

Thermal degradation of poly(2-methylphenylene oxide), poly(2,5-dimethylphenylene oxide) and poly(1,4-phenylene oxide)

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Polyoxyphenylenes were obtained from phenol, 2-methylphenol, 2,5-dimethylphenol in oxidative polycondensations using dimethylpyridine-CuCl complexes as catalysts. Samples of polymers from polycondensations were not completely linear as found by i.r. analysis. The m.s. and c.c.-m.s. analysis of degradation products of poly(2-methylphenylene oxide) (PMPO) and poly(2,5-dimethylphenylene oxide) (P2, 5DMPO) have shown that both polymers undergo Fries-type rearrangement prior to statistical scission of benzyl bonds. Ether linkages of poly(1,4-phenylene oxide) (PPO) decompose without rearrangement though cyclization to benzofurane systems has been observed.

INTRODUCTION

It was reported that poly(2,6-dimethyl-1,4-phenylene oxide) rearranges in the Fries-type mode prior to random scission¹. This mechanism seems to be general for the whole group of *ortho* alkyl substituted poly(phenylene oxides). Poly(2-methylphenylene oxide) and poly(2,5-dimethylphenylene oxide), are other examples of Fries-rearranging polymers, although their degradation reactions have not yet been examined.

EXPERIMENTAL

Oxidative polycondensations

100 ml of nitrobenzene or *o*-dichlorobenzene was put in a three-necked 250 ml flask, 0.001 mol CuCl and 0.003 mol of appropriate amine were added. The apparatus was filled with oxygen and the mixture stirred at room temperature until its colour turned from yellow to deep green in the case of nitrobenzene or from colourless to light green in the case of *o*-dichlorobenzene. When the catalyst was ready 2×10^{-2} mol of phenol was added and polycondensation was continued at appropriate temperature (25°–60°C) in an oxygen atmosphere with continuous stirring. The process was stopped by pouring the reaction mixture into 500 ml methanol containing 1% HCl. Coagulated polymer was filtered and then washed with methanol. After drying, the polymer was dissolved in chloroform, precipitated with methanol, filtered, washed and dried at 80°C in vacuum for 24 h.

Polymer degradation

The mixture of the degradation products, their silyl and deuterium analogues were obtained by the methods described in our previous papers^{1,2}.

Methods. Limiting viscosity numbers were determined in toluene at 25°C by using an Ubbelohde viscometer. N.m.r. spectra were recorded in CDCl₃ solutions on a Bruker HF 90 spectrometer. The infrared absorption spectra of polymer powders in KBr were obtained with a Specord 71 i.r. spectrometer. Gas chromatography-mass spectrometry analysis was carried out using a 2091 LKB gas chromatograph-mass spectrometer (g.c.-m.s.) connected with a PDP 11 digital computer.

Separating and recording conditions were the same as in our previous work¹. The spectra of the mixture of degradation products were obtained under the operating conditions 15eV, ion source temperature 25–250°C, accelerating voltage 3.5 kV and resolving power up to 1000.

RESULTS AND DISCUSSION

Polymer samples

Oxidative polycondensation of 2,6-dialkyphenols and 2,6-diphenylphenol has been extensively studied in many publications. Due to substituted *ortho* positions with respect to the hydroxyl group, high molecular and purely linear polymers can be obtained from these monomers. On the other hand, only a few publications have been devoted to the synthesis and investigations of poly(phenylene oxides) from unsubstituted or monosubstituted phenols. In this case, as substitution can be effected either in the *ortho* or *para* positions, products are not completely linear and high molecular weights cannot be achieved. The use of a catalytic complex with steric hindrance can diminish the extent of branching and crosslinking. Tsuchida *et al.*³ investigated the kinetics of oxidative polycondensation of various phenols in the presence of the complex CuCl-2,6-dimethylpyridine, but they did not characterize the polycondensation products. Several authors report the synthesis

Table 1 The results of oxidative polycondensation of 2-methylphenol, phenol, *p*-bromophenol and 2,5-dimethylphenol. Monomer concentration 2.10^{-1} mol/l, CuCl concentration 10^{-2} mol/l, amine concentration 3.10^{-2} mol/l

Monomer	Polymer number	Solvent	Catalyst	Polycondensation temperature (°C)	Polycondensation time (h)	Yield (%)	Viscosity (dl/g)
2-methylphenol	1	Nitrobenzene	CuCl/2,6-dimethylpyridine	30	40	70	0.06
2-methylphenol	2	Nitrobenzene	CuCl/2,6-dimethylpyridine	60	15	75	Partly soluble
2-methylphenol	3	<i>o</i> -Dichlorobenzene	CuCl/2,6-dimethylpyridine	35	24	70	0.07
2-methylphenol	4	Nitrobenzene	CuCl/2,4-dimethylpyridine	50	60	80	Partly soluble
2-methylphenol	5	Nitrobenzene	CuCl/2,3-dimethylpyridine	65	16	80	Partly soluble
phenol	6	Nitrobenzene	CuCl/2,6-dimethylpyridine	90	14	95	Insoluble
phenol	7	Nitrobenzene	CuCl/quinoline	90	24	55	Insoluble
phenol	8	<i>o</i> -Dichlorobenzene	CuCl/2,6-dimethylpyridine	85	24	25	Insoluble
<i>p</i> -bromophenol	9	1,4-Dimethoxybenzene	CuCl/pyridine	200	3	35	Soluble in boiling nitrobenzene
2,5-dimethylphenol	10	Nitrobenzene	CuCl/2,6-dimethylpyridine	40	25	45	Partly soluble
2,5-dimethylphenol	11	Nitrobenzene	CuCl/2,3-dimethylpyridine	55	19	90	Partly soluble
2,5-dimethylphenol	12	<i>c</i> -dichlorobenzene	CuCl/2,6-dimethylpyridine	40	24	87	Partly soluble

of high molecular polymers from 2-methylphenol in the presence of various catalytic complexes: *o*-substituted pyridine-CuCl⁴, pyridine-CuCl in conjunction with platinum on activated carbon and acetonitrile as a solvent⁵ and FeCl₃·6H₂O in a nitrogen atmosphere⁶. Synthesis of poly(2,5-dimethyl-phenylene oxide) has also been described⁷.

Linear poly(1,4-phenylene oxide) can be prepared from *p*-bromophenol under Ullmann condensation conditions⁸. Sample 9 of poly(1,4-phenylene oxide) was synthesized from *p*-bromophenol according to the procedure described in this paper⁸.

Results of oxidative polycondensations of 2-methylphenol, 2,5-dimethylphenol and phenol catalysed by complexes of CuCl-dimethylpyridines are recorded in Table 1. Viscosity measurements, i.r., n.m.r. and elemental analysis show that there is no effect of catalytic complex used in this work on the structure of obtained species. I.r. spectra of samples 1–5 were very similar. In all samples, strong absorption in the range of 860–910 cm⁻¹, indicating 1,2,4-substitution, was observed. Weak absorption in the range of 770–800 cm⁻¹ indicates the presence of 1,2,3-substituted rings, though the lack of absorption in the range of 840–850 cm⁻¹ excludes the formation of tetra-substituted branching sites in the polymer chain. N.m.r. spectra contain two multiplets: in the aromatic range the following peaks could be detected: 7.0 ppm (integration 32.3%), 6.71 ppm (100%), 5.86 ppm (2%), 5.76 ppm (2.8%), in aliphatic range: 2.17 ppm (84.9%), 1.97 ppm (57%). Overall integration ratio $S_{aromatic}/S_{aliphatic} = 1.04$.

I.r. spectra of samples 6–8 exhibit strong absorption at 800–860 cm⁻¹ (1,4-substitution) and at 700–780 cm⁻¹ (1,2-substitution). Weak absorption bands at 1960 cm⁻¹ and 1890 cm⁻¹ also confirm 1,2-substitution. Absorption bands at 970 cm⁻¹ and 1025 cm⁻¹ indicate 1,2,4-substitution and the strong absorption band 1190 cm⁻¹ is characteristic for aromatic ether linkage. It follows from the above that polymers obtained in oxidative polycondensation of phenol are not linear.

I.r. spectra of samples 10–12 exhibit a weak absorption band at 1900–1930 cm⁻¹ (ring substitution 1,2,3,4), absorption bands at 805, 875 and 1720 cm⁻¹ (substitution 1,2,4,5) indicating the presence of nonlinear structure. N.m.r. spectra of these samples contain two unresolved peaks: 6.62 ppm corresponding to aromatic protons and 2.17 ppm corresponding to methyl group protons.

Elemental analysis for C, H, O showed that the oxygen content in all samples obtained in oxidative condensations is increased by 1–5% compared to that calculated.

Pyrolysis products

Poly(2-methylphenylene oxide) (PMPO). 50 mg polymer samples from polycondensations 1–5 were pyrolyzed in a vacuum tube with a heating rate of 10°C/min in the temperature range 25–500°C. The mixture of the degradation products was transferred to the mass spectrometer in a methylene chloride solution and mass spectra were recorded in temperature range 25–200°C. Figure 1 shows an averaged mass spectrum. The peaks in each series correspond to molecular ions formed by random scission of rearranged chain. Oligomers in dimeric, trimeric etc. triads are shifted by 14 mass units i.e. differing by a methyl group (Table 2, columns 1–3). Simultaneously, scission of the ether bonds takes place yielding oligomers differing by a hydroxyl group i.e. shifted by 16 mass units. (Table 2, columns 4–6.) The spectra of the mixture of silylated degradation products reveal that oligomers resulting from random scission of benzyl bonds are partially rearranged. For example a triad of trimers M⁺ 306, 320, 334 yields the following triads of silylated derivatives: M⁺ 378, 392, 406 for unrearranged trimers, M⁺ 450, 464, 478 for once rearranged trimers and M⁺ 522, 536, 550 for twice rearranged trimers. Some monomeric, dimeric and trimeric compounds drawn in Table 2 can be identified on the chromatograms of degradation products and silylated degradation products which were the same for all polymer samples 1–5 (Figure 2 (a) and (b)). Table 3 shows the mass spectral analysis of separate compounds.

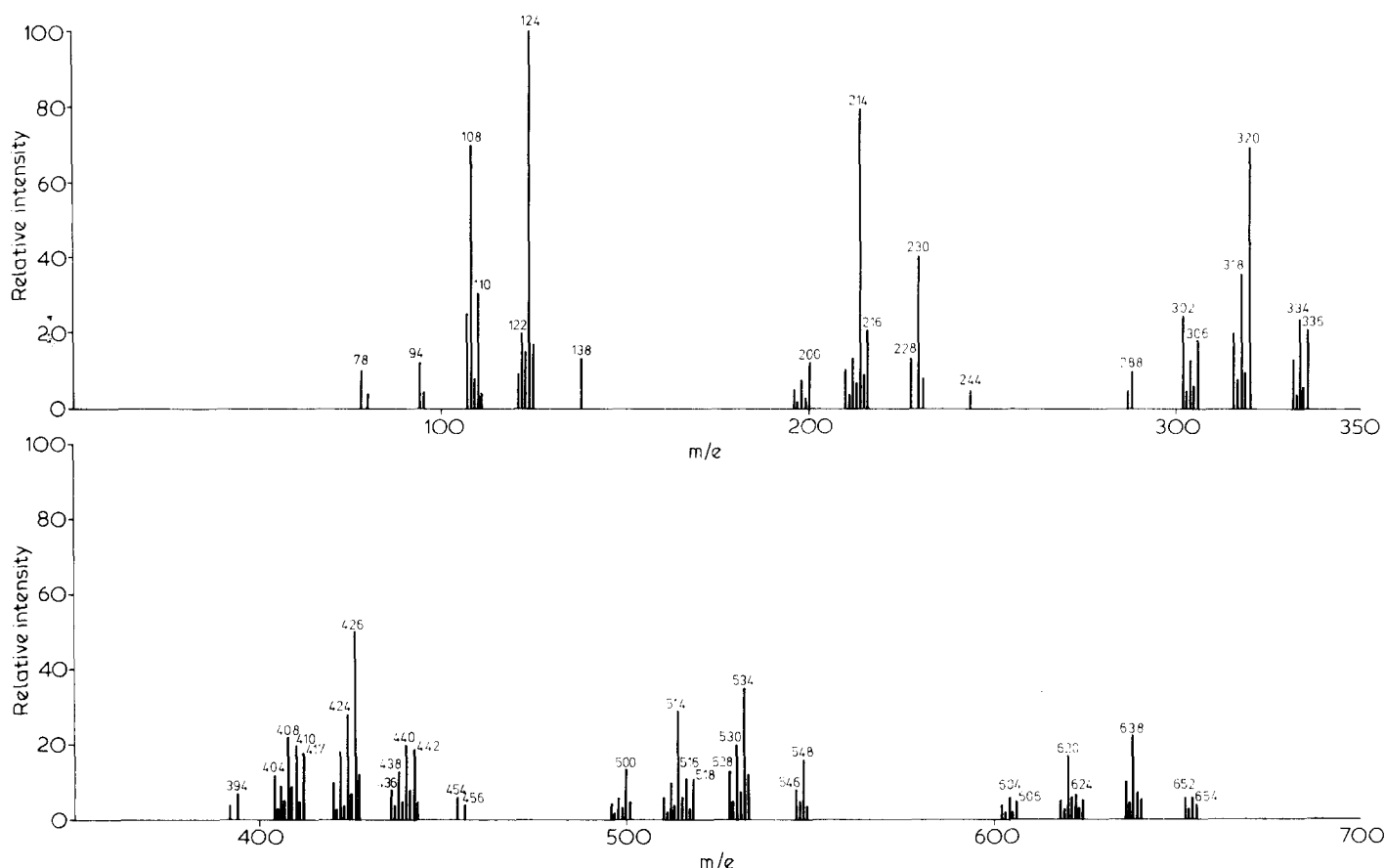
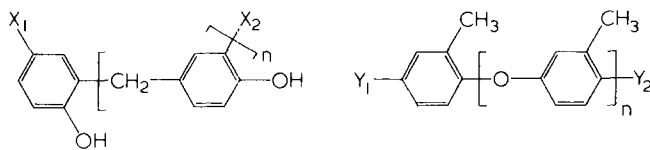


Figure 1 The mass spectrum of degradation products of poly(2-methylphenylene oxide)

Table 2 Rearranged and unrearranged products of poly(2-methylphenylene oxide) degradation



		M ⁺					
		1	2	3	4	5	6
<i>n</i>	X ₁ =H X ₂ =H	X ₁ =CH ₃ (H) X ₂ =H(CH ₃)	X ₁ =CH ₃ X ₂ =CH ₃	Y ₁ =H Y ₂ =H	Y ₁ =H(OH) Y ₂ =OH(H)	Y ₁ =OH Y ₂ =OH	
0		94	108	122	92	108	124
1		200	214	228	198	214	230
2		306	320	334	304	320	336
3		412	426	440	410	426	442
4		518	532	546	516	532	548
5		624	638	652	622	638	654

The analysis is based on the conclusions from our previous paper². Monomeric phenols were identified directly, using appropriate model compounds. Characteristic fragmentation of rearranged dimers, which were recognized by adding two silyl groups, was assumed to consist of α - or β -benzyl bond scission and *ortho* hydrogen transfer (Table 3, compounds 13, 14), while fragmentation of unrearranged dimers consists of ether or β -benzyl link cleavage, or *ortho* methyl or hydroxyl hydrogen transfer if rearrangement takes place on electron impact (Table 3, compounds 9, 12, 19). *Ortho* hydrogen transfer effect disappears in the case of double

silylated rearranged dimers and only odd mass fragmentation ions from α - and β -benzyl bond cleavage appear in the spectra (Table 3, compounds 12, 14, 15). On the other hand, silylated unrearranged dimers or trimers form even mass ions due to the presence of *ortho* methyl groups (Table 3, compounds 10, 17).

Poly(2,5-dimethylphenylene oxide) (P25DMPO). The averaged spectrum of P25DMPO degradation products was obtained in the same conditions as in the case of PMPO (Figure 3). Some low molecular degradation products were separated and identified by means of g.c.-m.s. (Figure 2c). In comparison with the poly(2,6-dimethyl-1,4-phenylene oxide) spectrum additional strong triads of peaks are observed.

These are 110, 124, 138 for monomeric products; 230, 244, 258 for dimeric products etc. Their appearance can be attributed to monomers containing two hydroxyl groups, dimers containing these hydroxyl groups etc. The presence of methyl groups in the 2,5 positions permits such a rearrangement of the polymer chain that two hydroxyl monomers can be obtained, as is shown below:

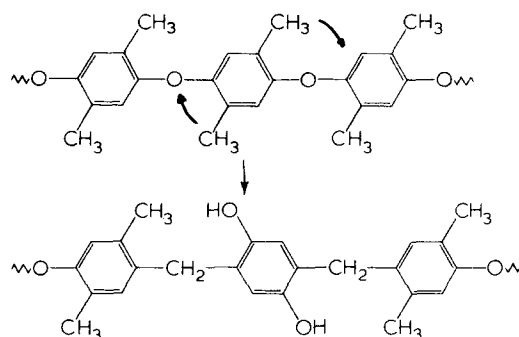


Table 3 Mass spectral analysis of poly(2-methylphenylene oxide) degradation products

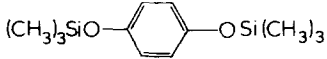
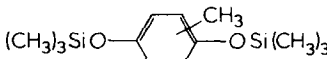
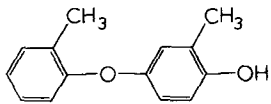
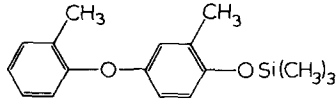
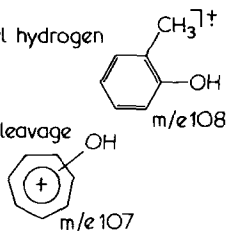
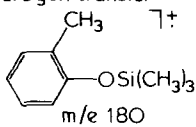
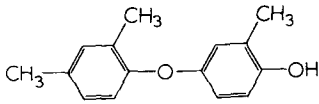
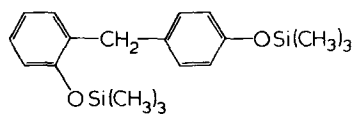
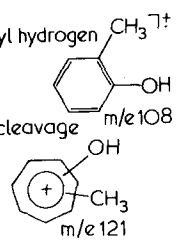
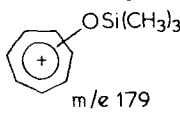
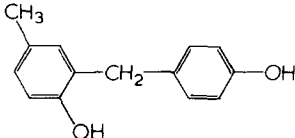
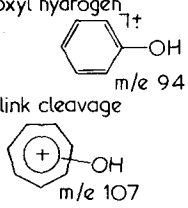
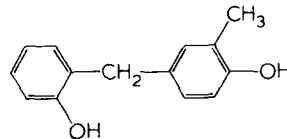
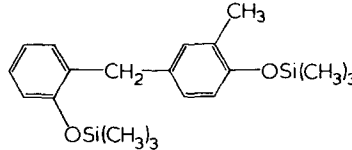
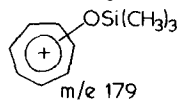
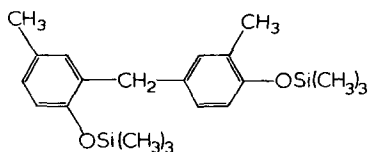
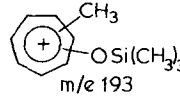
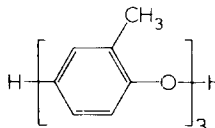
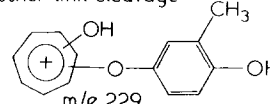
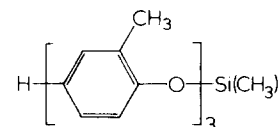
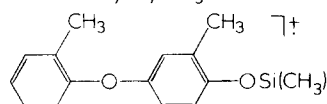
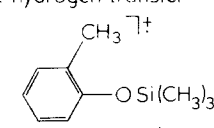
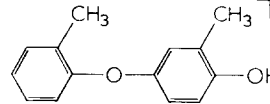
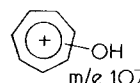
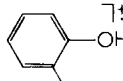
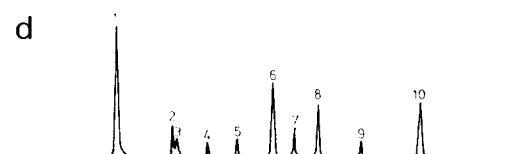
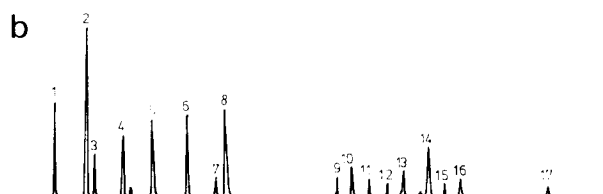
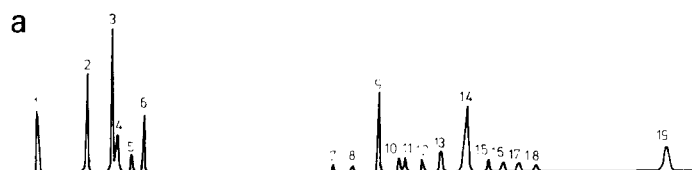
Degradation products			Silylated degradation products		
Peak number	Compound	Characteristic fragmentation	Peak number	Compound	Characteristic fragmentation
1	<i>p</i> -Xylene	—	—	—	—
2	Phenol	—	1	Silylphenol	—
3	2-Methylphenol	—	2	2-Methylsilylphenol	—
4	4-Methylphenol	—	3	4-Methylsilylphenol	—
5	Dimethylphenol	—	—	—	—
6	2,4-Dimethylphenol	—	4	2,4-Dimethylsilylphenol	—
7	Unidentified	—	5		$M^+ 254$
8			6		$M^+ 268$
9		$M^+ 214$ ortho methyl hydrogen transfer ether link cleavage	10		$M^+ 286$ ortho methyl hydrogen transfer
					
10	Unidentified	—	11	Unidentified	$M^+ 330$
11					
12		$M^+ 228$ ortho methyl hydrogen transfer ether link cleavage	12		$M^+ 344$ β - or α - cleavage
					
13		$M^+ 214$ ortho hydroxyl hydrogen transfer α - benzyl link cleavage	13	Unidentified	—
					
14		$M^+ 214$ ortho hydroxyl hydrogen transfer- m/e 108 β - benzyl link cleavage m/e 107 α - benzyl link cleavage m/e 121	14		$M^+ 358$ β - cleavage
					
15	Unidentified	—	15		$M^+ 372$ α - or β -cleavage
18					
			16	Unidentified	$M^+ 432$ Silylated dimer of <i>mw</i> 216/3 hydroxyl groups

Table 3 Mass spectral analysis of poly(2-methylphenylene oxide) degradation products

Degradation products			Silylated degradation products		
Peak number	Compound	Characteristic fragmentation	Peak number	Compound	Characteristic fragmentation
19		M^+ 320 ether link cleavage  m/e 229	17		M^+ 392 ortho methyl hydrogen transfer  m/e 286 $\downarrow -CH_3$ m/e 271 ortho methyl hydrogen transfer  m/e 130 $\downarrow -CH_3$ m/e 165
		ortho methyl hydrogen transfer  m/e 214 ether link cleavage  m/e 107 ortho methyl hydrogen transfer  m/e 108			



Poly(1,4-phenylene oxide) (PPO). The PPO samples were degraded in the temperature range 25–600°C (10°C/min) and mass spectra registered in the temperature range 25–220°C. Figure 4 shows the averaged spectrum of degradation products of sample 9 obtained in the Ullmann polycondensation process. The appearance of triads of molecular ions is the result of statistical scission of ether bonds. The oligomers in each triad differ by 16 mass units i.e. by hydroxyl group. The products corresponding to main molecular ions are collected in columns 1–3 of Table 4.

The products of molecular ions 2, 4, 6 mass units smaller than the mass of principle oligomer are probably formed by cyclization to benzofurane systems. Benzofurane dimers were identified by means of g.c.–m.s. (Figure 2d, compounds 5, 7). Oligomers corresponding to bromine substituted

Figure 2 Gas chromatograms of degradation products and silylated degradation products. (a) poly(2-methylphenylene oxide). (b) poly(2-methylphenylene oxide): silylated products. (c) poly(2,5-dimethylphenylene oxide): (1) 1,2,4-trimethylbenzene; (2) unidentified; (3) 1,2,4,5-tetramethylbenzene; (4) 2,5-dimethylphenol; (5) 3,4-dimethylphenol; (6) 2,4,5-trimethylphenol; (7) dihydroxymethylbenzene; (8) dihydroxydimethyl benzene; (9) unidentified; (10) dimer m.w. 254; (11) dimer m.w. 242; (12) dimer m.w. 242; (13) dimer m.w. 240; (14) dimer m.w. 256; (15) dimer m.w. 254; (16) dimer m.w. 242; (17) unidentified; (18) dimer m.w. 256. (d) poly(1,4-phenylene oxide), sample 9: (1) phenol; (2) hydroquinone; (3) *p*-bromophenol; (4) biphenyl ether [mass spectrum (10)]; (5) dibenzofurane [mass spectrum (11)]; (6) *p* phenoxyphenol [mass spectrum identical with a synthesized model]; (7) 2-hydroxybenzofuran [mass spectrum (11)]; (8) *p*-(*p*-hydroxyphenoxy) phenol; (9) *p*-phenoxy(biphenyl ether); (10) *p*-phenoxy phenol.

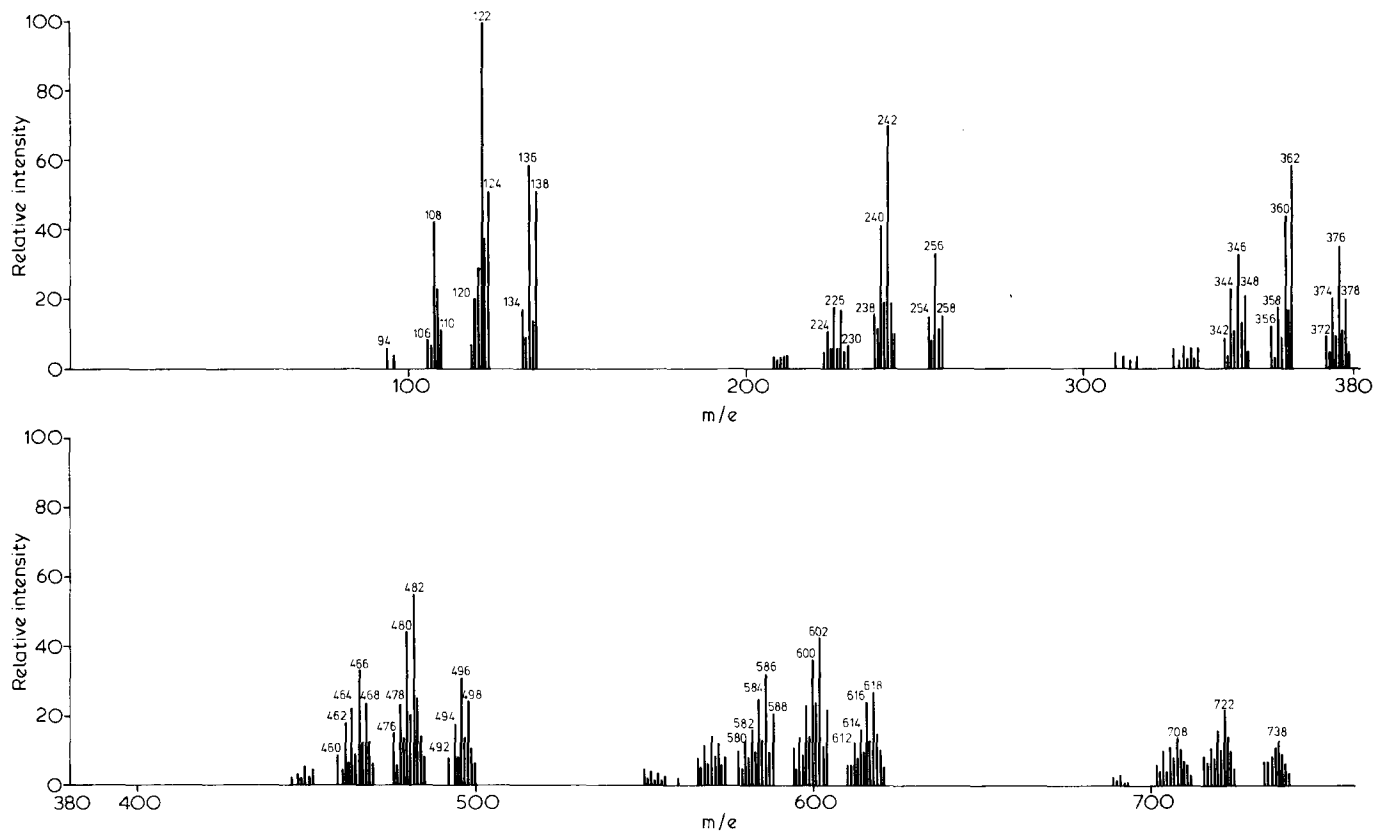


Figure 3 The mass spectrum of poly(2,5-dimethylphenylene oxide) degradation products

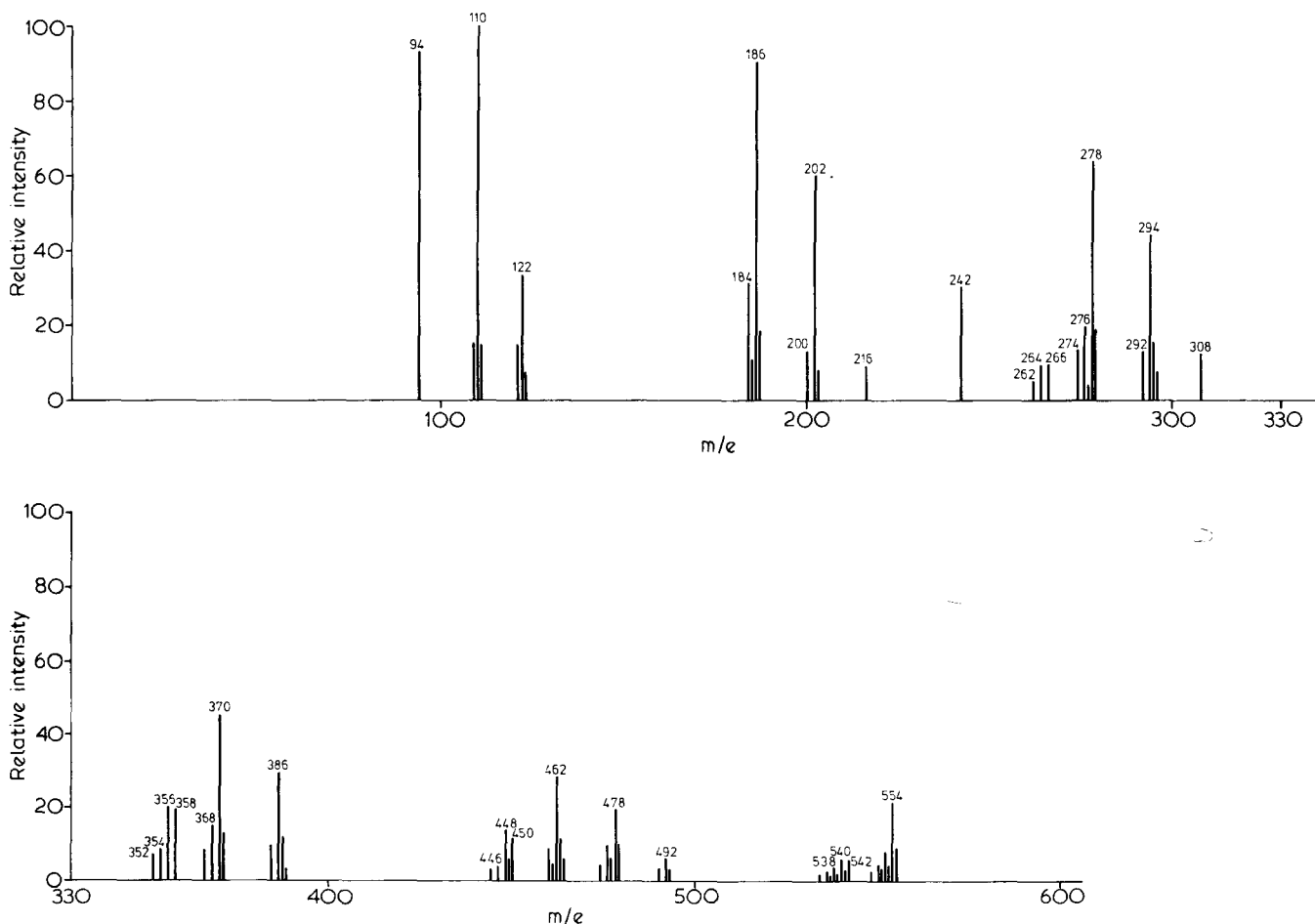
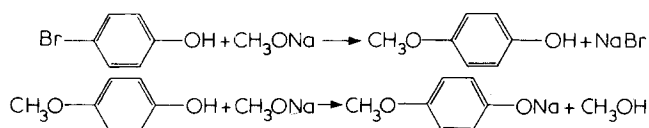


Figure 4 The mass spectrum of degradation products of poly(1,4-phenylene oxide)

Table 4 Products of Ullman poly(1,4-phenylene oxide) degradation

	M^+						
	1	2	3	4	5	6	7
	$X_1=H$ $X_2=H$	$X_1=H$ $X_2=OH$	$X_1=OH$ $X_2=OH$	$X_1=Br$ $X_2=H$	$X_1=Br$ $X_2=OH$	$X_1=H$ $X_2=OCH_3$	$X_1=OH$ $X_2=OCH_3$
$n=0$	78	94	110	156, 158	172, 174	108	124
$n=1$	170	186	202	248, 250	264, 266	200	216
$n=2$	262	278	294	340, 342	356, 358	292	308
$n=3$	354	370	386	432, 434	448, 450	384	400
$n=4$	446	462	478	524, 526	540, 542	476	492
$n=5$	538	554	570	—	—	—	—

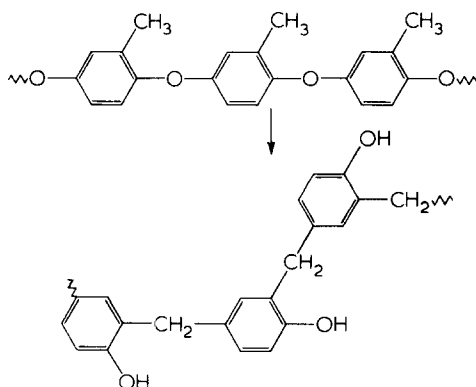
polymer ends which appear in mass spectrum are shown in columns 4, 5 of Table 4. One of them was directly identified in gas chromatogram of degradation products (Figure 2, compound 3). Each bromine derivative yields two molecular ions due to the presence of two bromine isotopes ^{79}Br and ^{81}Br . Methoxy group ended oligomers are also observed (Table 4, columns 6, 7). Polymer chains ending with $-\text{OCH}_3$ are probably formed in a side reaction during Ullmann polycondensation.



p-Methoxyphenolate can further condense with *p*-bromophenolate yielding a polyether chain, though the reaction of *p*-bromophenol with sodium methoxide moderates the growth of polymer chain. The mass spectra of degradation products of samples 6–8 are similar to those obtained for sample 9. They do not contain the peaks corresponding to Br and $-\text{OCH}_3$ substituted fragments.

Degradation mechanism

As in the case of poly(2,6-dimethyl-1,4-phenylene oxide) the presence of a methyl group brings about the Fries-type rearrangement in the first degradation step:

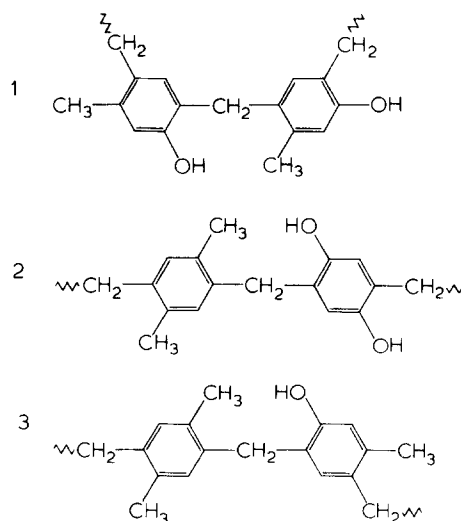


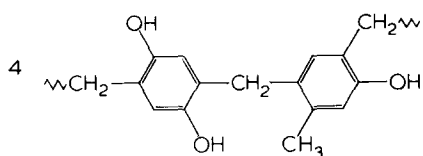
This process is followed by random scission of C–C bonds yielding as the main degradation products rearranged oligomeric phenols. All four theoretically possible monomeric phenols were identified (Table 3, compounds 2, 3, 4, 6) and

chromatogram a). Four rearranged dimers were identified either as phenols (Table 3, compounds 13, 14) or as their silyl derivatives (Table 3, compounds 12, 14, 15). The formation of unrearranged oligomers can be explained by assuming the scission of a partially rearranged polymer chain. Of four expected unrearranged dimers two were identified (Table 3, compounds 9, 12).

As was proposed in our previous paper¹, elementary scission reactions lead to the formation of two polymer ends – one reduced, yielding after further scissions mainly oligomeric phenols, the second oxidized, which is the source of oligomeric compounds with *para* or *ortho* quinomethyl system of bonds.

These products possess the molecular mass smaller by 2 and 4 mass units than the molecular mass of the principal phenolic oligomer. Molecular ions of these compounds appear in the mass spectra of the degradation products (Figure 1). Formation of compounds 5, 6, 7, 8, 16 (Figure 2b) and those drawn in Table 2 suggests the contribution of random scission of unrearranged ether bonds to the mechanism of degradation. Another possible explanation of their presence is that irregularities of polymer structure can cause the production of compounds which could not be derived from the proposed degradation scheme. There are, in fact, some unidentified peaks in the chromatograms which possibly correspond to irregular portions of polymer chain. In the case of poly(2,5-dimethylphenylene oxide) the rearrangement brings about four sequences of two monomer units:





That yields so complex a mixture of degradation products that they can not be separated by means of simple chromatographic columns.

Poly(1,4-phenylene oxide) obtained in Ullman polycondensation is more stable than oxidative polycondensation products. The data presented above indicate that this polymer undergoes direct scission of ether bonds. It has also been proved that a simultaneous process of cyclization takes place.

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