

Polymerization of Vinyl Ether by Use of Yttrium Silicate Gel as Solid Acid

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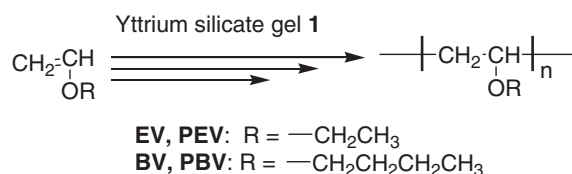
ABSTRACT: The gel of yttrium silicate was utilized as a solid catalyst for the polymerization of vinyl ethers. Several silicate gels showing the different element ratios of silicon and yttrium were prepared by the co-gelation of sodium metasilicate and yttrium(III) chloride from an acidic aqueous solution through neutralization by an aqueous ammonia. The polymerizations of ethyl vinyl ether and *n*-butyl vinyl ether proceeded readily in the presence of a catalytic amount of the silicate gel to give the corresponding polymers. When ethyl vinyl ether was used in benzene solution for the polymerization, the concentration of the monomer was not an essential factor which affected on the yield of the corresponding polymer. This demonstrated that the silicate gel provided an effective reaction environment for the polymerization with the catalytic sites. [doi:10.1295/polymj.PJ2005199]

KEY WORDS Yttrium Silicate / Rare Earth Metal / Vinyl Ether / Cationic Polymerization / Solid Acid /

Rare earth metal ion has been known and utilized as an effective Lewis acid in organic synthesis.^{1,2} Recently, the alkoxides and complexes of rare earth metals are applied to synthesis of polymeric compounds through ring opening polymerization.^{3–7} Furthermore, the solid silica derivatives containing the metals such as aluminum, chromium, zirconium, and vanadium have been employed for the well defined ring opening polymerization of 1,2-epoxide⁸ and lactones.^{9–12} In these ring opening reactions, the silicate structure is recognized to provide an appropriate reaction environment with Brønsted and Lewis acidity. In addition, the solid catalyst, which can be removed readily from the reaction system by a simple filtration, should provide a convenient and practical procedure in polymer synthesis.¹³ These facts lead to the expectation that the silicate gel of rare earth metals, which shows Brønsted and/or Lewis acidity, can be a useful solid catalyst for the polymerization through a cationic specie. On the other hand, the silicate gels containing rare earth metals are known to show the specific physical and optical properties.^{14–18} Therefore, a large part of the investigations concerning the rare earth metal silicates has been developed from the interests in their physical properties. In other words, the utility of rare earth metal silicates as a solid catalyst in organic reactions has not been exploited so much.

By considering the information mentioned above, we have begun the investigations on the catalytic use of rare earth metal silicate in the field of polymer

synthesis. As a first example, the ring-opening polymerization of oxetane by the catalytic uses of three kinds of the silicate gels such as yttrium (Y), neodymium, and samarium was studied.¹⁹ The obtained results indicated that yttrium silicate (**1**) was the most effective catalyst for the ring-opening polymerization among them. This seemed to reflect the reported Lewis acidities of the rare earth metals, in which Y shows a stronger acidity than neodymium and samarium.²⁰ The observations also demonstrated that the solid silicate is enough effective for the polymerization progressed through a cationic specie. Such facts led us to another examination on the catalytic use of the silicate gel of Y, which would provide an additional easy handling method for the cationic polymerization. As an appropriate example, our attention is directed to the polymerization of vinyl monomers. Since, the successful combination of vinyl monomers such as styrene and vinyl ethers with the resin containing sulfonic acid groups has been reported.²¹ In this report, to expand the usage of the silicate gel of Y in a cationic polymerization system, ethyl vinyl ether (**EV**) and *n*-



Scheme 1.

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butyl vinyl ether (**BV**) were chosen as the monomers and polymerized under various conditions.

EXPERIMENTAL

General

^1H NMR and ^{13}C NMR spectra were obtained on a JEOL FX-270 and JNM A-500 spectrometer in CDCl_3 . IR spectra were recorded on a JASCO FT/IR 230. The specific surface areas were obtained by the Brunaur-Emmett-Teller (BET) method with a Collter Omnisorp 100CX using nitrogen as the absorbate. Gel permeation chromatographic (GPC) analysis was carried out on a TOSO HLC-8020 chromatograph equipped with a refractive index detector. TSK gel G2500H, G2000H, and G1000H, were connected in series and tetrahydrofuran (THF) was used as an eluent. Calibration for number-average molecular weight (M_n) and polydispersity (M_w/M_n) was performed using standard polystyrenes. **EV** and **BV** were just distilled under argon atmosphere before use. Solvents employed for the reactions were distilled over an appropriate metal or a metal hydride before use. The alcohols were distilled over magnesium metal after the treatment with sodium metal. All other substrates including yttrium (III) chloride hexahydrate (YCl_3) were the best commercially available reagent grade and used as receipt.

Preparation of Rare Earth Metal Silicate Gel

The yttrium silicate gels **1** were prepared according to our reported procedure.¹⁹ To a solution of sodium metasilicate (Na_2SiO_3) (28.4 g, 0.10 mol) in water (100 mL), pH value of which was adjusted to be *ca.* 1 by using diluted hydrochloric acid (6 [M]), YCl_3 (15.2 g, 0.05 mol) in water (100 mL) was added. The aqueous solution was neutralized to pH = 7 by 10% of aqueous ammonia solution, which was added portion wise for over 3 h at room temperature. The solid precipitated from the solution was collected and washed several times with water and acetone. After drying at 700 °C for 3 h under air, the silicate gel **1a** (11.1 g, 61% based on Si, 58% based on yttrium, the element ratio of Si/Y = 2.1) was obtained. The contents of silicon and yttrium in **1a** were estimated by the results of gravimetric analysis and the specific surface area by BET method.

Analogously, the silicate gels containing the different ratios of silicon/yttrium such as Si/Y = 8.5 (**1b**) and 19.0 (**1c**) were prepared by changing the feed ratios of the starting materials. The analytical data of **1** was shown in Table I.

Polymerization of Vinyl Ether

Typical procedure was as follows: The silicate gel

1a (0.26 g, Y = 0.67 mmol equiv., 10 mol %) in a glass tube equipped with rubber septum was degassed and substituted with nitrogen at room temperature. Benzene (4 mL) and **EV** (0.49 g, 6.80 mmol) were injected by syringe and, then, the solution was stirred at 18 °C for 8 h. After the reaction, **1a** was filtered off and washed with methanol several times. The filtrate and washings were combined and evaporated under reduced pressure. The residual oil was dried under reduced pressure (*ca.* 15 mmHg) at room temperature to obtain the polymeric product of **EV** (**PEV**) (0.48 g, 98%) (Table II, Run 1); IR (neat) 2850 (CH_2 , strong), 1480 (CH_2 , medium), 1360 (CH_2 , medium), 1120 (C-O, strong) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.95 (m, 3H, CH_3 -), 1.54–1.75 (br m, 2H, $-\text{CH}_2-$); 3.30–3.65 (br m, 3H, $-\text{O}-\text{CH}-$, $-\text{O}-\text{CH}_2-$); ^{13}C NMR (CDCl_3) δ 15.67 ($-\text{CH}_3$), 39.92 ($-\text{CH}_2-$), 64.24 ($-\text{O}-\text{CH}-$), 73.61 ($-\text{O}-\text{CH}_2-$). $M_n = 8500$, $M_w/M_n = 3.72$.

Analogously, the polymerizations of **BV** to give the corresponding polymeric product were carried out in the presence of a catalytic amount of the silicate gel **1**, in which the polymers of **BV** (**PBV**) were isolated as an insoluble oil in methanol. The analytical data of **PBV** was as follows: IR (neat) 3450 (OH, weak), 2980 (CH_2 , strong), 2850 (CH_2 , strong), 1480 (CH_2 , medium), 1360 (CH_2 , medium), 1120 (C-O, strong) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90 (m, 3H, $-\text{CH}_3$), 1.54–1.84 (br m, 6H, $-\text{CH}_2-$), 3.30–3.65 (br m, 3H, $-\text{O}-\text{CH}-$, $-\text{O}-\text{CH}_2-$); ^{13}C NMR (CDCl_3) δ 14.01 ($-\text{CH}_3$), 19.55 ($-\text{CH}_2-$), 32.41 ($-\text{CH}_2-$), 40.52 ($-\text{CH}_2-$), 68.88 ($-\text{O}-\text{CH}-$), 73.69 ($-\text{O}-\text{CH}_2-$).

The results and conditions were listed in Table II. The polymerizations conducted in other solvents were also carried out. The results were listed in Table III.

For the time-conversion and the conversion- M_n and M_w/M_n curves shown in Figures 3, 4, and 5, the samples were taken by a syringe at the appropriate times during the polymerization which was carried out in 1.7 M benzene solution of the monomer. The samples were employed for the measurements of ^1H NMR and GPC without removal of the solvent, respectively.

Gravimetric Analysis

The contents of Y and Si in the silicate gels **1** were determined by the same treatment for gravimetric analysis reported previously.¹⁹

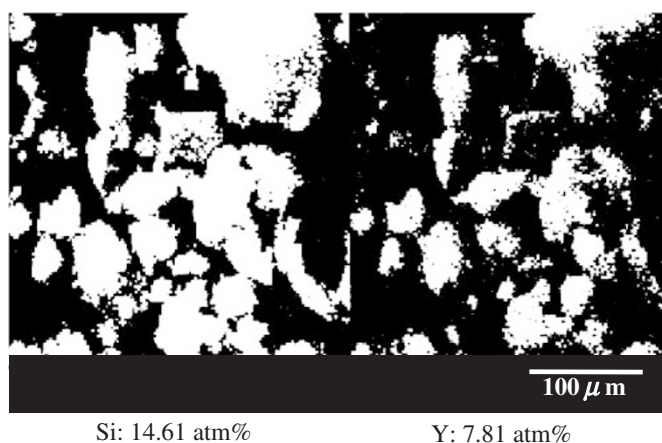
Scanning Electron Microscopy with Energy Dispersive X-ray Microanalysis (SEM-EDXA)

The silicate gel **1a** was measured with a SEM (HITACHI S-4700) equipped with an EDXA system (HITACHI E-1030). Micrograph of secondary electron images was taken at accelerating voltage of 5 keV, and EDXA was carried out at 20 keV for spectrum analysis and element mapping (256 by 256 pixels).

Table I. Preparation of the yttrium silicate gel **1**

Silicate gel	Yield of Si %	Yield of yttrium %	Content of Si mmol/g ^a	Content of yttrium mmol/g ^a	Molar ratio of Si/Yttrium	Surface area m ² /g ^b
1a	61	58	5.49	2.59	2.1	150
1b	68	71	8.59	1.01	8.5	195
1c	65	68	14.89	0.78	19.0	195

^aEstimated by gravimetric analysis. ^bMeasured by BET method using nitrogen as the absorbate.

**Figure 1.** SEM-EDXA images of **1a**.

The sample for SEM was fixed with photo-glue (vinyl acetate) on one end of copper tape adhered on a SEM stub and, then, adjusted the orientation by bending the copper tape. It was coated with Pt-Pd (80:20) in an ion-sputter coater (HITACHI OIE-6377) at 0.4 keV with an electron current of 15 mA for 30 s.

RESULTS AND DISCUSSIONS

Preparation of Silicate Gel

The silicate gels of yttrium **1** were prepared from Na₂SiO₃ and YCl₃ by the same procedure reported before.¹⁹ The aqueous solution of Na₂SiO₃ and YCl₃ was acidified by a diluted hydrochloric acid, where the pH value was adjusted to be *ca.* 2. Such acidic solution, in which polymeric or oligomeric silicic acid is reported to be hydrolyzed to monomeric one, was thought to be favorable for dispersing the rare earth metal species.²² The precipitation of the silicate gel was performed through neutralization of the acidic solution by using 10% aqueous ammonia solution. In this work, three kinds of the silicate gel **1a–c** were prepared by changing the feed molar ratios of Na₂SiO₃ and YCl₃. The results were shown in Table I. The contents of Si and Y in the gels, estimated by gravimetric analysis, were almost coincided with the feed molar ratios of Na₂SiO₃ and YCl₃. The estimated ratios of Si/Y were 2.1 for **1a**, 6.5 for **1b**, and 19.0 for **1c**, respectively. The surface areas of **1a–c** measured by BET method were in the range

from 150 m² g⁻¹ to 195 m² g⁻¹. These values may predict that the inner space of the gels is too narrow to progress the reaction in it and the reaction essentially proceeds on the surface. An additional evaluation of the silicate gel was made by SEM-EDXA analysis for the silicate gel **1a**, containing a half element ratio of Y to Si. As shown in Figure 1, the map for Y overlapped almost completely with that for Si and the measured ratio of Si/Y was 14.60/7.81 on the surface of **1a**. The atomic ratio of Y/Si on the surface showed good agreement with that estimated by gravimetric analysis of the gel **1a**, which should be Si/Y = 2.1. Such observations indicated that Y was dispersed well in polysiloxane network by forming Yttrium silicate structure.

Polymerization of Vinyl Ether

The polymerizations of **EV** and **BV** in the presence of a catalytic amount of the silicate gels **1** were conducted at 18 °C under a variety of conditions to elucidate the activities of the catalysts. The silicate gels **1** were calcined at 700 °C for 1 h before use. The conversion of the monomer was calculated on the basis of ¹H NMR spectral data. As shown in Figure 2, the signals assigned to the protons of methylene and methine bonded to oxygen in **PEV** were appeared at *ca.* 3.5 ppm. The signals due to other methylene and methyl protons were observed at *ca.* 1.5 and 0.95 ppm, respectively. The signals assigned to vinyl protons of the starting monomer **EV** were observed

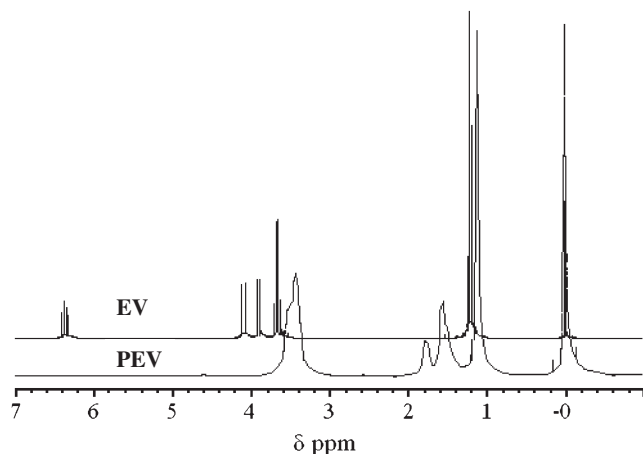


Figure 2. ^1H NMR spectra (CDCl_3) of **EV** and **PEV** (Table II, Run 1).

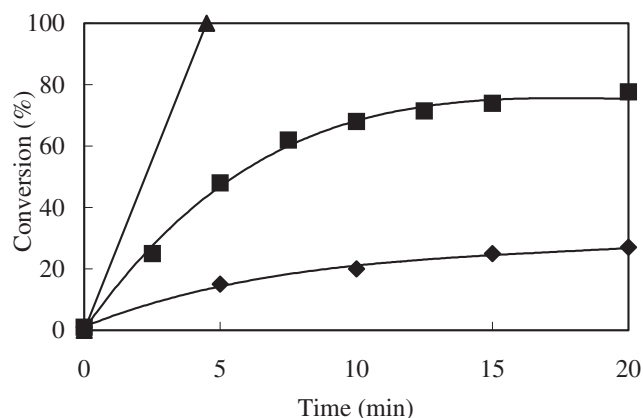


Figure 4. Relationships between time and conversion in the polymerization of [1.7M] of **BV** in benzene with **1a**: (◆): 1 mol %; (■): 5 mol %; (▲): 10 mol % of yttrium to **BV**.

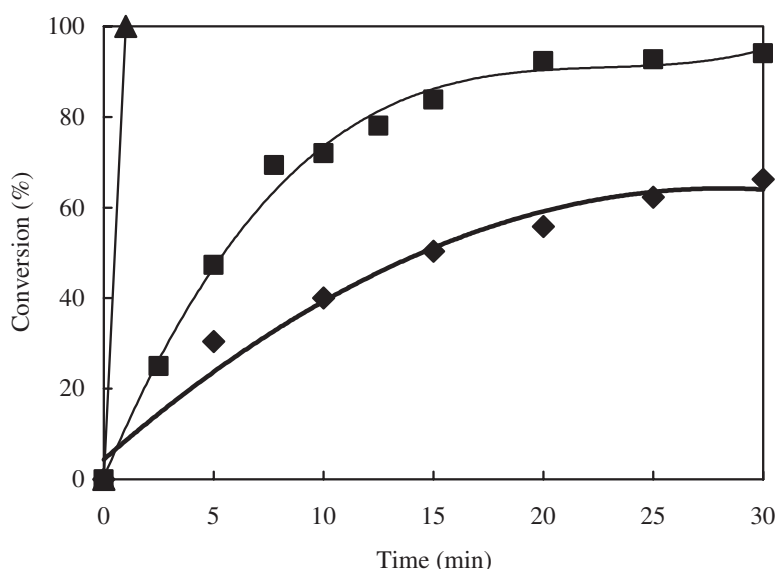


Figure 3. Relationships between time and conversion in the polymerization of [1.7M] of **EV** in benzene with **1a**: (◆): 1 mol %; (■): 5 mol %; (▲): 10 mol % of yttrium to **EV**.

at 3.91, 4.10, and 6.39 ppm. These were completely disappeared after the polymerization. In a similar manner, the corresponding signals due to methyl, methylene and methine protons of **BV** and **PBV** were observed in the ^1H NMR spectra with the additional signals for two methylene protons in the region from 1.36 to 1.82 ppm. These could be distinguished easily and were utilized for the calculations of conversion of the vinyl monomers in all the polymerizations mentioned here.

The relationships of time and conversion of the monomers were examined to obtain the information of the catalytic activity of **1**. Figure 3 and 4 showed the time-conversion curves of **EV** and **BV**, respectively, which were employed in 1.7M benzene solution at 18°C. In these polymerizations, the silicate gel **1a** was used as a representative catalyst and the contents of Y

in the polymerization system were adjusted to be 1, 5, and 10 mol % to the monomer by changing the amount of **1a**. The rate of consumption of the monomers reasonably increased according to the contents of Y. When the polymerization was carried out with **1a** containing 10 mol % of Y, the conversion of the monomer reached to 100% within 5 min in the both cases using **EV** and **BV**. The results demonstrated that the solid acid **1a** was enough effective for initiating the cationic polymerization of the monomers. However, the consumption of **BV** obviously became slow, when the content of Y decreased. In the uses of **1a** containing 1 and 5 mol % of Y to **BV**, the conversions could not reach to 80% even after 8 h reaction. With the measurements of the rate of the polymerization, the relationships of conversion with M_n and M_w/M_n in the above polymerization were also examined by

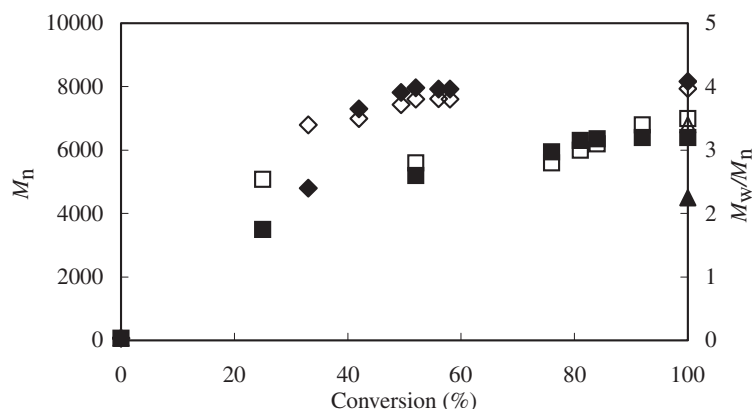


Figure 5. Relationships between conversion, M_n , and M_w/M_n in the polymerization of [1.7 M] of **EV** in benzene solution with **1a**. (\blacklozenge , \diamond): 1 mol %; (\blacksquare , \square): 5 mol %; (\blacktriangle , \triangle): 10 mol % of yttrium to **EV**.

Table II. Polymerization of vinyl ether in the presence of silicate gel **1**

Run	Conditions ^a			Poly(vinyl ether) ^a			
	Silicate gel (Molar ratio of Si/Y)	Monomer (Molar ratio of Y/Monomer)	Concentration of monomer [M] (Solvent)	Monomer conversion ^b %	Product (Yield, % ^c)	M_n ^d	M_w/M_n ^d
1	1a (2.1)	EV (0.01)	13.6 (Benzene)	>99	PEV (98)	8500	3.72
2	1b (8.5)	EV (0.01)	13.6 (Benzene)	>99	PEV (95)	7800	2.66
3	1c (19.0)	EV (0.01)	13.6 (Benzene)	>99	PEV (>99)	7000	3.25
4	1a (2.1)	BV (0.01)	13.6 (Benzene)	92	PBV (72)	9500	1.85
5	1c (19.0)	BV (0.01)	13.6 (Benzene)	68	PBV (46)	8000	1.51
6	1a (2.1)	EV (0.05)	13.6 (Benzene)	>99	PEV (>99)	6800	3.72
7	1a (2.1)	EV (0.10)	13.6 (Benzene)	>99	PEV (>99)	4600	3.86
8	1a (2.1)	EV (0.01)	— (None)	>99	PEV (>99)	6400	3.85
9	1a (2.1)	EV (0.01)	6.8 (Benzene)	>99	PEV (>99)	8400	3.60
10	1a (2.1)	EV (0.01)	3.4 (Benzene)	>99	PEV (97)	8200	3.62
11	1a (2.1)	EV (0.01)	0.9 (Benzene)	>99	PEV (89)	6200	3.20
12	1a (2.1)	BV (0.01)	— (None)	87	PBV (55)	9200	1.71
13	1a (2.1)	BV (0.01)	3.4 (Benzene)	72	PBV (55)	9400	1.83
14	1a (2.1)	BV (0.01)	0.9 (Benzene)	43	PBV (36)	7800	1.85
15 ^e	1a (2.1)	EV (0.01)	13.6 (Benzene)	>99	PEV (97)	8100	3.32

^a6.80 mmol of vinyl ether was used for the polymerization carried out at 18 °C for 8 h. ^bEstimated by ¹H NMR spectral data. ^cIsolated yield based on the weights of the materials. ^dEstimated by GPC (polystyrene standards). ^eRecycled **1a** was employed after using two times for the polymerization.

GPC using polystyrene standards. In the relationships using **BV** as the monomer, the meaningful changes of molecular weights and the polydispersities of the products according to the content of Y were hardly obtained due to the decreased rates of the polymerization. Therefore, the results were shown only in the cases using **EV**. Figure 5 showed that the M_n s of **PEV** increased with the increases of conversion of **EV**. When the conversion of **EV** was attained to 62% by the use of 1 mol % of Y, the M_n of **PEV** was ca. 8000. After complete consumption of **EV** in the polymerization containing 5 mol % of Y, the M_n of **PEV** was 6200. The use of the larger amount of **1a** such as 10 mol % of Y content resulted in the formation of the lower M_n of **PEV** as estimated to be

4600. The variation of M_n s according to the content of Y seemed to reflect the numbers of the active site on **1a** for generating the cation species. On the basis of the information mentioned above, the following polymerizations with the isolation of the resulting **PEV** and **PBV** were carried out for 8 h under various conditions.

As shown in Table II, the isolated yields of **PEV**, obtained by simple distillation of the reaction mixture under reduce pressure, were almost in accord with the conversions of the starting **EV**. This indicated that the reaction initiated by the silicate gel **1** proceeded primarily to form the corresponding polymeric product **PEV**. In the use of **BV**, the yields of **PBV** showed the smaller values compared to those of the conver-

Table III. Polymerization of vinyl ether in various solvents

Run	Conditions ^a		Poly(vinyl ether) ^a			
	Monomer	Concentration of monomer [M] (Solvent)	Monomer conversion ^b %	Product (Yield, % ^c)	M_n^d	M_w/M_n^d
1	EV	13.6 (Dichloromethane)	>99	PEV (>99)	8900	3.60
2	EV	1.7 (Dichloromethane)	>99	PEV (>99)	8300	2.15
3	EV	13.6 (Acetone)	>99	PEV (>99)	4900	2.34
4	EV	1.7 (Acetone)	62	PEV (62)	1800	1.60
5	EV	13.7 (Acetonitrile)	>99	PEV (95)	2600	1.65
6	EV	1.7 (Acetonitrile)	0	PEV (0)	—	—
7	EV	13.7 (Methanol)	>99	Unknown	—	—
8	EV	13.7 (<i>iso</i> -Propylalcohol)	>99	Unknown	—	—
9	BV	13.7 (Acetone)	17	PEV (17)	7500	1.95
10	BV	13.7 (Acetonitrile)	8	PEV (12)	—	—

^a6.80 mmol of vinyl ether was used for the polymerization carried out at 18 °C for 8 h with **1a**, the amount of which was adjusted to contain 1 mol % of Y to the monomer. ^bEstimated by ¹H NMR spectral data. ^cIsolated yield based on the weights of the materials. ^dEstimated by GPC (polystyrene standards).

sions. The lower yields of **PBV** in comparison with the corresponding conversions were thought to be caused by a difficulty to isolate an oily product, in which the mixture had to be cooled under 10 °C to separate **PBV** well from methanol and to collect by decantation after washings with methanol. In fact, in the ¹H NMR spectra used for the calculation of the conversion, no obvious signal assigned to the side products was observed.

In the polymerizations of **EV** with the gels **1a–c**, in which the content of Y was adjusted to be 1 mol % to the monomer, the conversions of **EV** and the yields of **PEV** showed the high values over 95% (Table II, Run 1–3). Even in the use of **1c** showing the smallest element ratio of Y to Si such as 1/19, the quantitative conversion and yield were recorded (Table II, Run 3). The increase of the molar ratios of Y to **EV** such as 5 and 10 mol % in the use of **1a** reasonably resulted in the quantitative formation of **PEV** (Table II, Run 6 and 7). The results demonstrated that the presence of only 1 mol % of Y to **EV** was enough effective for the polymerization. It was one of the characteristic features in the use of the silicate gel that the concentration of the monomer **EV** in benzene rarely affected on the efficiency of the polymerization. When the polymerizations of **EV** were carried out in 3.4 M benzene solution and without a solvent, the both yields of **PEV** were almost quantitative (Table II, Run 8 and 10). Even from the polymerization conducted in the diluted 0.9 M benzene solution, **PEV** was obtained in 89% yield.

The M_n s of **PBV** were estimated to be somewhat larger values over 7800 compared to those of **PEVs**. This seemed to be explained by the higher molecular weight of the monomer **BV**. In the polymerizations of **BV**, the decrease of the conversion from 92% to 68%

was observed, when the catalyst was changed from **1a** to **1c** (Table II, Run 4 and 5). In addition, in the use of **BV**, the yields of **PBV** decreased obviously with the increase of amount of the solvent (Table II, Run 12–14). Such differences of the experimental facts between the polymerization of **EV** and **BV** were interpreted that the polymerization of **EV** primarily progressed on the surface of the silicate gel **1**, but that of **BV** in a solution. This speculation was based on the steric effect of alkyl group involved in the monomer. The bulky butyl group should prevent the easy access of **BV** to the surface of the gel **1a**. Whereas, **EV** can readily approach to the surface and, further, may be adsorbed on **1a**. On the surface of the gel, the contact of the monomer with the active site neighboring yttrium should be favorable and the concentration of the substrates is possible. In the previous work, the possibility concerning such favorable effect of silica surface with the formation of ion pair intermediates was speculated.²³ Namely, as mentioned on the results using the gel **1c**, the silicate gel structure presented an appropriate reaction environment for **EV**, but **BV** could not utilize it effectively due to the steric factor.

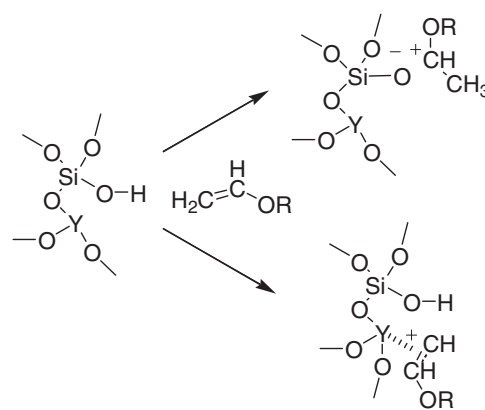
The results to examine the effects of solvent supported the above speculation. The polymerizations of **EV** conducted in dichloromethane, in which the concentrations of **EV** were adjusted to be 13.6 M and 1.7 M, respectively, afforded **PEVs** quantitatively (Table III, Run 1 and 2). The results coincided with those observed in benzene solution. However, in the polymerizations using the polar solvents such as acetone and acetonitrile, the yields of **PEV** varied markedly. The yields of **PEV** decreased from 100% to 62% with the decreases of the concentration of the monomer from 13.6 M to 1.7 M in acetone (Table III, Run 3 and 4). In a similar manner, the successful for-

mation of **PEV** was observed in 13.6M acetonitrile solution, but the polymerization of **EV** was failed in 1.7M solution (Table III, Run 5 and 6). In the cases using **BV**, the use of polar solvents such as acetone and acetonitrile was obviously unfavorable. The polymerizations conducted in those polar solvents gave **PBV** in the lower yields such as 17% and 12% (Table III, Run 9 and 10). These results suggested that the polar solvents covered the active sites on **1a** and/or the cationic species generated from the monomer located around Y, and made the contact of the activated specie with other vinyl ether monomers difficult. Consequently, the unfavorable effects due to the polar solvents seemed to appear more clearly in the cases using **BV**, which was difficult to stay on the surface of the gel by a steric hindrance of the bulky butyl group. The use of alcohols as the solvents gave unsuccessful results, in which no polymerization of **EV** progressed (Table III, Run 7 and 8). In these cases, the monomer was consumed completely, since no signal assigned to **EV** was detected in the ^1H NMR spectra after 8 h reaction. Although the detailed inspection on the spectra has not been done, the formation of acetal derivatives through the addition of the alcohol to **EV** was supposed. In addition, the catalyst was reusable. Even in the third use of **1a** after calcinations at 700°C for 1 h before reusing, **PEV** was obtained almost quantitative yield (Table II, Run 15).

CONCLUSION

The gel obtained from Na_2SiO_3 and YCl_3 , which consisted of metal silicate structures, was shown to be a usable solid catalyst for the polymerization of the vinyl ethers. The use of the solid catalyst enabled the simple handling. In the case of **EV**, after filtration of the silicate gel **1** and removal of volatile compounds by distillation under a reduced pressure, the pure **PEV** in the NMR spectral data was isolated. Furthermore, the catalyst **1** could be recycled at least third times without a loss of catalytic activity, although the calcination at 700°C was required before use.

The initiators for the polymerization were speculated to be silanol group and/or H_2O contained as an impurity, which generate a cation specie. Although the following results have not been listed in this report, it may present the preliminary information on such mechanistic aspects of the polymerization. The additions of 1 mol% of *n*-butylamine and 2, 6-dimethyl-1-pyridine in the polymerization system using **EV** with **1a** resulted in no formation of the polymeric product, but the conversions of **EV** were recorded to be 22% and 40%, respectively. Thus, the basic reagent, which should neutralize the acid site, obviously inhibited the polymerization. In addition, the use of



Scheme 2.

the later bulky base, which should show a difficulty to reach the active sites on the surface of **1a**, led to the somewhat higher conversion of **PEV** compared to that observed in the use of less bulky *n*-butylamine. The results suggested that the initiating step proceeds on the surface of the silicate gel and the generated cationic species stay around there, where the access of bulky substrate is unfavorable. Those speculated steps in the polymerization were shown in Scheme 2.

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