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# Novel Template Polymerization via Radical Ring-Opening Isomerization. 2. Polymerization of Copolymer Obtained from 4-Methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolanes with Styrene[1]

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ABSTRACT: Simultaneous separating template polymerizations of copolymers **4a** and **4b** obtained from 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolanes with styrene were carried out. Polymerizable functional groups on the side chain of **4** underwent chain reaction with a free radical initiator to afford poly(oxotrimethylene) as a newborn polymer **7N** accompanying release of copoly(vinylbenzophenone/styrene) as a template polymer **7T**. The postpolymers **7N** and **7T** were divided by fractional precipitation without postchemical treatment. The efficiency of separation was estimated by the composition of poly(oxotrimethylene) as K % in the fraction. All K % values on this paper were higher than the K % value of the template polymerization employing the homopolymer of 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane. It was attributed to dilution of the local concentration by the comonomer segment, which excluded the ring-intact addition to afford a grafting point between the newborn and template polymers. The prepolymer **4b** containing a methyl group on the dioxolane ring gave the most excellent K % value. GPC elution curves of the newborn polymer obtained from **4b** indicated that the newborn polymer was given by complete separation from the template polymer simultaneously.

## Introduction

The 4-methylene-1,3-dioxolanes have been investigated as rare monomers that can undergo radical ring-opening polymerization.[2-11] In particular, 2,2-diphenyl-4-methylene-1,3-dioxolane is interesting because it undergoes quantitative elimination polymerization to afford poly(oxotrimethylene) with equimolar benzophenone by radical initiation.[12] Recently, we have applied this reaction to novel template polymerization and achieved radical elimination polymerization of polyfunctional macromonomer 1 on its side chain (Scheme 1).[13] The obtained postpolymer **2** was divided into two parts by fractional precipitation without postchemical treatment. The DMF soluble part abounded with template polymer T, and the DMF insoluble part abounded with newborn polymer N, correspondingly. Thus it has demonstrated the new concept that *polymers bear polymers*.

However, each divided part contained some of another part; for example, solution polymerization of **1** in DMF (0.5 mol $L^{-1}$) gave the DMF insoluble polymer that consisted of 73% poly(oxotrimethylene) and 27% poly(vinylbenzophenone). It has been reported that the polymerization of 2,2-diphenyl-4-methylene-1,3-dioxolane in high concentration caused ring-intact polymerization as a side reaction.[12c] When ring-intact polymerization occurred on the side chain of **1** in a similar manner, the ring-intact unit would play the role of grafting point G between the newborn and template polymer, and the DMF insoluble part was contaminated by the template polymer. The polymerizable moiety of **1** was attached to the prepolymer's backbone, the local concentration of which may not be varied so much by the amount of solvent. The copolymer-type prepolymer was therefore a candidate to exclude the grafting point since the local concentration of the polymerizable moiety of **1** became lower than that of the homopolymer-type prepolymer. In this paper, preparation and template polymerization of copolymer-type prepolymer **4a** and its methyl-substituted prepolymer **4b** are disclosed.

## Experimental Section

**Measurements.** IR spectra were recorded on a JEOL JIR-5300 spectrophotometer. NMR spectra were obtained on a JEOL JNM PMX EX-90 (90 MHz) and a JEOL JNM PMX 60Si (60 MHz) spectrometer. Molecular weights were determined by a gel permeation chromatograph (GPC) based on standard polystyrene using a Toyo Soda HPLC CCP & 8000 system equipped with columns of TSK gels G2500H, G4000H, and G5000H at 35 °C or a JASCO TRIROTAR-III system equipped with Shodex KF-800P and A-8025 columns at 40 °C in tetrahydrofuran.

**Materials.** 4-Methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane (**3a**) was prepared by the reported method.[14] Styrene was washed with aqueous 5% sodium hydroxide, then distilled water, followed by drying over magnesium sulfate, and distilled under reduced pressure (63 °C/43 mmHg). Acrylonitrile was washed with diluted sulfuric acid, distilled water, aqueous sodium bicarbonate, and distilled water, followed by drying over magnesium sulfate, and then distilled (78 °C/1 atm). *N,N*-Dimethylformamide (DMF) was first stirred in vacuo (3 mmHg) to remove decomposed contaminants (dimethylamine and carbon monoxide) at ambient temperature for 1 h, followed by stirring over powdered calcium hydride for 30 min, then distilled under reduced pressure below 80 °C, and stored over 4 Å molecular sieves. Just before use, a small amount of decomposed contaminants was removed under vacuum. 2,2-Azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DTBP) were obtained commercially and used as received.

**Preparation of 2-(Chloromethyl)-3-methyloxirane (5b).** A mixture of *cis,trans*-crotyl chloride (15.00 g, 165.7 mmol) and *m*-chloroperoxybenzoic acid (35.73 g, 207.0 mmol) in 200 mL of methylene chloride was stirred at ambient temperature. After

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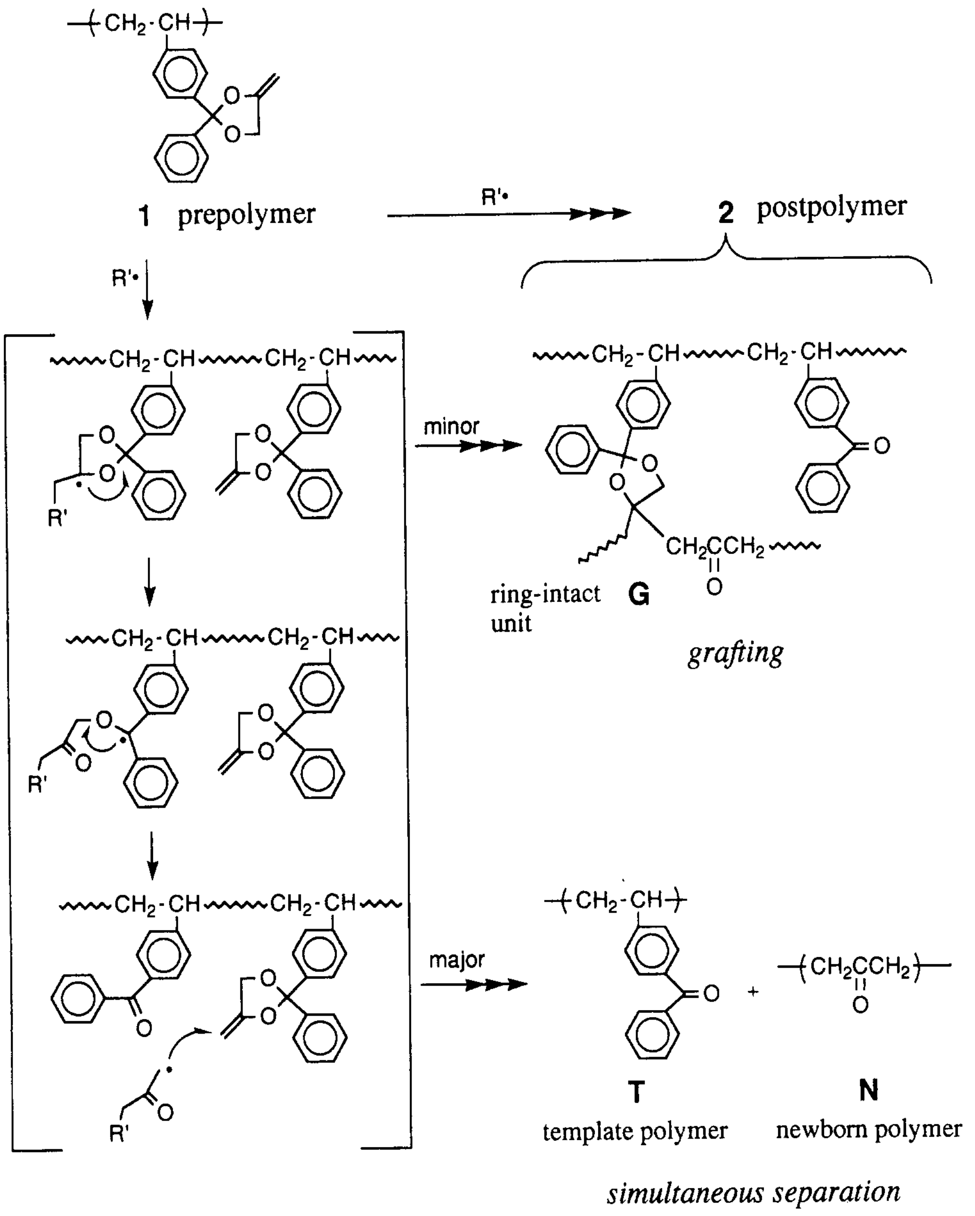
Scheme 1



6 h, the insoluble solid was filtered off, and the filtrate was chilled in a freezer. The obtained crystal was filtered off again, and then the crude product was collected in a cold trap by flush distillation (42–75 °C/760–56 mmHg). Pure **5b** was collected by fractional distillation (56 °C/56 mmHg) over calcium hydride as a colorless liquid. Yield: 6.79 g (38%).

**Preparation of 2-[4-(2-Bromoethyl)phenyl]-4-(chloromethyl)-5-methyl-2-phenyl-1,3-oxolane (6b).** To a solution of 4-(2-bromoethyl)benzophenone (20.27 g, 70.1 mmol) in 100 mL of dry methylene chloride was added boron trifluoride etherate (452 mg, 3.2 mmol) at ambient temperature. **5b** (6.79 g, 63.7 mmol) in 30 mL of dry methylene chloride was added dropwise over 15 min into the mixture, and then the solution was stirred for 1 h. The reaction was quenched by 1 mL of triethylamine and washed with saturated aqueous sodium bicarbonate. The organic layer was dried over magnesium sulfate and then concentrated. Subsequent column chromatography (benzene–hexane (1:1) mixture) on $SiO_2$ gave **6b** as a colorless liquid. Yield: 18.97 g (75%).

**Preparation of 5-Methyl-4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-oxolane (3b).** To a suspension of potassium *tert*-butoxide (26.93 g, 240.0 mmol) in 150 mL of dry tetrahydrofuran (THF) was added dropwise **6b** (18.97 g, 47.9 mmol) in 50 mL of THF over 40 min at 0 °C. After stirring for 15 h at ambient temperature, THF was removed by vacuum distillation, maintaining the temperature below 30 °C. When **3b** was heated under basic conditions, it isomerized to 4,5-dimethyl-2-phenyl-2-(4-vinylphenyl)-1,3-dioxole by a 1,3-hydrogen shift. Chilled water was added to the residue and then extracted with ether three times. The ether layer was washed with saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and then concentrated. The crude product was subjected to column chromatography (benzene–hexane (1:4) mixture) on activated aluminum oxide to afford **3b** as a colorless liquid. Yield: 7.00 g (52%).

**Typical Procedure of the Radical Copolymerization of 3.** A mixture of **3a** (15.00 g, 56.7 mmol), styrene (5.91 g, 56.7 mmol), azobis(isobutyronitrile) (AIBN) (373 mg, 2.3 mmol), and DMF (150 g) was heated at 60 °C in a glass tube sealed after degassing. After 12 h, the reaction mixture was poured into a 20-fold excess of basic methanol (methanol–triethylamine (200:1)). The polymer **4a** was collected by filtration as a white powder and purified by reprecipitation from methylene chloride in basic methanol. Yield: 8.50 g (41%).

**Typical Procedure of the Template Polymerization of 4a.** A mixture of **4a** (1300 mg), DTBP (25.8 mg, unit A:DTBP = 100:5), and DMF (14.1 mL) was heated at 130 °C in a degassed sealed glass tube for 12 h. Precipitate **7e** collected by centrifugation was dissolved in 10 mL of hot dimethyl sulfoxide (DMSO), and the solution was chilled to ambient temperature, following centrifugation. This procedure was repeated three times. The precipitate was suspended in methylene dichloride following reprecipitation into basic methanol, after centrifugation. This procedure was repeated once again, and the precipitate was dried *in vacuo*. Yield of **7e**: 85 mg (7 wt %). The composition of **7e** was estimated by $^1$H NMR at 120 °C in DMSO-$d_6$. The clarified supernatant of the reaction mixture and washings was poured into a 20-fold excess of basic methanol. Precipitate **7f** was collected by filtration through a Shibata 1G4 type crucible glass filter and dried *in vacuo*. Yield of **7f**: 1123 mg (86 wt%).

**Typical Procedure of the Template Polymerization of 4b.** A mixture of **4b** (2000 mg), DTBP (35.6 mg, unit A:DTBP = 100:5), and DMF (22.1 mL) was heated at 130 °C in a degassed sealed glass tube. After 36 h, the reaction mixture was poured into a 20-fold excess of basic methanol. Basic methanol insoluble polymer **7n** was collected by filtration as a white powder and reprecipitated from methylene chloride in basic methanol. Yield: 1783 mg (89 wt %). The filtrate was concentrated, the residue was dissolved in methylene dichloride (2 mL), and the solution was then poured into *n*-hexane (50 mL). *n*-Hexane insoluble polymer **7m** was collected by decantation, and dried *in vacuo*. Yield: 168 mg (8 wt %).

**Estimation of the Polymer Composition.** The concentration of units A, B, C, M, and K was calculated from $^1$H NMR integration. The composition of prepolymer **4a** was estimated to be $a_0$ and $m_0$ by eqs 1–4, where [aromatic] means the intensity

$$a_0 + m_0 = 100 \tag{1}$$

$$\frac{[\text{dioxolane}]}{[\text{aromatic}]} = \frac{a_0/100 \times 4}{a_0/100 \times 9 + m_0/100 \times 5} \tag{2}$$

$$a_0 = \frac{{}^5/_4[\text{dioxolane}]}{[\text{aromatic}] - [\text{dioxolane}]} \times 100 \tag{3}$$

$$m_0 = 100 - a_0 \tag{4}$$

of the signals for the aromatic protons ($\delta$ 6.1–8.1) and [dioxolane] means the intensity of the olefin and allylic protons of the 4-methylene-1,3-dioxolane ($\delta$ 3.7–4.7).

Relative concentrations of each unit in all the postpolymers were determined as $a'$, $b'$, $c'$, $m'$, and $k'$ by eqs 5–9, where

$$H_{\text{Ar}} = (9a_0 + 5m_0)/100 \tag{5}$$

$$a' = \frac{[\text{dioxolane}]/4}{[\text{aromatic}]/H_{\text{Ar}}} \times 100 \tag{6}$$

$$b' + c' = a_0 - a' \tag{7}$$

$$m' = m_0 \tag{8}$$

$$k' = \frac{[\text{polyketone}]/4}{[\text{aromatic}]/H_{\text{Ar}}} \times 100 \tag{9}$$

[polyketone] means the intensity of the oxotrimethylene's proton ($\delta$ 2.5–2.9). The number average of the aromatic proton per one repeating unit of the prepolymer was given as $H_{\text{Ar}}$ by eq 5, which was assumed to be equal even in the template polymer. According to the molecular ratio of ($a'$, $b'$, $c'$, $m'$, $k'$) and the weight yield, the compositions of the divided postpolymers were justified to ($a, b, c, m, k$), where $a_0 + m_0 = 100$ was employed for the criterion.

## Results and Discussions

**Preparation of the Prepolymer.** Comonomer 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane (**3**) was synthesized by acetalization of 4-(2-bromoethyl)benzophenone with substituted oxirane **5**, followed by dehydrohalogenation, as shown in Scheme 2. Prepolymers **4a–c** were prepared by copolymerization of **3** with styrene (St) or acrylonitrile (AN), as shown in Scheme 3.

The units in copolymer **4** were anticipated to be five units A, B, C, K, and M: unit A formed by polymerization of the styrene moiety of **3**, unit B formed by addition polymerization of both the styrene moiety and *exo*-methylene group of **3**, units C and K formed by elimination polymerization of unit A, and unit M formed from styrene or acrylonitrile. However, all the copoly(**3**/styrene)s as **4a** and **4b**, which were obtained under the condition summarized in Table 1, showed no IR absorption of the carbonyl group based on benzophenone or oxotrimethylene. The IR spectra of the polymer run 1 (**4a$_1$**) and run 5 (**4b**) are shown in Figures 1A and 4A. These spectra indicated that copolymers **4a** and **4b** included neither unit C nor K. The polymers in Table 1 except run 6 were easily dissolved in methylene chloride or THF, and GPC showed a unimodal elution curve. Thus including unit B was also denied. These results supported the solution copolymerization of **3** with styrene proceeding chemoselectively and affording the polymer consisting of units A and M only with retention of the *exo*-methylene group on dioxolane. Since the compositions of **4a** and **4b** were consistent with the feed ratio of the monomers, the reactivities of styrene and the styrene moiety of **3** might be nearly equal. Therefore **4a** and **4b** were assumed to be statistical copolymers and the local concentration of the *exo*-methylene groups might be diluted by styrene units.

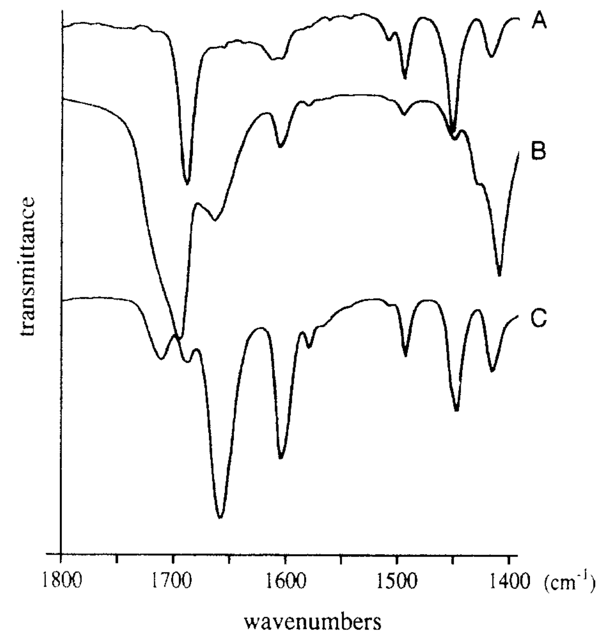
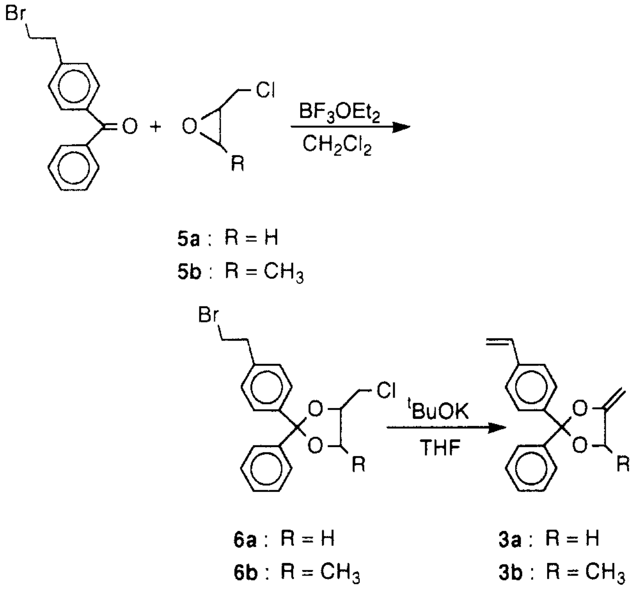


**Figure 1.** IR spectra of (A) prepolymer **4a$_1$**, (B) DMF insoluble postpolymer **7a**, and (C) DMF soluble postpolymer **7b**.

**Scheme 2**



**Scheme 3**

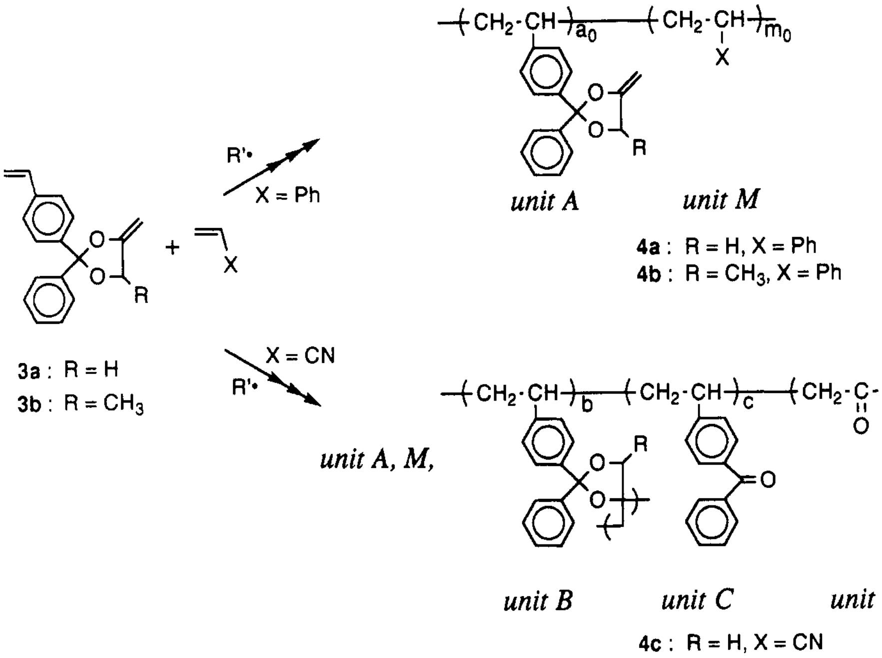


**Table 1. Radical Copolymerization of 3a with Styrene**[a]

| run | $M_1$ | $M_1$/St | solvent; concn, mol $L^{-1}$ | $P_1$[b] | yield,[c] wt % | $10^{-4}\bar{M}_n$[d] | $\bar{M}_w/\bar{M}_n$[d] | composition[e] $a_0/m_0$ |
|---|---|---|---|---|---|---|---|---|
| 1 | **3a** | 50/50 | DMF; 0.71 | **$4a_1$** | 41 | 1.9 | 2.2 | 50/50 |
| 2 | **3a** | 30/70 | DMF; 1.19 | **$4a_2$** | 48 | 1.1 | 1.8 | 31/69 |
| 3 | **3a** | 5/95 | DMF; 3.57 | **$4a_3$** | 34 | 1.7 | 1.9 | 6/94 |
| 4 | **3a** | 30/70 | PhCl; 1.40 | **$4a_4$** | 51 | 1.3 | 1.9 | 30/70 |
| 5 | **3b** | 50/50 | DMF; 0.71 | **4b** | 48 | 1.1 | 2.0 | 40/60 |
| 6 | **3a** | 30/70 | bulk | **$4a_6$** | 98 (gel) | | | |

[a] Heated at 60 °C for 12 h in a degassed sealed tube with AIBN (2 mol %). [b] Copolymer. [c] Insoluble in basic methanol. [d] Estimated by GPC (based on PSt). [e] Estimated by $^1H$ NMR.

**Table 2. Radical Copolymerization of 3a with Acrylonitrile**[a]

| run | 3a/AN | solvent; concn, mol $L^{-1}$ | time, h | yield,[b] wt % | $10^{-4}\bar{M}_n$[c] | $\bar{M}_w/\bar{M}_n$[c] |
|---|---|---|---|---|---|---|
| 7 | 50/50 | DMF; 0.71 | 12 | 79 (gel) | | |
| 8 | 50/50 | benzene; 0.66 | 12 | 74 (gel) | | |
| 9 | 30/70 | benzene; 0.66 | 12 | 72 (gel) | | |
| 10 | 50/50 | benzene; 0.66 | 2 | 21[d] | 2.9 | 3.3 |

[a] Heated at 60 °C in a degassed sealed tube with AIBN (2 mol %). [b] Insoluble in basic methanol. [c] Estimated by GPC (based on PSt). [d] Composition: $a_0/(b_0 + c_0 + k_0)/m_0 = 52/18/30$ (estimated by $^1H$ NMR).

The cross-linked polymer obtained from run 6 was based on the inclusion of unit B. Formation of unit B might be explained as follows: the terminal radical of the propagating polymer preferred to attack styrene or the styrene moiety of 3 rather than the *exo*-methylene group on the basis of each olefin's different polymerizability but could not attack selectively under high concentrations like the bulk conditions.

On the other hand, all of copoly(3a/acrylonitrile) 4c, which was obtained under the conditions summarized in Table 2, included units C and K, supported by IR absorptions (Figure 2). In particular one should note that run 10 showed that attack of free radical on the *exo*-methylene group frequently took place even at the initial stage without cross-linking. These results implied that the terminal radical of acrylonitrile having electrophilic character preferred attacking the *exo*-methylene group that was on one of the electron-rich olefins as a cyclic vinyl ether.

**Template Polymerization.** The prepolymers **4a** and **4b** consisting of units A and M only were used for the template polymerization. We have already reported[13] that DMF was appropriate for the solvent of this template polymerization because other solvents, e.g., chlorobenzene, could not well solvate the prepolymer and then unit B was formed. When **$4a_1$** (prepared from run 1, $a_0/m_0 = 50/50$) was treated with DTBP as a radical initiator at 120 °C for 12 h, postpolymer **7** was obtained as DMF insoluble part **7a** and DMF soluble part **7b** after centrifugation (Table 3,Scheme 4). The IR spectrum of **7b** showed an absorption at 1711 $cm^{-1}$ assignable to the usual aliphatic ketone's C—O stretching, whereas the spectrum of **7a** showed an overlapped bimodal absorption around 1693 $cm^{-1}$ assignable to the associated aliphatic ketones' C—O stretching (Figure 1B,C). This association of a carbonyl group might be based on the high concentration and/or long continuity of unit K. These characteristic absorptions coincided with the absorptions of the reported postpolymers **2T** and **2N** obtained from homopolymer **1**. Fraction **7a** abounded with newborn polymer **7N** because poly(oxotrimethylene) had a poor solubility in DMF or DMSO at ambient temperature. The $^1H$ NMR spectrum of **7a** indicated the existence of part of a template polymer since the aromatic protons' signal was observed (Figure 3). This signal did not disappear after another reprecipitation, indicating inclusion of unit B through which the template polymer connected to the newborn polymer by covalent bonding. The molar ratio of **7N** in **7a** was estimated to be K % which was calculated by (unit K)/(all units). The K % value was not affected by the reaction time (runs 11 and 12), but increased with increasing temperature (run 13).

Table 3. Template Polymerization of **4a**[a]

| run | $P_1$[b] | $a_0/m_0$ | temp, °C | time, h | $P_2$[b,c] | yield,[d] wt % | composition[e] *a* | *b* + *c* | *m* | *K* | K %[f] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | **4a$_1$** | 50/50 | 120 | 12 | **7a** i | 9 | 0 | 2.1 | 2.0 | 16.4 | 80 |
| | | | | | **7b** s | 88 | 10 | 39 | 49 | 8 | |
| 12 | **4a$_1$** | 50/50 | 120 | 24 | **7c** i | 7 | 0 | 1.7 | 1.6 | 13.6 | 80 |
| | | | | | **7d** s | 87 | 3 | 46 | 49 | 8 | |
| 13 | **4a$_1$** | 50/50 | 130 | 12 | **7e** i | 7 | 0 | 1.2 | 1.1 | 15.2 | 87 |
| | | | | | **7f** s | 86 | 2 | 48 | 49 | 6 | |
| 14 | **4a$_2$** | 31/69 | 120 | 24 | **7g** i | 6 | 0 | 0.9 | 2.0 | 8.9 | 76 |
| | | | | | **7h** s | 94 | 6 | 24 | 67 | 4 | |
| 15 | **4a$_3$** | 6/94 | 120 | 24 | **7i** ip | 3 | 0.1 | 0.1 | 2.8 | trace | |
| | | | | | **7j** sp | 97 | 4.3 | 1.9 | 91 | 0.3 | |
| 16 | **4b** | 40/60 | 120 | 24 | **7k** ih | 6 | 0 | 0.4 | 0.6 | 13.7 | 93 |
| | | | | | **7l** im | 81 | 18 | 18 | 53 | <4 | |
| 17 | **4b** | 40/60 | 130 | 36 | **7m** ih | 8 | 0 | 0.5 | 0.8 | 18.0 | 93 |
| | | | | | **7n** im | 89 | 11 | 29 | 61 | <8 | |
| 18[g] | **1** | 100/0 | 120 | 24 | **2a** i | 16 | 0 | 11.7 | | 32.0 | 73 |
| | | | | | **2b** s | 52 | 2 | 60 | | 12 | |

[a] Heated in DMF ($a_0 + m_0$ = 0.5 mol L$^{-1}$; run 15 PhCl) with DTBP ($a_0$:DTP = 1:0.05). [b] $P_1$ = Prepolymer; $P_2$ = postpolymer. [c] i = insoluble in DMF; s = soluble in DMF; ip = insoluble in PhCl; sp = soluble in PhCl; ih = insoluble in hexane; im = insoluble in basic methanol. [d] After centrifugation (run 15: after filtration). [e] Estimated by $^1$H NMR (based on $a_0 + m_0$ = 100). [f] K % = $k/(a + b + c + m + k)$. [g] Reference 13.

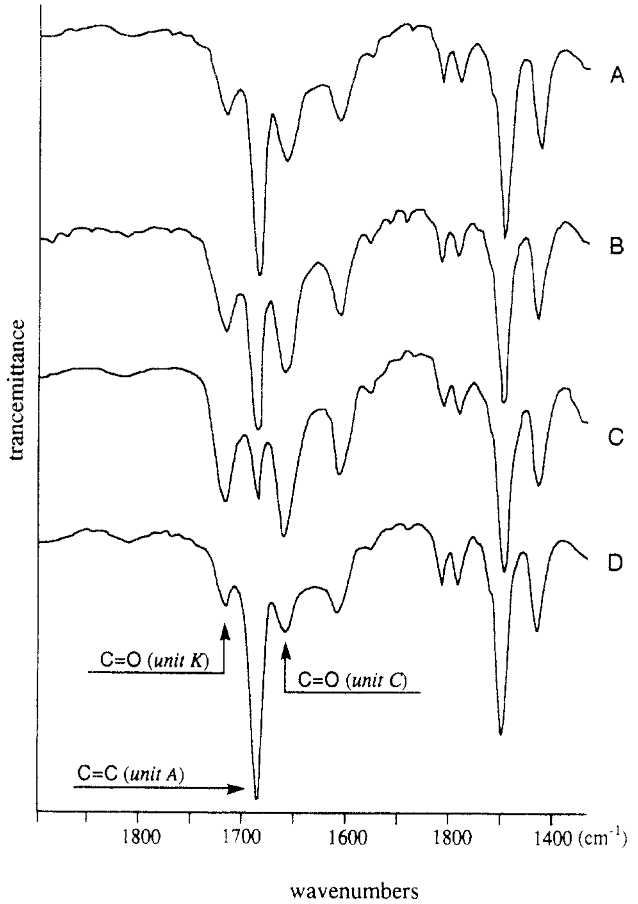
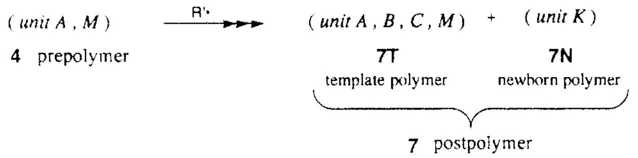


**Figure 2.** IR spectra of copoly(**3a**/acrylonitrile) **4c** obtained from (A) run 7, (B) run 8, (C) run 9, and (D) run 10.

### Scheme 4



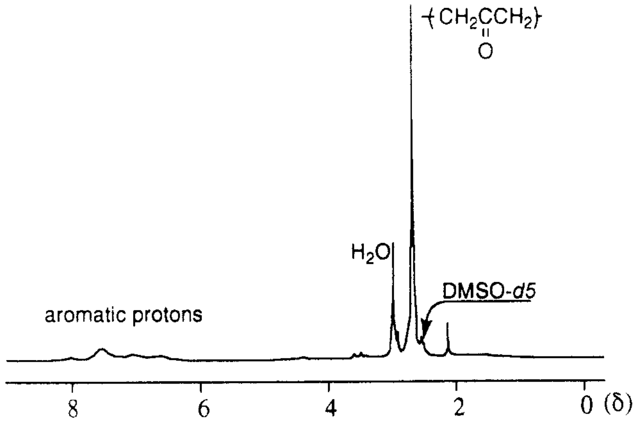


**Figure 3.** $^1$H NMR spectrum of postpolymer **7a**.

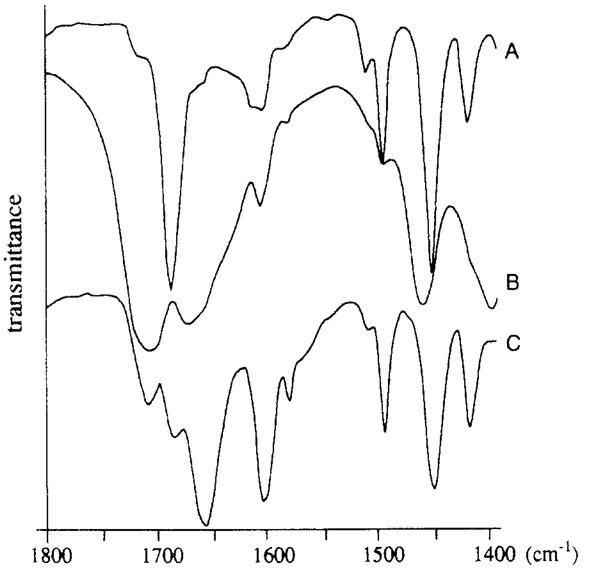
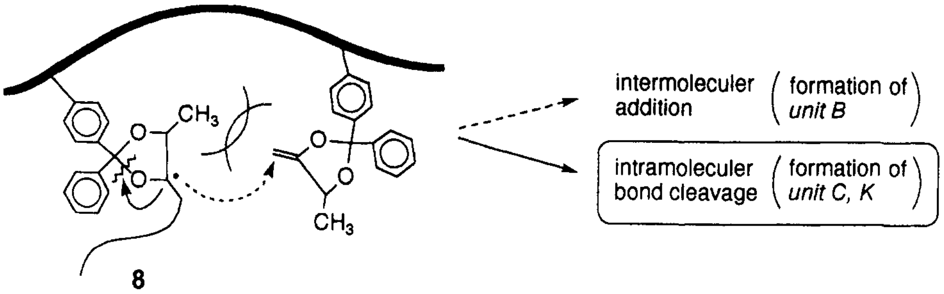


**Figure 4.** IR spectra of (A) prepolymer **4b**, (B) *n*-hexane insoluble postpolymer **7m**, and (C) basic methanol insoluble postpolymer **7n**.

More dilution of the local concentration using prepolymer **4a$_2$** did not afford a higher K % value.

The highest dilute prepolymer **4a$_3$** afforded a little insoluble postpolymer even in chlorobenzene solution where cross-linking would occur easily (run 15). When the concentration of free radical initiator is very low, polymerization might not progress efficiently. The results of runs 11–14 showed that all K % values were higher than the K % value in run 18 in which homopolymer **1** was used. Therefore suitable dilution of the local concentration

**Scheme 5**



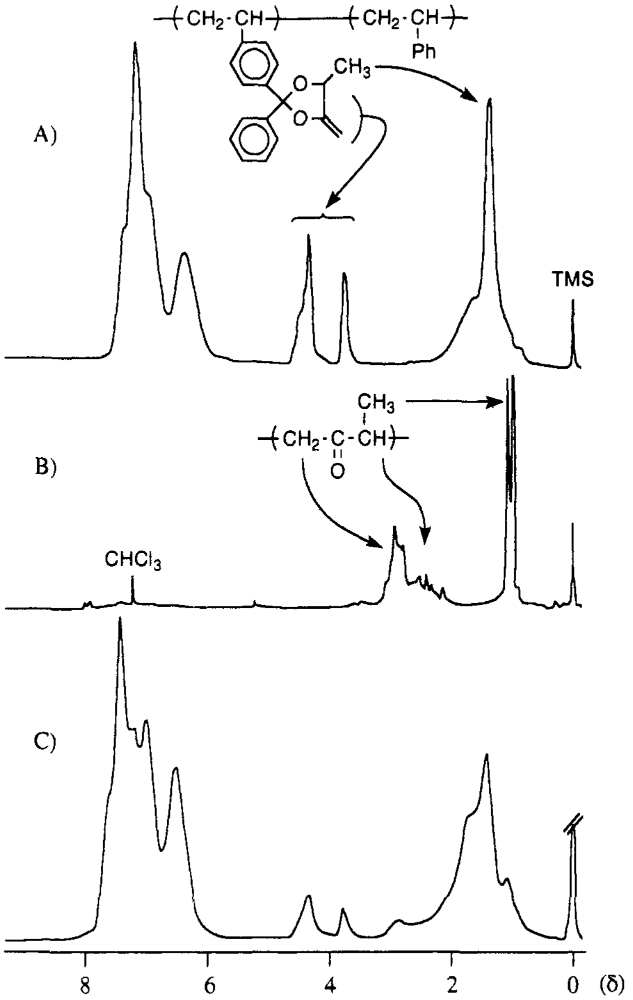


**Figure 5.** $^1$H NMR spectra of (A) prepolymer **4b**, (B) *n*-hexane insoluble postpolymer **7m**, and (C) basic methanol insoluble postpolymer **7n**.

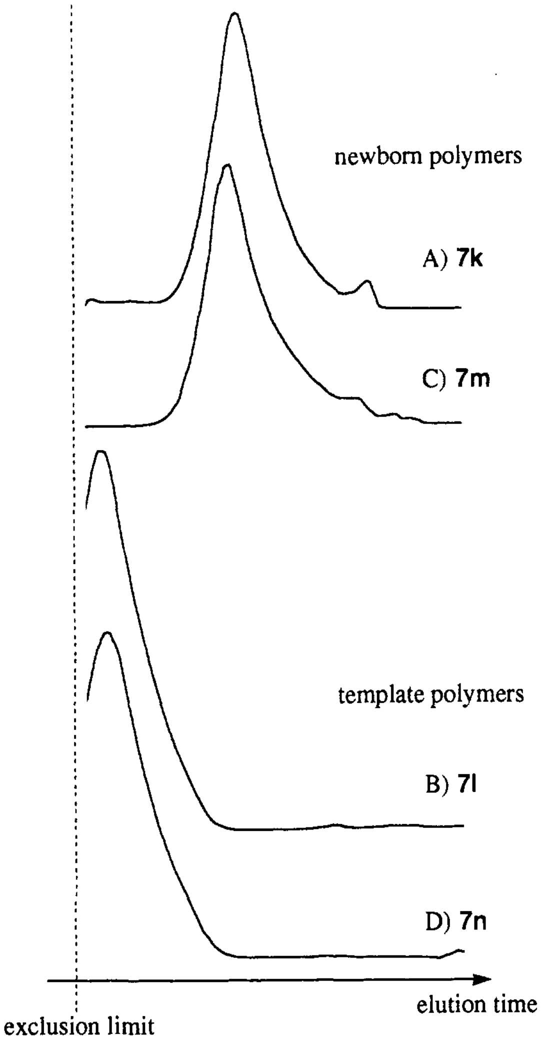


**Figure 6.** GPC curves of the postpolymers obtained from **4a** at (A, B) 120 °C and (C, D) 130 °C.

by comonomer around a 1:1 molar ratio was found to lead to good separation between the newborn and the template polymer.

Another approach for complete separation between **7T** and **7N** was examined by employing methyl-substituted prepolymer **4b**. If the ring-intact radical 8 has steric hindrance, it is anticipated that intramolecular bond cleavage may proceed rather than the attack on the next *exo*-methylene group without ring-opening isomerization (Scheme 5). When **4b** was treated at 130 °C with DTBP in DMF, the reaction mixture was transparent consistently. It was based on the good solubility of poly(1-methyl-2-oxotrimethylene).[12b] Template-rich part **7m** was collected as insoluble in basic methanol and newborn-rich part **7n** was collected as soluble in basic methanol. The IR spectrum of **7m** showed an absorption at 1705 cm$^{-1}$ of the usual aliphatic ketone's stretching, and the spectrum of **7n**, an absorption around 1671 cm$^{-1}$ on the associated ketones' stretching (Figure 4). $^1$H NMR spectra of **7m** and **7n** might support their structures (Figure 5). The K % values of **7k** and **7m** were the highest at 93%. A higher temperature could not affect the K % value but the yield of newborn polymer slightly increased (runs 16 and 17). The increase in the K % value is probably attributable to retardation of the undesirable formation of unit B by steric hindrance of the methyl group, as described above.

Improvement of the solubility of the newborn polymer by the methyl substituent introduction made it possible to analyze the postpolymers by GPC. The number average molecular weight and distribution, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$, of **7k** and **7m** were measured as 1.9 × 10$^3$ (1.2) and 2.0 × 10$^3$ (1.2), respectively (Figure 6). GPC curves of **7k** and **7m** approximately resembled unimodal peaks. If the newborn polymer connected to the template polymer, the peaks of the GPC curve would appear in a higher molecular weight area. However, **7k** and **7m** hardly absorbed the peaks around the high molecular weight area where the template polymer should be detected. It means that the newborn chains in **7k** and **7m** are almost independent of the template polymers. Consequently, it should be noted that the newborn polymer was isolated with complete separation from the template polymer.

## Conclusion

The prepolymer 4 as copoly(**3**/styrene) containing the 4-methylene-1,3-dioxolane skeleton on the side chain was prepared by selective radical copolymerization of **3** with styrene for the study of the simultaneous separating template polymerization. In the prepolymer synthesis, styrene was better than acrylonitrile for the comonomer to afford a linear and side-reaction-free polymer because the free radical originated from the electron-poor olefin such as acrylonitrile preferred attack on the *exo*-methylene group.

The template polymerization of the prepolymer **4a** was initiated by a free radical in DMF solution to afford a poly(oxotrimelthylene) as a newborn polymer **7N** with release of copoly(vinylbenzophenone/styrene) as a template polymer **7T**. Fractional precipitation in DMSO divided postpolymer 7 in **7N**- and **7T**-enriched parts. The separation efficiency between **7N** and **7T** was estimated by the K % value that indicated the composition of poly(oxotrimethylene) in the obtained polymer. All of the K % values in this paper were higher than previous values employing a homopolymer-type prepolymer. It was explained that the local concentration of the *exo*-methylene groups was diluted by the comonomer segment; as a result, isomerization of the ring-intact radical proceeded rather than attack without ring-opening.

The methyl-substituted prepolymer **4b** also afforded poly(1-oxo-2-methyltrimethylene) with release of copoly(vinylbenzophenone/styrene) and achieved the most excellent K % value. It might be explained that the methyl group on the ring-intact radical retarded the formation of unit B by steric hindrance. From the observed GPC curves of **7k** and **7m**, it was evident that the newborn chains were almost completely separated from the template polymers without postchemical treatment. Therefore our expectation for simultaneous separating elimination polymerization on the polymer's side chain was achieved.

## References and Notes

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