utes. The reaction mixture was stirred for 3 hours and then quenched by the addition of 20 ml. of water. The ether layer was extracted with 400 ml. of water; the water extract was boiled to remove excess ether and diluted to 500 ml. The Volhard method was used for the analysis for bromide ion. Iodide (from the methyl iodide used in the preparation of methyllithium) was removed by oxidation with 0.05 *N* nitrous acid.[17] Analyses were precise to 0.4%. The ether layer, which contained the unreacted bromoanisole, was washed with 400 ml. of 3 *N* hydrochloric acid to remove amines. The bromoanisole was distilled and then purified for analysis by vapor-phase chromatography.

Analysis of Mixtures of 3-Bromoanisole-2,4,6-$^2H_3$ and 3-Bromoanisole.—Mixtures were analyzed for deuterium by the "base-line" method at 11.061 μ[18] with a Perkin–Elmer (model 21) infrared spectrophotometer.

Transmittances of undiluted mixtures were measured in a 0.05-mm. cell. The 0.05-mm. cell in the reference beam was filled with pure protonated 3-bromoanisole. In this manner, the deuterium absorption peak was made sufficiently large for the desired accuracy without interference from adjacent hydrogen absorption. A calibration graph was prepared from several standard mixtures. The plots were linear to within 1% over the concentrations calibrated. Duplicate analyses agreed to within 1%.

Calculation of Kinetic Isotope Effects.—"Apparent" kinetic deuterium isotope effects were calculated on the basis of a concerted dehydrohalogenation mechanism (eq. 2). The following assumptions were made in formulating the kinetic expression below: only the 2-hydrogen of 3-bromoanisole is involved in the amination, the reactions of benzyne are not rate-determining nor reversible, and the initial elimination reaction is first order with respect to 3-bromoanisole. The rate of disappearance of 3-bromoanisole-2,4,6-$^2H_3$(D) and 3-bromoanisole (H), respectively, are

$$-\,\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_{\mathrm{D}}[\mathrm{D}][\mathrm{NR_2}'^{\ominus}]^n \qquad (5)$$

and

$$-\,\mathrm{d}[\mathrm{H}]/\mathrm{d}t = k_{\mathrm{H}}[\mathrm{H}][\mathrm{NR_2}'^{\ominus}]^n \qquad (6)$$

Division of (6) by (5) and integration yields

$$\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}} = \frac{\ln([\mathrm{D_t}]/[\mathrm{D_0}])}{\ln([\mathrm{H_t}]/[\mathrm{H_0}])} \qquad (7)$$

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[17] W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1939, p. 190.

[18] J. J. Heigel, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Polyethers. IX. Poly-(2,6-dimethyl-1,4-phenylene Oxide)

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The reaction of 4-bromo-2,6-dimethylphenolate ion with a number of oxidizing agents, such as ferricyanide ion, lead dioxide, iodine and oxygen and light, leads to the ready conversion at room temperature to polymer. The soluble polymer had molecular weights in the range 2000–10,000. Analysis indicates one bromine atom and one phenol group per chain. Efforts to polymerize 4-bromo-2,6-di-*t*-butylphenol, bromodurenol and pentabromophenol under the same conditions failed. A mechanism involving propagation by displacement of bromide ion by phenoxy radical is proposed.

In a series of papers, Hunter[2] reported on the polymerization of trihalophenols under a variety of conditions. Solid polymers with molecular weights around 2000 were reported. Hunter established that iodine was displaced somewhat more readily than bromine, which in turn was more reactive than chlorine, and that *p*-halogen reacted more readily than *ortho*.[3] Furthermore, only halogen in a ring with a free ionizable phenol group could be displaced.

Efforts on our part to prepare poly-(1,4-phenylene oxide) by a variety of methods either gave low yields of intractable, high melting, insoluble material or very low molecular weight product. Because of the potential thermal stability of a polymer system built on this backbone, we have investigated the polymerization of 4-bromo-2,6-dimethylphenol by procedures analogous to those of Hunter.

Experimental

2,4,6-Tribromophenol, m.p. 93.5°, was converted to the red silver salt,[4] which was polymerized by treatment with iodine in refluxing chloroform suspension. Precipitation with methanol after 12 hours gave 60% yield of amorphous polymer, softening about 235° and having a molecular weight of 3700 (cryoscopically in ethylene dibromide).

Silver *p*-bromophenoxide under similar conditions gave an amorphous solid, softening at 140–145°, with a reduced viscosity of 0.048.

Efforts to prepare **silver 4-bromo-2,6-dimethylphenoxide** were unsuccessful, yielding only black precipitates (evidently silver).

4-Bromo-2,6-dimethylphenol (0.8 g., m.p. 78°[5]) was dissolved in 10 ml. of Claisen alkali and 50 ml. of benzene and stirred in the dark for 22 hours. No polymer was formed. A similar reaction mixture exposed to a Hanovia ultraviolet lamp turned yellow. The benzene layer was washed and then added to ten volumes of methanol. The precipitated polymer was freeze-dried from benzene to yield 0.135 g. (27.6% conversion), softening at 212–218°.

Treatment of a similar reaction mixture with iodine (1–2 %) with stirring for 24 hours gave 87.5% recovery of starting phenol and 12.5% of amorphous polymer, softening at 205–210°, $[\eta]$ 0.23 (benzene, 25°).

When one equivalent of the phenol in Claisen alkali was shaken with one equivalent of iodine, the purple color faded to yellow almost immediately. After 5 minutes, the benzene layer yielded 70%[6] of polymer, softening at 218–222°.

Anal. Found: C, 77.65; H, 6.92; Br, 5.30.

Poly-(2,6-dimethyl-1,4-phenylene oxide) was prepared for fractionation by stirring a solution of 94.6 g. of 2,6-dimethyl-4-bromophenol in 2.3 l. of benzene with 26.4 g. of potassium hydroxide in 2.3 l. of water and adding 1.13 g. (1 mole %) of lead dioxide. After stirring for 45 hours at room temperature an aliquot from the aqueous layer was titrated for bromide ion, indicating 77% reaction. The benzene layer was separated, washed, concentrated to 500 ml.

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[1] Supported in part by Contract No. DA-19-129-QM-1265, U. S. Army Quartermaster Corps.

[2] See W. H. Hunter and M. A. Dahlen, *J. Am. Chem. Soc.*, **84**, 2459 (1932).

[3] W. H. Hunter and F. E. Joyce, *ibid.*, **39**, 2640 (1917).

[4] (a) A. Hantzsch, *Ber.*, **40**, 4875 (1907). (b) H. A. Torrey and W. H. Hunter, THIS JOURNAL, **33**, 194 (1911).

[5] T. C. Bruice, N. Kharasch and R. J. Wizzler, *J. Org. Chem.*, **18**, 83 (1953).

[6] W. H. Hunter and L. M. Seyfried, THIS JOURNAL, **43**, 151 (1921), reported yields of poly-(dichlorophenylene oxide) increasing sharply with the amount of iodine used.

TABLE I

FRACTIONATED POLY-(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

Fraction	Wt., g.[a]	[η]	Mol. wt.[b]	% C[c]	% H[c]	Br[c]	Br[d]	Mol. wt.[e]	Mol. wt.[f]	% C[g]	H%[g]
1A	1.25	0.29	....	79.06	6.63	0.76	1.07, 1.05	10,500	7540	79.39	6.67
1B	2.40	.20	6950 ± 200	78.45	6.61	1.31, 1.71	1.57, 1.53	5,390	5160	78.75	6.63
2	10.20	.20	7000 ± 200	78.60	6.55	1.04, 1.77	1.23, 1.18	6,100	6640	78.84	6.63
3	5.13	.16	5600 ± 150	78.66	6.71	1.42, 1.53	1.45, 1.42	5,400	5570	78.77	6.63
4	.942	.13	4250 ± 100	78.32	6.60	2.06, 2.09	1.73, 1.76	3,850	4570	78.29	6.60
5	6.31	.11	3700 ± 70	77.71	6.54	2.50, 2.20	2.17, 2.14	3,420	3710	78.07	6.58
6	1.91	.12	....	77.52	6.55	3.20, 2.83	....	2,660	..	77.53	6.55

[a] A total of 36.62 g. was recovered from 45.6 g. of original polymer. [b] Calculated from phenol titration with tetrabutylammonium hydroxide in pyridine–benzene–methanol (see R. H. Cundiff and P. C. Markunas, *Anal. Chem.*, **28**, 792 (1959)) assuming one phenol group per polymer molecule. [c] Analyses by Midwest Microlabs, Indianapolis, Ind. [d] Analyses by Microtech Labs., Skokie, Ill. [e] Calculated from Midwest bromine analyses. [f] Calculated from Microtech bromine analyses. [g] Calculated from mol. wt. (*e*).

and filtered into 1.5 l. of methanol to yield 46.5 g. (81%) of polymer, [η] 0.11 (benzene, 25°).

Fractionation was carried out by precipitation from ethylene dichloride by addition of nitromethane. Initially, 45.6 g. of polymer was dissolved in 2900 ml. of ethylene dichloride and 100 ml. of nitromethane was added. The turbid suspension was warmed until clear, and cooled with stirring in a bath at 30° for 24 hours. The 4.3 g. of precipitated polymer (fraction 1) was refractionated to samples 1A and 1B.

To the solution from fraction 1, a further 500 ml. of nitromethane was added. In this way eventually a total of seven fractions of increasing solubility was obtained (see Table I).

A 0.5-g. sample of fraction 4 (Table I) was dissolved in 65 ml. of benzene and treated with 0.53 g. of potassium hydroxide and 0.036 g. of potassium ferricyanide in 10 ml. of water. After shaking for 2 days, the polymer was reprecipitated, yielding 0.45 g., softening at 260°, [η] 0.43. The increase in viscosity cannot be explained by further polymerization through loss of bromine.[7]

Anal. Found: Br, 1.60, 2.19.

Kinetics.—Solutions of 0.01 mole of 4-bromo-2,6-dimethylphenol in 50 ml. of benzene were mixed with 0.01 mole of potassium hydroxide in 50 ml. of water. Lead dioxide (or potassium ferricyanide) was added to the stirred mixture. Aliquots were removed from the aqueous phase, quenched by addition of dilute acetic acid, and titrated for bromide liberated with standard silver nitrate solution. The data gave satisfactory linear plots for kinetics first order in monomer. The results are summarized in Table II.

TABLE II

RATE OF POLYMERIZATION OF 4-BROMO-2,6-DIMETHYLPHENOXIDE AT ROOM TEMPERATURE (26–28°)

Expt.	Catalyst	Mole %	$t_{1/2}$, sec.	$k \times 10^5$, sec.$^{-1}$
1	PbO_2	1	9360	7.40
2	PbO_2	1	7080	9.80
3	PbO_2	3	7440	9.3
4	PbO_2	0.5	9240	7.5
5	$K_3Fe(CN)_6$	1	8640	8.1
6	$K_3Fe(CN)_6$	1	7740	9.0

Cohesive Energy Density of Polymer.—A sample with a reduced viscosity of 0.14 was tested for solubility in a range of solvents by shaking 0.1 g. with 2 ml. of solvent at room temperature. The polymer dissolved in seven solvents with a cohesive energy density[8] between 8.5 and 10.1 (cal./ml.)$^{1/2}$ and was therefore assigned C.E.D. of 9.3 (cal./ml.)$^{1/2}$. It was insoluble in heptane (7.43), cyclohexane (8.2) nitropropane (10.38) and acrylonitrile (10.56).

The **ultraviolet spectrum** of poly-(dimethylphenylene oxide) was determined in chloroform. The results are compared with two simple analogs in Table III. The resemblance to the *para* model compound is clearly much closer than to the *meta*

TABLE III

ULTRAVIOLET SPECTRA

Ether	Max.₁, mμ	log ε	Min.₁, mμ	log ε	Max.₂, mμ	log ε
Poly-(dimethylphenylene oxide	244	3.72	258	2.84	280	3.14
4-Methoxydiphenyl ether	230	4.12	259	3.21	280	3.43
3-Methoxydiphenyl ether	..	..	253	3.01	273	3.49

The principal **infrared** absorption bands in chloroform solution are in μ (and % absorption): 6.25 (48), 6.82 (71), 7.25 (25), 7.67 (55), 8.48 (80), 9.84 (54), 10.47 (28), 11.72 (42), 12.08 (26).

Bromodurenol, pentabromophenol and 4-bromo-2,6-di-*t*-butylphenol were prepared but efforts to convert them to polymer by procedures successful for the 2,6-dimethyl product yielded no polymer.

4-Acetocymercuri-2,6-dimethylphenol was prepared from the dimethylphenol (12.2 g., 0.1 mole) in 300 ml. of ethanol by treatment with 21.6 g. (0.1 mole) of mercuric oxide in 100 ml. of 50% acetic acid. After standing overnight, the precipitate was collected and recrystallized from ethanol–acetic acid; m.p. 159–160°.

Anal. Calcd. for $C_{10}H_{12}HgO_3$: C, 31.54; H, 3.18. Found C, 31.81; H, 3.21.

When heated under vacuum for 45 minutes at 200°, this compound decomposed with the evolution of acetic acid to leave a brown residue and droplets of metallic mercury. Extraction with chloroform, leaving a brown insoluble resin, gave 12% conversion to soluble polymer having the same infrared spectra as poly-(2,6-dimethyl-1,4-phenylene oxide).

Discussion

The extensive recent work on the conversion of tri-*t*-butyl-[10] or triphenyl-[11] phenol to stable, colored free radicals by many of the reagents effective in polymerizing 4-bromo-2,6-dimethylphenol, suggests strongly that initiation is probably one-electron oxidation to an aryloxy radical.

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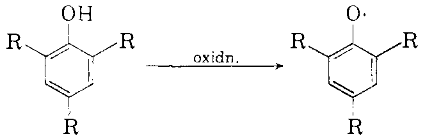
[7] Since 2,6-dimethylphenol has been found to polymerize under oxidizing conditions (Dr. A. S. Hay, General Electric Co., private communication), this may be an example of such oxidative polymerization, leading to branched polymer.

[8] J. Hildebrand and R. Scott, "The Solubility of Non-electrolytes," Reinhold, New York, 3rd Ed., pp. 129 and 361 (1949).

[9] H. E. Ungnade, E. E. Pickett, L. Rubin and E. Youse, *J. Org. Chem.*, **16**, 1319 (1951).

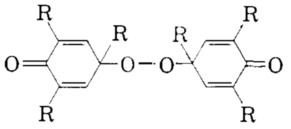
[10] (a) C. D. Cook, *et al.*, *J. Org. Chem.*, **18**, 261 (1853); **23**, 755 (1958); THIS JOURNAL, **78**, 2002, 3797, 4159 (1956); (b) E. Müller and K. Ley, *Ber.*, **87**, 922 (1954); **91**, 2682 (1958).

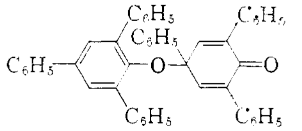
[11] K. Dimroth, F. Kalk, R. Sell and K. Schlömer, *ibid.*, **90**, 2058 (1957); *Ann.*, **624**, 57 (1959).



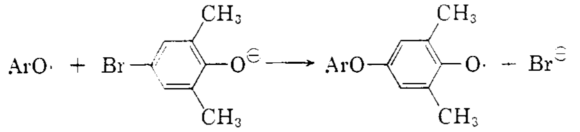
This view is supported by our observation that polymerizations run at −70° (in methanol–toluene) with iodine catalysis developed green colors which persisted at low temperature but faded at room temperature. Similarly, Hunter and Joyce[3] reported a transient blue color in the polymerization of the silver salt of 4-chloro-2,6-diiodophenol in benzene.

The ease of coupling through oxygen to the 4-position in these structures is indicated by the peroxide formed when R = *t*-Bu and the dimer when R = C_6H_5.





We therefore propose that the most likely course for the propagation step in the polymerization we have studied is the aryloxy displacement of bromide ion from the phenolate ion, perhaps through an intermediate ion–radical adduct.

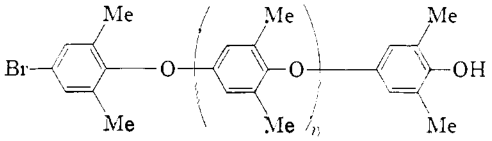


Since the polymer contains one bromine and one phenolic hydroxyl per chain, the termination must involve abstraction of a hydrogen atom from some molecule in the reaction mixture.

The propagation reaction, involving radical displacement at the 4-carbon of the ring, is evidently susceptible to steric hindrance. Flanking the oxy-radical center by two *t*-butyl groups, or the 4-bromine by two methyl or bromine atoms, blocks polymerization.

The polymerization seems to be most favored in systems with two liquid phases. Since the growing aryloxy polymer radical is soluble in the organic solvent, the phenoxide ion in the polar solvent, this is evidently as example of interfacial propagation. The great similarity in rate of polymerization for reactions initiated by 0.5 to 3% of lead dioxide or by 1% of potassium ferricyanide (Table II) suggests that the rate-controlling step is evidently not initiation.

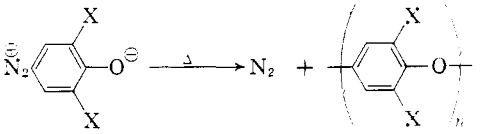
The end group determinations and the infrared and ultraviolet spectra are all in agreement with the following linear structure predicted by the mechanism proposed.

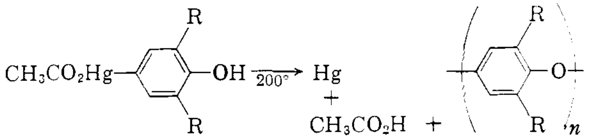


From the viscosity and molecular weight in Table I, it is possible to evaluate the constant in the Staudinger equation $[\eta] = KM^{\alpha}$ as $\alpha = 0.875$ and $K = 8.7 \times 10^{-5}$. These compare with $\alpha = 0.73$ and $K = 8.4 \times 10^{-5}$ for poly-(methyl methacrylate).[12] The high value for α suggests an unusually stiff, inflexible chain, which would seem reasonable for the structure proposed for the polymer. The considerable substitution around the ether links would limit the possible degrees of rotation.

One reason for our interest in these polymers was the potential thermal stability inherent in the diphenyl ether structural unit. The thermal stability of sample 1A, Table I, was studied by Dr. S. L. Madorsky at the National Bureau of Standards. On heating samples under vacuum for 30 minutes, he reported 1% weight loss at 320°, 13% at 370° and 69% at 420°. No products condensable at −190° were formed at 320 or 370°. At 420°, most of the product was condensable at room temperature.

Dewar[13] has reported that poly(phenylene oxide) structures could be prepared by pyrolysis of diazooxides. It occurred to us that a somewhat similar process might occur on the pyrolysis of phenol mercuriacetates.





The latter reaction was, however, accompanied by the formation of insoluble by-products.

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[12] P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 312.

[13] M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 917 (1958).