

# 1, 6-Diphenyl-4, 7-dioxaspiro[2.4]heptane의 합성 및 개환 중합

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(1991년 4월 10일 접수)

## Synthesis and Ring-Opening Polymerization of 1, 6-Diphenyl-4, 7-dioxaspiro[2.4] heptane

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(Received April 10, 1991)

**요 약 :** t-BuO<sup>-</sup>K<sup>+</sup> 존재하에서 (2,2-dichlorocyclopropyl)benzene과 (±)-1-phenyl-1,2-ethanediol을 반응시켜서 1,6-diphenyl-4,7-dioxaspiro[2.4]heptane (1)을 합성하였다. 단량체 1을 BF<sub>3</sub>와 같은 양이온 개시제로 중합시킨 결과 페닐기를 가지는 폴리에스테르 2를 얻었다. 양이온 중합은 이중 고리열림 메카니즘으로 진행되었다. 폴리에스테르 2는 상용 용매에 잘 녹았으며 고유점도는 0.10-0.12 dL/g을 보였다. 용액으로부터 만들어진 중합체 필름은 투명하고 취약성을 보였으며 유리전이 온도는 58°C였다.

**Abstract :** 1,6-Diphenyl-4,7-dioxaspiro[2.4]heptane (1) was prepared from (2,2-dichlorocyclopropyl)benzene and (±)-1-phenyl-1,2-ethanediol in the presence of potassium tert-butoxide. Compound 1 was polymerized by cationic initiators such as boron trifluoride etherate to obtain polyester (2) containing phenyl group. The cationic polymerization proceeded via double ring-opening mechanism. Polyester 2 was soluble in common solvents and the inherent viscosities were in the range of 0.10-0.12 dL/g. Solution-cast film was clear and brittle, showing T<sub>g</sub> value of 58°C.

### INTRODUCTION

Ring-opening polymerization of small carbocyclic compounds has long been the subject of curiosity to polymer chemists. Various substituted cyclopropanes have been polymerized via ring-opening mechanism.<sup>1-12</sup> The most important factors determining the ring-opening polymerizability of cyclopropanes are ring strain and positioning of proper

substituents. Aromatization energy also facilitates the ring-opening polymerization of spirocyclopropane compounds.<sup>12</sup>

Cyclic ketene acetals with radical stabilizing group undergo ring-opening polymerization to give polyesters.<sup>13-20</sup> They are especially interesting because it is possible to prepare various type of polyesters, which are difficult to obtain by conventional stepwise polymerization. These polyesters

also have received attention as biodegradable polymers.<sup>15</sup>

Recently Rasoul and his coworkers<sup>21</sup> have investigated the ring-opening polymerization of 1-phenyl-4,7-dioxaspiro[2.4]heptane. However, they obtained only low molecular weight viscous oil by cationic polymerization. To facilitate further the double ring-opening polymerization of spirocyclopropane compound we introduced a proper cation-stabilizing group into the cyclic acetal ring. We found that this substituent has enhanced ring-opening polymerizability of spirocyclopropane, which polymerized readily in double ring-opening fashion by cationic initiators.

The present report describes the synthesis and ring-opening polymerization of 1,6-diphenyl-4,7-dioxaspiro[2.4]heptane(1). Structure and properties of the resulting polyesters(2) were analyzed by spectroscopic and thermal methods.

## EXPERIMENTAL

### Materials

The reagent grade chemicals were purified by distillation or recrystallization before use. ( $\pm$ )-1-Phenyl-1,2-ethanediol, potassium tert-butoxide, and (2,2-dichlorocyclopropyl)benzene were purchased from Aldrich Co. Dichloromethane was dried with anhydrous calcium chloride, distilled over calcium hydride, and stored in a brown bottle. Chloroform was refluxed with phosphorus pentoxide, followed by fractional distillation. tert-Butyl alcohol was dried with anhydrous magnesium sulfate, filtered, and fractionally distilled. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure.

### Instrumentation

All measured temperatures are uncorrected. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. <sup>1</sup>H-NMR spectra were obtained on a Varian Midel EM 360L nuclear magnetic resonance spectrometer at 60 MHz. Elemental analyses were performed by Perkin-Elmer 24

00 CHN elemental analyzer. The glass transition temperature( $T_g$ ) was measured on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min up to 480°C was used for the thermal degradation study of polymers under nitrogen atmosphere. Viscosity values were obtained by using a Cannon-Fenske viscometer.

### Preparation of 1,6-Diphenyl-4,7-dioxaspiro[2.4]heptane(1)

A 250 mL four neck round bottomed flask was fitted with a condenser, thermometer, mechanical stirrer, and nitrogen inlet/outlet. ( $\pm$ )-1-Phenyl-1,2-ethanediol (97.0 g, 0.70 mole) and tert-butyl alcohol (44.3 mL, 0.47 mole) were placed in the flask. The mixture was heated gently to make a homogeneous solution and solid potassium tert-butoxide (36.0 g, 0.32 mole) was added. Then (2,2-dichlorocyclopropyl)benzene (11.2 g, 0.06 mole) was added dropwise during 5 min. The reaction mixture was refluxed with stirring for 10 hours under nitrogen, followed by stirring for 8 hours at room temperature. The reaction mixture was diluted with 250 mL of cold water and extracted twice with 250 mL of n-pentane. The organic layer was dried over anhydrous magnesium sulfate, filtered, and the solvent was removed by evaporation. The residue was placed in the refrigerator (5°C) for 24 hours. ( $\pm$ )-1-Phenyl-1,2-ethanediol crystallized was then removed by suction filtration and washed with 50 mL of n-pentane. The resulting filtrate was concentrated by evaporation under reduced pressure. Thus obtained crude product was purified by column chromatography (Slica gel, 70-230 mesh, 60 Å, ethyl acetate/n-hexane : 35/65, vol/vol). 1 : 7.5 g (50% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  1.13-1.80 (m, 2H), 2.08-2.53 (m, 1H), 3.31-4.34 (m, 2H), 4.78-5.20 (m, 1H), 7.30-7.45 (d, 10H) ; IR (neat) 3080, 3048, 3015 (aromatic C-H), 1602 (C=C), 760, 700 (aromatic) cm<sup>-1</sup>.

### Cationic Polymerization of 1,6-Diphenyl-4,7-dioxaspiro[2.4]heptane(1)

A representative cationic polymerization procedure

was as follows : In a polymerization tube capped by rubber septum was placed a dichloromethane (2 mL) solution of 1 (1.88 g, 7.5 mmole). The resulting solution was flushed with dry nitrogen for 20 min. The polymerization tube was then maintained at  $-50^{\circ}\text{C}$  under nitrogen, and  $9 \times 10^{-3}$  mL of boron trifluoride etherate was added to the solution. After 24 hours the polymerization tube was taken out and the polymerization mixture was poured into a large volume of ethanol. The precipitated polymer was collected and reprecipitated from chloroform into ethanol. Thus obtained white polymer was dried in a vacuum oven at room temperature. 2 : 0.57 g (30% yield) ;  $\eta_{\text{inh}} = 0.10$  dL/g (c, 0.5 g/dL in chloroform at  $25^{\circ}\text{C}$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.18-3.83 (m, 4H), 3.85-4.90 (m, 2H), 6.72-7.65 (s, 10H) ; IR (KBr) 3080, 3050, 3020 (aromatic C-H), 1736 (C=O), 1601 (C=C), 758,701 (aromatic)  $\text{cm}^{-1}$ . The degree of ring-ope-

ning was estimated from  $^1\text{H-NMR}$  and IR spectra.

## RESULTS AND DISCUSSION

Compound 1 was prepared according to a procedure similar to that reported already.<sup>21</sup> The crude compound was always contaminated by the reactant ( $\pm$ )-1-phenyl-1,2-ethanediol. After removal of ( $\pm$ )-1-phenyl-1,2-ethanediol by selective recrystallization the yellowish product was further purified by column chromatography. The chemical structure of the spirocyclopropane 1 was identified by  $^1\text{H-NMR}$ (Figure 1), IR (Figure 2(a)), and elemental analysis. All the spectral and elemental analysis data confirmed the expected structure.

We have tried polymerization of spiro compound 1 with various type of initiators such as boron trifluoride etherate, AIBN, and DTBP (di-tert-butyl-

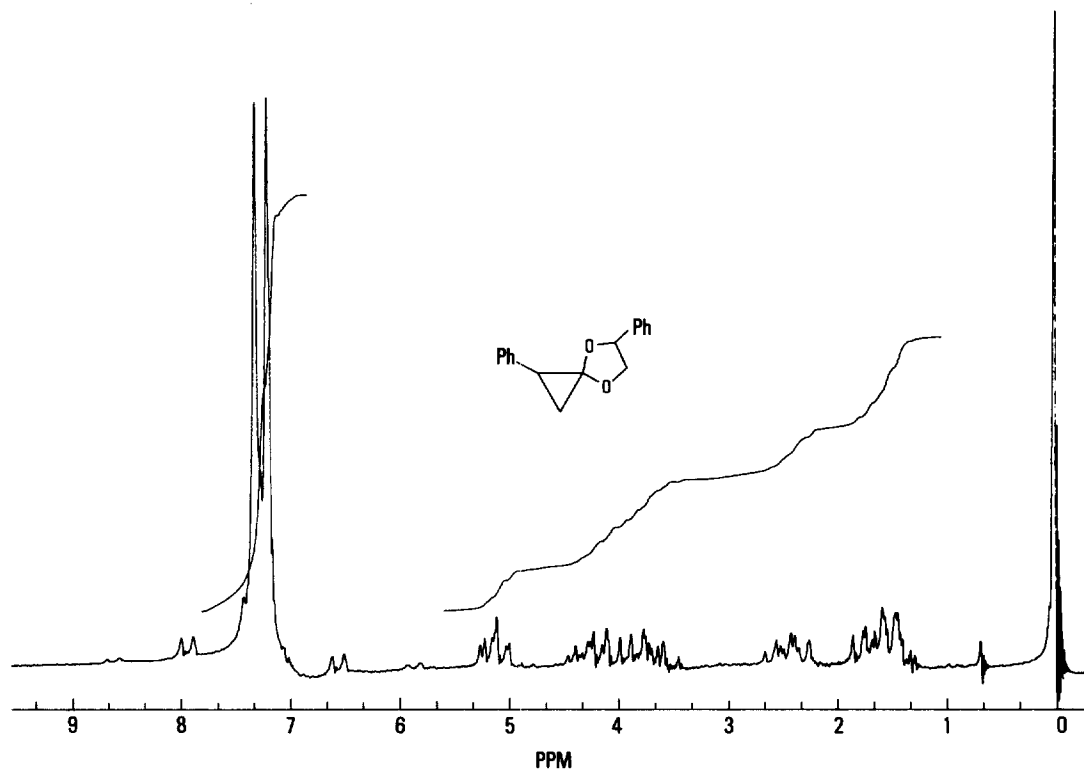


Fig. 1.  $^1\text{H-NMR}$  spectrum(60 MHz) of 1,6-Diphenyl- 4,7-dioxaspiro[2.4]heptane(1) taken in  $\text{CDCl}_3$  at room temperature.

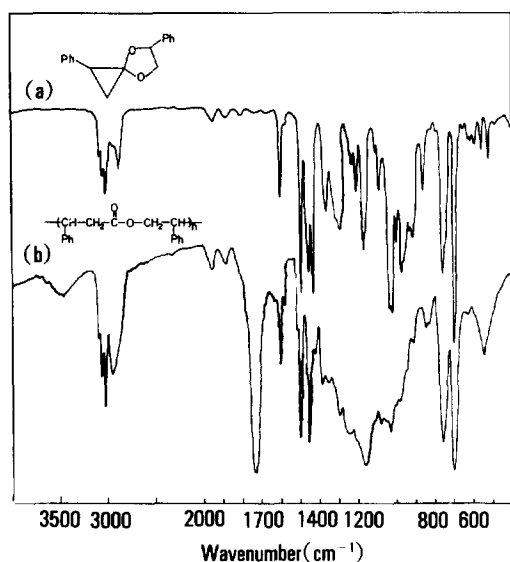
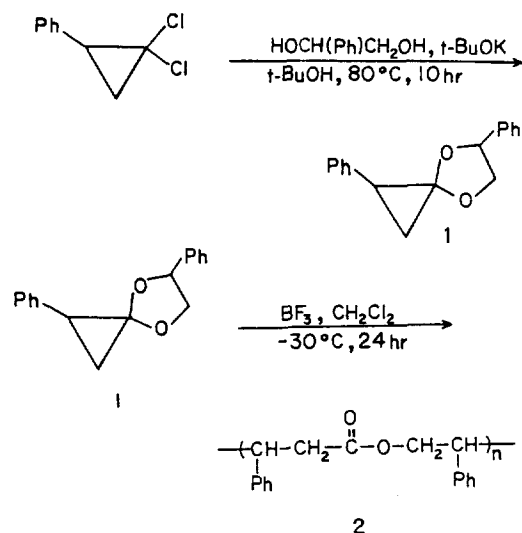


Fig. 2. Superimposed IR spectra of 1,6-Diphenyl-4,7-dioxaspiro[2.4]heptane 1(a) and its polymer 2(b).



(Scheme 1)

peroxide). Polymerization reactions were carried out in neat or in solution. The results of polymerizations are summarized in Table 1. As shown in Table 1, monomer 1 was double ring-open polymerized with cationic initiators in a low conversion (Scheme 1). However, all attempts to polymerize 1 with various radical initiators failed so far.

Structures of the resulting polymers were deter-

mined by IR (Figure 2(b)) and  $^1\text{H-NMR}$  spectra (Figure 3). The spectra of the polymer revealed that the polymer does not possess any ring moiety which would result from the polymerization of monomer 1 via 1,3-mode. In  $^1\text{H-NMR}$  spectra, no resonance peaks attributable to methylene protons ( $-\text{CH}_2-$ ,  $\delta=1.13-1.80$ ) of cyclopropane ring and benzyl proton ( $-\text{OCH}(\text{Ph})-$ ,  $\delta=4.78-5.20$ ) of cyclic ketal ring appeared. However, the same polymer showed strong absorption band at  $1736\text{ cm}^{-1}$  chara-

Table 1. Ring-Opening Polymerization of 1,6-Diphenyl-4,7-dioxaspiro[2.4]heptane (1)

Monomer	Solvent	Monomer/ Solvent, g/mL	Initiator to Monomer, mole %	Temp, °C	Time, hr	Yield of Product Polymer, %	Extent <sup>a</sup> of Ketal Ring-Opening, %	$\eta_{\text{inh}}^b$ dL/g
<u>1</u>	$\text{CH}_2\text{Cl}_2$	0.94	$\text{BF}_3$ , 1.0	-50	24	30	100	0.10
<u>1</u>	$\text{CH}_2\text{Cl}_2$	0.67	$\text{BF}_3$ , 0.9	-50	72	28	100	0.09
<u>1</u>	$\text{CHCl}_3$	0.75	$\text{BF}_3$ , 0.9	-30	48	20	100	0.12
<u>1</u>	$\text{CHCl}_3$	0.80	$\text{BF}_3$ , 1.0	-30	24	18	100	0.08
<u>1</u>	neat	—	AIBN, 0.7	65	24	nil	—	—
<u>1</u>	$\text{C}_6\text{H}_6$	0.70	AIBN, 0.8	65	20	nil	—	—
<u>1</u>	neat	—	DTBP, <sup>c</sup> 1.0	120	24	nil	—	—
<u>1</u>	$\text{C}_6\text{H}_5\text{Cl}$	0.50	DTBP, 1.2	120	20	nil	—	—

<sup>a</sup> Extent of ketal ring-opening was estimated from  $^1\text{H-NMR}$  and IR spectra.

<sup>b</sup> Concentration of 0.5 g/dL in chloroform at  $25^\circ\text{C}$ .

<sup>c</sup> Di-tert-butylperoxide.

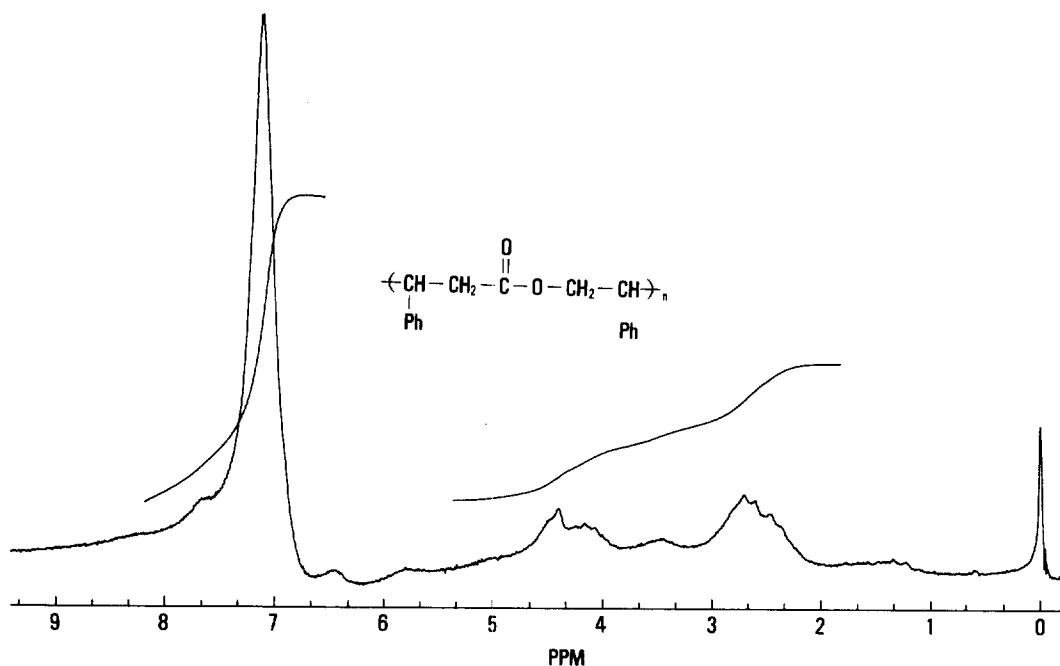


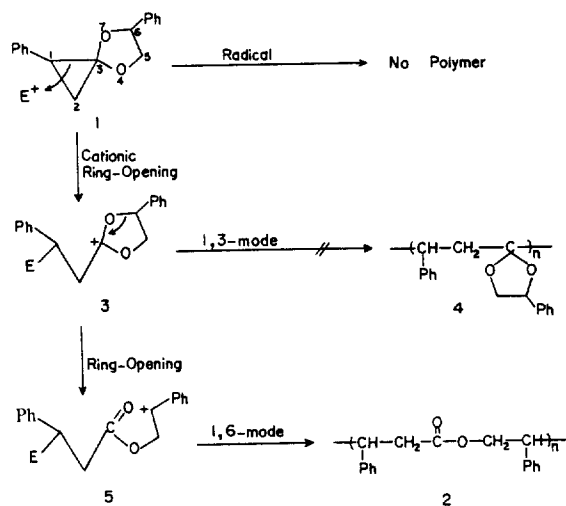
Fig. 3.  $^1\text{H-NMR}$  spectrum of polymer 2, 60 MHz, room temperature, arbitrary concentration in  $\text{CDCl}_3$ .

characteristic of an ester in the IR spectrum.

These spectral evidence seems to indicate that the spirocyclopropane compound 1 polymerizes cationically via double ring-opening mechanism(1, 6-mode). In the cationic double ring-opening polymerization depicted in Scheme 2, the catalyst initiates the polymerization by attacking a monomer molecule at C-1 of cyclopropane ring, thereby resulting in formation of a cation 3 by ring-opening. Cation 3 rearranges immediately by successive ring-opening to the well-investigated benzyl cation 5, which is usually involved in the cationic polymerization of styrene. Propagation by cation 3 is not favored in this situation for steric reason, which would lead to polymer 4.

The polyester 2 was soluble in common solvents such as chloroform and acetone, and the inherent viscosities measured in chloroform were in the range of 0.10-0.12 dL/g.

The thermal behavior of polyester 2 was investigated by thermogravimetric analysis(TGA) and differential scanning calorimeter(DSC) to deter-



<Scheme 2>

mine the thermal degradation pattern and glass transition temperature( $T_g$ ). The thermal analysis were carried out a scanning rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. The results are summarized in Table 2. The polyester showed single phase de-

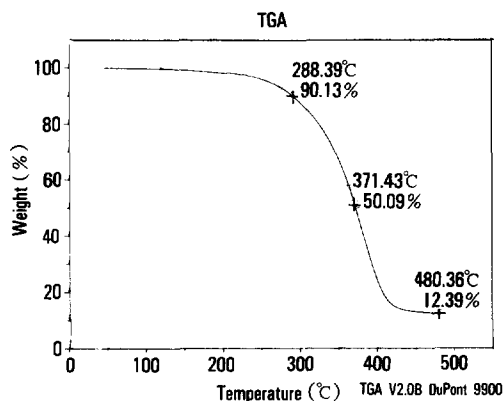


Fig. 4. TGA thermogram of polyester 2 (10°C/min, N<sub>2</sub>).

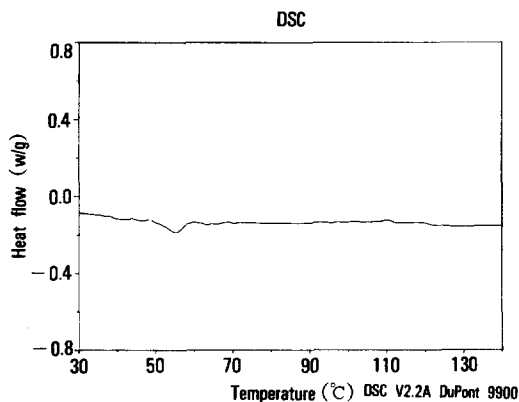


Fig. 5. DSC thermogram of polyester 2 (10°C/min, N<sub>2</sub>).

Table 2. Thermal Properties of Polyester 2

Polymer	T <sub>g</sub> , °C <sup>a</sup>	Degradation Temp, <sup>b</sup> °C		
		10% -loss	Half-loss	480°C, %
<u>2</u>	58	288	371	12.4

<sup>a</sup> Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

<sup>b</sup> Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

gradation pattern, exhibiting initial degradation (10% weight-loss) temperature of 288°C as shown in Figure 4. The glass transition temperature determined from DSC curve (Figure 5) was 58°C. Solution-cast films were clear and brittle, which could

be due to the low molecular weight.

We are now in the process of polymerization of other spirocyclopropane compounds.

**Acknowledgements** : We are deeply indebted to the Ministry of Education for support of this work.

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