Polymerization of 1-Oxaspiro[2.5]octa-4,7-dien-6-ones

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ABSTRACT: The polymerization of six spiro compounds such as 1-oxaspiro[2.5]octa-4,7-dien-6-one (**OSODO**), spiro[anthrone-10,2′-oxirane] (**SAO**), and 5,7-dibromo- (**Br_2-OSODO**), 5,7-di-*tert*-butyl- (**tBu_2-OSODO**), 5,7-difluoro- (**F_2-OSODO**), and 4,5,7,8-tetrachloro-1-oxaspiro[2.5]octa-4,7-dien-6-ones (**Cl_4-OSODO**) were examined. Spiro compounds which carry substituents at the 4 and 8 positions or bulky substituents at the 5 and 7 positions such as **SAO**, **tBu_2-OSODO**, and **Cl_4-OSODO** were reluctant to undergo polymerization. **Br_2-OSODO** gave a polymeric material in very low yield. **OSODO** and **F_2-OSODO** polymerized to give poly(1,4-phenylene oxide) and poly(2,6-difluoro-1,4-phenylene oxide), respectively. The polymerizability of these spiro compounds was explained by the steric effect of the substituents.

Introduction

Poly(phenylene oxide)s are of great interest for high performance polymers. The most investigated poly(phenylene oxide) is poly(2,6-dimethyl-1,4-phenylene oxide) whose blend with polystyrene has found a variety of commercial applications.[1] Other substituted poly(phenylene oxide)s including halogenated poly(phenylene oxide)s have the potential for materials with outstanding mechanical, chemical, and thermal properties.[2] Poly(2,6-dichloro-1,4-phenylene oxide) (**Cl_2-PPO**) has been prepared by several methods such as a free-radical-initiated decomposition of sodium 2,6-dichloro-4-bromophenolate with benzoyl peroxide,[3] a polymerization of 2,6-dichlorophenol by use of a cupric chloride−sodium methoxide system,[4] a thermal decomposition of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(I),[5] and an electrooxidative polymerization of 2,6-dichlorophenol.[6]

Recently, we found a novel preparation method for **Cl_2-PPO**. 5,7-Dichloro-1-oxaspiro[2.5]octa-4,7-dien-6-one (**Cl_2-OSODO**) was heated in 2-methoxyethanol in the presence of sodium 2-methoxyethoxide to give **Cl_2-PPO** via the elimination of formaldehyde (Scheme 1).[7]

Our idea was to extend this polymerization method to the syntheses of various substituted poly(phenylene oxide)s. In this work we report the polymerization of a series of spiro compounds such as 1-oxaspiro[2.5]octa-4,7-dien-6-one (**OSODO**), spiro[anthrone-10,2′-oxirane] (**SAO**), and 5,7-dibromo- (**Br_2-OSODO**), 5,7-di-*tert*-butyl- (**tBu_2-OSODO**), 5,7-difluoro- (**F_2-OSODO**), and 4,5,7,8-tetrachloro-1-oxaspiro[2.5]octa-4,7-dien-6-ones (**Cl_4-OSODO**).

Experimental Section

Instrumentation. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL EX-270 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G2500H and G2000H columns using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively.

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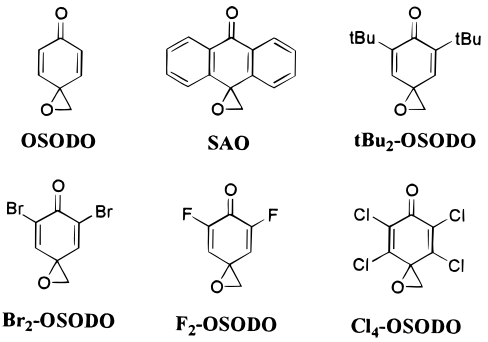
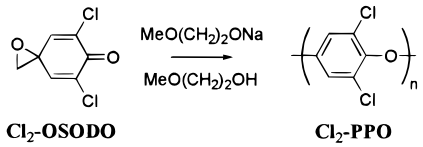
Chart 1



Scheme 1



1-Oxaspiro[2.5]octa-4,7-dien-6-one (OSODO). OSODO was prepared according to the literature.[8] It was purified by sublimation before polymerization: mp 49 °C (lit.[8] 51−52 °C); ^{1}H NMR ($CDCl_3$, δ) 6.51 (s, 4H), 3.35 (s, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1630, ν_{C-O} 1194.

Spiro[anthrone-10, 2′-oxirane] (SAO). Into the mixture of anthraquinone (3.3 g, 16 mmol) and sodium hydride (0.88 g, 22 mmol) in 100 mL of DMSO was added trimethylsulfonium iodide (4.5 g, 22 mmol) in 50 mL of DMSO dropwise at room temperature under nitrogen. The reaction mixture was poured into ice-cold water and extracted with dichloromethane. The organic extract was dried with anhydrous magnesium sulfate and placed under reduced pressure to remove the solvent. The residue was recrystallized from hexane to give **SAO** (1.0 g, 32%) as yellow needles: mp 117 °C; ^{1}H NMR ($CDCl_3$, δ) 8.31 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 6.8 Hz, 2H), 7.52 (t, J = 6.8 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 3.38 (s, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1628, ν_{C-O} 1291. Anal. Calcd for $C_{15}H_{10}O_2$: C, 81.07; H, 4.54. Found: C, 81.32; H, 4.67.

5,7-Dibromo-1-oxaspiro[2.5]octa-4,7-dien-6-one (Br_2-OSODO). The mixture of 2,6-dibromophenol (3.8 g, 15 mmol), 5 mL of 20% potassium hydroxide solution, and 2.5 mL of 37% formaldehyde solution was stirred at 50 °C for 24 h. It was

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poured into hydrochloric acid solution and extracted with ether. The organic extract was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was recrystallized from carbon tetrachloride to give 3,5-dibromo-4-hydroxybenzyl alcohol as colorless needles (2.5 g, 59%): mp 116−117 °C; ^{1}H NMR (DMSO-d_6, δ) 9.77 (brs, 1H), 7.45 (s, 2H), 5.3 (brs, 1H), 4.37 (d, J = 4.6 Hz, 2H); IR (KBr, cm^{-1}) ν_{O-H} 3294, ν_{C-Br} 550. Anal. Calcd for $C_7H_6Br_2O_2$: C, 29.82; H, 2.15; Br, 56.68. Found: C, 29.97; H, 2.01; Br, 57.02.

The mixture of 3,5-dibromo-4-hydroxybenzyl alcohol (5.8 g, 21 mmol), sodium bismuthate (11.7 g, 42 mmol), acetic acid (160 mL), and water (40 mL) was stirred at room temperature for 1 h and filtered. The filtrate was poured into water and extracted with dichloromethane. The extract was washed with sodium hydrogen carbonate solution, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was recrystallized from isopropyl ether to give **Br$_2$-OSODO** as pale yellow needles (2.1 g, 37%): mp 113 °C; ^{1}H NMR ($CDCl_3$, δ) 6.99 (s, 2H), 3.44 (s, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1634, ν_{C-O} 1004. Anal. Calcd for $C_7H_4Br_2O_2$: C, 30.04; H, 1.44; Br, 57.09. Found: C, 29.87; H, 1.67; Br, 57.25.

5,7-Di-*tert*-butyl-1-oxaspiro[2.5]octa-4,7-dien-6-one (tBu$_2$-OSODO). Into the mixture of 2,6-di-*tert*-butyl-1,4-benzoquinone (1.0 g, 4.5 mmol) and sodium hydride (0.25 g, 6.4 mmol) in 16 mL of DMSO was added trimethylsulfonium iodide (1.3 g, 6.4 mmol) in 8 mL of DMSO dropwise at room temperature under nitrogen. The reaction mixture was poured into ice-cold water and extracted with dichloromethane. The organic extract was dried with anhydrous magnesium sulfate and placed under reduced pressure to give **tBu$_2$-OSODO** (0.74 g, 70%) as pale yellow plates: mp 98 °C; ^{1}H NMR ($CDCl_3$, δ) 6.17 (s, 2H), 3.29 (s, 2H), 1.24 (s, 18H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1602, ν_{C-O} 1231. Anal. Calcd for $C_{15}H_{10}O_2$: C, 76.88; H, 9.46. Found: C, 77.10; H, 9.56.

5,7-Difluoro-1-oxaspiro[2.5]octa-4,7-dien-6-one (F$_2$-OSODO). The mixture of 2,6-difluorophenol (5.0 g, 38 mmol), 12 mL of 20% potassium hydroxide solution, and 6 mL of 37% formaldehyde solution was stirred at 50 °C for 20 h. It was poured into hydrochloric acid solution and extracted with ether. The organic extract was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using chloroform as an eluent. After the first band was collected to remove the unreacted 2,6-difluorophenol, the eluent was changed to isopropyl ether and the second band was collected to give 3,5-difluoro-4-hydroxybenzyl alcohol as colorless plates: mp 80 °C; ^{1}H NMR (DMSO-d_6, δ) 9.95 (brs, 1H), 6.95 (d, J = 9.2 Hz, 2H), 5.3 (brs, 1H), 4.39 (s, 2H); IR (KBr, cm^{-1}) ν_{O-H} 3374, ν_{C-F} 1312. Anal. Calcd for $C_7H_6F_2O_2$: C, 52.51; H, 3.78. Found: C, 52.40; H, 3.55.

The mixture of 3,5-difluoro-4-hydroxybenzyl alcohol (1.6 g, 10 mmol), sodium bismuthate (5.6 g, 20 mmol), acetic acid (80 mL), and water (20 mL) was stirred at room temperature for 1 h and filtered. The filtrate was poured into water and extracted with dichloromethane. The extract was washed with sodium hydrogen carbonate solution, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using dichloromethane as an eluent. The first band was collected and recrystallized from isopropyl ether to give **F$_2$-OSODO** (0.65 g, 41%) as pale yellow plates: mp 71 °C; ^{1}H NMR ($CDCl_3$, δ) 6.17 (d, J = 5.4 Hz, 2H), 3.42 (s, 2H); IR (KBr, cm^{-1}) $\nu_{C=O}$ 1653, ν_{C-O} 999. Anal. Calcd for $C_7H_4F_2O_2$: C, 53.18; H, 2.55. Found: C, 53.03; H, 2.69.

4,5,7,8-Tetrachloro-1-oxaspiro[2.5]octa-4,7-dien-6-one (Cl$_4$-OSODO). Cl$_4$-OSODO was prepared according to the literature.[9] It was purified by recrystallization from hexane: mp 165 °C (lit.[9] 165−166 °C); ^{13}C NMR ($CDCl_3$, δ) 169.81, 146.29, 133.94, 56.96, 55.15; IR (KBr, cm^{-1}) $\nu_{C=O}$ 1642, ν_{C-O} 1104, ν_{C-Cl} 722.

Polymerization. A given amount of spiro compound was dissolved in a suitable solvent and the resulting solution was thermostated at constant temperature under nitrogen. Into the solution was added a sodium alkoxide solution prepared by dissolving a given amount of sodium in ethanol or 2-methoxyethanol, and the reaction mixture was stirred for the time of polymerization. The reaction mixture was poured into excess methanol, and the deposited polymeric material was repeatedly washed with methanol. When the polymeric product was not deposited, the methanol solution was concentrated to ca. 20 mL. It was poured into hydrochloric acid solution and extracted with dichloromethane. The organic extract was placed under reduced pressure to remove the solvent, and the residue was subject to IR and NMR analyses.

Scheme 2

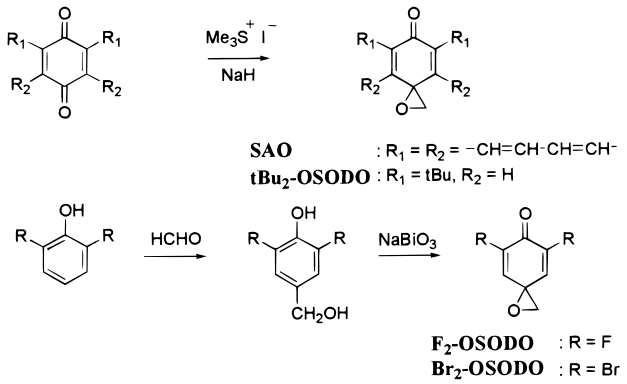


Table 1. Polymerization of OSODO

run	initiator[a]	solvent	temp, °C	time, h	yield, %	M_n(pSt)[b]
1	EtONa	THF	50	24	0	
2	EtONa	DMF	50	24	0	
3	EtONa	dioxane	50	24	0	
4	EtONa	EtOH	50	10	31	2400
5	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	50	24	88	3500

[a] [**OSODO**]/[initiator] = 50. [b] Determined by GPC.

Results and Discussion

Preparation of Spiro Compounds. Four novel spiro compounds were prepared according to Scheme 2. **SAO** and **tBu$_2$-OSODO** were prepared by the methylene transfer reaction with dimethylsulfonium methylide using anthraquinone and 2,6-di-*tert*-butyl-1,4-benzoquinone as a starting quinone compound, respectively. **Br$_2$-OSODO** and **F$_2$-OSODO** were prepared in two steps using 2,6-dibromophenol and 2,6-difluorophenol, respectively, as a starting material. The phenols were reacted with formaldehyde, followed by oxidation with sodium bismuthate.

Polymerization. Table 1 summarizes the polymerization results of **OSODO**. Unreacted spiro compounds were recovered in runs 1−3. The polymeric materials were obtained when protic solvents were employed (runs 4 and 5). In these cases the reaction mixture became heterogeneous during the reaction due to the precipitation of polymeric materials. The polymers obtained were not soluble in methanol, hexane, or benzene but were partially soluble in acetone, THF, and DMSO. The ^{1}H NMR spectrum of the DMSO soluble part exhibited a broad peak at 7.6−6.8 ppm assigned to aromatic protons and a small peak at 4.6 ppm assigned to terminal phenolic protons. Its IR spectrum was compared with that of authentic poly(1,4-phenylene oxide) (**PPO**) which was prepared by the thermal disproportionation reaction of 4,4′-dihydroxydiphenyl ether according to the literature.[10] Figure 1 shows the IR spectrum of the product obtained in run 4 together with that of **PPO**. Both spectra were quite similar. The elemental analysis of the product was in good agreement

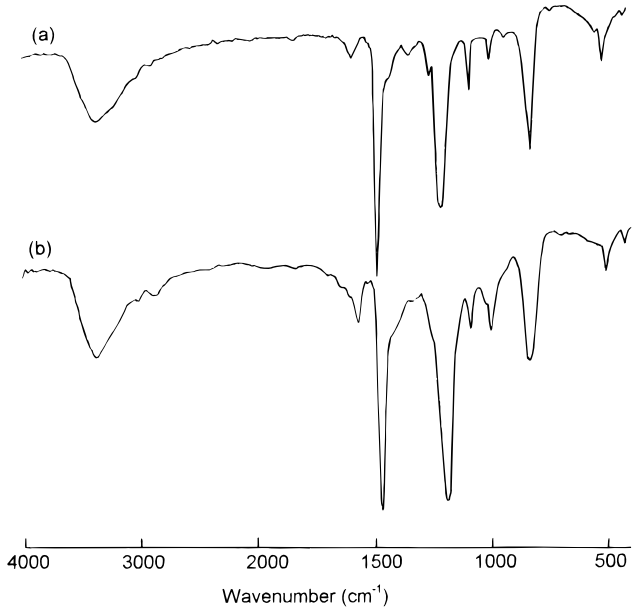
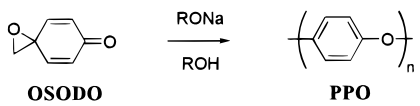


Figure 1. IR spectra of (a) the product obtained from run 5 (Table 1) and (b) **PPO** prepared by the thermal disproportionation of 4,4′-dihydroxydiphenyl ether.

Scheme 3



with the calculated value for **PPO** (Anal. Calcd for $(C_6H_4O)_n$: C, 78.25; H, 4.38. Found: C, 78.58; H, 4.11). It was concluded that **OSODO** gave **PPO** on heating in alcoholic solution in the presence of alkoxide (Scheme 3).

We examined the polymerization of substituted **OSODO**s. Table 2 summarizes the polymerization results of **SAO**, **Br_2-OSODO**, **F_2-OSODO**, **tBu_2-OSODO**, and **Cl_4-OSODO** together with that of **Cl_2-OSODO**. In the case of **SAO**, **tBu_2-OSODO**, and **Cl_4-OSODO**, no polymeric product was obtained. Only unreacted spiro compound was recovered (runs 1, 2, 5, 6, 9, and 10). **Br_2-OSODO** gave a trace amount of polymeric material whose molecular weight was 1400−1900 on polystyrene

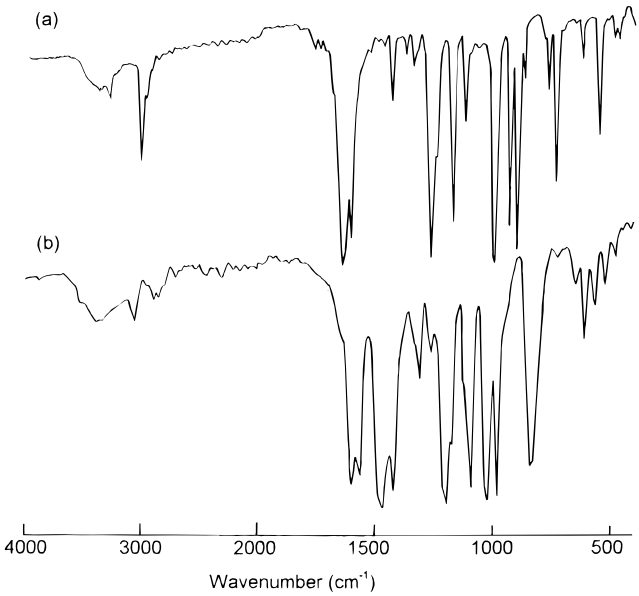


Figure 2. IR spectra of (a) **F_2-OSODO** and (b) the product obtained from run 7 (Table 2).

standards (runs 3 and 4). However, this polymer was not characterized further due to the very low yield. **F_2-OSODO** gave a polymeric product (runs 7 and 8). As the reaction proceeded, the initially homogeneous solution gradually became heterogeneous with a white precipitation of the product. Figure 2 shows IR spectra of the product and **F_2-OSODO**. The IR spectrum of the product exhibited no peak at 1654 cm^{-1} or at 3024, 1180, 998, or 737 cm^{-1}, assignable to a carbonyl or epoxy moiety, respectively, but a new peak at 1092 cm^{-1} assignable to an ether bond was observed. Its ^1H NMR spectrum is shown in Figure 3. Although there are small unknown peaks around 3−4.5 ppm, it exhibited mainly a doublet peak at 6.92 ppm (J = 10.8 Hz). The small broad peak at 8.7 ppm can be assigned to the terminal phenolic protons. Its ^{13}C NMR exhibited four absorptions at 102.3 (d, J = 27 Hz), 127.9 (s), 158.0 (s), and 158.2 ppm (d, J = 250 Hz). The elemental analysis of the product was in good agreement with poly(2,6-difluoro-1,4-phenylene oxide) (**F_2-PPO**) (Anal. Calcd for $(C_6H_2F_2O)_n$: C, 56.27; H, 1.57. Found: C, 56.79; H,

Table 2. Polymerization of SAO, Br_2-OSODO, tBu_2-Osodo, F_2-OSODO, Cl_4-OSODO, and Cl_2-OSODO

run	initiator[a]	solvent	temp, °C	time, h	yield, %	M_n(pSt)[b]	$\overline{DP}$
			SAO				
1	EtONa	EtOH	50	24	0		
2	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	120	24	0		
			Br_2-OSODO				
3	EtONa	EtOH	40	24	trace	1900	8
4	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	80	24	trace	1400	6
			tBu_2-OSODO				
5	EtONa	EtOH	50	5	0	0	
6	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	80	10	0	0	
			F_2-OSODO				
7	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	40	24	76	5600	44
8	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	80	24	68	4800	38
			Cl_4-OSODO				
9	EtONa	EtOH	50	24	0		
10	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	100	24	0		
			Cl_2-OSODO				
11	EtONa	EtOH	60	12	14	3400	21
12	$MeO(CH_2)_2ONa$	$MeO(CH_2)_2OH$	80	24	56	4200	26

[a] [spiro compound]/[initiator] = 30. [b] Determined by GPC.

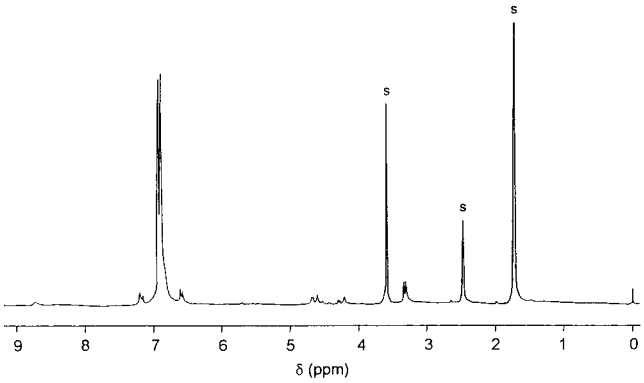
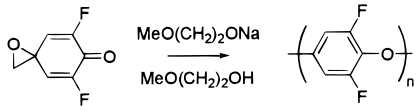


Figure 3. 270-MHz ^{1}H NMR spectrum of the product obtained from run 7 (Table 2) in THF-d_8. The signals marked with s are assigned to the solvents.

Scheme 4



F_2-OSODO **F_2-PPO**

Table 3. Solubilities[a] of PPO, F_2-PPO, and Cl_2-PPO

	solvent				
polymer	benzene	2-methoxyethanol	$CHCl_3$	DMSO	THF
PPO	−	−	−	±	±
F_2-PPO	−	−	−	±	+
Cl_2-PPO	−	+	+	+	+

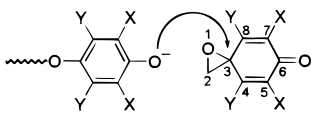
[a] Key: +, soluble; ±, partially soluble; −, insoluble.

1.66.) Thus, **F_2-OSODO** was found to polymerize to give **F_2-PPO** (Scheme 4).

The solubilities of **PPO**, **Cl_2-PPO**, and **F_2-PPO** were summarized in Table 3. The solubility decreases in the sequence **Cl_2-PPO**, **F_2-PPO**, and **PPO**, indicating that poly(phenylene oxide) having a larger substituent exhibited higher solubility.

Polymerizability. As can be seen from the yield data in Table 2, the following order of polymerization reactivity can be drawn in a series of 5,7-disubstituted **OSODO**: **tBu_2-OSODO** < **Br_2-OSODO** ≪ **Cl_2-OSODO** < **F_2-OSODO**. The degree of polymerization of **F_2-PPO** was about twice that of **Cl_2-PPO** despite the premature precipitation of **F_2-PPO**. In the case of **SAO** and **Cl_4-OSODO**, which carry substituents at the 4 and 8 positions of **OSODO**, a polymerization reaction did not occur at all. We ascribe the differences in reactivities to the steric effect of the substituents. The polymerization formally involves the binding between phenoxy anion and the spiro carbon on the six-membered ring. This reaction step is conceivable to be seriously influenced by the steric hindrance effect between the substituents of the spiro compounds as shown in Scheme 5. In fact, the reaction of sodium phenoxide with equivalent of **SAO** or **Cl_4-OSODO** was carried out in 2-methoxyethanol at 60 °C only to recover the starting materials quantitatively, indicating that the substituents at the 4 and 8 positions hinder the reactivity of the spiro compounds. The low polymerizability of **tBu_2-OSODO** can be explained by the generation of a hindered phenoxy anion which no longer binds with the spiro carbon. **Br_2-OSODO** barely gave a polymeric material. **Cl_2-OSODO** and **F_2-OSODO**, carrying relatively small substituents, can undergo polymerization. Apart from the steric effects mentioned, inductive effects may play a role. Strong electron-accepting substituents decrease the reactivity of the terminal phenoxy anion. On the other hand, such substituents can compensate for the reactivity of the spiro carbon since they make the spiro carbon electron-deficient. The large difference between **Cl_2-OSODO** and **Br_2-OSODO** in polymerizability is hard to explain by only the difference of the electron-withdrawing natures of the halogens. It was concluded that the polymerizability of compounds based on 1-oxaspiro[2.5]octa-4,7-dien-6-one depends on mainly the steric hindrance effect of the substituents. Unsubstituted **OSODO** was expected to be the most reactive in view of the steric effect. However, the low solubility of the resulting **PPO** may be responsible for the rather modest molecular weight. Finally, we successfully prepared a novel substituted poly(phenylene oxide), **F_2-PPO**, using **F_2-OSODO** as a starting material. Further studies on the polymerization mechanism are now underway.

Scheme 5



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