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A Novel Living Polymerization of 5,7-Dichloro-1-oxaspiro[2.5]octa-4,7-dien-6-one

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ABSTRACT: The polymerization of 5,7-dichloro-1-oxaspiro[2.5]octa-4,7-dien-6-one (Cl_2-OSODO) was carried out in 2-methoxyethanol using potassium 4-methoxyphenoxide as an initiator. The molecular weights of the polymers increased linearly with conversion. Monomer incremental addition and end-capping experiments exhibited the living characters of this polymerization. From kinetic studies of model reactions, a combination of fast initiation and slow propagation rates in this polymerization system was confirmed.

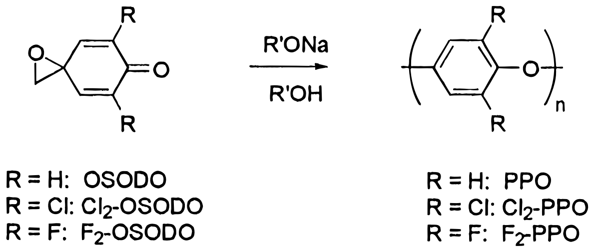
Introduction

Living polymerization is a chain growth polymerization where termination or chain transfer reaction is absent. The degree of polymerization is proportional to monomer conversion and the resultant polymer has narrow molecular weight distribution. The living polymerization technique can provide various tailor-made polymers including monodisperse polymers, block copolymers, and macromonomers. Thus, a discovery of a novel living polymerization is of great importance from the viewpoint of developing a new material.

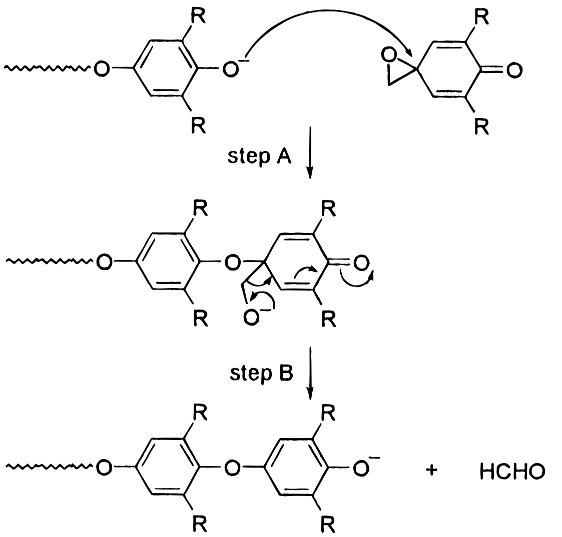
In the previous papers, we reported a novel synthetic method for 2,6-disubstituted poly(1,4-phenylene oxide)s using oxaspiro compounds as starting materials (Scheme 1).[1,2] Our proposed polymerization mechanism is shown in Scheme 2. The propagation reaction consists of two reaction steps. The first one is the binding of the phenoxy anion with the spiro carbon of the oxaspiro compound (step A). The second one is the retro aldol reaction accompanying an elimination of formaldehyde to generate a new phenoxy anion (step B). The first reaction (step A) is conceivable to be rate-determining because the latter reaction (step B) involves an aromatization process which should be rapid.

In the case of the polymerization of 5,7-dichloro-1-oxaspiro[2.5]octa-4,7-dien-6-one (Cl_2-OSODO), the propagation reaction corresponds to the reaction of the relatively hindered 2,6-dichlorophenoxide anion with Cl_2-OSODO. Our idea is to use the less hindered phenoxide anion as an initiator, which will achieve a combination of fast initiation and slow propagation (Scheme 3). In this study we examined the polymerization behavior of Cl_2-OSODO using potassium 4-methoxyphenoxide as an initiator.

Scheme 1



Scheme 2



Experimental Section

Instrumentation. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. ^1H 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. High-performance liquid chromatography (HPLC) was performed on Tosoh CCPE and UV-8011 instruments (column, ODS-$80T_M$; eluent, $CH_3OH/H_2O/AcOH/NEt_3$ (70/30/0.2/0.2); flow rate, 0.8 mL/min; UV detector, 277 nm).

Polymerization. In a typical example, into a solution of 4-methoxyphenol (12 mg, 0.10 mmol) and potassium *tert*-butoxide (11 mg, 0.10 mmol) in 6 mL of 2-methoxyethanol was added Cl_2-OSODO (380 mg, 2.0 mmol), and the mixture was stirred at constant temperature for the time of polymerization. The reaction mixture was poured into excess methanol to precipitate the polymeric material, which was repeatedly washed with methanol. The polymer was dried under reduced pressure to constant weight.

Monomer Incremental Addition Experiment. Into a solution of 4-methoxyphenol (12 mg, 0.10 mmol) and potassium

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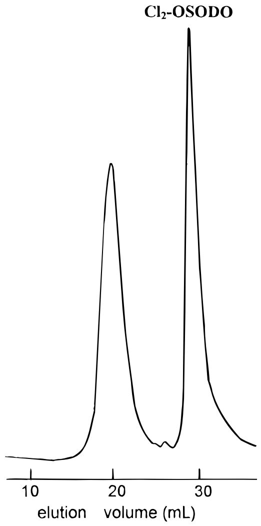
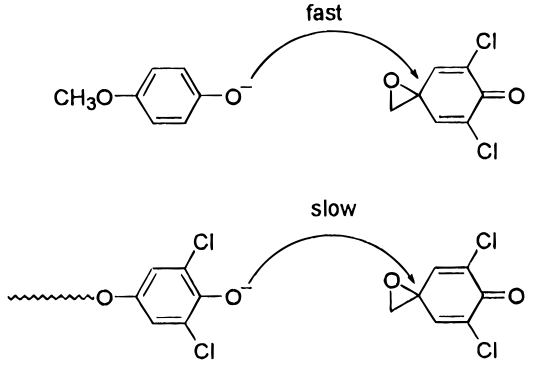


Figure 1. GPC curve of the reaction mixture: time, 6 h; temperature, 10 °C; [Cl_2-OSODO]$_0$ = 0.3 mol/L; [Cl_2-OSODO]$_0$/[potassium 4-methoxyphenoxide] = 20.

Scheme 3



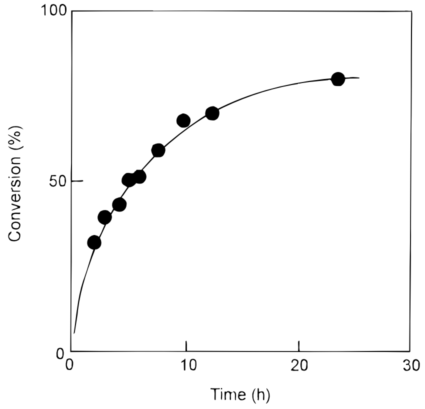


Figure 2. Time–conversion curve for the polymerization of Cl_2-OSODO at 10 °C. [Cl_2-OSODO]$_0$ = 0.3 mol/L; [Cl_2-OSODO]$_0$/[potassium 4-methoxyphenoxide] = 20.

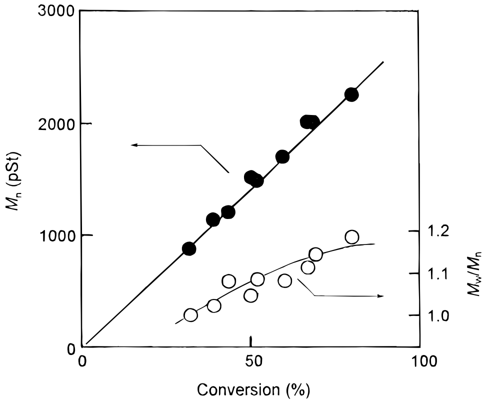


Figure 3. M_n and M_w/M_n vs conversion for the polymerization of Cl_2-OSODO at 10 °C. [Cl_2-OSODO]$_0$ = 0.3 mol/L; [Cl_2-OSODO]$_0$/[potassium 4-methoxyphenoxide] = 20.

tert-butoxide (11 mg, 0.10 mmol) in 4 mL of a mixed solvent of 2-methoxyethanol and THF (1:1 v/v) was added Cl_2-OSODO (100 mg, 0.5 mmol), and the mixture was stirred at 60 °C. Additional amounts of Cl_2-OSODO (100 mg, 0.5 mmol) were supplied to the reaction mixture after 1 and 2 h, respectively.

End-Capping Experiment. Into a solution of 4-methoxyphenol (12 mg, 0.10 mmol) and potassium *tert*-butoxide (11 mg, 0.10 mmol) in 4 mL of 2-methoxyethanol was added Cl_2-OSODO (190 mg, 1.0 mmol), and the mixture was stirred for 20 h at 10 °C. Then, benzyl bromide (35 mg, 0.2 mmol) was added, and the mixture was stirred for 16 h at 80 °C. The reaction mixture was poured into methanol to precipitate the polymeric material to give benzyl-terminated Cl_2-PPO as a white powder (170 mg, 93%). ^{1}H NMR ($CDCl_3$, δ): 7.6–6.8 (m, aromatic), 5.0 (s, CH_2), 3.9 (s, CH_3O). GPC(pSt): $M_n = 1770$, $M_w/M_n = 1.12$.

Kinetic Study. Into a solution of potassium *tert*-butoxide (89 mg, 0.80 mmol) and 4-methoxyphenol (99 mg, 0.80 mmol) or 2,6-dichlorophenol (130 mg, 0.80 mmol) in 6 mL of 2-methoxyethanol were added Cl_2-OSODO (190 mg, 0.80 mmol) and benzophenone (18 mg, 0.1 mmol) as a reference compound for HPLC analysis. The mixture was stirred at −10 °C, and aliquots were subjected to HPLC at regular intervals. The concentration of unreacted Cl_2-OSODO was determined from the relative peak area ratio of Cl_2-OSODO to benzophenone.

Results and Discussion

Polymerization. Figure 1 shows an example of a gel permeation chromatogram for the reaction mixture with feed Cl_2-OSODO concentration of 0.3 mol/L in 2-methoxyethanol at 10 °C for the reaction time of 6 h. The reaction mixture consisted of no compound other than Cl_2-OSODO and the polymer. Figure 2 shows a time–conversion plot of the polymerization of Cl_2-OSODO at 10 °C. It was noted that the reaction mixture became turbid after 20 h probably due to the partial precipitation of the polymer because the resulting Cl_2-PPO is not very soluble in 2-methoxyethanol. Figure 3 shows M_n and M_w/M_n vs conversion for the polymerization of Cl_2-OSODO. The molecular weight increased linearly with conversion while the molecular weight distribution remained narrow ($M_w/M_n < 1.2$).

Monomer Incremental Addition Experiment. To estimate the stability of the propagating end group of polymerization, a monomer incremental addition experiment was carried out. As stated before, the solubility of the resulting Cl_2-PPO in 2-methoxyethanol is not high enough; the polymerization was carried out in a mixed solvent of 2-methoxyethanol and THF (1:1 v/v) at 60 °C. In this case the polymerization proceeded throughout homogeneously. Figure 4 shows GPC curves of the polymerization mixture. The molecular weight of the polymer increased in the second and third stages without significant broadening of the molecular weight distribution. It was concluded that all polymer chains formed in the first stage polymerization undergo propagation when additional Cl_2-OSODO was supplied.

End-Capping Experiment. The end-capping experiment was carried out using benzyl bromide as an electrophilic agent according to Scheme 4. Figure 5 shows the ^{1}H NMR spectrum of the end-capped polymer. The peak at 5.8 ppm assignable to terminal phenolic protons disappeared. The singlet peak at 5.0 and 3.9

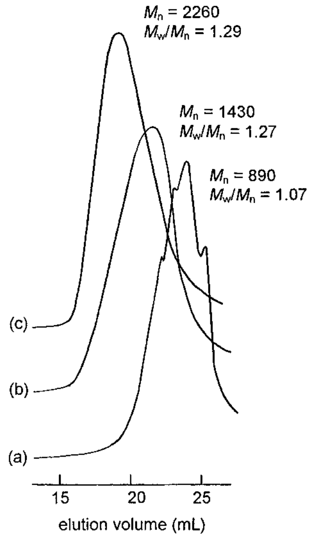


Figure 4. GPC curves of **Cl_2-PPOs** produced by (a) first addition, (b) second addition, and (c) third addition.

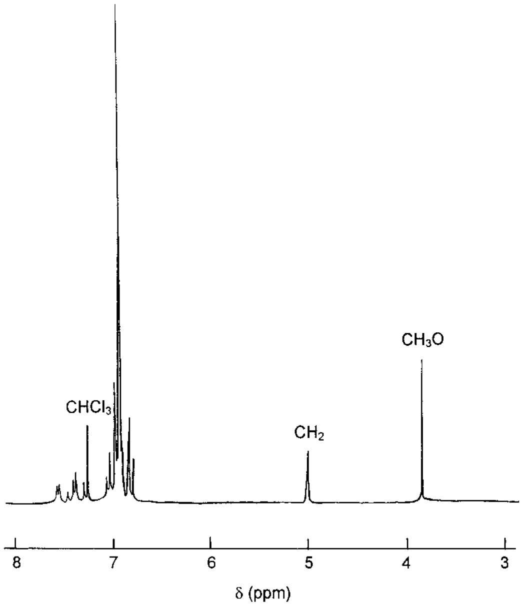
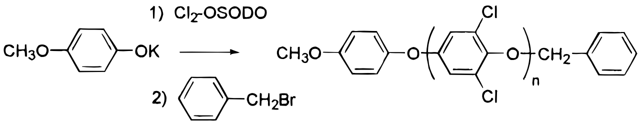


Figure 5. ^1H NMR spectrum of the end-capped Cl_2-PPO in $CDCl_3$.

Scheme 4



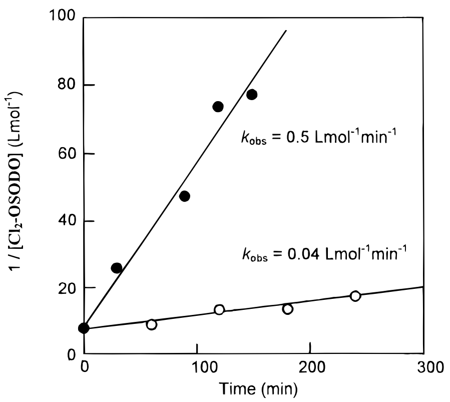
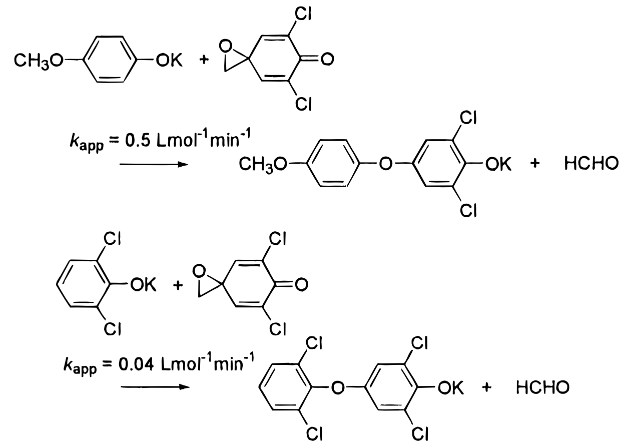


Figure 6. Kinetic plots for the reactions of Cl_2-OSODO with (closed symbols) potassium 4-methoxyphenoxide and (open symbols) potassium 2,6-dichlorophenoxide in 2-methoxyethanol at −10 °C.

Scheme 5



ppm were assignable to terminal benzyl and head methoxy protons, respectively. The amounts of methoxy and benzyl groups were estimated from the peak areas of these peaks. It was found that the ratio of methoxyphenyl head to benzyl end is 1.0, indicating a well-defined polymer. The degree of polymerization of the polymer was determined from the peak area ratio of head methoxy protons to aromatic protons to be 10.3, which was close to the theoretical value of 10.0. These experimental results support that the polymerization of Cl_2-OSODO proceeded through a living mechanism.

Kinetic Study. The rate of initiation was compared with that of propagation in this polymerization. The initiation reaction was evaluated by the equimolar reaction of Cl_2-OSODO with potassium 4-methoxyphenoxide in the presence of a small amount of benzophenone as a standard for HPLC analysis. Similarly, the equimolar reaction of Cl_2-OSODO with potassium 2,6-dichlorophenoxide was carried out as a model reaction for propagation reaction. These equimolar reactions were carried out at −10 °C to prevent further propagation reaction. The conversion of Cl_2-OSODO was determined by the peak area ratio between Cl_2-OSODO and benzophenone. The second-order plots are shown in Figure 6, which exhibited two straight lines. The apparent reaction rate constants of Cl_2-OSODO with potassium 4-methoxyphenoxide and potassium 2,6-dichlorophenoxide were obtained to be 0.5 and 0.04 L mol^{-1} min^{-1}, respectively (Scheme 5). It was found that the reaction between Cl_2-OSODO and potassium 4-methoxyphenoxide was much faster than that between Cl_2-OSODO and potassium 2,6-dichlorophenoxide. These experimental results support the combination of fast initiation and slow propagation.

Molecular Weight Control. The polymerization results of Cl_2-OSODO under various conditions are summarized in Table 1. A well-defined Cl_2-PPO with a degree of polymerization of 10 was obtained (run 1). When [Cl_2-OSODO]/[initiator] ratio was increased to 20, the resulting polymer precipitated from the reaction mixture (run 2). The living character was lost when the reaction temperature was elevated to 90 °C for solubilizing the polymer (run 3). This problem was solved by changing the polymerization solvent from 2-methoxyethanol to a mixture of 2-methoxyethanol and THF (1:1

Table 1. Polymerization of Cl_2-OSODO[a]

run	[Cl_2-OSODO]/ArOK	solvent[b]	temp, °C	yield, %	M_n		M_w/M_n[c]
					calcd	exp[c]	
1	10	A	10	94	1730	1800	1.12
2	20	A	10	87	3340	2100[d]	1.18
3	20	A	90	67	3340	5200	1.80
4	20	B	60	92	3340	3360	1.30
5	30	B	60	75	4950	2360[d]	1.25

[a] Polymerization was run for 24 h. [Cl_2-OSODO]$_0$ = 0.3 mol/L. Ar = 4-MeO−C_6H_4. [b] A = 2-methoxyethanol; B = a mixture of 2-methoxyethanol and THF (v/v = 1/1). [c] Determined by GPC. [d] Polymer precipitation was observed.

v/v) although its molecular weight distribution was somewhat broad (run 4). When the [Cl_2-OSODO]/[initiator] ratio was increased to 30, polymer precipitation occurred even in a mixed solvent at 60 °C (run 5).

Cl_2-PPO has been prepared by several methods including a free-radical-initiated decomposition of sodium 2,6-dichloro-4-bromophenolate with benzoyl peroxide,[3] a polymerization of 2,6-dichlorophenol by 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] We have demonstrated the first example for the preparation of Cl_2-PPO with controlled molecular weight, although a precise molecular weight control is limited up to 20-mers due to the limited solubility of the resulting polymer in protic solvent such as 2-methoxyethanol.

References and Notes

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