

Syntheses and Ring-Opening Polymerizations of 7-Methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene and 7-Methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene

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ABSTRACT: 7-Methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene (**1**) and 7-methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene (**2**) were prepared by [4 + 2] Diels–Alder reaction in a Parr-reactor. While monomer **1** polymerized only *via* opening of pyran ring, monomer **2** which has the oxygen atoms properly positioned to facilitate the double ring-opening underwent cationic polymerization with mainly double ring opening. Volume expansion (6.7%) was observed in polymerization of monomer **2**.

KEY WORDS Cationic Double Ring-Opening Polymerization / 7-Methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene / 7-Methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene / Volume Expansion /

We have previously reported¹ the ring-opening polymerization of 8-cyano-7-ethoxy-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene. In the polymerization of cyclic ortho ester containing dihydro-2*H*-pyran ring, only dihydro-2*H*-pyran ring was opened. In order to facilitate the double ring-opening polymerization of the spiro compounds, an oxygen atom was repositioned in the structure of cyclic ortho ester. 7-Methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene (**1**) and 7-methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene (**2**) were prepared by [4 + 2] cycloaddition reaction of methyl vinyl ketone with 2-methylene-4-phenyl-1,3-dioxolane^{2,3} and methyl vinyl ketone with 4-methylene-2-phenyl-1,3-dioxolane⁴ and their polymerization behavior were investigated. This type of adduct formation was first reported by Hall and co-workers,⁵ and we also have reported the formation of similar adducts and their ring-opening polymerization.⁶

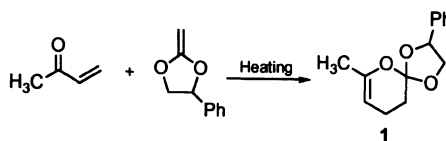
In this article, we describe the polymerization

behavior of monomers **1**, **2** and the volume expansion in polymerization.

EXPERIMENTAL

Preparation of 7-Methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene (**1**)

A mixture of 18.5 g (260 mmol) of methyl vinyl ketone and 11.0 g (68 mmol) of 2-methylene-4-phenyl-1,3-dioxolane in 20 ml of acetonitrile was heated at 150°C with 3 g of hydroquinone in a stainless steel bomb (Scheme 1). After 4 days the solvent was evaporated, the crude product was purified by fractional distillation in vacuum, followed by simple distil-

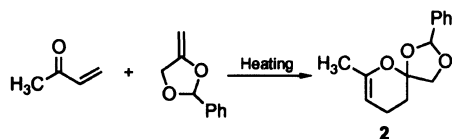


Scheme 1.

lation. bp 94°C at 0.10 Torr, yield 14.5 g (92%). ¹H NMR (CDCl₃, δ = ppm): 1.8 (s, 3H), 2.0—2.4 (m, 4H), 3.8—4.1 (t, 1H), 4.2—4.8 (m, 2H), 5.3—5.5 (t, 1H), 7.4—7.5 (m, 5H). IR (cm⁻¹): 690, 760 (aromatic =CH out of plane bending), 1690 (strong, stretching of internal vinyl ether). ¹³C NMR (CDCl₃, ppm): 21.2, 29.9, 30.3, 72.7, 73.1, 79.0, 97.0, 121.3, 127.7, 128.1, 129.6, 130.0, 140.6, 150.2.

Preparation of 7-Methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene (2)

A mixture of 25.3 g (360 mmol) of methyl vinyl ketone and 24.5 g (151 mmol) of 4-methylene-2-phenyl-1,3-dioxolane in 20 ml of acetonitrile was heated at 200°C with 3 g of hydroquinone in a stainless steel bomb (Scheme 2). After 7 days the solvent was evaporated, the crude product was purified by fractional distillation in vacuum, followed by simple distillation. bp 96°C at 0.10 Torr, yield 21.0 g



Scheme 2.

(60%). ¹H NMR (CDCl₃, δ = ppm): 1.8 (s, 3H), 1.8—2.3 (m, 4H), 4.0—4.1 (dd, 2H), 4.6 (s, 1H), 6.1 (s, 1H), 7.4—7.5 (m, 5H). IR (cm⁻¹): 690, 760, 1690 (strong, stretching of internal vinyl ether). ¹³C NMR (CDCl₃, ppm): 17.9, 20.0, 28.4, 75.7, 96.1, 103.4, 103.6, 126.8, 128.2, 129.4, 136.6, 148.3.

Cationic Polymerization of 1 and 2

A methylene chloride solution of **1** and **2** (0.5 g, 2.16 mmol) was placed in a rubber septum stopper capped pyrex glass ampule under nitrogen. The resulting solution was flushed with dry nitrogen for 1 h. The ampule was then placed in dry ice-acetone bath under nitrogen, and 13.5 μl (5 mol%) of boron trifluoride etherate was added to the solution. After the appropriate time, the reaction mixture was quenched with ammonia water and the solution was pured into a large volume of hexane. The white polymer precipitates were filtered and dried in vacuum at room temperature.

Polymer 1p. ¹H NMR (CDCl₃, δ = ppm): 1.7—2.2 (m, 7H), 3.0 (m, 1H), 3.7 (m, 1H), 4.1—4.3 (m, 1H), 4.9—5.1 (m, 1H), 7.3 (m, 1H). IR (cm⁻¹): 690, 760, 1710 (strong, C=O).

Table I. Polymerizations of the 7-methyl-2-phenyl-1,4,6-trioxaspiro[4,5]dec-7-ene (**1**) and 7-methyl-2-phenyl-1,3,6-trioxaspiro[4,5]dec-7-ene (**2**)

Monomer ^a (g ml ⁻¹)	Initiator (BF ₃ ·OEt ₂)	Temp	Time	Conv.	<i>M_w</i> ^b (<i>M_w</i> / <i>M_n</i>)	Mode of ring opening
		°C	h	%		
1 (0.5)	2 mol%	-30	27	77	4635 (1.46)	Pyran ring- opening mixed
	2 mol%	20	12	82	6675 (3.66)	
2 (0.5)	2 mol%	-78	12	70	10674 (4.38)	Mainly DROP ^c
	2 mol%	-30	27	80	7823 (4.25)	Mainly DROP
	2 mol%	20	12	85	2621 (2.27)	Mixed

^a Methylene chloride (1 ml) was used as solvent.

^b Weight-average molecular weight, Waters GPC-150 instrument, using a calibration curve for polystyrene.

^c DROP, double ring-opening polymerization.

^{13}C NMR (CDCl_3 , ppm): 20.3, 31.0, 32.0, 59.1, 71.8, 77.9, 111.5, 126.0, 127.7, 128.0, 128.2, 128.4, 137.3, 137.5, 209.5.

Polymer 2p. ^1H NMR (CDCl_3 , δ =ppm): 1.2–2.4 (m, 9H), 2.8 (m, 1H), 3.4–3.8 (m, 2H), 4.3–4.7 (m, 1H), 7.1–7.3 (m, 5H). IR (cm^{-1}): 690, 760, 1716 (broad, C=O). ^{13}C NMR (CDCl_3 , ppm): 21.6, 31.4, 36.2, 37.7, 57.4, 58.3, 73.1, 82.4, 84.5, 116.0, 126.5–128.7, 137.5–138.3, 206.6, 207.3, 209.6, 211.1.

Volume Change on Polymerization

The volume changes during polymerizations,

as calculated from densities of monomer and polymers ($\{[\text{density}(\text{monomer}) - \text{density}(\text{polymer})]/\text{density}(\text{monomer})\} \times 100$). Densities of monomer and polymers were measured by the density gradient tube method at 20°C (density of monomer **2**=1.268, density of polymer **2p**=1.183).

RESULTS AND DISCUSSION

The polymerizations were carried out at various temperatures in the presence of boron trifluoride etherate and dry methylene chloride

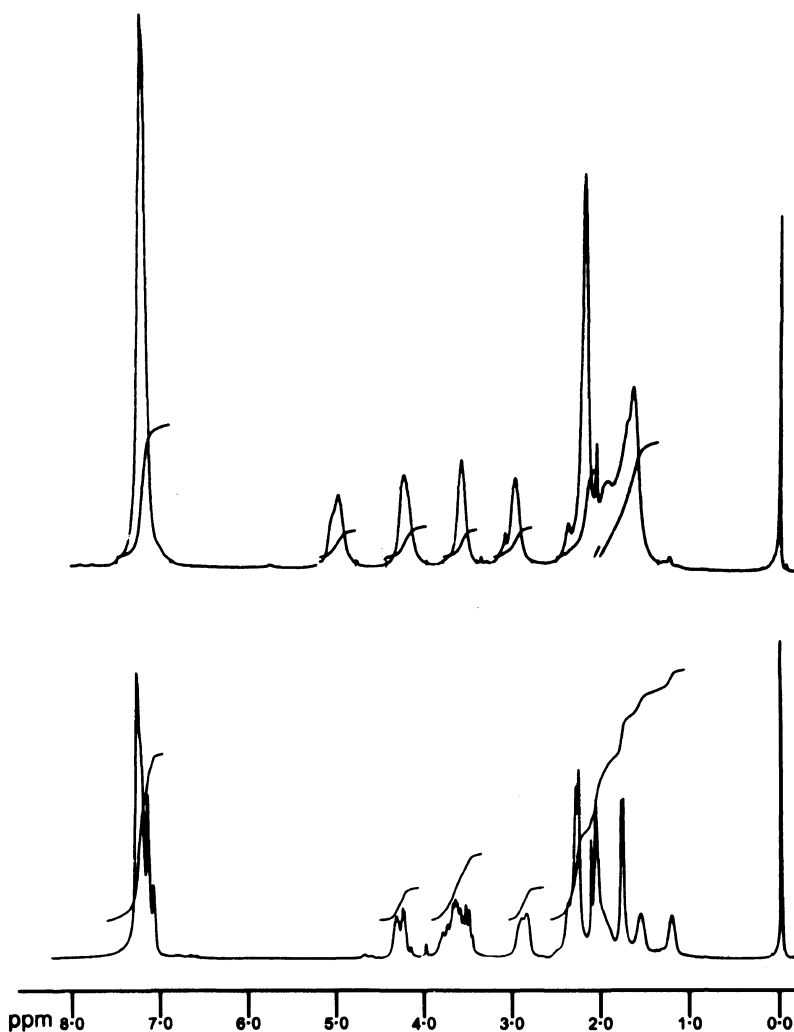


Figure 1. ^1H NMR spectrum of polymer **1p** (upper) and **2p** (lower) obtained by cationic polymerization.

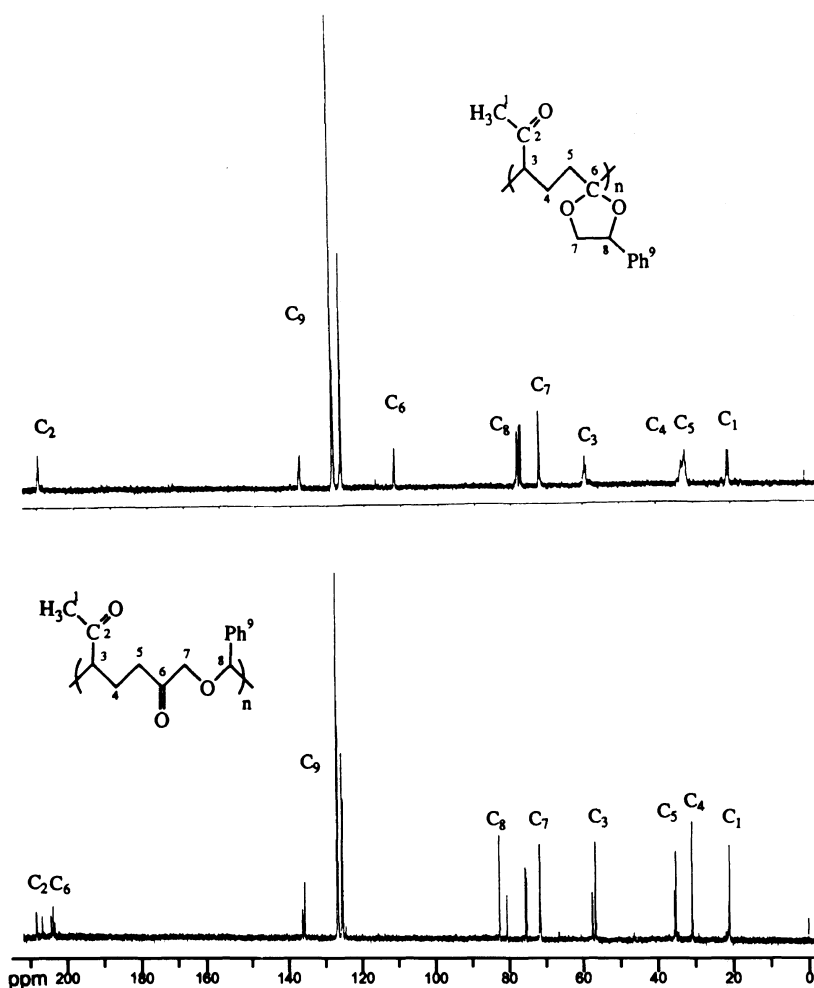


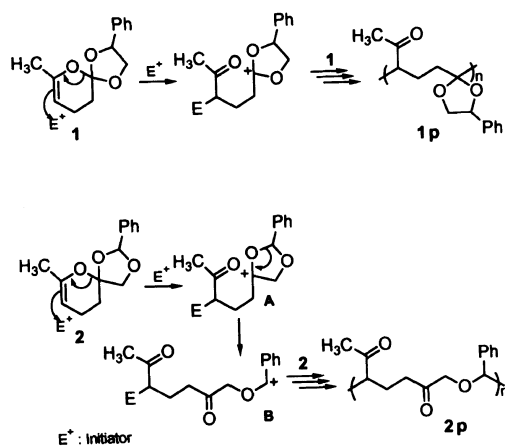
Figure 2. ^{13}C NMR spectrum of polymer **1p** (upper) obtained by cationic ring-opening polymerization and **2p** (lower) obtained by cationic double ring-opening polymerization.

as solvent under nitrogen. The polymers obtained were reprecipitated from methylene chloride into petroleum ether or hexane, which gave white powders. The results of polymerizations are summarized in obtaining Table I.

The structures of the polymers were confirmed by IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectrum of the polymer **1p** consists of a strong absorption band at 1710 cm^{-1} which is attributable to carbonyl group of the ring-opened pyran, no absorption related to another type of carbonyl group was observed.

Monomer **1** shows absorption band of internal double bond at 1690 cm^{-1} which were not observed in those spectra of the polymer. The ^1H NMR spectrum (Figure 1) exhibits three peaks of the remaining phenyl-substituted dioxolane ring proton at $\delta = 3.7\text{ ppm}$ (m, 1H), 4.1–4.3 ppm (m, 1H) and 4.9–5.1 ppm (m, 1H). And, the presence of one signal of the carbonyl carbon in the ^{13}C NMR spectrum (Figure 2) at 209.5 ppm indicate that monomer **1** was polymerized *via* pyran ring-opening only.

The IR spectrum of polymer **2p** shows broad



Scheme 3.

absorption band around $1700\text{--}1720\text{ cm}^{-1}$, attributable to carbonyl groups. The ^1H NMR spectrum (Figure 1) exhibits three proton peaks of the pyran ring opened and those of opened dioxolane ring at $\delta = 2.8\text{ ppm}$ (m, 1H), $3.4\text{--}3.8\text{ ppm}$ (m, 2H) and $4.3\text{--}4.7\text{ ppm}$ (m, 1H). And, the ^{13}C NMR spectrum (Figure 2) shows four peaks of the two carbonyl groups around $206.6\text{--}211.1\text{ ppm}$. These spectral data indicate that the polymerization of **2** proceeded *via* double ring-opening process.

Density measurements revealed that the double ring-opening polymerization of monomer **2** proceeded with 6.7% expansion of the volume.⁷

From the proposed polymer structure a

consistent mechanism of polymerization was extracted (Scheme 3). A cationic initiator (E^+) attacks first the double bond of the monomer, forming a cation that rearranges with ring-opening pyran to alkoxy-carbenium ion.

In the polymerization of monomer **1** the resulting growing dialkoxy-carbenium ion are sufficiently stabilized by oxygen atom, the polymerization reaction then proceeds continuously. However, the stabilization is more pronounced for the growing cation B (benzyl alkoxy carbenium ion) compared with cation A (alkoxy-carbenium ion), and the opening of second ring becomes more favorable. Monomer **2** polymerizes mainly *via* double ring-opening at low temperature.

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