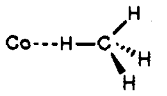
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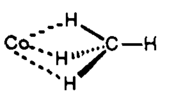
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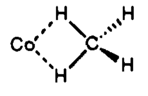
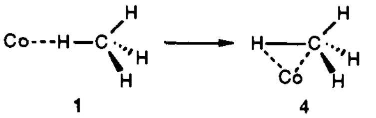

3

stable. Another argument in favor of **2** is the facile insertion of the Co atom into a C–H bond of methane to yield CH$_3$CoH.[10] Complex **1** would require extensive reorganization (**1** → **4**) prior to C–H activation.



The Co=CH$_2$ intermediate illustrated in Scheme I can be isolated and characterized in the absence of dihydrogen. The vibrational frequencies assigned to this species as well as those of the isotopically labeled species, Co=^{13}CH$_2$, Co=CD$_2$, and Co=CHD, used to make the vibrational assignments are presented in Table II.[21]

Future studies will extend this work to other metal atom–alkane adducts.

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[21] Co=^{13}CH$_2$, Co=CD$_2$, and Co=CHD were prepared from ^{13}CH$_2$N$_2$, CD$_2$N$_2$, and CHDN$_2$, respectively.

Production of Polymers from Polymers. Novel Template Polymerization via Radical Ring-Opening Isomerization

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The 4-methylene-1,3-dioxolanes have been investigated[1-7] as rare monomers which can undergo radical ring-opening polymerization. However, their polymers consist of two or more kinds of repeating units, since the polymerization is sometimes accompanied by not only ring-opening but also elimination of carbonyl compounds R$_2$C=O. Recently, Hiraguri et al. reported the first example of radical ring-opening polymerization accompanied by quantitative elimination of the carbonyl compound, achieved by using 2,2-diphenyl-4-methylene-1,3-dioxolane (**1**), which affords polyketone and benzophenone[7] (eq 1).

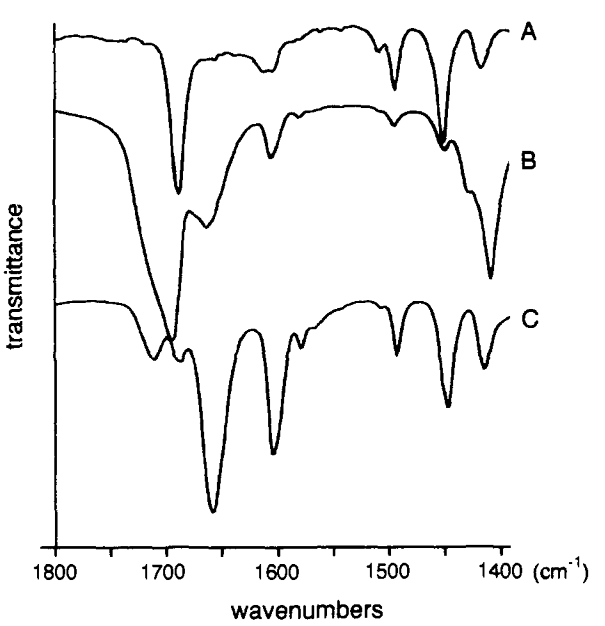
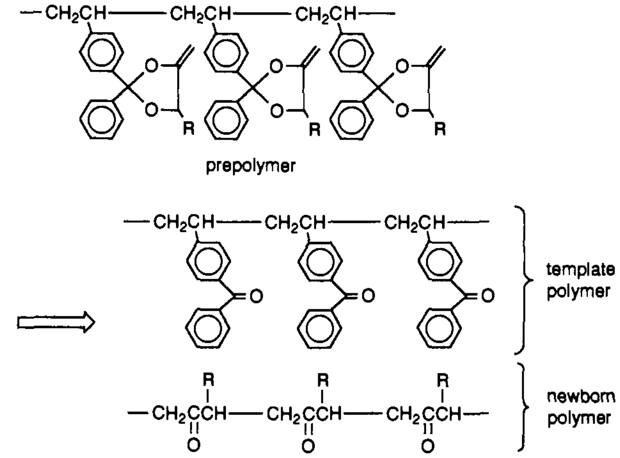
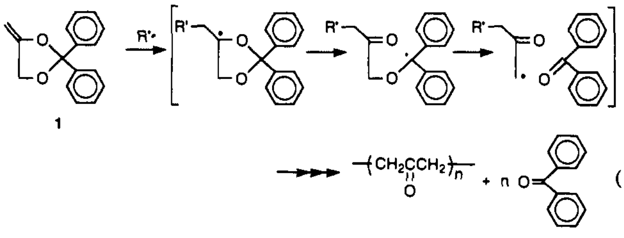


Figure 1. IR absorption of **2a**, **4a**, and **5a**. (A) Prepolymer **2a**. (B) Newborn polymer **4a**. (C) Template polymer **5a**.

Scheme I




(1)

1

This quantitative elimination in the radical ring-opening polymerization stimulated us to establish a novel template polymerization. It is anticipated that if the polymer (named prepolymer) has the structure of **1** in the side chain of repeating units, then the polyketone (newborn polymer) will also be formed from the prepolymer with radical initiation. This means that *polymers bear polymers* (Scheme I). This polymerization differs from conventional template polymerizations in that polymerization and separation take place simultaneously on the *prepolymer* to afford both the *newborn* and the *template polymer* without chemical treatment after polymerization.

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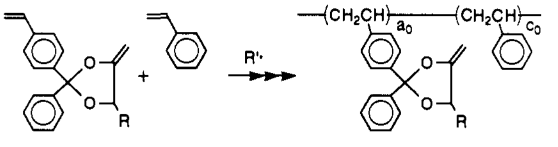
Table I. Template Polymerization of **2a** and **2b**

P1	T, °C	T, h	P2	composition^b				K%^{c}	IR absorption, cm^{-1}		
				a	*b*	*c*	*k*		C═O	C═C	C═O
2a	120	12	**4a**	0	2	2	16	80	1693		
			5a	10	39	49	8		1710	1687	1659
2a	130	12	**4a′**	0	1	1	15	87	1693		
			5a′	2	48	49	6		1710		1659
2b	130	36	**4b**	0	0.5	0.8	18	93	1705 1670		
			5b	11	29	61	<8		1707	1684	1655

^{a}P1 = prepolymer; P2 = postpolymer. ^{b}Estimated by ^{1}H NMR based on $(a_0,c_0) = (50,50)$ (**2a**) or $(a_0,c_0) = (40,60)$ (**2b**). ^{c}K% = $k/(a + b + c + k)$.

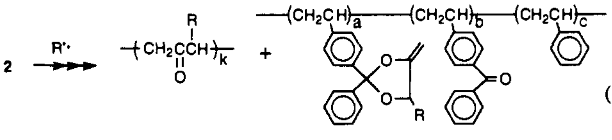
The prepolymers **2a** and **2b** were prepared by selective radical copolymerization of styrene and the corresponding monomer **3a**[8a] or **3b**[8b] (eq 2). The polymerization of **2a** was carried out at 120–130 °C in dimethylformamide (DMF) in the presence of di-*tert*-butyl peroxide (DTBP) as a radical initiator.[9a] After 12 h, the newborn polymer **4a** was collected by centrifugation from the chilled reaction mixture; **4a** was insoluble in DMF at room temperature (eq 3). The obtained **4a** was not cross-linked because it could be dissolved in hot dimethylsulfoxide (DMSO). The IR spectrum of **4a** showed an absorption at 1693 cm^{-1} assigned to the C═O group of the continuous ketone unit (Figure 1B), and the ^{13}C NMR spectrum showed signals at 207.06 and 35.27 ppm as carbonyl and methylene carbons of unit K, respectively. Furthermore, the ^{1}H NMR spectrum showed a major signal at 2.62 ppm corresponding to the methylene protons on a carbon atom adjacent to the ketone group and small signals at 7–8 ppm as aromatic protons of inseparable template polymer. From the ratio of the intensity of the signals for the methylene protons to the intensity of the signals for the aromatic protons, ketone composition (K%) of **4a** on the basis of whole repeating units was estimated to be 80–87% (Table I).



(2)

3a : R = H
3b : R = Me

R	a_0 / c_0		$\overline{M}n(\overline{M}w/\overline{M}n)$
2a : H	50	50	1.9x10^4(1.9)
2b : Me	40	60	1.1x10^4(2.0)



(3)

unit K *unit A* *unit B* *unit C*

4a : R = H
4b : R = Me
5a : R = H
5b : R = Me

The template polymer **5a** was collected by precipitation in methanol from DMF solution. The IR spectra of **5a** showed an absorption at 1659 cm^{-1} assigned to a C═O group of released benzophenone side chain accompanied by a small absorption at 1710 cm^{-1} assigned to a C═O group of isolated ketone unit, which was incompletely separated unit K (Figure 1C). The composition of **5a** was estimated by ^{1}H NMR and summarized in Table I. The template polymer **5a** was completely recovered (yield >98%), and unit A in the **2a** was decreased from 50 mol % to 2–10 mol % after polymerization, indicating that unit A was converted to unit K with releasing unit B. These results mean that radical elimination polymerization actually occurred on the side chain of prepolymer **2a**, thus, **2a** changed to template **5a** by producing newborn polymer **4a**.

The methyl-substituted prepolymer **2b** was also polymerized by radical initiation at 130 °C.[9b] The **4b** was obtained from the methanol-soluble and hexane-insoluble part, whereas the template **5b** was obtained from the methanol-insoluble part. The obtained **4b** was built in higher ketone composition (93%) than **4a**. It should be noted that the polymerization of **2b** proceeds with nearly complete separation of the newborn polymer **4b** and the template **5b**. This phenomenon is probably attributable to retardation of the undesirable vinyl polymerization, which would lead to connection between the template and the newborn polymer by a covalent bond, prevented by the steric hindrance of the methyl group of **2b**.

In conclusion, the prepolymers **2** afforded polyketones, and they themselves were converted to poly(vinylbenzophenone). Both poly(vinylbenzophenone) as template and polyketones as newborn polymer were easily separated by fractional precipitation without any particular chemical treatment after polymerization. This novel template polymerization via radical isomerization demonstrates the new concept that *polymers bear polymers.*

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(8) (a) Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.*, submitted for publication. (b) In the same way as **3a**, **3b** was synthesized by acetalization of 4-(2-bromoethyl)benzophenone using 2-chloromethyl-3-methyloxirane, followed by dehydrohalogenation.

(9) (a) Prepolymer **2a** (1300 mg), DTBP (25.8 mg, 2 mol % based on unit A), and DMF (14.1 mL) was heated at 120 °C in a degassed sealed tube. After 12 h, the reaction mixture was chilled in a refrigerator, and white powdery **4a** was collected by centrifugation. The **4a** was purified by reprecipitation from cooling of hot DMSO solution and repeating centrifugation (111 mg). The supernate was poured into a methanol/triethylamine (200/1) mixture, and **5a** (1141 mg) was collected as a white powder. (b) After polymerization, the reaction mixture was poured into a methanol/triethylamine mixture, and **5b** was collected as a white powder by filtration. After the filtrate was concentrated by evaporation, the residue was dissolved in methylene chloride and the solution was poured into hexane. The polyketone **4b** was collected by decantation as hexane-insoluble viscous liquid. All of the collected polymers were dried in vacuo over 12 h.

First Total Synthesis of Scopadulcic Acid B

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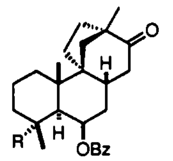
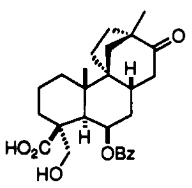
The medicinal plant *Scoparia dulcis* L. has long been used in Paraguay, India, and Taiwan for treating a variety of medical problems.[2] In recent investigations of the Paraguayan crude drug "Typychá kuratû (*Scoparicdulcis* L., Scrophulariaceae), Hayashi and co-workers isolated a number of structurally unique tetracyclic diterpenes, exemplified by the scopadulcic acids B (**1**) and A (**3**) and scopadulciol (**2**) that are its active ingredients.[3] Scopadulcic acid B and some semisynthetic derivatives are powerful inhibitors of H$^+$,K$^+$-adenosine triphosphatase and as such are potential



scopadulcic acid B (**1**) R = CO_2H
scopadulciol (**2**) R = CH_2OH



scopadulcic acid A (**3**)

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