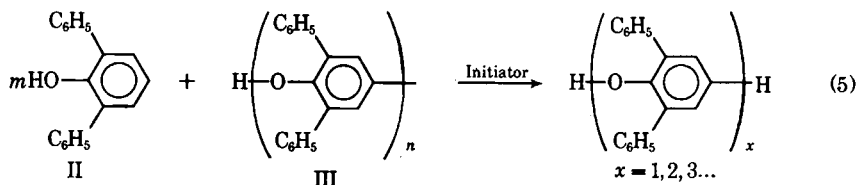
i.e., $m \simeq n$ in reaction (5).*

Phenol was equilibrated with polymer III [reaction (6)] and the components of the mixture converted to their acetate derivatives.

(6)
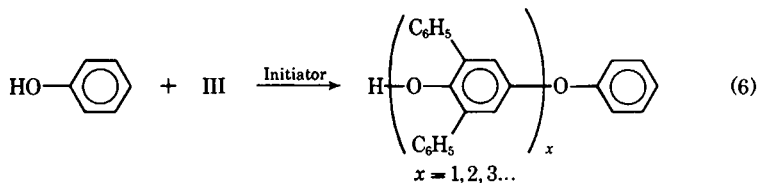
From the product mixture, the lowest boiling principal product was isolated and identified as 4-phenoxy-2,6-diphenylphenyl acetate (VII). The yield based on the formation of one molecule of VIII per repeating unit of polymer was 12%. A small amount of IX was also isolated.

* For reactions (3) and (5) under nitrogen with only a trace of initiator, the number-average degree of polymerization $\overline{DP}_n$ of the equilibrated mixture is essentially the same as that of the starting mixture. Thus, when $n = m$ in reaction (5), $\overline{DP}_n = 2$ as in the case with the dimer [reaction (3)].

C_6H_5
CH_3CO_2—⟨⟩—O—⟨⟩
C_6H_5
VIII

C_6H_5 C_6H_5
CH_3CO_2—⟨⟩—⟨⟩—O_2CCH_3
C_6H_5 C_6H_5
IX

C_6H_5 C_6H_5
HO—⟨⟩—⟨⟩—OH
C_6H_5 C_6H_5
X

Compound IX arose primarily from the initiator, VII, after reduction to X during the initiation process. For this equilibration reaction, a low molecular weight polymer which had been found to undergo extensive equilibration when heated with II was used to provide a relatively high conversion to products. As a result, product yields in this case were greater than in another equilibration with phenol and a higher molecular weight polymer which is described in the next section.

Reaction Variables

To assess the effects of reaction conditions, solvents, polymer structure and type of initiator on the extent to which reaction (5) proceeded, the yields of recovered (methanol-insoluble) polymer were measured after equal weights of polymer III and 2,6-diphenylphenol were heated at reflux, usually in chlorobenzene. A 100% yield of recovered polymer indicated no equilibration, and lower yields indicated increasing extents of reaction. The extents of reaction were qualitatively proportional to the concentration of lower molecular weight products by gas and thin layer chromatographic analysis.

A comparison of the effectiveness of initiators for reaction (5) is presented in Table IV. Except for the benzoyl peroxide reaction which was in benzene at 80°C, the other reactions were in chlorobenzene at 132°C. Although the molar quantities of the initiators vary, their effectiveness toward

TABLE IV
Equilibration of II (500 mg) and III (500 mg)
With Various Initiators

Initiator	Wt. of initiator, mg	Recovered polymer, %
VII	50	35
3,3',5,5'-Tetramethyl-4,4'-diphenoquinone	50	98
Dicumyl peroxide	50	100
Benzoyl peroxide	100	67
tert-Butyl hydroperoxide	50	99
tert-Butyl perbenzoate	50	40

promoting equilibration can be assessed qualitatively. Three oxidizing agents were ineffective: 3,3',5,5'-tetramethyl-4,4'-diphenoquinone, *tert*-butyl hydroperoxide, and dicumyl peroxide. The remaining materials, 3,3',5,5'-tetraphenyldiphenoquinone, VII, *tert*-butyl perbenzoate, and benzoyl peroxide were initiators. Benzoyl peroxide was used at 80°C because of its relatively low decomposition temperature, yet was moderately effective. Compound VII appeared to be the most versatile initiator, since it could be used over a wide temperature range.

Initiator concentrations were varied for VII in chlorobenzene at 132°C and for benzoyl peroxide in benzene at 80°C. The effect on recovered polymer yield is listed in Table V. With VII, a quantity of ca. 50 mg/500

TABLE V
Equilibration of II (500 mg) and III (500 mg)
with Various Quantities of Initiators

Initiator	Wt. of initiator, mg	Recovered polymer, %
VII	5	73
VII	15	58
VII	50	35
VII	150	45
Benzoyl peroxide	20	91
Benzoyl peroxide	50	80
Benzoyl peroxide	100	67

mg polymer was most effective. Possibly, with the higher concentration of VII, the equilibration products were being oxidized to higher molecular weight insoluble products. With benzoyl peroxide quantities of 100 mg/500 mg polymer or more appeared to be required for extensive equilibration.

Polymer recovery from reaction (5) with VII as an initiator is listed in Table VI for four solvents at temperatures ranging from 80 to 180°C.

TABLE VI
Equilibration of II (500 mg) and III (500 mg) in
Various Solvents at Reflux Temperatures

Solvent	Reaction temperature, °C	Recoverd polymer, %
Benzene	80	71
Toluene	111	83
Chlorobenzene	132	35
o-Dichlorobenzene	180	14

Although there is a general trend toward more extensive equilibration with increased reaction temperature, the type of solvent appears to be of some importance since with toluene the least amount of equilibration occurred even though it was used at an intermediate temperature.

Three equilibration reactions were run in chlorobenzene at reflux for various time intervals (Table VII).

TABLE VII
Extent of Equilibration of II (500 mg) and III (500 mg) with Time

Reaction time, hr	Recovered polymer, %
0.5	53
2.0	35
18.0	22

Initially the reaction proceeded rapidly, but then became slower. This may have been due primarily to the loss of the initiator by reaction with 2,6-diphenylphenol:*

$$2II + VII \rightarrow 2X$$

During the course of the reaction, a decrease in the color of VII was noted. Chromatographic analysis indicated the formation of 4,4'-dihydroxy-3,3',-5,5'-tetraphenylbiphenyl (X). The isolation of the diacetate of X was described above for the equilibration in which III was co-redistributed with phenol.

3,3',5,5'-Tetramethyldiphenoquinone was used as an initiator at lower temperatures to minimize side reactions. The reaction was very slow at 80°C. Yields of recovered polymer were: 99% after 0.5 hr, 98% after 2 hr, and 97% after 16 hr.

A variety of samples of polymer III with different molecular weights and from different catalyst systems were described previously.[1] Some of these samples were equilibrated with 2,6-diphenylphenol with initiation by VII in benzene at 80°C. Yields of recovered polymer are compared in Table VIII

TABLE VIII
Equilibration of Polymers Prepared from Various
Catalysts with II in Chlorobenzene at 132°C

[η] dl/g	Amine in polymerization catalyst	Recovered polymer, %
0.05	N,N'-Dimethyl-1,3-propane-diamine	37
0.06	N,N,N',N'-Tetramethyl-1,6-hexanediamine	42
0.07	N,N,N',N'-Tetramethyl-1,3-butanediamine	39
0.44	"	95
0.32	N,N,N',N'-Tetramethylethylene-diamine	71
0.19	Di-n-butylamine	95
0.39	"	97
0.31	n-Butylamine	91

* The analogous oxidation of 2,6-xylenol by 3,3',5,5'-tetramethyldiphenoquinone has been reported.[10,11]

for polymers prepared with various amines in the catalyst and with the viscosity of the polymer before equilibration.

Polymers prepared with diamine catalysts showed a general progression of less equilibration with increasing intrinsic viscosity. When the catalyst contained either a primary or secondary monoamine, the polymers neither attained high molecular weights in the polymerization[5] nor equilibrated appreciably. Thus, it is possible that the monoamines reacted with the phenolic end of the polymer to both terminate polymerization and deactivate the "redistribution-active" portion of the polymer.

To determine whether low molecular weight polymers did equilibrate more readily than high molecular weight polymers, six polymers which were isolated at different times from the same polymerization reaction were equilibrated with 2,6-diphenylphenol in o-dichlorobenzene at 180°C for 2 hr. The molecular weights of these samples ranged from $\bar{M}_n$ <5000 to ca. 80,000. Yields of recovered polymer are listed in Table IX.

TABLE IX
Effect of Molecular Weight on Extent of Equilibration

[η] dl/g	Recovered polymer, %
0.09	4
0.11	10
0.19	19
0.24	16
0.30	16, 17
0.41	28

The tendency toward less equilibration with higher molecular weight is similar to the behavior of poly(2,6-dimethylphenylene oxide), I, equilibrations, in which case both molecular weight (i.e., changes in endgroup concentration) and endgroup abnormalities affect the reactivity.[1]

The reactivity of four phenols toward equilibration with III in chlorobenzene at 132°C with VII as an initiator was measured (Table X). 2,6-Diphenylphenol caused the most extensive equilibration. 2-Methyl-6-phenylphenol, with a structure closer to that of 2,6-diphenylphenol than the other phenols, was more reactive than the other two phenols. A somewhat similar reactivity series has been found for poly(2-methyl-6-phenylphenylene oxide). In this case, 2-methyl-6-phenylphenol equilibrated more extensively with the polymer than did phenol or 2,6-xylenol which do not contain an o-phenyl group.[12]
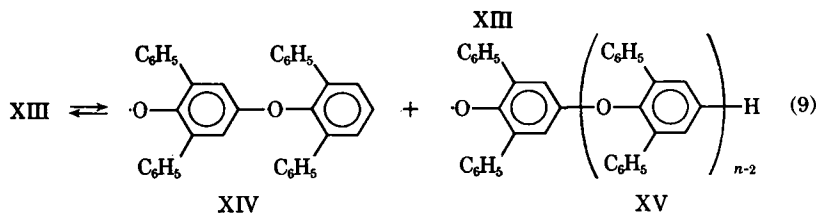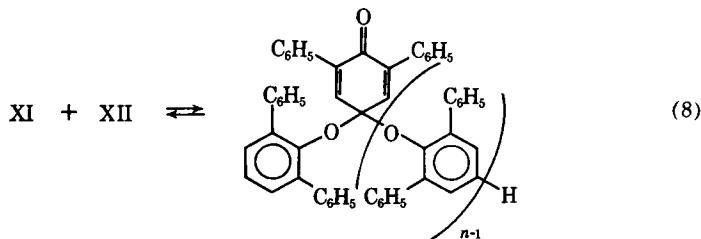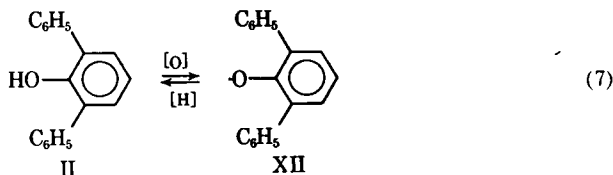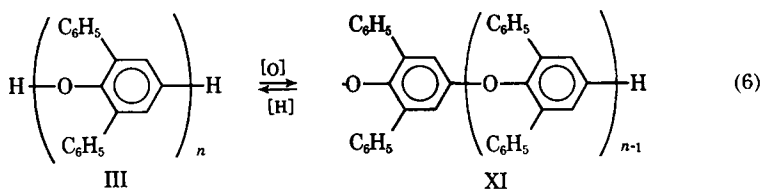
TABLE X
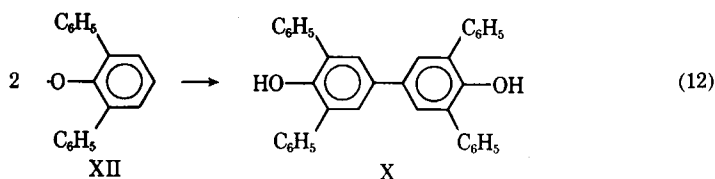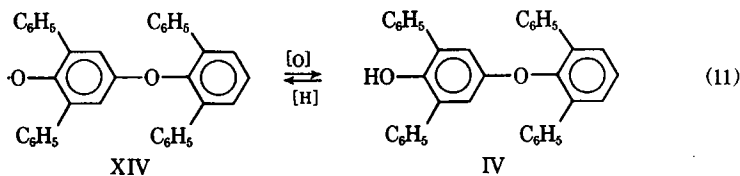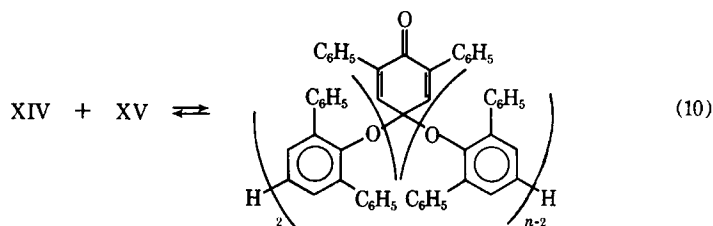Equilibration of III with Various Phenols (1 mole phenol/monomer unit)

Phenol	Recovered polymer, %
Phenol	93
2,6-Dimethylphenol	94
2-Methyl-6-phenylphenol	60
2,6-Diphenylphenol	35

DISCUSSION

The reaction conditions which are required to equilibrate polymer III with phenols are more strenuous than for the equilibration of the corresponding polymer, I, from 2,6-dimethylphenol with phenols. Higher temperatures and higher concentrations of initiator are required. Furthermore, initiators with higher oxidation potentials are more effective (e.g., VII instead of the tetramethyl-substituted analog). The initiators also have to be able to oxidize the phenols at the higher temperatures without extensive side reactions.

There are many similarities between equilibration of phenols with III and with I. The extensiveness of both reactions depends on the molecular weight of the polymer and the method of polymerization. In both cases, one of the most effective initiators is the tetrasubstituted diphenoquinone which is obtained as a side product during the preparation of the polymer. The similarities of the two systems and the product analyses after equilibration indicate similar mechanisms for equilibration. Thus, for the case of reaction (5) with VII as initiator, the reactions (6)–(12) seem likely.

$$\text{XIV} \; + \; \text{XV} \; \rightleftharpoons \; \left(\quad \right)_2 \left(\quad \right)_{n-2} \tag{10}$$

$$\text{XIV} \quad \xrightleftharpoons[\text{[H]}]{\text{[o]}} \quad \text{IV} \tag{11}$$

$$2 \quad \text{XII} \quad \longrightarrow \quad \text{X} \tag{12}$$

Reactions (6) and (7) represent initiation reactions. The oxidizing agent can be either VII or the semiquinone of VII. The reaction sequence is continued by carbon–oxygen coupling reactions and dissociation reactions which are illustrated by the reactions in equilibria (8), (9), and (10). Hydrogen abstraction reactions as (11) convert the radical species to the free phenol and either generate new aryloxy radicals or oxidize the reduced forms of VII. Termination is represented by the carbon–carbon coupling reaction (12).

Polymer III must have a free phenolic hydroxyl group at the end of the polymer chain to participate in the equilibration sequence described above; otherwise, co-redistribution should not occur. This requirement was demonstrated by an attempt to equilibrate polymer with the hydroxyl groups quantitatively acetylated. No low molecular weight co-redistribution products were detected, and the polymer was recovered quantitatively. Presumably then, the polymers which did not co-redistribute extensively with 2,6-diphenylphenol (Table VII) contain structural irregularities in the head ring. These inactive polymers are also inert toward further oxidation to high molecular weights in polymerization systems which normally produce high molecular weight polymers.

Further support for the presence of structural irregularities is presented by the reduced reactivity of higher molecular weight polymers toward equilibration. Two reasons why the differences in molecular weight alone do not account for variations in reactivity are described here. First, the lower molecular weight polymers should react at a more rapid rate than higher polymers since equal weights were used resulting in higher end group concentrations for solutions of low polymers. However, due to the high

reaction temperature (170°C), the reaction time was sufficient to approach a steady state condition even for the higher polymers. This was demonstrated by using longer reaction times and finding almost no further decrease in the yields of recovered polymer. Second, the possibility that complete equilibration of high molecular weight polymer would produce a larger concentration of higher molecular weight (and thereby methanol-insoluble) oligomers than would a low polymer is not the case since the molar concentration of II is so much greater than the molar concentration of either high or low polymer that the $\overline{DP}_n$ of both reaction mixtures is almost identical.

The possibility that some of the polymer chains do not contain 4-hydroxy-2,6-diphenylphenoxy "head" endgroups and that there is a decrease in the percentage of chains bearing these end groups as polymerization proceeds can account for decreasing reactivity with increasing molecular weight. If the "head" end-groups can react during polymerization in an abnormal manner, i.e., to form stable products by reactions other than the normal oxidative coupling reactions for chain growth, or if intermediates such as the quinone-ketal moiety can rearrange or be intercepted by other species in the reaction medium, abnormal structural units can arise. Two types of abnormal reactions would be, for example, head-to-head coupling reactions [other than the normal quinone-ketal formation reaction such as reactions (8) or (10)] which would result in either unreactive polymers containing 2,6-diphenylphenoxy groups on each end of the chain instead of only on one end of the chain or in reactions in which another species such as the amine in the catalyst reacted with the "head" endgroup to form a new abnormal endgroup. The gradual incorporation of nitrogen into the polymer with increased polymerization time[5] supports the possibility of reactions of polymer with the amine.

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