

Homopolymerization and Copolymerization with Styrene of Various Alkoxyvinylsilanes and Oxidative Transformation of C-Si Bond in the Resulting Copolymers to Afford Poly[(vinyl alcohol)-*co*-styrene]s

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Radical (co)polymerization behavior of alkoxyvinylsilanes [tri(isobutoxy)vinylsilane **1**, triethoxyvinylsilane **2**, di(isobutoxy)methylvinylsilane **3**, di(isobutoxy)phenylvinylsilane **4**, diethoxymethylvinylsilane **5**, and diethoxyphenylvinylsilane **6**] was systematically investigated. Homopolymerization and copolymerization with styrene of these alkoxyvinylsilanes were performed under various conditions in order to find appropriate initiating systems for the radical polymerizations. Transformation of some of the copolymers into poly[(vinyl alcohol)-*co*-styrene]s was examined *via* oxidative cleavage of the Si-C bonds in the alkoxyvinylsilane repeating units.

KEY WORDS: Radical Polymerization / Copolymerization / Poly(alkoxyvinylsilane) / Polystyrene / Polymer Reaction /

Radical polymerization of vinylsilanes followed by oxidative cleavage of C-Si bonds in the resulting repeating units could be a useful method for preparing poly(vinyl alcohol) (PVA) and its derivatives. The strategy, which was for the first time proposed by T. E. Hogen-Esch, *et al.* in 1996,¹ had not been realized until we recently demonstrated that copolymers of di(isobutoxy)methylvinylsilane **3** and styrene prepared by radical copolymerization can be transformed into poly[(vinyl alcohol)-*co*-styrene]s (Scheme 1).² In fact, that is the first example of the synthesis of poly[(vinyl alcohol)-*co*-styrene]. Although the copolymer should be prepared by hydrolysis of poly[(vinyl acetate)-*co*-styrene], the synthesis of the precursor copolymer *via* radical copolymerization is not practical due to the large difference of the monomer reactivity ratios [r_1 (styrene) = 56, r_2 (vinyl acetate) = 0.01].³ On the other hand, the oxidation of the homopolymer poly**3** afforded an insoluble product, whose elemental analysis agreed well with the composition of PVA.²

Although the results are highly promising for further development, the problem with the process is that the copolymerization initiated by 1,1'-azobis(cyclohexane-1-carbonitrile) (VAZO) at 130 °C did not proceed efficiently, giving rather low molecular weight copolymers in low yields ($M_n < 8600$, yield < 35%).² Accordingly, in order to establish this strategy as a practical synthetic method for polymeric materials containing vinyl alcohol (VA) repeating units, we should find more efficient conditions for the polymerization of **3** or other vinylsilanes, which can be polymerized to give higher molecular weight (co)polymers and can provide an appropriate C-Si bond for the following oxidative cleavage.

According to the literatures,⁴ the requirement for the oxidative cleavage to successfully proceed is the presence

of at least one -OR or -NR₂ group on Si. Thus, as for alkoxyvinylsilanes, because we have found that the repeating unit of a monoalkoxyvinylsilane [dimethyl(isobutoxy)vinylsilane] in the copolymer with styrene could not be efficiently transformed into VA repeating unit after oxidation,² we have trialkoxyvinylsilane and dialkoxyvinylsilane as candidates. Whereas there have been some reports and patents describing polymerization of alkoxyvinylsilanes,⁵⁻⁸ systematic investigation into radical polymerization behavior of various alkoxyvinylsilanes is needed for our purpose. As such alkoxyvinylsilanes other than **3**, we additionally chose tri(isobutoxy)vinylsilane **1**,⁵ triethoxyvinylsilane **2**,⁶ di(isobutoxy)phenylvinylsilane **4**, diethoxymethylvinylsilane **5**,^{6a,6d,7} and diethoxyphenylvinylsilane **6**,^{6a,6b} and investigated their radical (co)polymerization behavior in detail (Figure 1). In order to avoid the complexity caused by the high propensity for hydrolysis of C-O-Si linkage, vinylsilanes with SiOMe group^{6c,6d,8} were excluded. In addition, the results of oxidative transformation to give poly[(vinyl alcohol)-*co*-styrene]s will be described for some of the resulting poly(alkoxyvinylsilane-*co*-styrene)s.

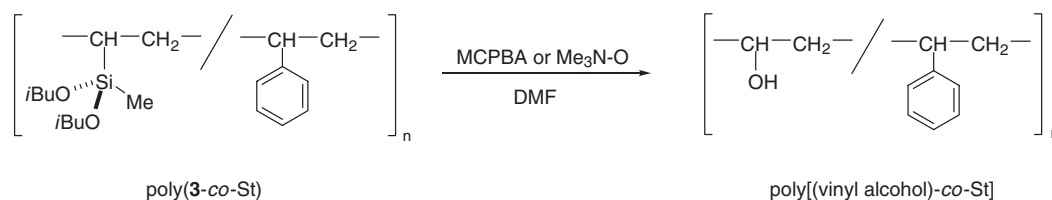
EXPERIMENTAL

Materials

DMF (Nacalai, 99%), AIBN (Nacalai, 98%), BPO (Kishida chemical), VAZO (Wako, 95%), VAm-111 (Wako, 95%), DCPO (Nacalai, 98%), MCPBA (Nacalai, 65%, including 25% of H₂O), trimethylamine oxide dihydrate (TMA-O, Kanto Chemical, >95%), KF (Nacalai, 99%), and KHF₂ (Wako, 99%) were used as received. Styrene (Aldrich, 99%) was dried over CaH₂ and distilled before use. Among the alkoxyvinylsilane monomers **1-6**, only **4** is a new compound, whose

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Scheme 1. Synthesis of Poly[(vinyl alcohol)-*co*-styrene].

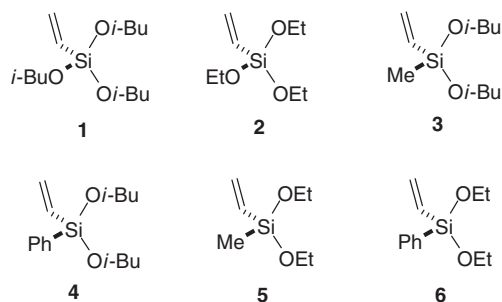


Figure 1. Alkoxyvinylsilanes Used in This Study.

synthetic procedure and characterization data are described below. Other monomers are commercially available or can be easily prepared from appropriate vinylsilane compounds *via* substitution of Si-Cl to Si-OR with ROH/Et₃N or Si-OR to Si-Ph with PhMgBr.

Measurements

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethylsilane as an internal standard in chloroform-*d* (CDCl₃) at room temperature (for monomers) or 50 °C (for polymers).

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-Bowin system (ver. 1.50) equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C. For the measurement of the samples obtained in run 9 in Table I, runs 5 and 6 and 11–14 in Table II, runs 4–7 in Table IV, runs 2 and 4 in Table V, calibration was carried out with polystyrene standards ($M_n = 10000$, $M_w/M_n = 1.08$, $M_n = 4000$, $M_w/M_n = 1.07$, and $M_n = 740$, $M_w/M_n = 1.04$), and the column used for the analyses were Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20 K for polystyrene). For the other samples than those mentioned above, calibration was carried out with polystyrene standards ($M_n = 4000$ – 200000 , $M_w/M_n = 1.02$ – 1.04), and the column used for the GPC analyses was a combination of G6000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 4000 K for polystyrene), G4000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 400 K for polystyrene), and G3000H_{HR} (TOSOH; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 60 K for polystyrene).

Table I. Radical polymerization of 3^a

run	initiator (I)	[M]/[I]	temp (°C)	yield (%)	M_n^b	M_w/M_n^b
1	AIBN	50	85	no polymerization	—	—
2	VAZO	50	130	34	7700	1.69
3	VAZO	50	110	33	6300	1.91
4	VAZO	50	90	25	6300	2.10
5	VAZO	200	90	19	9900	1.46
6	VAm-111	50	130	39	7900	1.61
7	VAm-111	50	110	45	10100	1.58
8	VAm-111	50	100	39	10300	1.57
9	BPO	50	130	43	1000	1.77
10	DCPO	50	160	55	2200	1.85
11	DCPO	50	130	57	8700	2.20
12	DCPO	100	130	70	9800	1.88
13	DCPO	200	130	77	9100	1.69
14	DCPO	50	100	45	10900	1.75
15	—	—	130	no polymerization	—	—

^aBulk; polymerization period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution.

Table II. Radical polymerization of various alkoxyvinylsilane^a

run	alkoxyvinylsilane (M)	initiator (I)	yield (%)	M_n^b	M_w/M_n^b
1	1	VAZO	54	13600	1.47
2	1	VAm-111	55	12600	1.57
3	1	DCPO	79	20800	2.80
4 ^c	2	VAZO	52	9300	2.38
5	4	VAZO	23	6600	1.51
6	4	VAm-111	26	4900	1.63
7	4	DCPO	51	8000	1.51
8	5	VAZO	47	6200	2.50
9	5	VAm-111	61	10400	3.10
10	5	DCPO	insoluble product	—	—
11	6	VAZO	29	3200	1.47
12	6	VAm-111	16	1600	1.39
13	6	DCPO	30	1700	1.38

^aBulk; [M]/[I] = 50; temperature = 130 °C; polymerization period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution. ^cReaction period = 7 h.

Purification by preparative recycling GPC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm × 20 mm i.d., exclusion molecular

weight of 70 K for polystyrene) and a JAIGEL-2H (600 mm × 20 mm i.d., exclusion molecular weight of 20 K for polystyrene) using CHCl₃ as eluent at a flow rate of 3.8 mL/min at 25 °C. The sample solution (3 mL containing *ca.* 0.3 g of the crude product) was injected and recycled before fractionation.

Elemental analyses were performed on a YANAKO MT-5 analyzer at Integrated Center for Science (INCS) in Ehime University.

Preparation of Di(isobutoxy)phenylvinylsilane (4)

Under a nitrogen atmosphere, a THF (100 mL) solution of **1** (24.8 g, 90.4 mmol) was placed in a round bottomed flask and cooled to 0 °C. After PhMgBr (80.0 mL of 1.13 M solution in THF, 90.4 mmol) was added at 0 °C, the mixture was stirred for 8 h at 0 °C to room temperature. After H₂O (100 mL) and CHCl₃ (150 mL) were added, the organic layer was extracted by using a separatory funnel, washed with 100 mL of H₂O, dried over Na₂SO₄, and filtrated. After the volatiles were removed under reduced pressure, the residual liquid was distilled under reduced pressure to give **4** as colorless liquid (23.9 g, 95.0%). ¹H NMR (400 MHz, CDCl₃) δ 7.12–7.64 (m, 5H, Ph), 5.86–6.23 (m, 3H, CH₂=CH-), 3.45 (d, *J* = 7.2 Hz, 4H, -O-CH₂-), 1.81 (m, 2H, CH₂-CHMe₂), 0.90 (d, *J* = 8.4 Hz, 12H, -CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 136.8 (CH₂=CH-), 134.7 (Ph), 133.3 (Ph-*ipso*), 132.2 (CH₂=CH-), 130.0 (Ph), 127.7 (Ph), 69.3 (-O-CH₂-CHMe₂), 30.7 (-O-CH₂-CHMe₂), 19.0 (-CH₃). Anal. Calcd for C₁₆H₂₆O₂Si: C, 69.01; H, 9.41. Found: C, 68.86; H, 9.43.

Radical Homopolymerization of Alkoxyvinylsilane

As a typical procedure for the homopolymerization of alkoxyvinylsilanes, the procedure for run 1 in Table II is described as follows. Under a nitrogen atmosphere, **1** (1.0 mL, 3.3 mmol) and VAZO (16.3 mg, 0.0669 mmol) were placed in a Schlenk tube, and the mixture was degassed three times by freeze-thawing. Then, the mixture was heated for 18 h at 130 °C. After the volatiles were removed under reduced pressure, the residue was purified by using preparative recycling GPC to give 0.495 g (54%) of poly**1** as colorless viscous oil.

¹H NMR (400 MHz, CDCl₃) δ 3.4–3.6 (br, 6H, -O-CH₂-), 1.7–1.9 (br, 3H, -OCH₂-CHMe₂), 1.5–1.7 (br, 2H, main chain -CH₂-), 0.7–1.1 (d, *J* = 6.0 Hz, 18H, -CH₃), 0.4–0.7 (br, 1H, main chain -CH-). Anal. Calcd for (C₁₄H₃₀O₃Si)_n: C, 61.26; H, 11.02. Found: C, 61.40; H, 8.83).

Other radical homopolymerizations of alkoxyvinylsilanes in Tables I and II were carried out in similar procedures.

Poly**2**; ¹H NMR (400 MHz, CDCl₃) δ 3.7–3.9 (br, 6H, -O-CH₂-), 1.4–1.8 (br, 2H, main chain -CH₂-), 1.0–1.4 (s, 9H, -CH₃), 0.4–0.9 (br, 1H, main chain -CH-). Anal. Calcd for (C₈H₁₈O₃Si)_n: C, 50.49; H, 9.53. Found: C, 50.30; H, 8.93).

Poly**4**; ¹H NMR (400 MHz, CDCl₃) δ 6.8–7.7 (br, 5H, Ph-H), 3.0–3.6 (br, 4H, -O-CH₂-), 1.6–2.0 (br, 2H, CH₂-CHMe₂), 1.1–1.60 (br, 2H, main chain -CH₂-), 0.2–1.0 (br, 12H, -CH₃ and 1H, main chain -CH-). Anal. Calcd for (C₁₆H₂₆O₂Si)_n: C, 69.01; H, 9.41. Found: C, 68.56; H, 8.96).

Poly**5**; ¹H NMR (400 MHz, CDCl₃) δ 3.6–3.8 (br, 4H, -O-CH₂-), 1.3–1.9 (br, 2H, main chain -CH₂-), 1.1–1.3 (br, 6H, -OCH₂CH₃), 0.4–1.0 (br, 1H, main chain -CH-), 0.0–0.4 (br, 3H, Si-CH₃). Anal. Calcd for (C₇H₁₆O₂Si)_n: C, 52.45; H, 10.06. Found: C, 52.63; H, 9.49).

Poly**6**; ¹H NMR (400 MHz, CDCl₃) δ 6.8–7.8 (br, 5H, Ph-H), 3.3–4.1 (br, 4H, -O-CH₂-), 1.3–2.0 (br, 2H, main chain -CH₂-), 0.8–1.2 (br, 6H, -CH₃), 0.3–0.8 (br, 1H, main chain -CH-). Anal. Calcd for (C₁₂H₁₈O₂Si)_n: C, 64.82; H, 8.16. Found: C, 64.31; H, 8.06).

Radical Copolymerization of Alkoxyvinylsilanes with Styrene

Bulk radical copolymerizations of alkoxyvinylsilanes with styrene in Tables III–VI were carried out in similar procedures as described for homopolymerization of **1**, heating a mixture of alkoxyvinylsilane, styrene, and VAZO in a Schlenk tube under a nitrogen atmosphere for 18 h at 130 °C after the degassing procedure. Isolation of the products was carried out by using preparative recycling GPC (for the samples obtained with feed ratios of [alkoxyvinylsilane] > [styrene]) or by reprecipitation from CHCl₃ into MeOH (for the samples obtained with the feed ratio of [alkoxyvinylsilane] = [styrene] or [alkoxyvinylsilane] < [styrene]).

Poly(**1**-*co*-styrene); ¹H NMR (400 MHz, CDCl₃) δ 6.0–7.5 (br, Ph-H), 2.9–3.7 (br, -O-CH₂-), 1.2–2.6 (br, main chain Hs on styrene repeating unit, main chain CH₂ on alkoxyvinylsilane repeating unit), 0.5–1.1 (br, -CH[CH₃]₂, main chain CH on alkoxyvinylsilane repeating unit). Anal. Calcd for a sample with a composition of [1]:[St] = 1:4.0: C, 79.95; H, 9.04. Found: C, 79.93; H, 8.97 for a sample with *M_n* = 4790, *M_w*/*M_n* = 1.51, [1]:[St] = 1:4.0 (composition by ¹H NMR).

Poly(**2**-*co*-styrene); ¹H NMR (400 MHz, CDCl₃) δ 6.0–7.5 (br, Ph-H), 3.2–3.9 (br, -O-CH₂-), 1.2–2.6 (br, main chain Hs on styrene repeating unit, main chain CH₂ on alkoxyvinylsilane repeating unit), 0.5–1.2 (br, -CH₃, main chain CH on alkoxyvinylsilane repeating unit). Anal. Calcd for a sample with a composition of [2]:[St] = 1:9.1: C, 85.27; H, 8.04. Found: C, 85.00; H, 8.08 for a sample with *M_n* = 4400, *M_w*/*M_n* = 1.30, [1]:[St] = 1:9.1 (composition by ¹H NMR).

Poly(**4**-*co*-styrene); ¹H NMR (400 MHz, CDCl₃) δ 6.0–7.7 (br, Ph-H), 2.8–3.6 (br, -O-CH₂-), 1.1–2.6 (br, main chain Hs

Table III. Radical copolymerization of alkoxyvinylsilane **3** with styrene^a

run	initiator (I)	temp (°C)	yield (%)	<i>M_n</i> ^b	<i>M_w</i> / <i>M_n</i> ^b	composition in copolymer, [3]:[St] (mol % of 3) (¹ H NMR)
1	DCPO	130	36	7900	1.54	1.0:6.1 (14%)
2	DCPO	120	33	7700	1.73	1.0:6.0 (14%)
3	DCPO	110	31	10600	2.18	1.0:9.8 (9.3%)
4	DCPO	100	24	15500	2.07	1.0:13 (7.1%)
5	—	130	9.9	37300	1.95	1.0:20 (4.8%)
6	—	100	2.2	107000	1.81	1.0:24 (4.0%)

^aBulk; [3]:[St] = 1:1; ([3]:[St])/[I] = 50; polymerization period = 18 h.
^b*M_n* and *M_w*/*M_n* were obtained by GPC calibration using standard polystyrenes in THF solution.

Table IV. Radical copolymerization of alkoxyvinylsilane **3** with styrene with various initiator concentration at 130 °C^a

run	initiator (I)	[3]:[St]	([3] + [St])/[I]	yield (%)	M_n^b	M_w/M_n^b	composition in copolymer, [3]:[St] (mol % of 3) (¹ H NMR)
1	DCPO	10:1	25	54	3100	2.22	4.5:1.0 (82%)
2	DCPO	10:1	50	38	2300	1.55	2.0:1.0 (67%)
3	DCPO	10:1	100	23	2300	1.36	1.3:1.0 (57%)
4	DCPO	10:1	200	16	2300	1.38	0.76:1.0 (43%)
5	VAZO	1:1	50	21	4500	1.27	1.0:9.0 (10%)
6	VAZO	1:1	100	21	5900	1.31	1.0:10 (9.1%)
7	VAZO	1:1	200	23	8400	1.49	1.0:11 (8.3%)

^aBulk; polymerization period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution.

Table V. Radical copolymerization of various alkoxyvinylsilanes with styrene at 130 °C^a

run	monomer (M)	initiator (I)	[M]:[St]	yield (%)	M_n^b	M_w/M_n^b	composition in copolymer, [M]:[St] (mol % of M) (¹ H NMR)
1	1	VAZO	1:1	19	4600	1.27	1.0:5.6 (15%)
2	1	VAZO	5:1	10	1600	1.34	1.0:1.1 (48%)
3	2	VAZO	1:1	29	4400	1.30	1.0:9.1 (9.9%)
4 ^c	5	VAZO	1:1	34	4800	1.33	1.0:12 (7.7%)

^aBulk; ([M] + [St])/[I] = 50; polymerization period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution. ^cReaction temperature = 120 °C.

Table VI. Radical copolymerization of alkoxyvinylsilanes with styrene: Synthesis of high molecular weight copolymers^a

run	monomer (M)	initiator (I)	[M]:[St]	temp (°C)	yield (%)	M_n^b	M_w/M_n^b	composition in copolymer, [M]:[St] (mol % of M) (¹ H NMR)
1	3	VAZO	1:1	90	22	11900	1.79	1.0:16 (5.9%)
2	3	VAm-111	1:1	100	5.9	22600	2.09	1.0:17 (5.6%)
3	3	VAm-111	3:1	100	4.8	7800	1.75	1.0:7.2 (12%)
4	3	DCPO	1:1	100	17	15500	2.14	1.0:16 (5.9%)
5	3	DCPO	3:1	100	4.8	6200	1.63	1.0:5.4 (16%)
6	4	VAZO	1:1	90	15	13400	1.78	1.0:11 (8.3%)
7	4	VAm-111	1:1	100	5.3	16500	1.76	1.0:7.2 (12%)
8	4	DCPO	1:1	100	8.4	13100	2.01	1.0:7.5 (12%)

^aBulk; ([M] + [St])/[I] = 200; polymerization period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution.

on styrene repeating unit, main chain CH₂ on alkoxyvinylsilane repeating unit), 0.5–1.0 (br, -CH₃, main chain CH on alkoxyvinylsilane repeating unit). Anal. Calcd for a sample with a composition of [4]:[St] = 1:3.3: C, 81.85; H, 8.49. Found: C, 81.40; H, 8.16 for a sample with M_n = 3520, M_w/M_n = 1.40, [1]:[St] = 1:3.6 (composition by ¹H NMR). Poly(**5-co-styrene**); ¹H NMR (400 MHz, CDCl₃): δ 6.0–7.5 (br, Ph-H), 3.0–3.8 (br, -O-CH₂-), 1.2–2.8 (br, main chain Hs on styrene repeating unit, main chain CH₂ on alkoxyvinylsilane repeating unit), 0.5–1.2 (br, -OCH₂CH₃), -0.6–0.2 (br, Si-CH₃). Anal. Calcd for a sample with a composition of [5]:[St] = 1:9.4: C, 86.66; H, 8.07. Found: C, 86.24; H, 8.08 for a sample with M_n = 4760, M_w/M_n = 1.33, [5]:[St] = 1:12 (composition by ¹H NMR).

Poly(**6-co-styrene**); ¹H NMR (400 MHz, CDCl₃): δ 6.0–7.7 (br, Ph-H), 3.0–3.9 (br, -O-CH₂-), 1.2–2.8 (br, main chain Hs

on styrene repeating unit, main chain CH₂ on alkoxyvinylsilane repeating unit), 0.5–1.2 (br, -CH₃). Anal. Calcd for a sample with a composition of [6]:[St] = 1:4.4: C, 83.29; H, 7.88. Found: C, 83.53; H, 7.69 for a sample with M_n = 4470, M_w/M_n = 1.55, [6]:[St] = 1:3.8 (composition by ¹H NMR).

Oxidative Cleavage of Poly(alkoxyvinylsilane-co-St)

As a typical procedure for the oxidative cleavage of poly(alkoxyvinylsilane-co-St) with MCPBA, the procedure for run 1 in Table VII is described as follows. Under a nitrogen atmosphere, poly(**2-co-styrene**) (0.249 g), KF (131 mg, 2.25 mmol), and DMF (25 mL) were placed in a Schlenk tube. After a DMF (15 mL) solution of MCPBA (506 mg, 2.20 mmol) was added dropwise at room temperature, the mixture was heated for 18 h at 60 °C. After 50 mL of H₂O was added to the mixture, it was extracted with 50 mL of Et₂O

Table VII. Oxidative cleavage of poly(alkoxyvinylsilane-*co*-St)^a

run	monomer (M)	prepolymer		oxidant	yield (%)	after oxidative cleavage
		GPC M_n M_w/M_n	composition [M]:[St] mol % of M (¹ H NMR)			GPC M_n^b M_w/M_n^b
1	2	4400	1:9.1	MCPBA	80.3	3840
		1.30	9.9%			1.34
2	3	22600	1:15	MCPBA	86.9	16900
		2.65	6.3%			2.76
3	3	22600	1:15	TMA-O	93.2	16600
		2.65	6.3%			2.81
4	5	4760	1:12	MCPBA	79.2	3760
		1.33	7.7%			1.31
5	5	4760	1:12	TMA-O	64.0	3990
		1.33	7.7%			1.31
6	6	4470	1:3.8	MCPBA	87.5	4070
		1.55	21%			2.06

^aPoly(alkoxyvinylsilane-*co*-St) (0.20–0.30 g) was reacted in 40 mL of DMF; [MCPBA or TMA-O] = [KF or KHF₂] = 5 × [repeating unit of alkoxyvinylsilane in the copolymers]; temperature = 60 °C; reaction period = 18 h. ^b M_n and M_w/M_n were obtained by GPC calibration using standard polystyrenes in THF solution.

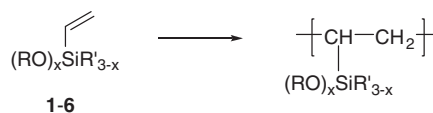
twice, and the combined organic phase was washed with 0.20 M NaHSO₃ aqueous solution (50 mL × 2), saturated NaHCO₃ aqueous solution (50 mL × 2), 50 mL of H₂O. The organic phase was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give 0.175 g (80.3%) of poly[(vinyl alcohol)-*co*-styrene] as a white powder. Other oxidative cleavage in Table VII were carried out in similar procedures with MCPBA/KF or TMA-O/KHF₂. Data for characterization of poly[(vinyl alcohol)-*co*-styrene] were reported in our previous paper.²

RESULTS AND DISCUSSION

Homopolymerization of Alkoxyvinylsilanes

In our previous paper² describing radical polymerization of **3** and dimethyl(isobutoxy)vinylsilane using benzoyl peroxide (BPO) and VAZO as initiators (bulk, at 130 °C), molecular weights of the resulting polymers were rather low ($M_n < 6500$). Thus, in order to find an initiating system to give higher molecular weight poly(alkoxyvinylsilane)s, radical polymerization of **3** was examined under various reaction conditions (Scheme 2, Table I). Whereas the radical polymerization in our previous paper² was carried out without deoxygenation of the reaction mixture, all the polymerizations in this study were performed after degassing procedure, because of which the results here were somewhat different from those we previously reported.

Although AIBN could not initiate the polymerization of **3** at 85 °C, VAZO was effective for initiating the polymerization. For example, poly**3** with $M_n = 7700$ was obtained in a 34%



Scheme 2. Radical Polymerization of Alkoxyvinylsilanes.

yield at 130 °C with [M]/[I] = 50 (run 2). Whereas lowering the polymerization temperature resulted in lower yields and M_n s (runs 3 and 4), a higher molecular weight polymer ($M_n = 9900$) was obtained by reducing the initiator concentration to [M]/[I] = 200 at 90 °C (run 5). Although 2,2'-azobis(*N*-cyclohexyl-2-methylpropionamide) (VAm-111), whose decomposition is much slower than VAZO (10 h half-life decomposition temperature; VAZO = 88 °C in toluene, VAm-111 = 111 °C in ethylbenzene)⁹ showed similar initiating activity at 130 °C as VAZO (run 6), the molecular weights of the polymers increased by lowering the polymerization temperature, reaching up to 10000 at 110 and 100 °C without yield reduction (runs 7 and 8).

As a non-azo type initiator other than BPO, which gave a low molecular weight poly**3** at 130 °C (run 9), a slowly decomposing radical initiator, dicumyl peroxide (DCPO, k_d in chlorobenzene; DCPO = 1.93×10^{-5} at 112 °C, BPO = 1.93×10^{-3} at 113 °C),¹⁰ was employed for the polymerization of **3**. Whereas DCPO afforded poly**3** with a low M_n at 160 °C (run 10), a higher molecular weight polymer ($M_n = 8700$) was obtained in a moderate yield (57%) by the polymerization at 130 °C (run 11). By increasing the [M]/[I] ratio to 100 and 200, the yield increased significantly along with slight increase in M_n (runs 12 and 13). Lowering the polymerization temperature to 100 °C slightly increased the M_n to 10900 (run 14), but the polymer yield became significantly lower. These results reveal that polymerization should be conducted at lower temperature in order to obtain higher molecular weight poly**3**s. In addition, at least for the polymerization of **3**, initiators with slower decomposition rate (VAm-111 and DCPO) are more suitable for obtaining higher molecular weight polymers, because the lower concentration of radical species would suppress termination *via* bimolecular radical coupling. Furthermore, we should mention that because the polymerization temperatures employed throughout this study are basically too high for the radical initiators, there would be more appropriate initiators that would give much better polymerization results. Spontaneous polymerization of **3** did not proceed at 130 °C (run 15).

Radical polymerization of other alkoxyvinylsilanes **1**, **2**, and **4–6** was examined at 130 °C with [M]/[I] = 50 using VAZO, VAm-111, and DCPO as initiators, and the results are summarized in Table II. All the monomers were converted into poly(alkoxyvinylsilane)s, whose structures were confirmed by ¹H NMR and elemental analyses (see Experimental Section). In particular, the elemental analyses indicate that the hydrolysis of the Si-O-C bond does not occur at least for several days after the polymerization for all the poly(alkoxyvinylsilane)s. However, after standing for longer period at

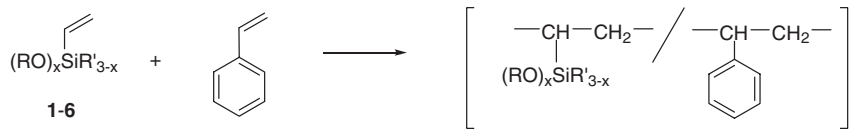
ambient temperature in the air, all the polymers including poly**3** became insoluble, which would be ascribed to the hydrolysis followed by cross-linking *via* Si-O-Si bond formation.

Tri(isobutoxy)vinylsilane **1** was found to be effectively polymerized (runs 1–3, Table II), and a polymer with $M_n = 20800$ was obtained in a good yield by using DCPO as an initiator (run 3). Similarly, polymerization of triethoxyvinylsilane **2** proceeded to give a polymer with $M_n = 9300$ (run 4). Di(isobutoxy)phenylvinylsilane **4** was polymerized to give polymers with lower M_n s and in lower yields compared to the poly**3**s obtained under the same conditions (run 5–7). Although diethoxymethylvinylsilane **5** gave a polymer with $M_n = 10400$ in a 61% yield with the initiation of VAm-111, DCPO-initiated polymerization of **5** resulted in the formation of an insoluble product, probably because cross-linking of alkoxyvinyl moiety occurred in this case (runs 8–10). Polymerization of **6** afforded only low molecular weight polymers (runs 11–13).

These results in Table II indicate that the combination of isobutoxy-containing monomers with DCPO as an initiator is suitable for obtaining high molecular weight poly(alkoxyvinylsilane)s with moderate stability in relatively good yields, and it is actually possible to prepare poly(alkoxyvinylsilane)s with M_n over 10000 by choosing appropriate polymerization conditions. As representative examples, ^1H NMR spectra of poly**5** and poly**6** are shown in Figure 2.

Copolymerization of Alkoxyvinylsilane with Styrene

Radical copolymerization of **3** with styrene in a feed ratio of $[\mathbf{3}]:[\text{St}] = 1:1$ was investigated at various temperatures (Scheme 3) and the representative results are summarized in Table III. Because styrene is much more reactive than **3** in the copolymerization as we previously reported $[r_1(\text{St}) = 20.0, r_2(\mathbf{3}) = 0.11]$,² the incorporation of **3** is not effective. In addition, compared to homopolymerization of each monomer, the copolymer yields are generally low. As an example, runs 1–4 show the copolymerization results in the temperature range of 130–100 °C initiated by DCPO, which gave better results than VAZO and VAm-111 with respect to M_n , copolymer yields, and incorporation of **3**. As expected for conventional radical polymerization, increase of M_n with the decrease of the temperature was observed because bimolecular termination should be suppressed at lower temperatures due to lower radical concentration. On the other hand, the observed dependence of incorporation of **3** on polymerization temperature suggests that because reactivity of **3** diminishes with decreasing temperature, relative reactivity for styrene was enhanced at lower temperatures, resulting in the low incorporation of **3** in the products. At the maximum, a copolymer with 14 mol % composition of **3** was obtained with the copolymerization (runs 1 and 2).



Scheme 3. Radical Copolymerization of Various Alkoxyvinylsilanes with Styrene.

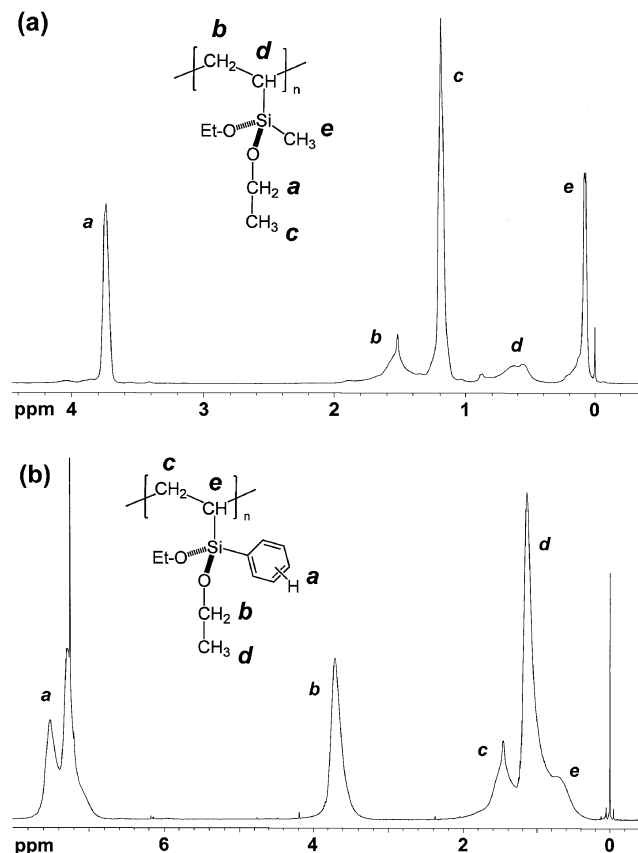


Figure 2. ^1H NMR spectra poly**5** (a) and poly**6** (b).

When VAZO and VAm-111 were used as initiators under the same conditions, compared to the results with DCPO, slightly lower **3** incorporation was observed for both azo initiators, whereas significantly decreased and slightly increased M_n s were observed for VAZO- and VAm-111-initiated polymerization, respectively.

Without adding radical initiators, copolymers with low **3** content were obtained in very low yields by heating (runs 5 and 6). However, it is interesting to note that the M_n s of the copolymers were much higher than those of the copolymers obtained with the radical initiators.

Then, the copolymerization of **3** with styrene with various feed ratios was carried out using DCPO as an initiator at 130 °C. Figure 3 shows the dependence of M_n and composition of **3** on the feed ratio of **3** (mol %). As can be clearly seen from the figure, the incorporation of **3** increased corresponding to the feed ratio of **3**, indicating that the copolymer composition can be controlled by changing the feed ratio. However, M_n s of the copolymers decreased with the increase of the feed ratio of **3**

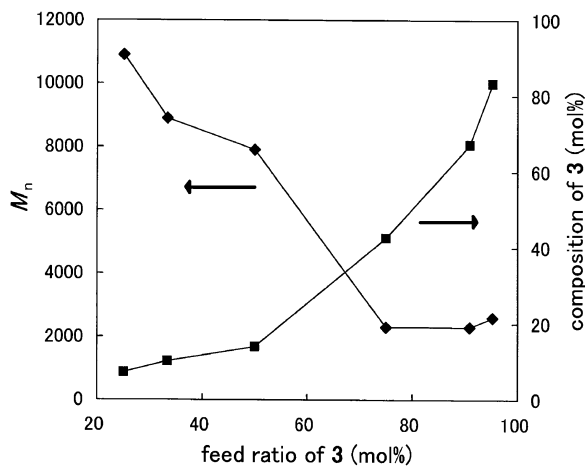


Figure 3. Plots of GPC-estimated M_n (◆) and composition of **3** (mol %) (■) against feed ratio of **3** (mol %) for the DCPO-initiated radical copolymerization (bulk) of **3** with styrene at 130 °C. ([**3**] + [St])/[DCPO] = 50. Polymerization period = 18 h.

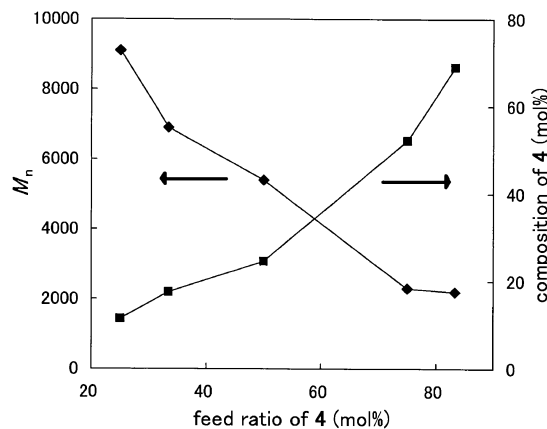


Figure 5. Plots of GPC-estimated M_n (◆) and composition of **4** (mol %) (■) against feed ratio of **4** (mol %) for the DCPO-initiated radical copolymerization (bulk) of **4** with styrene at 130 °C. ([**4**] + [St])/[DCPO] = 50. Polymerization period = 18 h.

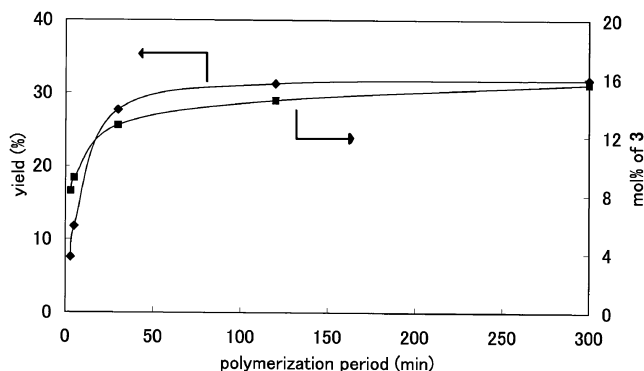


Figure 4. Plots of polymer yield (%) (◆) and composition of **3** (mol %) (■) against polymerization period (min.) for the VAZO-initiated radical copolymerization (bulk) of **3** with styrene at 130 °C. [**3**]:[St] = 2:1; ([**3**] + [St])/[VAZO] = 50. M_n (GPC) of the copolymers = 1800–2300.

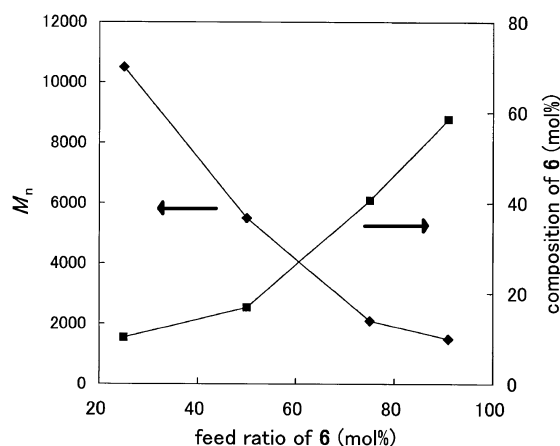


Figure 6. Plots of GPC-estimated M_n (◆) and composition of **6** (mol %) (■) against feed ratio of **6** (mol %) for the DCPO-initiated radical copolymerization (bulk) of **6** with styrene at 130 °C. ([**6**] + [St])/[DCPO] = 50. Polymerization period = 18 h.

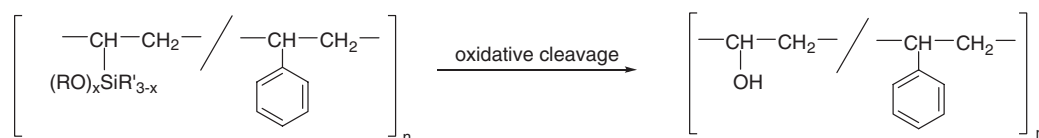
because of the lower reactivity of **3** compared to styrene in this copolymerization system.

Then, expecting the formation of high molecular weight copolymers with relatively high **3** composition, we conducted the copolymerization of **3** with styrene with a constant feed ratio of [**3**]:[St] = 10:1 with various initiator concentration as shown in runs 1–4 in Table IV. However, contrary to our expectation based on the conventional radical polymerization behavior, M_n s of the copolymers did not increase with the decrease of the initiator concentration, whose reason is not clear at present. On the other hand, the expected dependence of M_n on the initiator concentration was clearly observed for the copolymerization when the feed ratio was [**3**]:[St] = 1:1 as shown in runs 5–7. As for the dependence of **3** incorporation on the initiator concentration in runs 1–4, we can assume that the incorporation corresponds to the conversion. Because styrene should be converted much faster than **3** as the reactivity ratio mentioned,² styrene would be preferentially consumed at the

early stage of the polymerization. Accordingly, higher conversions under the conditions with such high initial concentration of **3** resulted in the formation of copolymers with higher **3** incorporation.

Although we have demonstrated the reactivity difference between styrene and **3** by showing the r_1 and r_2 ratio for these monomers,² the preferential consumption of styrene in the copolymerization was confirmed by measuring the composition of the copolymers after a certain period of the polymerization (Figure 4). It was actually demonstrated that the composition of **3** in the copolymers gradually increased with the polymerization period.

The copolymerization of other alkoxyvinylsilanes **1**, **2**, and **4–6** with styrene was carried out. The plots of M_n and composition of alkoxyvinylsilanes **4** and **6** obtained by DCPO-initiated copolymerization with styrene against the feed ratios are illustrated in Figures 5 and 6, respectively, where the similar behaviors are observed as that in Figure 3. Together



Scheme 4. Oxidative Cleavage of Poly(alkoxyvinylsilane-co-St).

with the representative results for the VAZO-initiated copolymerization of **1**, **2**, and **5** with styrene listed in Table V, we can conclude that it is possible to prepare copolymers of these alkoxyvinylsilanes **1–6** with styrene with a variety of compositions, although molecular weights become lower with higher composition of **1–6** and the efficiency of the incorporation of **1–6** somewhat depends on the monomer structures.

In contrast to the aforementioned homopolymers of **1–6**, the copolymers are basically stable without becoming insoluble while being kept in the air at room temperature. In addition, the elemental analysis for these copolymers confirmed that hydrolysis of Si-O-C did not occur (Experimental Section).

In order to prepare high molecular weight copolymers, the copolymerization with low initiator concentration ($[M]:[I] = 200:1$) was conducted at relatively low temperatures (90–100 °C) as listed in Table VI. For the copolymerization of **3** with styrene in a $[3]:[St]$ ratio of 1:1, copolymers with M_n s over 10000 and 5–6% composition of **3** were obtained in low yields (runs 1,2,4). In particular, M_n of the copolymer obtained by VAm-111 reached 22600 (run 2). On the other hand, when **4** was used as an alkoxyvinylsilane, the composition of **4** in the copolymers were higher than those of **3** under the same conditions, although the copolymer yields became lower. Runs 7 and 8 furnished copolymers with M_n over 10000 and alkoxyvinylsilane incorporation over 10 mol %.

Oxidative Cleavage of C-Si in Poly(alkoxyvinylsilane-co-styrene): Transformation into Poly[(vinyl alcohol)-co-styrene]

Oxidative cleavage of C-Si bond in copolymers of alkoxyvinylsilanes **2**, **3**, **5**, and **6** with styrene was carried out by using 5 equiv of MCPBA or TMA-O as an oxidant at 60 °C for 18 h in DMF to obtain poly[(vinyl alcohol)-co-styrene]s (Scheme 4). As summarized in Table VII, GPC-estimated M_n s of all the products of the oxidation are lower than those of the corresponding prepolymers. In a similar manner as was demonstrated in our previous paper,² signals derived from the silyl groups almost disappeared in the ¹H NMR spectra of these oxidized polymers in Table VII. Along with the disappearance of absorptions assignable to Si-O stretch at around 1100 cm⁻¹ in their IR spectra, we can suppose that the oxidative transformation proceeded rather efficiently, although we do not have any quantitative data for the efficiency. Developing the method for quantifying the progress of the transformation is our current important objective.

CONCLUSIONS

We have demonstrated that alkoxyvinylsilanes **1–6** can be used as monomers for radical (co)polymerization to afford poly(alkoxyvinylsilane)s and poly(alkoxyvinylsilane-co-styrene)s. As for homopolymerization of the alkoxyvinylsilanes, although the homopolymers tend to become insoluble because of hydrolysis of alkoxyvinyl groups followed by crosslinking, poly(alkoxyvinylsilane)s with $M_n > 10000$ can be obtained in good yields. On the other hand, copolymerization of alkoxyvinylsilane with styrene gives stable copolymers, although the copolymer yields are rather low. The composition of the two kinds of the repeating units can be controlled by changing the monomer feed ratios, although higher incorporation of alkoxyvinylsilane units results in the lower yields and M_n s. Not only for the synthesis poly[(vinyl alcohol)-co-styrene] by the transformation of the alkoxyvinylsilane repeating units into vinyl alcohol repeating units described in this paper, the polymers derived from the alkoxyvinylsilanes would be useful for various applications.

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