

2-Phenyl-4-methylene-1,3-dioxolane의 광개시 라디칼 중합

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Photoinitiated Free Radical Polymerization of 2-Phenyl-4-methylene-1,3-dioxolane

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요 약 : 2-Phenyl-4-methylene-1,3-dioxolane(2-PMDO)을 benzoin methylether 존재하에 광개시 라디칼 중합(254nm)을 시킨 결과, 개환이 지배적인 중합체를 66%의 수율로 얻었다. 한편, 125°C에서 di-t-butyl peroxide를 사용한 라디칼 중합에 의해서는 비닐, 개환, 탈리가 혼합되어 일어난 구조를 가진 중합체를 얻었다. 2-PMDO는 benzoin methylether 존재하에서 254nm의 광을 조사한 공중합에 있어서 acrylonitrile, methyl methacrylate 등과 쉽게 공중합되어 거의 개환되지 않은 단위를 포함하는 공중합체가 얻어졌다. Acrylonitrile과 2-PMDO의 공중합시 두 모노머 단위의 구성비는 혼합비에 관계없이 두배의 차이가 크지 않았으며 반면에, methyl methacrylate와의 공중합체들은 같은 조건에서 methyl methacrylate의 단위가 우세한 공중합체가 얻어졌다.

Abstract : 2-Phenyl-4-methylene-1,3-dioxolane(2-PMDO) underwent photoinitiated free radical ring-opening polymerization with benzoin methylether at 254nm to yield the polymer in 66% of conversion with virtually exclusive ring-opening. On the other hand, thermal free radical polymerization with di-t-butyl peroxide at 125°C generated the polymer with mixed modes of polymerization : vinyl, ring-opening and elimination polymerization. In copolymerization, 2-PMDO was shown to copolymerize readily with acrylonitrile, methyl methacrylate in the presence of benzoin methylether at 254nm to produce copolymer containing most of unopened unit. The ratios of two monomer units of copolymer of 2-PMDO with acrylonitrile varied insignificantly as the feed ratio change, whereas the copolymer with methyl methacrylate were predominantly composed of methyl methacrylate unit.

INTRODUCTION

The photoinitiated radical ring-opening polymerization is particularly interesting topic in polymerization of various monomers.

Although a variety of unsaturated cyclic ethers such as cyclic ketene acetal,¹⁻⁴ cyclic vinyl ether,^{5,6} and unsaturated orthoester⁷⁻⁹ were synthesized and found to undergo thermal free radical ring-opening polymerization. However, photoinitiated free-radical ring-opening polymerization of those monomers are comparatively rare. Recently Endo has reported that 2-methylene-1,3-dioxepane¹⁰ and 2-methylene-4-phenyl-1,3-dioxolane¹¹ undergo quantitative ring-opening to form polyesters by both radical and photolytic polymerization.

In the case of 2-phenyl-4-methylene-1,3-dioxolane(2-PMDO), Bailey carried out free radical polymerization and obtained the polymers resulting from the mixed modes of polymerization; vinyl, ring-opening and elimination polymerization.¹²

We are also interested in this particular 2-PMDO and like to report its clean ring-opening polymerization by photoinitiation, rate of polymerization and copolymerizability with comonomers.

EXPERIMENTAL

Materials and Instruments

The monomer 2-PMDO was synthesized by using the modified procedure previously reported.¹² Benzoin methylether(BME) was purified by recrystallization from ethanol. Acrylonitrile, styrene, methyl methacrylate and vinyl acetate were distilled over calcium hydride under a nitrogen atmosphere.

¹H-NMR spectra were recorded with a T-60A Varian nuclear magnetic resonance spectrometer. ¹³C-NMR spectra were obtained by Druker AM 200 NMR spectrometer. The infrared spectra were taken on a Perkin-Elmer Model 1310 spectrophotometer. Size exclusion chromatography was carried out with two columns(Waters μ -Styrogel 10³

and 10⁴ Å), calibrated with polystyrene standards, in chloroform as eluent at 254nm. Photopolymerization was carried out with Annular photoreactor Model APQ-40 and 400 W medium pressure Hg-lamp(254 nm) or 40W Hg-lamp(366nm).

Photopolymerization of 2-Phenyl-4-methylene-1,3-dioxolane (2-PMDO)

1 g of 2-PMDO was photoirradiated in a quartz tube in bulk after degassing with the freeze-thaw method, by using a 400 W mercury-lamp(254 nm) at 25°C in the presence of benzoin methylether(3 mole%) as initiator.

The distance between the lamp and ampoule was ca. 10 cm. After 2 hr, the mixture was dissolved in methylene chloride and the solution was added dropwise into stirred cold petroleum ether to obtain white powdery polymers. (yield : 66%). IR(film) : 3060, 3020, 2880, 1735(s), 1350, 760, 710 cm⁻¹. ¹H-NMR(CDCl₃) : δ =7.2(s, 5H, phenyl), 4.65(broad triplet, 1H, $-\text{CH}\Phi-\text{O}-$), 3.7(s, 2H $-\text{CO}-\text{CH}_2-\text{O}-$), 3.1-2.2(broad multiplet, 2H, $-\text{CH}_2-\text{CO}-$). ¹³C-NMR(CDCl₃) : 48.6($-\text{CO}-\text{CH}_2-$), 75.9($-\text{CO}-\text{CH}_2-\text{O}-$), 79.6($-\text{O}-\text{C}\Phi$), 128.1, 129.7, 130.1, 141.4, (aromatic C's), 206.5($-\text{CO}-$).

Similar procedure was applied to the synthesis of polymer with 40W Hg-lamp at 366nm for 12hr in Exp. No. 1. In Exp. No. 3, 2-PMDO in the Pyrex tube was exposed to the sun light for 120 hr at 30°C.

Radical Polymerization of 2-PMDO

In a sealed polymerization tube, a solution of 1 g of 2-PMDO and DTBP 0.024 g(2 mole %) was placed. After degassing, the tube was heated in an oil bath and kept at 125°C for 48 hr. The polymer was purified by precipitation from methylene chloride into cold petroleum ether. The collected solid was dried in vacuo at 50°C for 5 hr to give 0.72 g of white powdery polymer. (yield : 72%) IR (film) : 3060, 3010, 2880, 1733(s), 1600, 1490, 1450, 1360, 1110(s), 760, 700 cm⁻¹.

¹H-NMR(CDCl₃) : δ =7.2(s, 5H, phenyl), 5.8(broad, 1H, $-\text{O}-\text{CH}(\text{Ph})-\text{O}-$), 4.7(broad, 1H, $-\text{O}-\text{CH}\Phi-$), 4.2-3.4($-\text{CO}-\text{CH}_2-\text{O}-$ and

$-O-CH_2-C(CH_2)-$, 3.0-2.2(m, $-CH_2-CO-$ and $-CH_2-CO-CH_2-$), 2.2-1.8(m, $-CH_2-$), $^{13}C-NMR(CDCl_3)$: $\delta=38, 48.7, 75.7, 79.5, 103.1, 128.2, 129.3, 133.1, 142.1, 195.6, 205.1, 207$.

Measurement of the Rate of Photoinitiated Radical Polymerization

In a rubber-septum stopper-capped quartz tube was placed a solution of freshly distilled 2-PMDO (2 g : 12 mmol) and BME(54 mg, 2 mol%). The resulting solution was stirred and photoirradiated with 400W of medium pressure Hg-lamp(254nm) at 25°C after degassing with freeze-thaw method and charging with nitrogen. The bulb jacketed with quartz condensor was placed about 10 cm from the polymerization tube to be irradiated. The samples in controlled amount were withdrawn by means of syringes, at corresponding time and analyzed by NMR.

Copolymerization of 2-PMDO

The mixture of 1g of 2-PMDO and 0.33g acrylonitrile in a quartz tube was irradiated with a 400 W mercury lamp(254nm) at 25°C for 2 hr in the presence of benzoin methylether (3 mole %) as initiator.

The distance between the lamp and the quartz tube was 10 cm. After the reaction, the mixture was dissolved in chloroform and the solution was added dropwise into a stirred petroleum ether to obtain 1.18g of a white powdery polymer.

(Yield : 89%) IR(film) : 3020, 2900, 2220, 1720,

1450, 1400, 1200, 1110, 760, 690 cm^{-1} . $^1H-NMR(CDCl_3)$ $\delta=7.2$ (s, 5H, phenyl), 5.8(s, 1H, benzyl), 3.7(s, 2H, $-O-CH_2-$), 2.6(s, $-CH_2-CH-(CN)-$, 1H), 1.8(s, $-CH_2-$ in PAN and $-CH_2-$ in 2-PMDO).

Similar procedure was applied to the synthesis of copolymers with AN, MMA, vinylacetate and styrene according to the corresponding composition of two monomers.

RESULTS AND DISCUSSION

Photopolymerization of 2-PMDO was carried out by irradiation with mercury lamp(254nm) in bulk using benzoin methylether($\lambda_{max}=247, 326nm$) as a photoinitiator. The radical polymerization with di-tert-butyl peroxide(DTBP) and 2,2'-azo-isobutyronitrile(AIBN) were performed to compare the result with the photoinitiated radical polymerization. The results of these polymerizations are summarized in Table 1.

NMR spectra of the polymers obtained by thermal and photoinitiated radical polymerization were somewhat different as shown in Fig. 1. The absence of a peak at 5.8 ppm assignable to benzyl proton of 1,3-dioxolane ring indicates that 2-PMDO undergoes virtually exclusive ring-opening by photopolymerization as shown in Fig. 1(a).

The appearance of the benzyl signal at 5.8 ppm in Fig. 1(b) compared with that of Fig. 1(a)

Table 1. The Conditions and Results of Polymerization of 2-PMDO

| EXP. No. | Initiator in mole % | Temp. (°C) | Time (hr) | Yield (%) | Mw | Composition of polymer in % ^d | | |
|----------------|---------------------|------------|-----------|-----------|-------|--|-----|-----|
| | | | | | | RI | RO | E |
| 1 ^a | BME, 3 | 25 | 12 | 78 | 8,500 | 0 | 100 | 0 |
| 2 ^b | BME, 3 | 25 | 2 | 66 | 9,000 | 0 | 100 | 0 |
| 3 ^c | none | 30 | 120 | 82 | 6,400 | 0 | 100 | 0 |
| 4 | AIBN, 2 | 65 | 48 | 42 | 5,500 | <20 | 65 | <15 |
| 5 | DTBP, 2 | 125 | 48 | 72 | 6,300 | 20 | 57 | 23 |

^a Benzoin methylether at 366nm (40 W)

^b Benzoin methylether at 254nm (400 W)

^c This experiment was performed by exposing the Pyrex tube to the sunlight without any sensitizer.

^d RI : ring intact, RO : ring opening, E : elimination. These values were determined by the method previously reported.¹²

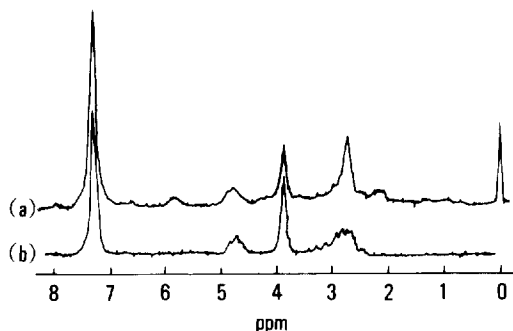


Fig. 1. ^1H NMR spectra of polymers obtained by (a) radical polymerization (DTBP; 2 mol%) and (b) photoinitiated polymerization (BME; 3 mol%) of 2-PMDO.

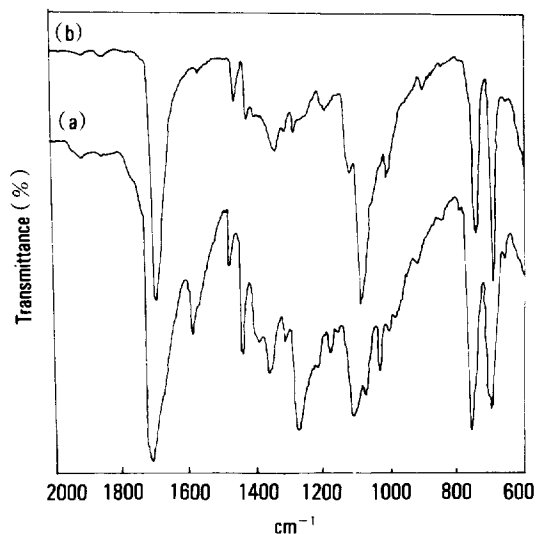


Fig. 2. Infrared spectra of polymers obtained by (a) radical polymerization (DTBP, 2 mol%, 125°C) and (b) photoinitiated polymerization (BME, 3 mol%, 25°C) of 2-PMDO.

suggests that the radical polymerization proceeded in complicated manner involving vinyl, ring opening and elimination. This result is analogous to that obtained by Bailey.¹² IR spectra (Fig. 2) of all the polymers show a strong band at 1735 cm^{-1} indicating the presence of carbonyl group. The polymer obtained thermally as well as photochemically exhibited relatively strong band at 1735 cm^{-1} assignable to carbonyl group formed by ring-opening

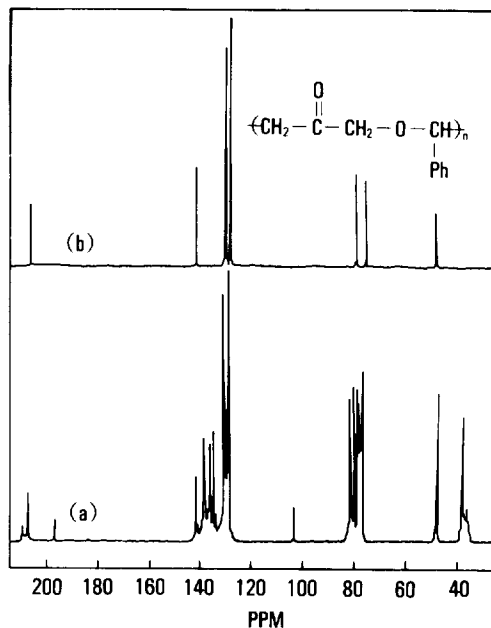


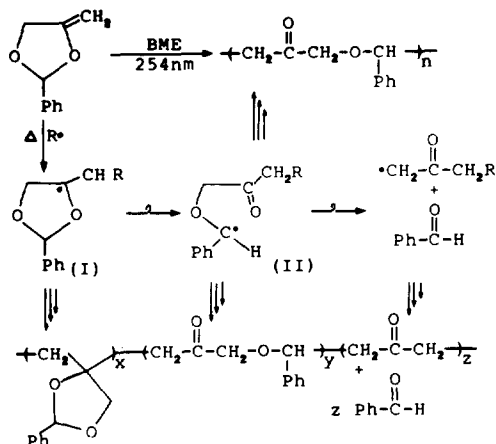
Fig. 3. ^{13}C -NMR spectra of polymers obtained by (a) radical polymerization (DTBP, 2 mole%, 125°C) and (b) photoinitiated polymerization (BME, 3 mole%, 25°C) of 2-PMDO.

and elimination polymerization, thus increasing the intensity of carbonyl absorption.

^{13}C -NMR spectra (Fig. 3) of the polymers obtained by thermal and photoinitiated radical polymerization were quite different from each other. The polymer obtained photochemically shows no peak around 103 ppm corresponding to an acetal carbon in the ring indicating that 2-PMDO underwent completely ring opening, while the peaks at 103 ppm observed in the polymer obtained by thermal radical polymerization indicate the presence of unopened ring structure.

In photopolymerization carried out at lower temperature than that of thermal radical polymerization, it is thought that attack of radical(I) on the monomer is slow enough to be isomerized to more stable benzyl radical(II). Moreover radical(II) reacts with monomer rapidly to form ring-opened poly(keto-ether) without further elimination of benzaldehyde.

The rate of photoinitiated polymerization of 2-



PMDO was determined at 25°C in bulk with BME as a photoinitiator to compare the result with that obtained by thermal radical polymerization. When the relationship between conversion and time was measured, the rate of photoinitiation polymerization was exclusively higher than that of thermal radical polymerization as illustrated in Fig. 4. This result was consistent with those obtained for cyclic ketene acetals by Endo.^{10,11} However, it is also thought that the excitation of 2-PMDO itself by UV light was partly responsible for the mode of polymerization as well as the rate of polymerization.

Typical common monomers such as AN, MMA, styrene and vinylacetate were adopted as comonomers for the copolymerization study of 2-PMDO. 2-PMDO was readily copolymerized with comonomers by irradiation with Hg-lamp(254nm) in the presence of BME. The copolymerization results are shown in Table 2.

Since 2-PMDO is electron donor, it can be copolymerized well with electron accepting monomer, AN via weak charge-transfer complex^{14,15} which could not cause spontaneous polymerization at 25°C. Upon varying the monomer ratio in feed, the ratio of two monomer units in the copolymer varies insignificantly with feed ratio as illustrated in Exp. No 1-5.

In the NMR spectrum(Fig. 5), the presence of a peak at 5.6~6.0 ppm assignable to an acetal

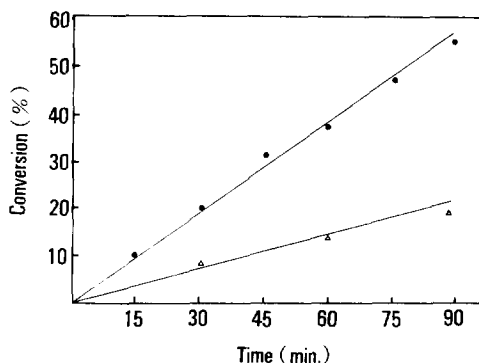


Fig. 4. Rate of photoinitiated radical polymerization (●) and thermal radical polymerization(△) of 2-PMDO.

Table 2. Conditions and Results of Photoinitiated Copolymerization of 2-PMDO with Comonomers 25°C in bulk

| Exp. No | Comonomer | 2-PMDO/Comonomer in mole | Yield (%) | Composition ^{a)} of Copolymer 2-PMDO/Comonomer |
|------------------|-----------|--------------------------|-----------|---|
| 1 | AN | 5 | 35 | 60/40 |
| 2 | AN | 2 | 55 | 56/44 |
| 3 ^{b)} | AN | 1 | 85 | 50/50 |
| 4 | AN | 1/2 | 89 | 38/62 |
| 5 | AN | 1/5 | 88 | - ^{c)} |
| 6 | MMA | 5 | 40 | 37/63 |
| 7 | MMA | 2 | 33 | 34/66 |
| 8 ^{c)} | MMA | 1 | 80 | 33/67 |
| 9 | MMA | 1/2 | 74 | 20/80 |
| 10 | MMA | 1/5 | 84 | 12/88 |
| 11 ^{d)} | VAc | 1 | 33 | 65/35 |
| 12 | St. | 1 | oligomer | 20/80 |

a) These values were determined by integration ratio of phenyl peak of 2-PMDO at 7.1 ppm and corresponding characteristic peaks of comonomer.

b), c), and d) Ring-opening contents were 5%, 10% and 100% respectively. These values were measured by the integration of NMR peak of the benzyl proton (monomer : 5.8 ppm, polymer : 4.8 ppm).

e) Crosslinked polymer.

proton of 1,3-dioxolane ring indicated that the structural unit of 2-PMDO in the copolymer with the AN contained 95 mole % of nonring-opened

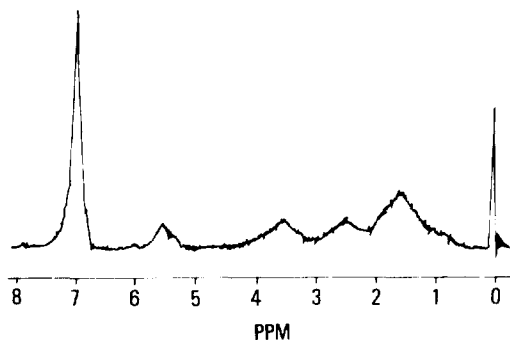


Fig. 5. ^1H NMR spectrum of copolymer of 2-PMDO with AN obtained by photoinitiated polymerization with 3 mol% of BME at 25°C , feed ratio : 2-PMDO/AN = 1/1.

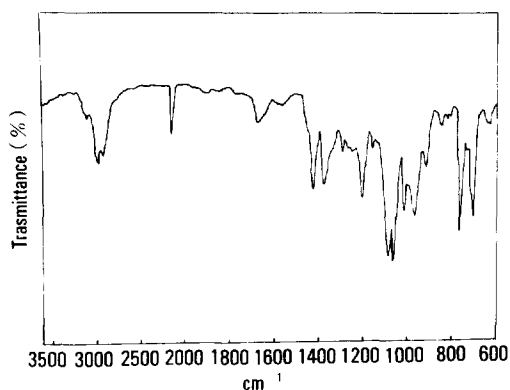


Fig. 6. Infrared spectrum of copolymer of 2-PMDO with AN obtained by photoinitiated polymerization with 3 mol% BME at 25°C , feed ratio : 2-PMDO/AN = 1/1.

unit and 5% of keto-ether linkage formed by ring opening. IR spectrum in Fig. 6 shows a weak band at 1720 cm^{-1} attributable to carbonyl group by ring-opening. Anyway the results obtained in Exp. No. 1~5 verify the possibility of alternating tendency of 2-PMDO with electron accepting monomers.¹⁵

In the case of MMA as a comonomer, the copolymer was predominately composed of MMA in most case in Exp. No. 6~10. Moreover, 10% of 2-PMDO unit was incorporated into the copolymer obtained by Exp. No. 8 with ring-opening.

This result implies that the reactivity of MMA is much higher than that of 2-PMDO. When 2-PMDO was copolymerized with vinylacetate,

resulting copolymer was consisted of 65% of 2-PMDO unit only with ring-opened structure.

The absence of a peak at 5.8 ppm due to the methine proton in the dioxolane ring indicates that copolymerization of 2-PMDO with vinylacetate undergoes with quantitative ring-opening. The above results support that 2-PMDO is more reactive than vinylacetate toward radical.

Monomer, 2-PMDO could not copolymerized well with styrene. The copolymers contained less than 20% of 2-PMDO unit.

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