

CHROMSYMP. 1436

## HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF OXIDATION PRODUCTS OF 2,6-DIMETHYLPHENOL

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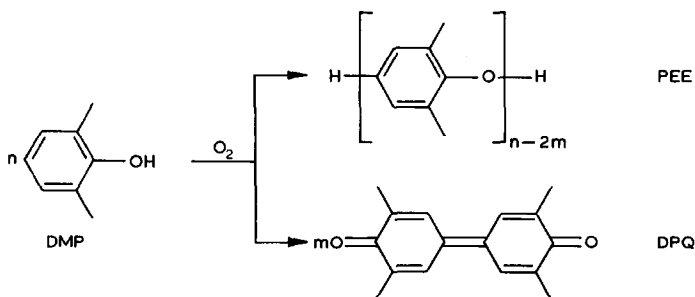
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### SUMMARY

The oligomers of poly(2,6-dimethyl-1,4-phenylene oxide) ( $M < 1000$ ) have been separated by gradient elution. Poly(2,6-dimethyl-1,4-phenylene oxide) is prepared by oxidative coupling of 2,6-dimethylphenol. At low conversions the concentrations of the oligomers from  $n = 2$  to  $n = 10$  follow the normal distribution of Schulz and Flory. A linear extrapolation of these values ( $n = 2-10$ ) yields a value for the monomer ( $n = 1$ ), which amounts only to 1/20 of the experimental value. By a side reaction, 3,3',5,5'-tetramethyl-4,4'-diphenyl-1,4-dione (DPQ) is formed. From the chromatograms recorded simultaneously at different wavelengths, DPQ can be determined together with the oligomers during a single HPLC experiment. Experimental results confirming the principle of "equal reactivity" (Flory) for oligomers ( $n < 10$ ) are presented.

### INTRODUCTION

Polyphenylene ether (PPE) is a hard, tough material with exceptional properties<sup>1</sup>. Blends of PPE with high impact polystyrene are outstanding, combining excellent mechanical properties with good flame retardancy<sup>2</sup>. High-molecular-weight PPE is prepared by allowing 2,6-dimethylphenol (DMP) to react with oxygen in the presence of a catalyst (a cupric amine complex).



3,3',5,5'-Tetramethyl-4,4'-diphenyl-1,4-dione (DPQ)<sup>3</sup> is a by-product, which cannot be avoided. Hitherto the oligomeric reaction products have been investigated by gas chromatography as trimethylsilyl ethers<sup>4</sup> or by gel permeation chromatography

(GPC)<sup>5</sup>. In this work a simple high-performance liquid chromatographic (HPLC) method is described, which allows a separation of the monomer and of the reaction products directly without any derivatization.

## MATERIALS AND METHODS

### *Oxidation of 2,6-dimethylphenol*

For the oxidative coupling of DMP the recipe reported by Brandt<sup>1</sup> was used. The reactor contained all of the monomer at the beginning of the oxidation (batch operation). The catalyst mixture, (a suspension of 0.36 g copper(I) bromide in 19.5 g dibutylamine and 13 g toluene), was added to a solution of 116 g 2,6-dimethylphenol in 374 g toluene. With vigorous agitation, air was passed into the solution at room temperature. (The use of air instead of pure oxygen reduced the reaction rate. Thus it was possible to withdraw samples having different degrees of conversion during a single experiment).

### *Analytical procedure*

The oxidation reaction was stopped by adding a small sample of the reactor solution (2 ml) to an excess of methanol (10 ml) acidified with concentrated aqueous hydrochloric acid (0.5 ml). At low conversions, an homogenous mixture was obtained, which was washed with water after diluting it in chloroform (20 ml). The chloroform solution was injected immediately into the chromatograph.

A HP 1090 liquid chromatograph (Hewlett-Packard, Analytical Division, Waldbronn, F.R.G.) equipped with an autosampler and diode-array detector HP 1040 was used. The eluents were delivered by two dual syringe metering pumps, operating at low pressure (around 3 bar).

### *Chromatographic conditions*

Columns were from E. Merck (Darmstadt, F.R.G.) and were 250 mm × 4 mm. The stationary phase was LiChrosorb Si 60 (5 μm) (Merck) at an oven temperature of 40°C.

Gradient elution (0 to 95% B, 30 min) was used, with eluent A (73% dichloromethane + 27% cyclohexane), eluent B (99.2% dichloromethane + 0.8% tetrahydrofuran) and a flow-rate of 1 ml/min. The detection system was operated simultaneously at two wavelengths (277 and 420 nm). The data were evaluated by an analytical work station HP 79994 A (Hewlett-Packard).

## RESULTS

Figs. 1 and 2 show chromatograms after 3 h of air oxidation. At 277 nm the monomer (DMP) peak appears after 5.8 min. Between 7 and 12 min, the oligomers  $n=2$  to  $n=10$  are separated. The polymer (PPE) appears after about 20 min (not shown). The by-product, diphenoquinone (DPQ) is eluted later (after 26 min). Optimum detection of DPQ is obtained at 420 nm. The oligomer distribution in Fig. 1 is close to equilibrium; the DMP content of the undiluted reactor sample shows little change (−5%) after standing overnight under nitrogen.

A single HPLC experiment is sufficient to determine the starting material, the oligomeric intermediates and the by-product.

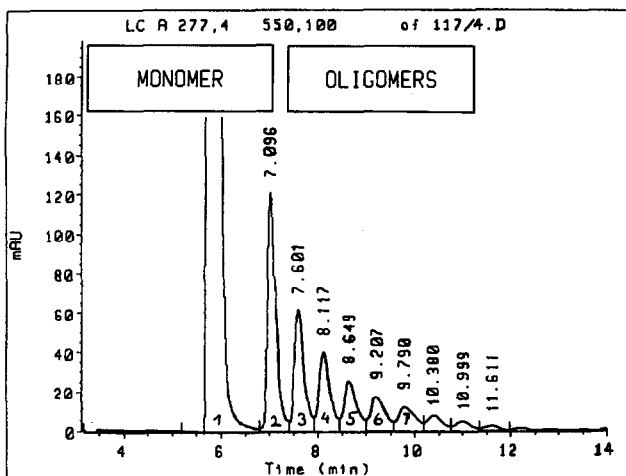


Fig. 1. HPLC separation of the reaction products after oxidation of dimethylphenol (DMP), detected at 277 nm.

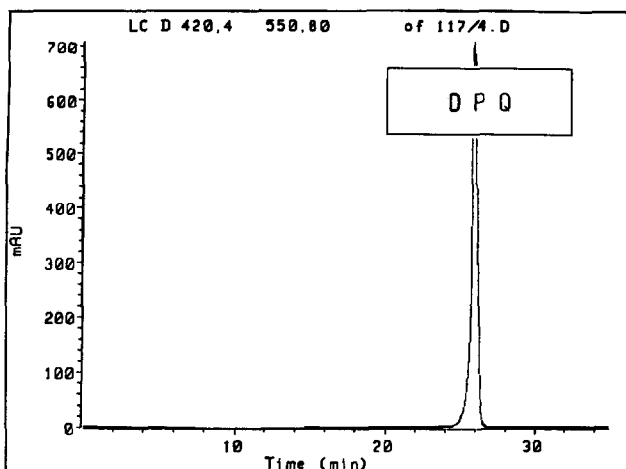


Fig. 2. HPLC separation of the reaction products after oxidation of dimethylphenol, detected at 420 nm; otherwise as in Fig. 1.

## DISCUSSION

The oxidative coupling of DMP is reported to proceed in a manner analogous to a linear polycondensation<sup>6</sup>. Formally the coupling reaction can be treated as a polycondensation with elimination of hydrogen, the quinone ketal equilibration resulting in a redistribution reaction<sup>4,7</sup>. For a linear polycondensation a normal distribution of molecular weights as postulated by Schulz<sup>8</sup> and Flory<sup>9</sup> is expected.

For a normal distribution a linear plot of  $\log(c_n/n)$  vs.  $n$  can be deduced ( $c_n$  = concentration by weight of the species with degree of polymerization (P)

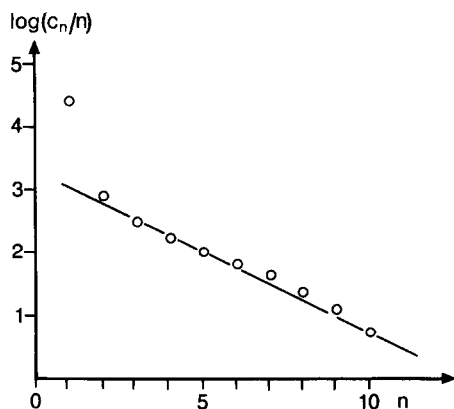


Fig. 3. Molar concentrations ( $c_n/n$ ) of the oligomers (logarithmic plot). From the principle of equal reactivity, a linear plot is expected.

=  $n$ ).  $c_n$  is proportional to  $a_n$  ( $a_n$  = HPLC peak area of the  $n$ th peak). When  $\log(a_n/n)$  is plotted vs.  $n$ , the molar concentrations of the oligomers from  $n = 2$  to  $n = 10$  follow the normal distribution of Schulz and Flory. A linear extrapolation of these values yields a value for the monomer ( $n = 1$ ) which amounts to only 1/20 of the experimental value (Fig. 3).

Flory<sup>10</sup> formulated a "principle of equal reactivity" for the functional groups of long chain molecules. Our chromatographic results confirm this principle for the oligomers in the range between  $n = 2$  and  $n = 10$ . The reactivity is different for the first step in the oxidative coupling of DMP. Heitz<sup>11</sup> proposed a single electron process (SET)<sup>12</sup> in the growth reaction of PPE to explain the deviation of the concentration of DMP determined by his measurements (GPC)<sup>5</sup> at low conversion.

Apart from liquid chromatography, PPE oligomers have been investigated by gas chromatography after fractional distillation of derivatives<sup>6</sup> or by less specific methods such as thin-layer chromatography<sup>13</sup>.

HPLC offers a rapid and specific method of separation for PPE oligomers. Equal reactivity is a fundamental principle of macromolecular chemistry. Its validity may be extended down to small molecules ( $M > 200$ ) by our HPLC results.

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