# Radical Polymerization of 4-Methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane as a Bifunctional Monomer Containing Differential Reactivity

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ABSTRACT: Polymerization of a bifunctional monomer, 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane (**3**), is described. The monomer **3** has both styrene and unsaturated cyclic monomer moieties, which were polymerizable by radical initiation. Additionally, the latter functional moiety could proceed by not only addition but also elimination polymerization; therefore, **3** is anticipated to undergo polymerization of the styrene moiety, addition polymerization of the unsaturated cyclic monomer moiety, and elimination polymerization with formation of benzophenone derivative. However, selective polymerization of the styrene moiety of **3** is achieved in dimethylformamide solution, with complete retention of another radical polymerizable group as a pendant on side chain. Furthermore, bulk polymerization gave a crosslinked polymer, and low concentration reaction caused back biting of its own side chain. These results mean that the reaction concentration has an important effect on the structure of the resulting polymer. The polystyrene-like **poly-3** afforded by dimethylformamide solution polymerization can be regarded as a novel polyfunctional macromonomer for the template polymerization via elimination polymerization.

## Introduction

Bifunctional monomers for radical polymerization such as divinylbenzene, alkylene di(meth)acrylates, and diallyl quaternary ammonium salts are used for crosslinking or cyclopolymerization. Both functional groups of these monomers react in the same way; thus, it is difficult to polymerize selectively one of the functional groups and retain another functional group in the side chain to afford a linear backbone. If the monomer has two kinds of polymerizable groups which are a low copolymerizing combination and have large differences in reactivity, a noncrosslinked soluble polymer whose main chain is formed by a higher reactive functional group will be obtained with suspending pendants of the remaining lower reactive group. Furthermore, the remaining functional group on the side chain in every repeating unit does not lose reactivity and will be allowed to undergo polymer reaction under the more fitting condition. These functional polymers can be used for self-crosslinkable materials.

Recently, Hiraguri and Endo[1] proposed a new radical elimination polymerization to give a polyketone using an unsaturated cyclic monomer, 2,2-diphenyl-4-methylene-1,3-dioxolane (**1**). The monomer **1** gave a poly(2-oxotrimethylene) (**2**) with quantitative elimination of benzophenone initiated by di-*tert*-butyl peroxide in chlorobenzene at 120 °C (Scheme I). The well-known monomers for elimination polymerization release gaseous molecules, e.g., diazomethane, to give a polymethylene with nitrogen or *N*-carboxyamino acid anhydride, to give a polyamino acid with carbon dioxide. Therefore, it is a novel style that the polymerization of **1** accompanies elimination of nonvolatile compound.

Herein we wish to describe the polymerization of a novel bifunctional monomer, 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane (**3**), which has a styrene and an unsaturated cyclic monomer **1** moiety. From the presented result,[2] equimolar bulk copolymerization of **1** with styrene at 120 °C provided a styrene-rich copolymer of poly(2-oxotrimethylene) (composition: St./**2** = 67/33). It indicated that cyclic monomer **1** is less active than styrene, and therefore selective vinyl polymerization of the styrene moiety of **1** is anticipated to take place with suspension of the remaining cyclic monomer moiety, notwithstanding both C–C double bonds have radical polymerizability. Worthy of special mention, the polystyrene-like **poly-3** is different from a general polyfunctional macromonomer because it can proceed with elimination polymerization on the side chain. This means that poly(2-oxotrimethylene) is born from the orderly unsaturated cyclic monomer moiety in the side chain, and it can be regarded as a novel template polymerization (Scheme II).

## Experimental Section

**Measurements.** IR spectra were recorded on a JEOL JIR-5300 spectrophotometer. NMR spectra were obtained on JEOL JNM PMX EX-90 (90 MHz) and JEOL JNM PMX60SI (60 MHz) spectrometers. Molecular weights were determined by a gel permeation chromatograph (GPC) based on standard polystyrenes using a Toyo Soda HPLC CCP & 8000 system equipped with TSK gels G2500H, G4000H, and G5000H columns at 35 °C in tetrahydrofuran (THF).

**Materials.** The synthesis of 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane (**3**) was carried out by the reported method[3] and purified by column chromatography (benzene–hexane (1:4), activated aluminum oxide) before use. Chlorobenzene was washed several times with concentrated sulfuric acid, aqueous sodium bicarbonate, and water followed by drying with anhydrous magnesium sulfate. Distillate over calcium hydride was stored over 4-Å molecular sieves. Dimethylformamide (DMF) was reduced at 3 mmHg to remove decompose contaminants (dimethylamine and carbon monoxide) at ambient temperature for 1 h, followed by stirring over powdered calcium hydride for 30 min, and then distilled under reduced pressure below 80 °C and stored over 4-Å molecular sieves. Before use, a small amount of decomposition contaminants was removed under vacuum. 2,2-

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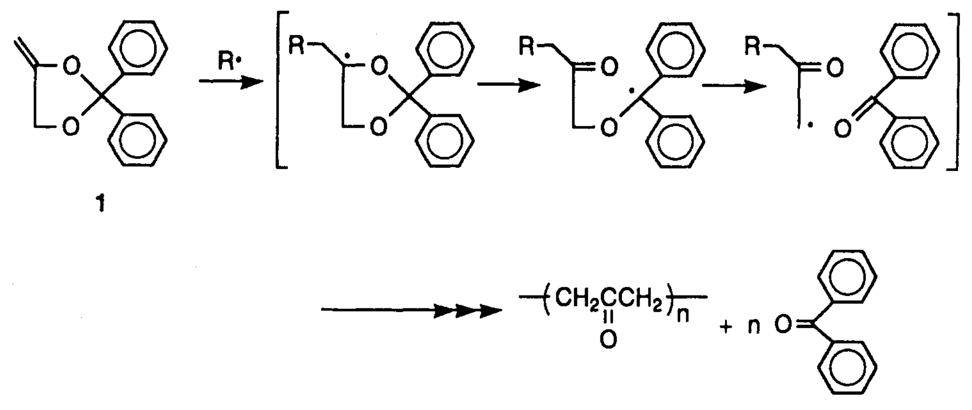
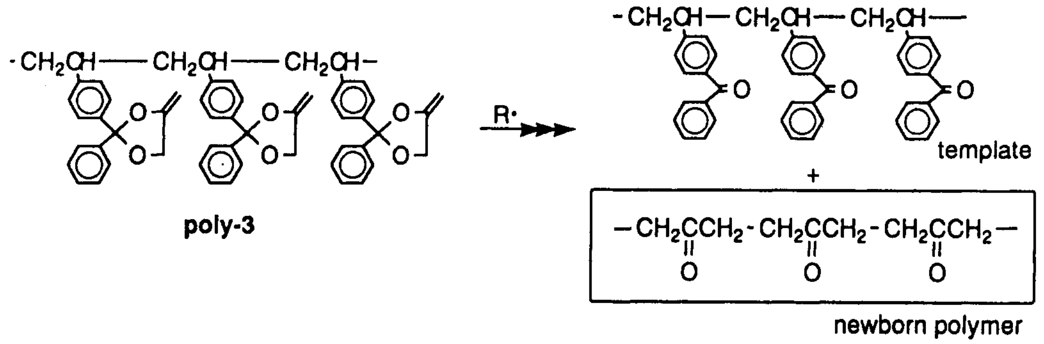
Scheme I



Scheme II



Azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DTBP) were obtained commercially and used as received.

**Typical Procedure of Radical Polymerization.** A mixture of 3 (6010 mg, 22.7 mmol), AIBN (74.7 mg, 2 mol %), and DMF (30.05 g, 500 wt %) was heated in a degassed sealed glass tube at 60 °C. After 10 h, the reaction mixture was dropped into a 20-fold amount of methanol–triethylamine (200:1) solvent mixture. The polymer obtained was corrected by filtration and purified by dissolution in methylene chloride, followed by reprecipitation in basic methanol. **4e** (consisting of unit A): IR (KBr) 1687 (C=C), 1448, 1279, 1070 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) 0.3–2.8 (br, 3H), 3.5–4.1 (br, 1H), 4.1–4.7 (br, 3H), 5.7–7.7 (br, 9H). Dilution method: a mixture of **3** (1057 mg, 4.0 mmol), AIBN (13.1 mg, 2 mol %), and DMF (80 mL) was heated for 24 h and then poured into 1600 mL of basic methanol. The collected polymer was purified by reprecipitation.

**Estimation of the Polymer Composition.** The polymer which showed unimodal elution curve by GPC was estimated excluding unit B. If the polymer showed no IR absorption at 1657 (ArC=OAr) or 1711 ($-CH_2C{=}OCH_2-$) $cm^{-1}$, it was estimated including neither unit C nor K. For the rest, the composition of units A, C, and K was calculated by ratio of the intensity of the signals of $^1H$ NMR spectra. The ratio of units A, C, and K was determined by the following eqs 1–3.

$$a = \frac{[\text{dioxolane}]/4}{[\text{aromatic}]/9}100 \qquad (1)$$

$$k = \frac{\{[\text{aliphatic}] - 3/9[\text{aromatic}]\}/4}{[\text{aromatic}]/9}100 \qquad (2)$$

$$c = 100 - a \qquad (3)$$

Herein, [aromatic] means intensity of the signals for the aromatic protons (5.7–7.7, 9H of units A and C), [dioxolane] means intensity of the olefinic and allylic protons of the methylenedioxolane (3.5–4.7, 4H of unit A), and [aliphatic] means intensity of the backbone and polyketone's methylene protons (0.3–2.8, 3H of units A and C + 4H of unit K). The intensity of the [polyketone] (4H of unit K) was calculated after subtracting [backbone] (3H of units A and C) from [aliphatic], and [backbone] was given by three ninths of [aromatic].

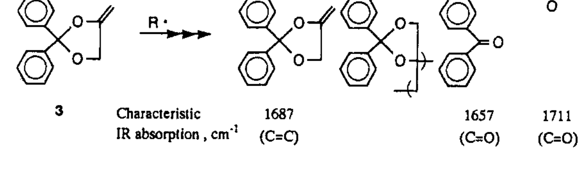
Table I. Radical Polymerization of 3[a]

| run | solvent, wt % | time, h | polymer | yield,[b], wt % | $\bar{M}_n$, $10^{-4}$ | $\bar{M}_w/\bar{M}_n$[c] | solubility[d] to THF |
|---|---|---|---|---|---|---|---|
| 1 | bulk | 1 | **4a** | 74 | | | – |
| 2 | bulk | 0.25 | **4b** | 11 | | | – |
| 3 | PhCl, 500[e] | 12 | **4c** | 69 | 2.1[h,i] | | ± |
| 4 | PhCl, 500[e] | 1 | **4d** | 11 | 4.6[h] | 2.2[h] | ± |
| 5 | DMF, 500[f] | 10 | **4e** | 60[g] | 2.9 | 3.1 | + |

[a] Heated at 60 °C in a degassed sealed tube with AIBN (2 mol %). [b] Insoluble in hexane. [c] Estimated by GPC (based on PSt). [d] Key: +, soluble; ±, partially soluble and swollen part remained; –, insoluble. [e] 0.84 mol $L^{-1}$. [f] 0.71 mol $L^{-1}$. [g] Insoluble in basic methanol. [h] Filtrate of THF suspension. [i] Bimodal.

## Results and Discussion

**Solvent Effect on Radical Polymerization of 3.** The monomer **3** has polymerizable styryl and exomethylene groups, and the polymerization rate of the styryl group is expected to be much faster than the exomethylene group. Thus, four types of units in the polymer were anticipated: unit A formed by addition polymerization of the styryl moiety, unit B formed by addition polymerization of both the styryl and the exomethylene moiety, and units C and K formed by elimination polymerization of unit A (eq 4).



(4)

The polymerization was carried out in the presence of AIBN at 60 °C in a degassed sealed tube. The results are shown in Table I.

In bulk polymerization, crosslinking took place after 1 h. In the initial stage (15 min), the reaction mixture still had fluidity and gave a homogeneous solution by addition of methylene chloride, but the polymer obtained after

**Table II. Radical Polymerization in Dilute Solution**[a]

| run | solvent[b] | time, h | polymer | yield,[c] wt % | $\bar{M}_n$,[d] $10^{-3}$ | $\bar{M}_w$/$\bar{M}_n$[d] | composition[e] A/C/K |
|---|---|---|---|---|---|---|---|
| 6 | PhCl | 12 | **4f** | 9 | 7.8 | 2.9 | 56/44/20 |
| 7 | DMF | 12 | **4g** | 18 | 9.7 | 2.3 | 66/34/32 |
| 8 | DMF[f] | 12 | **4h** | 27 | 10.5 | 3.1 | 73/27/12 |
| 9 | DMF | 24 | **4i** | 29 | 7.1 | 2.0 | 62/38/41 |

[a] Heated at 60 °C with 2 mol % of AIBN in sealed tube. [b] 0.05 mol $L^{-1}$. [c] Insoluble in basic methanol. [d] Estimated by GPC (based on PSt). [e] Estimated by $^1$H NMR. [f] 0.1 mol $L^{-1}$.

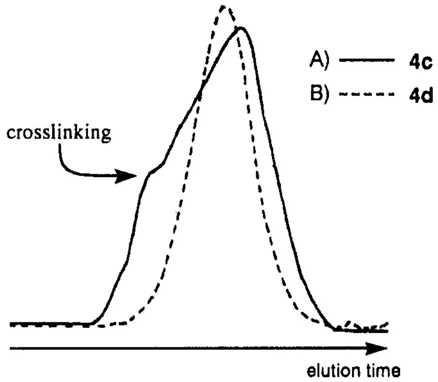
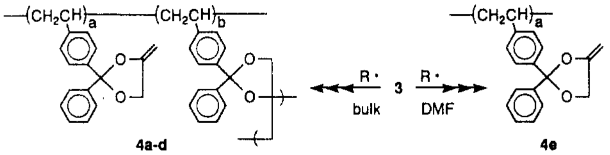


**Figure 1.** GPC curves of the polymers prepared at 60 °C in PhCl reacted for (A) 12 h (**4c**) and (B) 1 h (**4d**).

precipitation into hexane was not redissolved completely in methylene chloride or THF any more. This insolubilization was caused by formation of unit B. Since any IR absorption was not detected at 1657 cm$^{-1}$ based on benzophenone's C=O bond or 1711 cm$^{-1}$ based on 2-oxotrimethylene's C=O bond, the polymer obtained by bulk polymerization was supposed to consist of units A and B without C or K (runs 1 and 2). Under the high monomer concentration like the bulk condition, a propagating terminal radical is assumed to attack not only the styryl group but also the exomethylene group, followed by addition to the next monomer before ring-opening isomerization (eq 5).



(5)

On the other hand, solution polymerization in DMF proceeded homogeneously (run 5). The corrected polymer which did not have any absorption of C=O bond (1657 or 1711 cm$^{-1}$) was easily dissolved in methylene chloride or THF, and the GPC profile showed a unimodal elution curve. It indicated that neither ring-opening polymerization nor crosslinking took place, and the polymer consisted of only unit A (eq 5).

The solution polymerization in chlorobenzene (runs 3 and 4) also gave the polymer without ring-opening. However, the GPC profile of **4c** showed a discernible shoulder at a higher molecular weight region, which implied inclusion of a few crosslinking points in the polymer due to unit B (Figure 1, A). This tendency was not conspicuous at the initial stage (Figure 1, B). Since the propagating polymer is thought to be less solvated in chlorobenzene than DMF, aggregation of the polymer might be induced, and crosslinking like as in bulk polymerization could not be avoided in chlorobenzene.

**Dilute Polymerization.** By comparison of the results between bulk and DMF solution reaction, low concentration of the exomethylene moiety might be responsible for exclusion of the unit B. Thus, high dilute polymerization would expect to give the polymer containing no unit B even in chlorobenzene (Table II). The settled concentration was 0.05 mol L$^{-1}$, about the 1/17 of run 3.

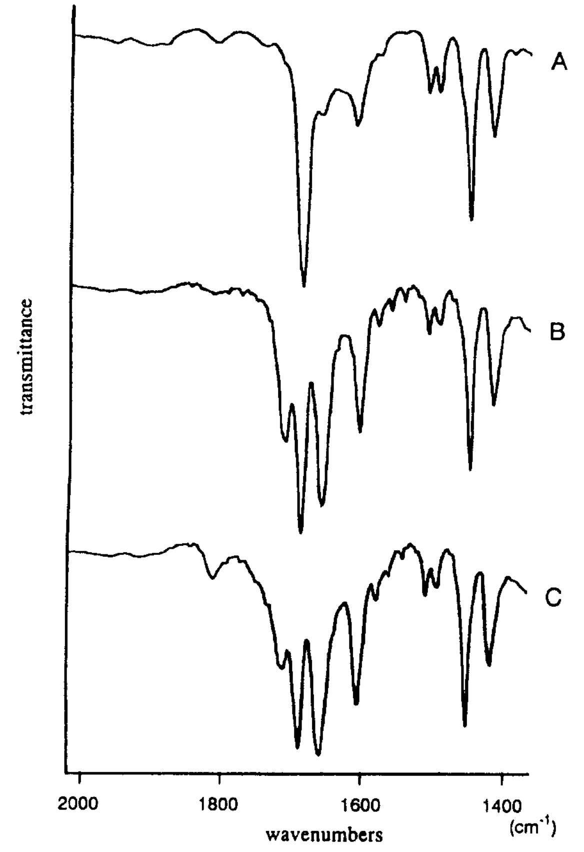


**Figure 2.** IR spectra of the polymers: (A) **4e** from DMF solution method at 60 °C, (B) **4i** from DMF dilution method at 60 °C; (C) **4j** from PhCl solution method at 120 °C.

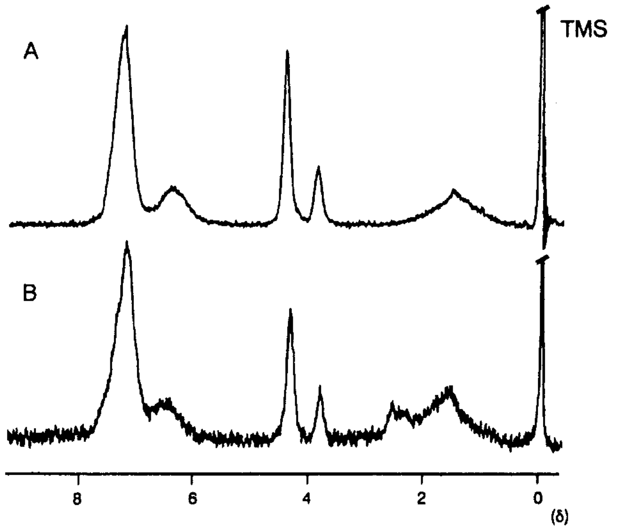
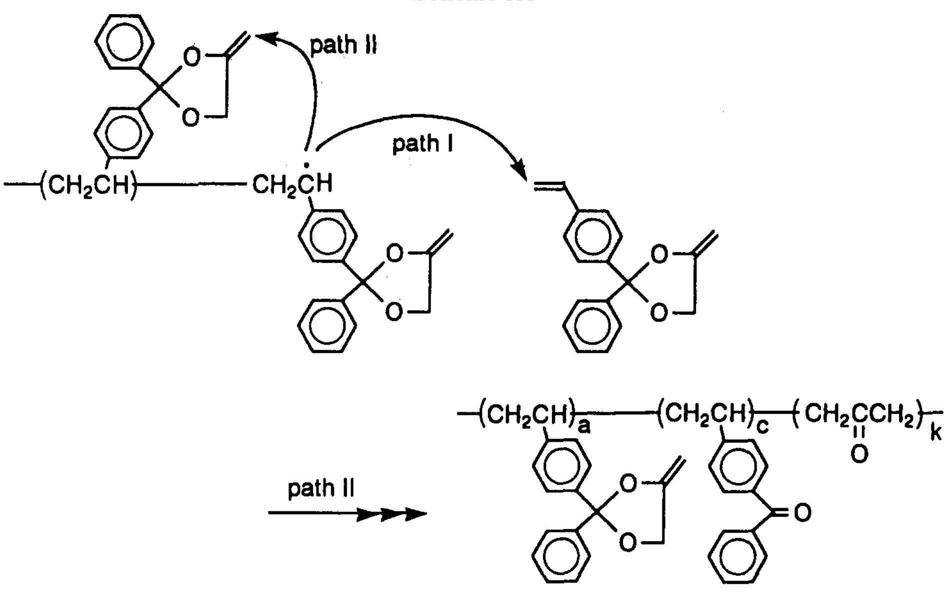


**Figure 3.** $^1$H NMR spectra of the polymers: (A) **4e** from DMF solution method at 60 °C; (B) **4i** from DMF dilution method at 60 °C.

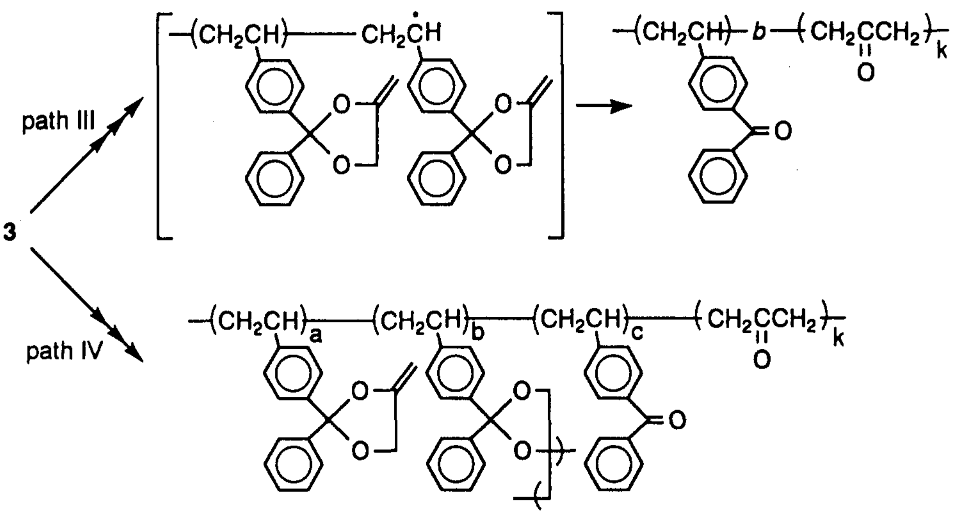
Although the yields became lower than run 3 or 5, all of the obtained polymers were easily dissolved in methylene chloride or THF, and GPC showed unimodal elution curves. It was in accord with the expectation that crosslinking based on unit B did not occur. However, these polymers had IR absorptions at 1657 and 1711 cm$^{-1}$ attributable to the units C and K (Figure 2, B). The $^1$H NMR spectra of the polymer showed that unit A was decreased to 56–73% (Figure 3).

**Scheme III**



**4f-i**

**Scheme IV**



**4j**

Since the length between a propagating radical and the styrene moiety of the next monomer became much longer as compared with the monotonous length between the radical and its own neighboring side chain in a dilute solution, the intermolecular polymerization rate (Scheme III, path I) may be decreased with respect to the intramolecular polymerization rate (path II), although the styryl moiety has higher reactivity than the exomethylene group. Consequently, back biting of the terminal radical often occurred, followed by smooth isomerization to acetonyl radical and polyvinylbenzophenone unit to afford terpolymer consisting of units A, C, and K.

**Polymerization at High Temperature.** Polymerization was also carried out at higher temperature, expecting speedy formation of polystyrene-like polymer followed by elimination polymerization at once in one pot to make a block copolymer (Scheme IV, path III). Then, 3 in 500 wt % of chlorobenzene was heated at 120 °C for 6 h with 2 mol % of DTBP. The obtained polymer 4j (yield 89 wt %) showed IR absorptions of the units C and K, indicating that the elimination polymerization also proceeded. However, an absorption at 1687 cm$^{-1}$ based on the C=C bond of unit A remained (Figure 2, C). Furthermore, this polymer was not soluble but swollen in methylene chloride, which suggested inclusion of the unit B also. In this condition, one pot reaction without crosslinking could not be attained, and all four of the units were formed (Scheme IV, path IV).

Table III. Contents of the Obtained Polymers

| method | polymer | unit[a] A | unit[a] B | unit[a] C | unit[a] K |
|---|---|---|---|---|---|
| A, 60 °C, bulk | **4a,b,c,d** | O | O | X | X |
| B, 60 °C, solution | **4e** | O | X | X | X |
| C, 60 °C, high dilution | **4f,g,h,i** | O | X | O | O |
| D, 120 °C, solution | **4j** | O | O | O | O |

[a] O: include. X: exclude.

## Conclusion

The bifunctional monomer 3 showed three kinds of reaction, polymerization of the styrene moiety, addition polymerization of the 4-methylene-1,3-dioxolane moiety, and elimination polymerization in the presence of radical initiator. Combination of them supplied four kinds of polymers summarized in Table III: (A) bulk method at 60 °C included crosslinking (units A and B), (B) solution method at 60 °C excluded crosslinking (unit A), (C) high-dilution method at 60 °C excluded crosslinking but included ring-opening (units A, C, and K), and (D) solution method at 120 °C included crosslinking and ring-opening (units A, B, C, and K). This conclusion is interesting for chemoselective addition polymerization of two differential functionalized monomers because concentration dramatically affects the polymer product structure, irrespective of the same initiation system by AIBN.

In closing, it was shown that the prepolymer for the described template polymerization was prepared by solution method at 60 °C. A new template polymerization of **poly-3** (**4e**) via radical ring-opening isomerization will be reported soon.

## References and Notes

(1) Hiraguri, Y.; Endo, T. *J. Am. Chem. Soc.* **1987**, *109*, 3779.

(2) Hiraguri, Y.; Endo, T. *J. Polym. Sci., Polym. Lett. Ed.* **1989**, *27*, 1.

(3) Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.*, in press.