

## Novel preparation of poly(oxy-1,2-phenylene-oxymethylene)

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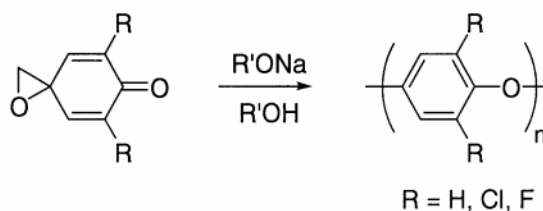
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### Summary

7-Iodo-1-oxaspiro[2.5]octa-5,7-dien-4-one undergoes melt polymerization to yield poly(oxy-4-iodo-1,2-phenylene-oxymethylene). The polymerization involved a nucleophilic attack of the terminal hydroxy group of the growing polymer chain at the methylene carbon in oxirane followed by cleavage of the oxirane ring and simultaneous aromatization of cyclohexadienone to generate a new phenol to continue the polymerization.

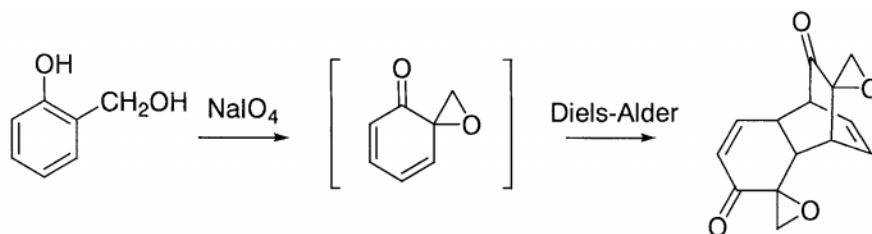
### Introduction

Poly(2,6-dimethyl-1,4-phenylene oxide) has developed into important commercial engineering thermoplastics (1). Recently, we found a novel synthetic method for 2,6-disubstituted poly(1,4-phenylene oxide)s using oxaspiro compounds as starting materials (Scheme 1) (2-4).



**Scheme 1.** Preparation of poly(1,4-phenylene oxide)s using oxaspiro compounds

In these oxaspiro compounds an oxirane ring is connected to 2,5-cyclohexadienone. We were interested in the polymerization of 1-oxaspiro[2.5]octa-5,7-dien-4-one in which oxirane is connected to 2,4-cyclohexadienone moiety. However, 1-oxaspiro[2.5]octa-5,7-dien-4-one is reported to undergo a Diels-Alder reaction to give a dimer at room temperature (5).



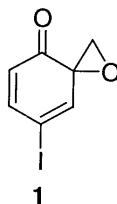
**Scheme 2.** Diels-Alder dimerization of 1-oxaspiro[2.5]octa-5,7-dien-4-one

Introducing bulky substituents onto the cyclohexadienone moiety can prevent this

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Diels-Alder dimerization (6). We report here the polymerization of 7-iodo-1-oxaspiro[2.5]octa-5,7-dien-4-one (**1**).



## Experimental

### Material

The monomer, 7-iodo-1-oxaspiro[2.5]octa-5,7-dien-4-one (**1**), was prepared according to the literature (6). It was purified by recrystallization from hexane.

### Solution polymerization

A given amount of **1** was dissolved in 2-methoxyethanol and the resulting solution was thermostated at constant temperature under nitrogen. Into the solution was added a potassium 4-methoxyphenoxide solution prepared by dissolving given amounts of potassium *tert*-butoxide and 4-methoxyphenol in 2-methoxyethanol, and the reaction mixture was stirred for the time of polymerization. The reaction mixture was poured into excess methanol.

### Melt polymerization

A given amount of **1** and initiator was mixed well and the mixture was heated under nitrogen at 120 °C for the time of polymerization. The reaction mixture was poured into excess methanol, and the deposited polymeric material was repeatedly washed with methanol.

### Model reaction of **1** with 4-methoxyphenol (**3**) in a molten state

A mixture of **1** (100 mg, 0.4 mmol) and **3** (50 mg, 0.4 mmol) was heated at 75 °C for 20 min under nitrogen. The reaction mixture was dissolved in a small amount of dichloromethane and separated by preparative thin layer chromatography (Merck 105717) using dichloromethane as an eluent to obtain 40 mg of 4-iodo-2-[(4-methoxyphenoxy)methoxy]phenol (**4**) and 15 mg of 5-iodosalicylaldehyde (**5**).

**4**: IR (KBr) 3316, 2882, 1249, 1203, 1179, 971 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.49 (s, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.71 (d, *J* = 8.6 Hz, 1H), 5.65 (s, 2H), 3.78 (s, 3H). Anal. Calcd for C<sub>14</sub>H<sub>13</sub>IO<sub>4</sub>: C, 45.18; H, 3.52. Found: C, 45.32; H, 3.36.

## Results and discussion

Table 1 summarizes the polymerization of oxaspiro compound **1**. In contrast to the polymerization of substituted 1-oxaspiro[2.5]octa-4,7-dien-6-ones (**3**), solution polymerizations using potassium 4-methoxyphenoxide as an initiator gave poor results (run 1,2). No polymeric material was obtained when the reaction mixture was poured into methanol. On the other hand, bulk polymerization was effective. Melt polymerization was observed on heating above the melting point (103 °C) of **1** in the

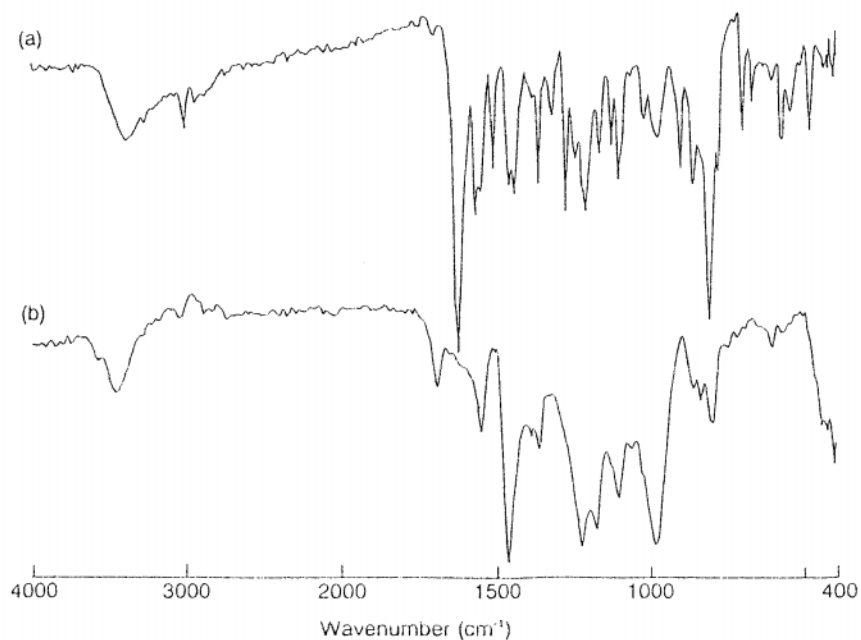
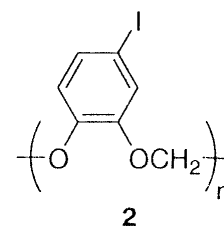
presence of a catalytic amount (5 mol%) of a nucleophilic initiator such as cesium fluoride or potassium 4-methoxyphenoxide (run 3,4). Polymerization occurred even in the absence of initiator (run 5). The obtained polymer was not soluble in methanol or hexane but was soluble in THF and dimethyl sulfoxide (DMSO) at room temperature.

**Table 1.** Polymerization of 7-iodo-1-oxaspiro[2.5]octa-5,7-dien-4-one (**1**)

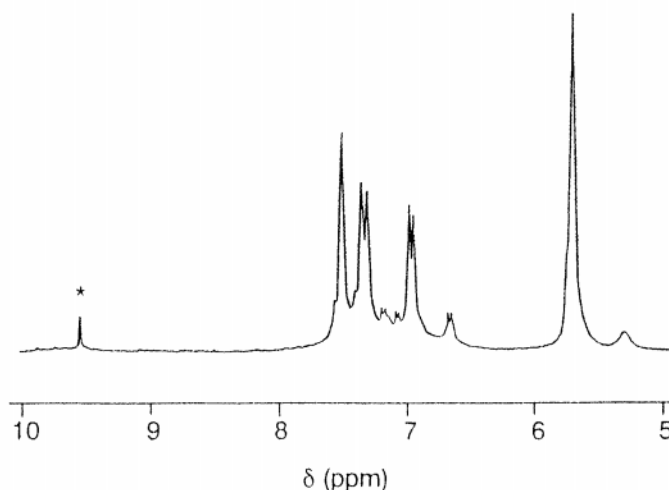
run	initiator <sup>a</sup>	solvent	temp., °C	time, h	yield <sup>b</sup> , %	$M_n$ (pSt) <sup>c</sup>
1	4-MeOC <sub>6</sub> H <sub>4</sub> OK	MeO(CH <sub>2</sub> ) <sub>2</sub> OH	20	20	-	-
2	4-MeOC <sub>6</sub> H <sub>4</sub> OK	MeO(CH <sub>2</sub> ) <sub>2</sub> OH	60	24	-	-
3	CsF	none	120	0.5	84	4100
4	4-MeOC <sub>6</sub> H <sub>4</sub> OK	none	120	0.5	76	4000
5	none	none	120	0.5	74	4000

<sup>a</sup> [1]/[initiator] = 20. <sup>b</sup> Methanol insoluble part. <sup>c</sup> Determined by GPC.

The structure of the polymer was investigated with IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. The IR spectrum of the obtained product exhibited no peak at 1634 or 3002 cm<sup>-1</sup> nor at 1279, 904 or 810 cm<sup>-1</sup>, assignable to a carbonyl or oxirane moiety, respectively (Figure 1). The <sup>1</sup>H NMR spectrum exhibited three peaks in aromatic region and a singlet peak at 5.7 ppm which is assignable to oxymethylene protons (Figure 2). The <sup>13</sup>C NMR exhibited seven peaks at 147.6, 146.7, 132.2, 126.2, 119.8, 92.0, and 86.1. ppm. These experimental results indicated that the obtained polymer is poly(oxy-4-iodo-1,2-phenylene-oxymethylene) (**2**). Elemental analysis was in good agreement with the calculated values for polymer **2** (Anal. Calcd for C<sub>7</sub>H<sub>5</sub>IO<sub>2</sub>: C, 33.90; H, 2.03. Found: C, 33.64; H, 2.17.).

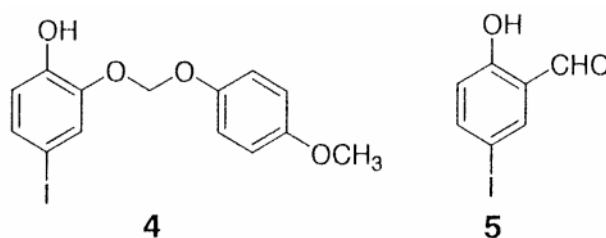


**Figure 1.** IR spectra of (a) **1** and (b) the polymer obtained from run 3 (Table 1).

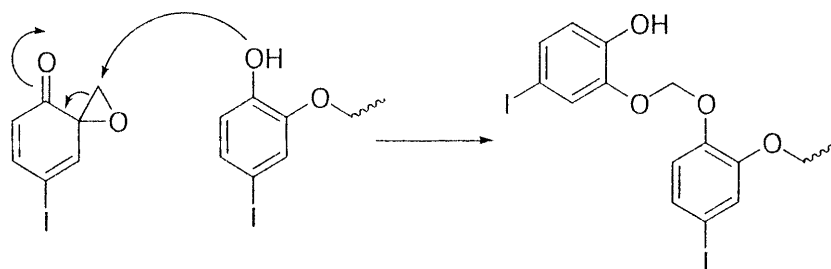


**Figure 2.**  $^1\text{H}$  NMR spectrum of the polymer obtained from run 3 (Table 1) in  $\text{DMSO-}d_6$ .

In order to clarify the polymerization mechanism, an equimolar reaction of **1** and 4-methoxyphenol (**3**) was carried out at  $75\text{ }^\circ\text{C}$  in the molten state for 20 min. The reaction products were separated by preparative thin layer chromatography to obtain 1:1 adduct **4** in 25% yield along with **5** and oligomeric products.



These experimental results indicated that the polymerization mechanism includes a nucleophilic attack of the terminal hydroxy group of the growing polymer molecule at the methylene carbon in the oxirane ring of **1**, followed by cleavage of oxirane and simultaneous aromatization of cyclohexadienone to generate a new phenol to continue the polymerization as shown in Scheme 3.



**Scheme 3.** Plausible polymerization mechanism

The fact that the aldehyde **5** was detected in the thermal reaction between **1** and **3** indicated the presence of thermal isomerization of **1** to **5**. The aldehyde **5** carrying phenolic hydroxy group may be the actual initiator. The IR spectrum of polymer **2** exhibited an absorption peak at  $1699\text{ cm}^{-1}$  probably due to 2-formyl-4-iodophenoxy group as an initiator fragment (Figure 1). Furthermore, NMR signal at 9.5 ppm is assignable to aldehyde protons as seen in Figure 2 (marked with \*).

In conclusion, we have demonstrated a novel preparation of a poly(oxy-1,2-phenylene-oxymethylene)-based polymer formally representing an alternating copolymer of 1,2-phenylene oxide and formaldehyde.

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