addition was complete, the mixture was refluxed for 2 h, cooled and poured into water and worked up as described above. Fractionation yielded 0.73 g (14 %) of 2,3,5-trimethylthiophene, b.p. 60–65°C/14 mmHg, identified by combined VPC-mass spectrometry and 2.26 g (42 %) of the title compound, b.p. 89–90°C/14 mmHg, m.p. 34–35°C. IR: C≡C 2220 cm^{-1}, C=C 1590 cm^{-1}. NMR (CCl_4): τ_{C-CH_3}=8.02 ppm, τ_{S-CH_3}=7.72 ppm, τ_{CH}=4.75 ppm. [Found: M.wt. 126; C 66.62; H 8.05; S 25.08. Calc. for $C_7H_{10}S$ (126): C 66.61; H 7.99; S 25.40].

2,5-Dimethyl-3-thiophenecarboxylic acid. Ethereal methyllithium (50 ml, 0.7 N) was added drop-wise under nitrogen with stirring to a solution of 5.00 g (0.0210 mole) of 2,5-dimethyl-3-iodothiophene in 40 ml of anhydrous ether cooled to −70°C. The mixture was allowed to stand at −70°C for 6 h and was then carbonated. The usual work-up yielded 2.51 g (76 %) of 2,5-dimethyl-3-thiophenecarboxylic acid, m.p. 117–118°C. Literature value,[5] m.p. 119–120°C.

The neutral phase contained 0.35 g of a mixture of 2,5-dimethylthiophene and 2,5-dimethyl-3-iodothiophene but no ring-opened product.

NMR spectra were recorded with a Varian A60 or a Varian HR-100 NMR spectrometer. Mass spectra were obtained with an LKB A 900 combined gas chromatograph mass-spectrometer. IR spectra were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer. Gas chromatographic analysis was carried out with a Perkin-Elmer model 900 gas chromatograph using an NPGS (5 %) column.

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Pyrolysis Products of Poly(2,6-dimethoxy-1,4-phenylene ether)

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Direct GLC analysis of the products of pyrolysis of methoxy-substituted polyphenylene oxides detects only partly demethylated fragments. To achieve a more complete analysis, we have studied by combined gas chromatography and mass spectrometry acetylated products of pyrolysis of poly(2,6-dimethoxy-1,4-phenylene ether) (PPOO). In addition, the oligomers formed were fractionated by gel permeation chromatography and their molecular weight distribution was investigated by vapour pressure osmometry (VPO).

Experimental. About 300 mg of PPOO (M_n=8000), synthetized as described in Ref. 2, was pyrolyzed at 500°C for 25 min in a nitrogen atmosphere as reported earlier.[1] The volatile reaction products were collected in a receiver held in a salt-ice bath. The pyrolysis residue was eluted with chloroform and the resulting solution was evaporated to dryness. The combined fractions were acetylated with a pyridine-acetic anhydride mixture for 6 h at 60–70°C.

The acetylated fractions were dissolved in chloroform and a sample of the solution was analyzed at 70 eV on a Perkin-Elmer Model 270 GC-DF mass spectrometer combined with a Model 900 gas chromatograph. A 3 % SE-30 column (length 1.5 m. diameter 6 mm) was used. The fractions were identified by comparing their mass spectra and retention times with those of model compounds.

Another sample of the mentioned solution was fractionated on a Sephadex LH-20 column using chloroform as eluent and the fractions were analyzed by UV spectroscopy at 260 and 270 nm. The column was calibrated with polystyrene standards. In addition molecular weights of representative oligomeric fractions of the pyrolyzed PPOO were investigated by VPO using a Hitachi-Perkin Elmer Model 115 instrument and chloroform as solvent.[3]

Non-aromatic degradation products were not analyzed.

Results. The principal results of the MS analysis are collected in Table 1 and those of the GPC analysis in Table 2.

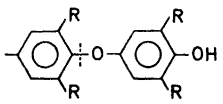
Table 1. Mass spectra and percentages of the most abundant acetylated pyrolysis products. Intense peaks are in italics.

Acetylated compound	Abundance %	Molecular weight	Mass numbers (*m/e*)
Hydroquinone	6	110	194—152—*110*—43
2,6-Dimethoxyphenol	19	154	196—*154*—139—124—110—93—83—65
3,5-Dimethoxyphenol?	17	154	196—*154*—125—94—69
4-Hydroxy-6-methoxyphenol	24	140	224—182—168—*140*—125—110—97
4-Hydroxy-2-methoxy-6-methylphenol	10	154	238—224—196—182—154—*140*—126
2,4-Dihydroxyphenol	4	126	252—210—168—*126*
4-Hydroxy-2,6-dimethoxyphenol	15	170	254—212—170—*156*—155—126—69
Mixture of dimers	< 5		290—272—257—191—177—148—134 119—109—95—81—*69*

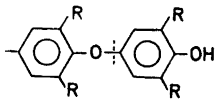
Table 2. Abundances of monomers and oligomers with M_n <4000 as analyzed by GPC and VPO.

Molecular weight range	Abundance, %
4000—1000	10
1000— 400	25
400— 150	65
Total	100

From the data obtained it can be seen that more than 40—50 % of the pyrolysis products are trimers or larger fragments and carbon. However, the results depend greatly on the molecular weight of the polymer and also on the reaction conditions. Comparison of these results with the results for non-acetylated fragments [1] reveals that the chief reaction in addition to demethylation is chain scission which can take place either at the bond



or the bond



In addition, some indications of methyl group migration and radical reactions can be noted.

The mass spectra may be compared with the spectra obtained by Kovàčik *et al.*[4] for phenolic lignin models and seem to be explicable in terms of similar degradation schemes.

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