Macromolecules

Volume 27, Number 8 April 11, 1994

Novel Template Polymerization via Radical Ring-Opening Isomerization. 1. Polymerization of 4-Methylene-1,3-dioxolane on the Polymer Side Chain[1]

Jun-ichi Sugiyama,[†] Tsutomu Yokozawa,[‡] and Takeshi Endo[*,§]

Department of Materials Science and Engineering, Yamagata University, 4-3-16 Jounan, Yonezawa, Yamagata 992, Japan, Department of Applied Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan, and Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

Received October 5, 1993; Revised Manuscript Received January 19, 1994[®]

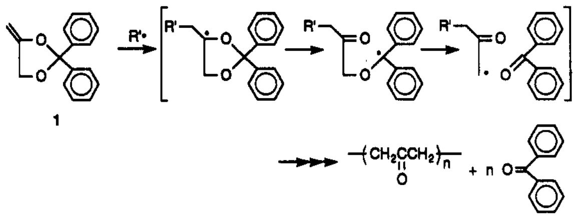
ABSTRACT: Novel template polymerization of prepolymer poly(4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane) (7) was carried out. Polymerizable function groups on the side chain of 7 underwent a chain reaction with a free radical initiator to afford a poly(oxotrimethylene) as a newborn polymer via radical ring-opening isomerization accompanying release of a poly(vinylbenzophenone) as a template polymer. This reaction was influenced dramatically by used solvents. Although an insoluble polymer of the newborn-template network was obtained from the reaction in chlorobenzene solution, the elimination polymerization was found to occur in DMF solution. Each of the newborn-rich and the template-rich polymers was collected by fractional precipitation without postchemical treatment. It meant a first example of simultaneous separating template polymerization via radical polymerization; like polymers bear polymers.

Introduction

Template polymerization has been expected as one of the high-performance reactions because translation of information may be anticipated from templates to second generation polymers. There are many transferable subjects such as sequence, orientation, molecular weight, molecular weight distribution, tacticity, higher order structure, etc. In previous reports, many connection styles between templates and polymerizable parts have been reported, e.g., covalent bonding,[2] hydrogen bonding,[3,4] electrostatic force of attraction,[5] and charge-transfer interaction.[6]

Generally, conventional template polymerization using synthesized polymer is made up of two chemical reaction stages. The first stage is construction of a new main chain among the polymerizable part that is already connected to the template. This connection usually retains even if whole polymerizable parts change to second generation polymer's backbone. Therefore conventional template polymerization invariably needs the second stage where scission of connection takes place. After the postpolymer is treated chemically, the second generation polymer should be isolated from the template polymer.

Recently Hiraguri and Endo have reported that an unsaturated cyclic monomer, 2,2-diphenyl-4-methylene-1,3-dioxolane (1), can undergo radical ring-opening polymerization to obtain a polyketone with quantitative elimination of benzophenone[7] (eq 1). Our attention has now been directed to application of this unique polymerization style to novel template polymerization. If the prepolymer has the structure identical to 1 in a repeating unit, this polyfunctional macromonomer 2 maybe expected to yield a second generation (newborn polymer) by radical initiation (Scheme 1). This concept means that *polymers bear polymers*. It is obviously different from the conventional template polymerization described above since simultaneous separation between the template and the newborn polymer would occur without postchemical treatment. In this paper, the radical polymerization of prepolymer 2 prepared by polymer modification reaction method and chemoselective polymerization method is disclosed.



(1)

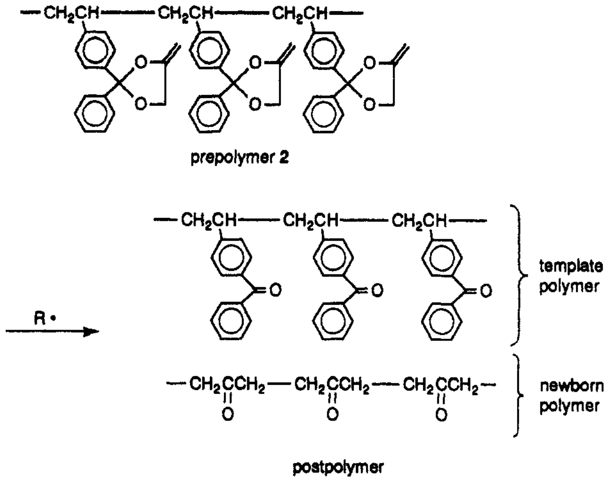
[†] Yamagata University.

[‡] Kanagawa University.

[§] Tokyo Institute of Technology.

[®] Abstract published in *Advance ACS Abstracts*, March 1, 1994.

Scheme 1



Experimental Section

Measurements. IR spectra were recorded on a Hitachi I-5020 FT-IR spectrometer. NMR spectra were obtained on JEOL JNM EX-270 (270 MHz) spectrometer. Molecular weights were determined by a gel permeation chromatography (GPC) based on standard polystyrenes using a Toyo Soda HPLC CCP & 8000 system equipped with a TSK gels G2500H, G4000H, and G5000H columns at 35 °C in tetrahydrofuran (THF).

Materials. 4-Vinylbenzophenone[8] and 4-methylene-2-phenyl-2-(4-vinylphenyl)-1,3-dioxolane[9] were prepared by the reported method. Benzene and chlorobenzene were washed several times with concentrated sulfuric acid, aqueous sodium bicarbonate, and water, followed by drying over anhydrous magnesium sulfate. Distillate over calcium hydride was stored over 4-Å molecular sieves. *N,N*-Dimethylformamide (DMF) was reduced at 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 bellow 80 °C, and stored over 4-Å molecular sieves. Before use, a small amount of decomposed contaminant was removed under vacuum. 2,2-Azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DTBP) were obtained commercially and used as received.

Preparation of Poly(vinylbenzophenone) 3. A mixture of 4-vinylbenzophenone (4.36 g, 20.9 mmol), AIBN (114 mg, 3.3 mol %), and benzene (6.53 g, 400 mol %) was heated at 60 °C in a degassed sealed glass tube. After 48 h, the reaction mixture was diluted with methylene chloride (40 mL), and the solution was poured into an *n*-hexane (1500 mL). The obtained polymer was purified by dissolution in methylene chloride (50 mL), followed by reprecipitation with *n*-hexane (1500 mL). The polymer collected by filtration was dried *in vacuo*. Yield was 101 wt % (4.42 g) as white powder. $\bar{M}n(\bar{M}w/\bar{M}n) = 2.32 \times 10^4$ (2.90).

Acetalization of 3. 3-Chloro-1,2-propanediol (6.9 g, 300 mol %), **3** (4.42 g), *p*-toluenesulfonic acid (72 mg, 2 mol %), and xylene (120 mL) were mixed in a round-bottomed flask fitted with a Dean-Stark condenser. The mixture was heated at 150 °C, and water was separated as the xylene azeotrope. After 7 h, the reaction mixture was poured into methanol (2000 mL) and precipitate was collected by filtration. This acetalization procedure was repeated two more times. The obtained polymer 4 (x:y = 17:83) weighed 3.83 g and was composed of a slightly gray powder. $\bar{M}n(\bar{M}w/\bar{M}n) = 2.19 \times 10^4$ (3.27).

Dehydrochlorination of 4. A mixture of **4** (3.70 g), sodium methoxide (prepared from 895 mg of sodium and absolute methanol), and DMF (150 mL) was heated at 60 °C for 7 h, and then 130 mL of DMF was removed under reduced pressure. Residue was poured into water (500 mL) and precipitate was collected by centrifugation. Precipitate was dissolved into methylene chloride (30 mL), washed with water, and poured into methanol (500 mL). Brown powder polymer **5** was collected by filtration and then dried *in vacuo*. Yield was 2.51 g (x:z = 19:81). $\bar{M}n(\bar{M}w/\bar{M}n) = 1.14 \times 10^4$ (2.66).

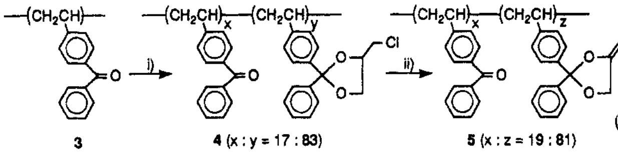
Preparation of 7. A mixture of **6** (12.93 g, 48.9 mmol), AIBN (161 mg, 2 mol %), and DMF (64.65 g, 500 wt %) was heated at 60 °C in a degassed sealed glass tube. After 10 h, the reaction mixture was poured into a 20-fold amount of methanol–triethylamine (200:1). The polymer obtained was collected by filtration and purified by dissolution into methylene chloride, followed by reprecipitation in basic methanol. Yield was 7.37 g (57%): IR (KBr) 1687 (C=C), 1448, 1279, 1070 cm^{-1}; ^{1}H 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); $\bar{M}n(\bar{M}w/\bar{M}n) = 1.76 \times 10^4$ (4.27).

Template Polymerization of 5. A mixture of **5** (2300 mg), DTBP (32 mg), and chlorobenzene (23 mL) was heated for 72 h at 130 °C in a degassed sealed glass tube. Chlorobenzene was removed by vacuum distillation, and then residual postpolymer **8** was collected. *m*-Cresol (10 mL) solution of **8** was poured into 200 mL of methylene chloride–triethylamine mixture (10:1), and then the insoluble part (6.6 mg) was collected by filtration through a Shibata 1G4 type crucible glass filter. The filtrate was washed with $NaHCO_3$ aqueous and water, followed by concentration at reduced pressure, and poured into methanol (800 mL). The precipitate (2080 mg) was collected by filtration and dried *in vacuo*.

Template Polymerization of 7. A mixture of **7** (1057 mg, 4.0 mmol), DTBP (29.2 mg, 5 mol %), and DMF (8 mL, 0.5 mol L^{-1}) was heated at 120 °C in a degassed sealed glass tube for 24 h. The reaction mixture suspension was diluted with DMF (20 mL) and centrifuged. Collected precipitate **9c** was rinsed–centrifuged in DMF (30 mL, twice) and methanol (30 mL, three times) and then dried *in vacuo*. Yield of **9c** was 169 mg (16 wt %). Composition of **9c** was estimated by ^{1}H NMR at 120 °C in DMSO-d_6. The clarified supernatant of reaction mixture and washings were poured into 20-fold methanol–triethylamine mixture (400:1). Precipitate **9d** was collected by filtration through a Shibata 1G4 type crucible glass filter and dried *in vacuo*. Yield of **9d** was 545 mg (52 wt %).

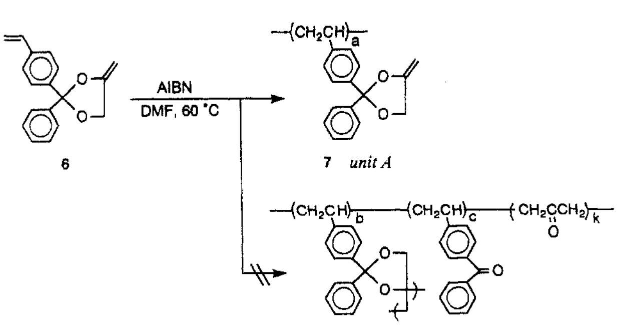
Results and Discussion

Preparation of Prepolymer. The prepolymers **5** and **7** containing 4-methylene-1,3-dioxolane structure in a repeating unit were prepared by polymer modification reaction or polymerization of the corresponding monomer **6**, shown as eqs 2 and 3, respectively. The polymer modification reaction method was first examined.



(2)

i) 3-Chloro-1,2-propanediol, *p*-TsOH, xylene azeotrope. ii) MeONa, DMF, 60 °C.



(3)

Poly(vinylbenzophenone) **3** was prepared by radical polymerization of 4-vinylbenzophenone. When **3** reacted with 3-chloro-1,2-propanediol in the presence of acid catalyst, the acetal polymer **4** was afforded as a slightly gray powder after reprecipitation. However, the IR spectrum of the polymer still showed an absorption based on benzophenone at 1658 cm^{-1}. This absorption did not disappear although acetalization was repeated two more

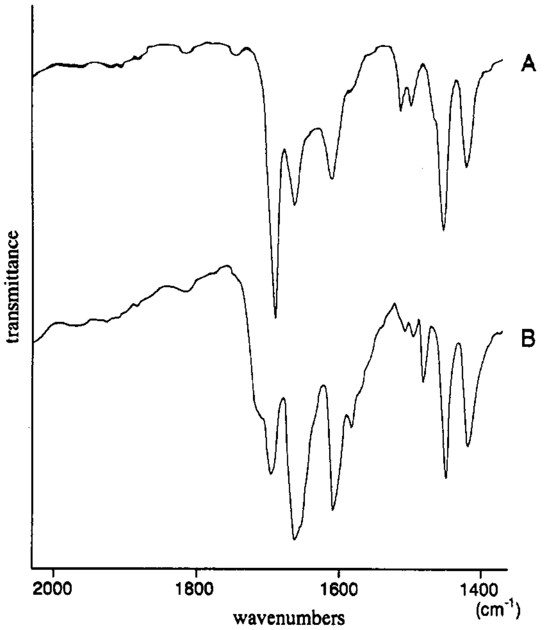


Figure 1. IR spectra of the polymers: (A) prepolymer **5** prepared by polymer modification reaction and (B) postpolymer **8** from polymerization in PhCl solution.

times. The composition of **4** obtained finally was estimated to be $x{:}y$ = 17:83 by ^{1}H NMR. Incomplete acetalization might be attributable to steric hindrance of neighboring side chains, which increased with reaction progress. On the other hand, dehydrochlorination of the polymer **4** with sodium methoxide proceeded smoothly and completely. Disappearance of all the chloromethyl groups was supported by the frame reaction of **5** showing an absence of the element chlorine. Characteristic absorption of C–C double bond could be observed in the IR spectroscopy at 1686 cm^{-1} as well as absorption of C–O double bond of benzophenone at 1658 cm^{-1} (Figure 1A). Composition of the polymer **5** was estimated to be $x{:}z$ = 19:81 by ^{1}H NMR, which could also support the statement that the dehydrochlorination proceeded quantitatively. However this reaction might include some side reactions because **5** was a brown colored polymer, never bleached by washing with water and methylene dichloride.

The prepolymer for the template polymerization could be prepared as **5**, but a part of the repeating units did not contain polymerizable structures. Recently we have reported that a bifunctional monomer **6** afforded a polymer **7** via radical selective polymerization in DMF solution at 60 °C.[9] Prepared polymer **7** was soluble easily in methylene chloride, chlorobenzene, and DMF, meaning it was free from cross-linking by unit B. Furthermore, the IR spectrum of **7** did not show absorptions assignable to benzophenone or trimethylene-2-one (Figure 2A); it excluded unit C and K and consisted of unit A only. The polymer **7** was a white powder unlike polymer **5**. It might mean that the amount of contaminant in **7** was less than in **5**.

Template Polymerization of 5. Hiraguri and Endo have reported that the monomeric compound **1** can polymerize by radical initiation via ring-intact and elimination polymerizations.[7] Ring-intact polymerization could be excluded at higher temperatures above 120 °C or in dilute conditions.[7b] Thus, prepolymer **5** was treated with DTBP as a radical initiator at 130 °C in chlorobenzene. After 72 h a slightly suspended solution of postpolymer **8** was obtained, followed by removal of solvent. In the crude **8**, presence of unit K could be supported by IR absorption of aliphatic ketone (1707 cm^{-1}, Figure 1B) and ^{1}H NMR signal of $-CH_2COCH_2-$ (δ 2.72). These data might suggest that the elimination polymerization on the side chain of **5** proceeded to afford a newborn polymer **8N** (Scheme 2). It has been known that poly(oxotrimethylene), which is the same structure of this newborn polyketone, is soluble in *m*-cresol or hot dimethyl sulfoxide (DMSO) but insoluble in methylene chloride, whereas poly(vinylbenzophenone) is easily soluble in all of these solvents. Accordingly, fractional precipitation into methylene chloride would be effective to collect newborn polymer **8N** from postpolymer **8**. Solution of **8** in *m*-cresol was poured into the methylene chloride–triethylamine mixture (10:1); however, the mixture was slightly suspended, and the insoluble part scarcely collected on a glass filter (0.3 wt %). Filtrate was still suspended but was never clarified by filtration or centrifugation. These results indicated that the postpolymer **8** could not be divided to the newborn polymer **8N** and the template polymer **8T** by fractional precipitation. It might be attributed to inclusion of the ring-intact unit B as a connecting point between **8N** and **8T**. Since **8** was soluble in DMSO completely at 120 °C, the concentration of unit B was not so high enough to make a newborn-template network. The composition of **8** before fractional precipitation was calculated by ^{1}H NMR integration to be a:b + c:k = 25:75:12, based on $x + z$ = a + b + c = 100. Comparing the prepolymer with the postpolymer in Scheme 2 meant that 25%-unit A in the prepolymer **5** was retained but 56%-unit A converted to unit B or C with production of 12%-unit K. Molar yield of the newborn polymer based on the converted unit A was low (12/56 = 21%). It might be presumed that a contaminant in prepolymer **5** often caused side reactions such as hydrolytic cleavage of acetal or inhibition of radical reaction.

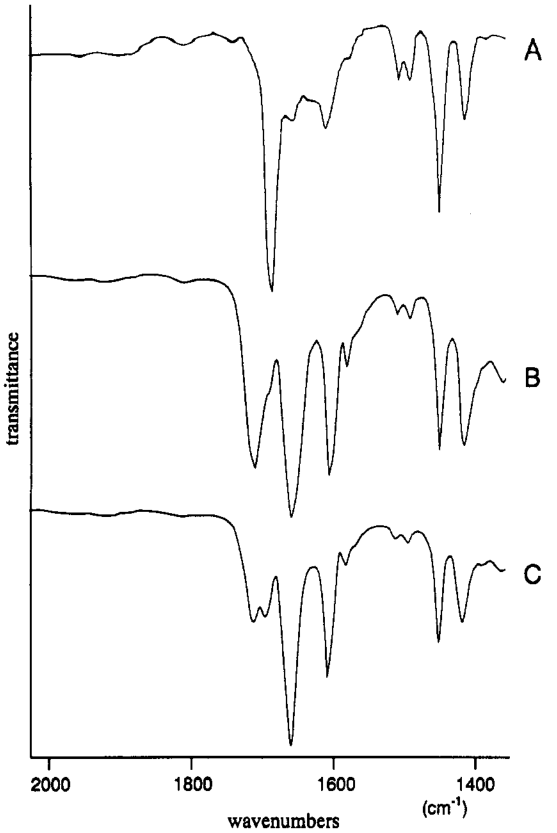
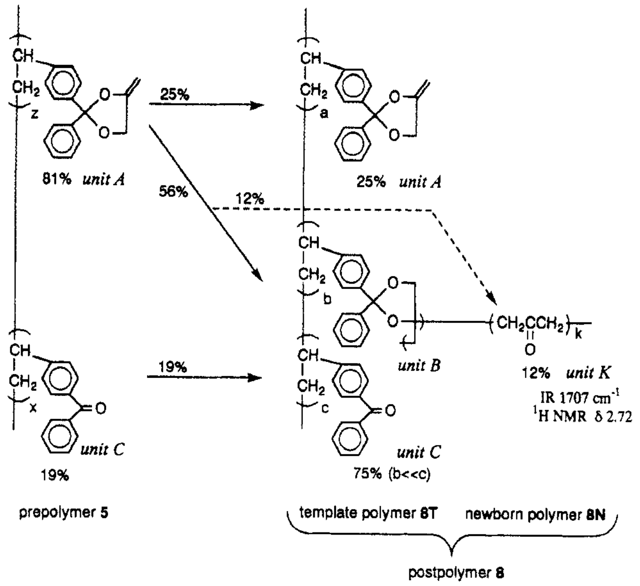


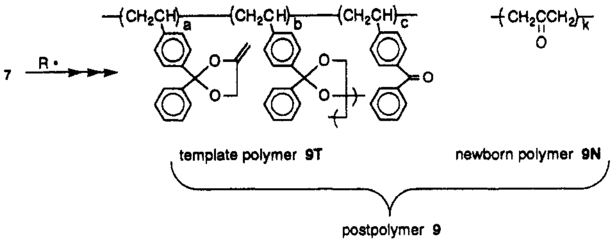
Figure 2. IR spectra of the polymers: (A) prepolymer **7** prepared by polymerization of **6**, (B) postpolymer **9a**, and (C) postpolymer **9b**.

Template Polymerization of 7. In contrast to the template polymerization of **5**, the reaction of **7** proceeded

Scheme 2



clearly, shown in eq 4 and Table 1. When **7** was heated at 120 °C with DTBP in chlorobenzene, most of the postpolymer was solidified and separated from the solution within 2 h. The swollen polymer at 2 h was colorless and became pale brown with reaction proceeding. The postpolymer **9** was divided to swollen part **9a** and well-solvated part **9b** in chlorobenzene by filtration. **9a** was collected as a brown solid after purification by washing with methylene chloride, followed by vacuum drying. After pouring the filtrate into basic methanol, chlorobenzene soluble part **9b** was also collected as a white powder by filtration. Cross-linking of **9a** during polymerization indicated that unit B was easily formed to provide a newborn-template network. Quick cross-linking was not found when **5** was used for prepolymer; it might explain that effective chain reaction of free radical occurred when **7** was used. Template and newborn polymer ratio of **9b** was estimated as 81:19 by ^{1}H NMR. The composition of **9a** could not be estimated because insolubility of the postpolymer hampered recording of NMR spectra, but IR spectrum of **9a** showed the absorption of unit K (1711 cm^{-1}) and unit C (1655 cm^{-1}) and decreasing of the absorption of unit A. This observation might support that radical ring-opening isomerization involved in **9a** as well as in **9b**. Relative intensity ratio of absorption of unit C based on absorption of unit K would generously indicate the template and newborn polymer ratio. Figure 2B,C provided evidence that the newborn polymer content of **9a** was higher than **9b**.



(4)

Interestingly, the cross-linking reaction of **7** was found to dominate dramatically by solvent employed. When polymerization took place under the same condition using DMF instead of chlorobenzene, the reaction mixture changed suspension state within 2 h, but was not solidified even after desired time. The postpolymer **9** was divided into insoluble part **9c** and soluble part **9d** in DMF by centrifugation. Each part was not crosslinked because **9c** was completely soluble in DMSO at 120 °C and **9d** showed unimodal curve in GPC.

Table 1. Template Polymerization of the Prepolymer 7[a]

run	solvent	concn, mol L^{-1}	PP[b]	yield, wt%	**9T:9N**[c]
1	PhCl	0.5	**9a**[d]	70	
			9b[e]	24	81:19
2	DMF	0.5	**9c**[f]	16	27:73
			9d[g]	52	83:17
3	DMF	0.05	**9e**[f]	1.3	18:82
			9f[g]	84	86:14

[a] Heated at 120 °C for 24 h (run 3: 48 h) with DTBP (5 mol%). [b] Postpolymer. [c] Molar ratio of repeating unit (a + b + c:k), estimated by ^{1}H NMR. [d] Insoluble in PhCl. [e] Filtrate through grass filter, insoluble in MeOH. [f] Insoluble in DMF. [g] Soluble in DMF, insoluble in MeOH.

The formation of non-cross-linked postpolymer might be explained by assumptions that (1) a sufficient solvation of the prepolymer by DMF led repulsion between each repeating unit to disturb an addition of intermediate radical **10** to next exomethylene group, or (2) relative isomerizing rate of the radical **10** solvated by DMF is faster than the rate using chlorobenzene. This solvent effect had also been found in the polymerization of **6**.[9] As described above, **6** gave the polymer which consisted of unit A only by radical reaction in DMF; however, in chlorobenzene it gave a partially cross-linked polymer containing a small amount of unit B an addition to unit A. This phenomenon could be regarded as similar to the result of **7**. In the polymerization of **6** in DMF, non-cross-linked polymer formation was unrelated with the rate of isomerization of **10** because **10** was absent. When a poor solvent was used, formation of unit B might be explained by the fact that each prepolymer was intimate and **10** attacked another exomethylene group in the repeating unit before ring-opening isomerization (Scheme 3). Solvation ability of DMF and chlorobenzene could not be estimated quantitatively; however, it was observed that polymer **7** could dissolve immediately in DMF but gradually in chlorobenzene. The authors therefore conjectured DMF might have a greater solvation ability rather than chlorobenzene and proposed the former assumption might be a principal factor of the solvent effect.

Solubility difference of **9c** and **9d** might be based on the polymer composition supported by ^{1}H NMR and IR spectra. As shown in Table 1, the content of the newborn polymer **9N** (unit K) was higher in DMF-insoluble part **9c** (73%) than in DMF-soluble part **9d** (17%). The IR spectrum of **9d** showed an absorption at 1711 cm^{-1} that could be assignable to a usual ketone's C–O stretching, whereas the spectrum of **9c** showed an overlapped bimodal absorption around 1693 cm^{-1} area (Figure 3). The latter absorption would be assigned to an associated ketone's stretching overlapping on the usual ketone's stretching. This carbonyl association in the newborn polymer was supposed to be due to high concentration and/or long continuity of unit K. It might be explained that the newborn polymer consisting of a long or continuous repeating unit K, which had the association property, could not be dissolved in DMF, while a short newborn polymer connected to the template polymer could be dissolved. Hence the newborn **9N**, which was produced by efficient elimination polymerization, might exist in **9c**, rather than in **9d**.

Although the polymerization of **7** to obtain **9c** would satisfy our concept for simultaneous separating template polymerization, the newborn polymer **9N** could not be completely isolated from template polymer **9T**. Repeating

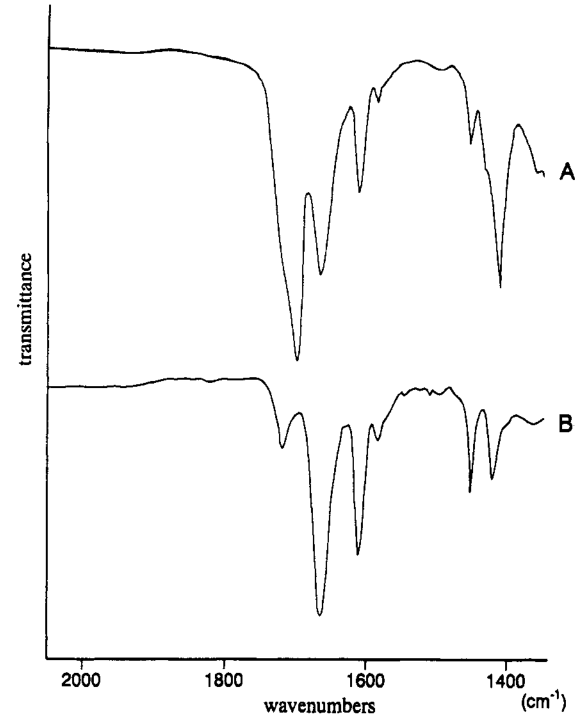
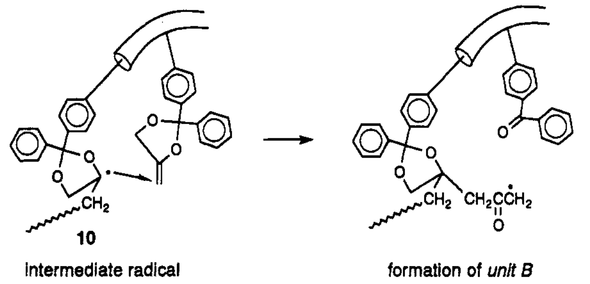


Figure 3. IR spectra of the polymers: (A) postpolymer **9c**, insoluble in DMF, and (B) postpolymer **9d**, soluble in DMF and insoluble in MeOH.

Scheme 3



fractional reprecipitation did not change the composition of **9c**, and thus the newborn **9N** and template **9T** might be connected by covalent bonding as in unit B. In order to exclude the formation of unit B, the polymerization of **7** was carried out in dilute solution (run 3). From the reaction of **7** in 0.05 mol L^{-1} DMF solution, DMF-insoluble polymer **9e** and DMF-soluble polymer **9f** were obtained. Yield of **9e** was very low (1.3 wt %); however, it was found that the newborn polymer's ratio in **9e** (82%) was higher than in **9c** (73%) supported by IR (Figure 4A) and ^1H NMR (Table 1). IR spectrum of **9f** showed inclusion of a short newborn polymer like **9d** (Figure 4B), and the template polymer's ratio in **9f** (86%) was also higher than in **9d** (83%). This result might be ascribed as a disturbance of the intermolecular attack of the ring-intact radical **10** to other exomethylene among the prepolymer molecules. Therefore the radical **10** smoothly isomerized to the terminal radical of newborn polymer, and formation of unit B was reluctant. Well separation between the newborn and the template polymer led to a higher content of **9N** and **9T** in **9e** and **9f** than in **9c** and **9d**.

Conclusion

The polymer containing radical elimination polymerizable skeletons on the side chain was prepared for the study of template polymerization. In the prepolymer synthesis, the polymerization method using monomer **6** was better than the polymer modified reaction method, judging from comparison of the prepolymer purity. The template polymerization of the prepolymer **7** was initiated by free radical in DMF solution to afford a poly(oxotrimethylene) as a newborn polymer **9N** with releasing of a poly(vinylbenzophenone) as a template polymer **9T**. Solubility difference of **9N** and **9T** was capable for separation between them, and fractional precipitation in DMF divided postpolymer **9** into **9N** or **9T** rich polymer. On the other hand, polymerization of **7** in chlorobenzene afforded only a newborn-template network. It showed the solvation ability of solvent might influence dramatically to radical isomerization step. Sufficient solvation of the reaction site led smooth division between the template and the terminal radical of the newborn, although chlorobenzene might not be satisfied to solvate.

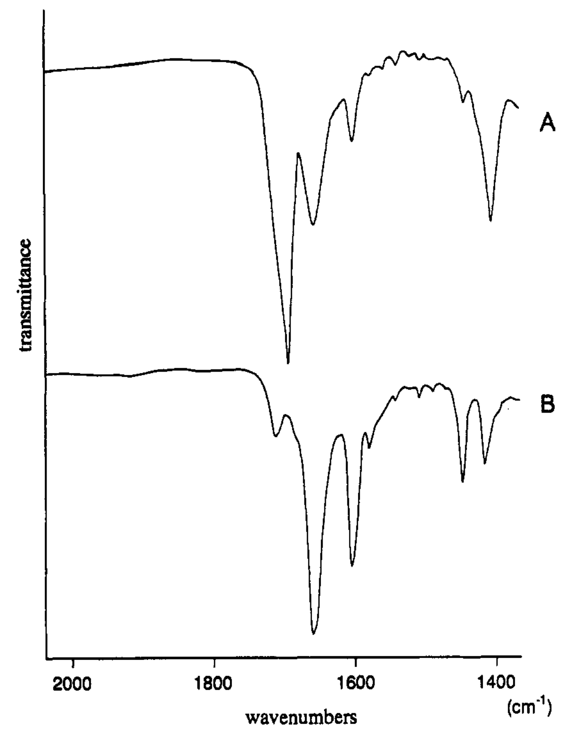


Figure 4. IR spectra of the polymers: (A) postpolymer **9e**, insoluble in DMF, and (B) postpolymer **9f**, soluble in DMF and insoluble in MeOH.

Our concept for elimination polymerization on the polymer's side chain was achieved since the IR spectra of **9c** or **9e** showed absorptions of associated carbonyl group based on the long or continuous polyketone. It was remarkable that the template polymerization described in this paper was different from the conventional method because template and newborn polymers were separated simultaneously.

References and Notes

(1) Preliminary report dealing with certain aspects of this work: Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Am. Chem. Soc.* **1993**, *115*, 2041.
(2) Kämmerer, H.; Shukla, J. S. *Makromol. Chem.* **1968**, *116*, 62.
(3) Kargina, O. V.; Kabanov, V. A.; Kargin, V. A. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *16*, 1079.
(4) Endo, T.; Numazawa, R.; Okawara, M. *Makromol. Chem.* **1971**, *146*, 247.
(5) Blumstein, A.; Kakivaya, S. R.; Salamone, J. C. *J. Polym. Sci., Part C, Polym. Lett. Ed.* **1974**, *12*, 651.
(6) Shima, K.; Kakui, Y.; Kinoshita, M.; Imoto, M. *Makromol. Chem.* **1972**, *154*, 247.
(7) (a) Hiraguri, Y.; Endo, T. *J. Am. Chem. Soc.* **1987**, *109*, 3779. (b) Hiraguri, Y.; Endo, T. *Macromolecules* **1990**, *23*, 1.
(8) Braun, V. D.; Newmann, W.; Faust, J. *Makromol. Chem.* **1965**, *85*, 143.
(9) (a) Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 2173. (b) Sugiyama, J.; Yokozawa, T.; Endo, T. *Macromolecules*, **1993**, *26*, 2842.