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ORIGINAL PAPER

Preparation of poly[(vinyl alcohol)-*co*-(methyl methacrylate)] by oxidative transformation of C–Si bond in poly[di(isobutoxy)phenylvinylsilane-*co*-(methyl methacrylate)]

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Abstract Radical copolymerization of di(isobutoxy)methylvinylsilane **1** and di(isobutoxy)phenylvinylsilane **2** with methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BA) was carried out, and the oxidative cleavage of Si–C bonds in the resulting copolymers was examined to prepare copolymers having repeating units of vinyl alcohol (VA). Although the incorporation of **1** and **2** in the copolymerization of these alkoxyvinylsilanes with MMA was not so effective (**1** or **2** content < 18 mol%), MCPBA-induced oxidative transformation of a poly(**2**-*co*-MMA) with 9.0 mol% of **2** content proceeded efficiently, giving a poly[(vinyl alcohol)-*co*-MMA]. On the other hand, whereas poly(**1** or **2**-*co*-*n*-BA)s with relatively higher **1** or **2** contents (up to 45 mol%) can be prepared by the radical copolymerization of **1** or **2** with *n*-BA, oxidation of the copolymers afforded insoluble products.

Keywords Radical copolymerization · Alkoxyvinylsilane · Alkyl (meth)acrylate · Polymer reaction

Introduction

Oxidative cleavage of a certain type of Si–C bond has been reported to give C–OH groups efficiently [1–4]. When the transformation is applied for Si–C bonds in vinylsilane repeating units in polymers, the products should include a repeating unit structure derived from vinyl polymerization of vinyl alcohol (VA) [5]. Although the VA repeating unit is generally prepared by saponification of a repeating unit from vinyl acetate (VAc), the new strategy via oxidative cleavage would be a useful method for preparing poly(vinyl alcohol) (PVA) derivatives, which cannot be

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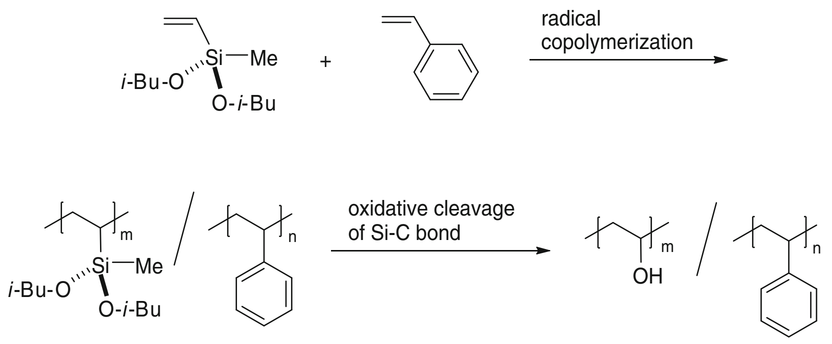
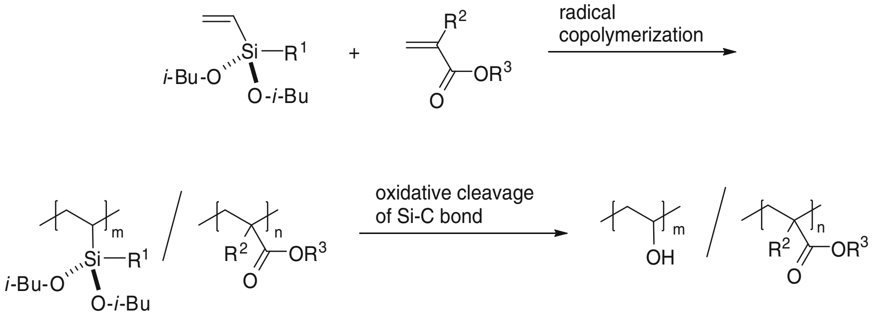


Scheme 1 Synthesis of poly(VA-*co*-styrene) via oxidative transformation of poly(alkoxyvinylsilane-*co*-styrene)



Scheme 2 Synthesis of poly{VA-*co*-[alkyl (meth)acrylate]}

obtained using VAc as a starting material. Accordingly, we have chosen some alkoxyvinylsilanes whose Si–C bond after their polymerization could be oxidatively cleaved, and we have explored radical (co)polymerization of such alkoxyvinylsilanes and subsequent oxidative transformation of the resulting polymers [6, 7]. Although the oxidation of polyalkoxyvinylsilane homopolymers resulted in the formation of insoluble products, whose elemental analyses agreed with the values expected for PVA, the oxidative cleavage actually proceeded for poly(alkoxyvinylsilane-*co*-styrene), giving poly(VA-*co*-styrene) (Scheme 1) [6, 7]. Whereas the structure of poly(VA-*co*-styrene) should be essentially given by saponification of poly(VAc-*co*-styrene), to our knowledge, synthesis of the OH-containing copolymer had not been reported until our previous publication [6].

In this article, the same strategy is applied for copolymerization of alkoxyvinylsilane with alkyl (meth)acrylate followed by the oxidative transformation, in order to prepare poly{VA-*co*-[alkyl (meth)acrylate]} (Scheme 2). The structure of poly{VA-*co*-[alkyl (meth)acrylate]} cannot be simply obtained from copolymers of VAc and alkyl (meth)acrylate, because saponification of poly{VAc-*co*-[alkyl (meth)acrylate]} should give poly{VA-*co*-[(meth)acrylic acid]}.

Experimental

Materials

DMF (Nacalai, 99%), VAZO (Wako, 95%) (Nacalai, 98%), MCPBA (Nacalai, 65%, including 25% of H_2O), and KF (Nacalai, 99%) were used as received. Methyl methacrylate (MMA) (Nacalai, 99%) was dried over CaH_2 and distilled before use. *n*-BA (Nacalai, 99%) were treated with 1N NaOH aqueous solution, dried over Na_2SO_4, and used without further purification. Synthetic procedures for alkoxyvinylsilane monomers **1** [5] and **2** [6] are described in our previous publications.

Measurements

^1H (400 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer using tetramethysilane as an internal standard in chloroform *d* ($CDCl_3$) at 50 °C.

Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured by means of gel permeation chromatography (GPC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using tetrahydrofuran as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with poly(MMA) standards. The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 600 K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm i.d., 5 μm average particle size, exclusion molecular weight of 20 K for polystyrene), and poly(MMA) standards (Shodex M-75, $M_n = 200{,}000$, $M_w/M_n = 1.05$, $M_n = 47{,}300$, $M_w/M_n = 1.02$, $M_n = 21{,}700$, $M_w/M_n = 1.02$, $M_n = 5{,}220$, $M_w/M_n = 1.06$, $M_n = 2{,}190$, $M_w/M_n = 1.08$) and dibutyl sebacate (MW = 314.5) were used for the calibration.

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 $CHCl_3$ 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.

Radical copolymerization of alkoxyvinylsilanes with MMA or *n*-BA

Under a nitrogen atmosphere, alkoxyvinylsilane (**1** or **2**), alky (meth)acrylate (MMA or *n*-BA), and radical initiator (VAZO or DCPO) 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 a certain temperature defined in Tables 1 and 2. After the volatiles were removed under reduced pressure, the residue was purified by reprecipitation from $CHCl_3$ into hexane or by using preparative recycling GPC.

Table 1 Radical copolymerization of di(isobutoxy)methylvinylsilane **1** with MMA and *n*-BA

Run	Comonomer (*M*)	Initiator (*I*)	Temp. (°C)	[**1**]:[M]	Yield (%)	M_n^a	M_w/M_n^a	Composition (mol% of **1**, ^{1}H NMR)
1	MMA	VAZO	80	1:1	22.9	20,600	3.7	7.8
2	MMA	VAZO	80	2:1	8.3	15,600	2.1	13.0
3	MMA	DCPO	80	1:1	25.0	47,100	3.3	7.1
4	MMA	DCPO	80	2:1	9.4	49,200	2.4	10.7
5	*n*-BA	VAZO	100	1:3	62.8	19,800	6.7	12.3
6	*n*-BA	VAZO	80	1:3	52.5	254,000	2.7	11.7
7	*n*-BA	VAZO	100	1:1	53.1	5,300	4.1	32.4
8	*n*-BA	VAZO	80	1:1	43.0	8,000	8.0	22.2
9	*n*-BA	DCPO	100	1:1	48.4	7,700	7.4	30.4
10	*n*-BA	DCPO	80	1:1	33.1	42,700	4.4	18.9

Bulk; ([**1**] + [M])/[I] = 50; polymerization period = 18 h

[a] M_n and M_w/M_n were obtained by GPC calibration using standard polyMMAs in THF solution

Table 2 Radical Copolymerization of Di(isobutoxy)phenylvinylsilane **2** with MMA and *n*-BAP

Run	Comonomer (*M*)	Initiator (*I*)	Temp. (°C)	[**2**]:[M]	Yield (%)	M_n^b	M_w/M_n^b	Composition (mol% of **2**, ^{1}H NMR)
1	MMA	VAZO	80	1:2	43.4	58,100	3.1	6.5
2	MMA	VAZO	80	1:1	29.6	36,400	1.6	12.4
3	MMA	VAZO	80	2:1	15.4	24,800	1.5	15.4
4	MMA	VAZO	80	3:1	4.7	18,100	1.4	18.0
5	MMA	DCPO	80	1:2	40.4	98,700	4.3	8.6
6	MMA	DCPO	80	1:1	24.5	60,000	2.7	10.5
7	*n*-BA	VAZO	120	1:3	66.8	6,600	3.6	18.6
8	*n*-BA	VAZO	120	1:1	57.0	3,200	2.7	40.3
9	*n*-BA	VAZO	100	1:1	64.7	4,900	3.4	35.0
10	*n*-BA	VAZO	80	1:1	48.5	5,900	5.2	26.8
11	*n*-BA	DCPO	120	1:1	87.1	4,700	4.0	44.5
12	*n*-BA	DCPO	100	1:1	47.8	6,000	3.8	32.4
13	*n*-BA	DCPO	80	1:1	25.7	10,500	4.3	23.7

Bulk; ([**2**] + [M])/[I] = 50; polymerization period = 18 h

[a] M_n and M_w/M_n were obtained by GPC calibration using standard polyMMAs in THF solution

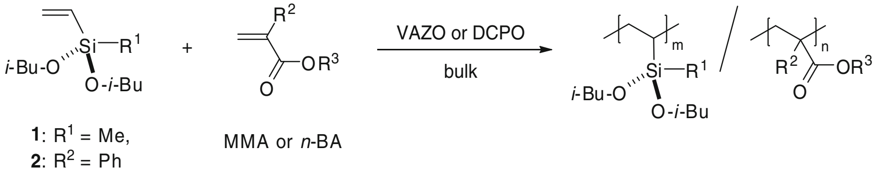
Oxidative cleavage of poly(alkoxyvinylsilane-*co*-MMA)

Under a nitrogen atmosphere, poly(alkoxyvinylsilane-*co*-MMA) (0.1–0.4 g, KF, and DMF (20 mL) were placed in a Schlenk tube. After a DMF (20 mL) solution of MCPBA was added dropwise at room temperature, the mixture was heated for 18 h at 120 °C. After 50 mL of 0.20 M $NaHSO_3$ aqueous solution was added to the mixture, it was extracted with 140 mL of $CHCl_3$, and the organic phase was washed with 100 mL of H_2O. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give crude poly(VA-*co*-MMA), which was purified by reprecipitation into MeOH.

Results and discussion

Radical copolymerization of di(isobutoxy)methylvinylsilane 1 with MMA and *n*-BA

Although a few literatures reported radical copolymerization of alkoxyvinylsilanes with alkyl (meth)acrylates [8, 9], detailed studies on the copolymerization behavior of these monomers have not been conducted so far. In particular, radical copolymerization of alkoxyvinylsilanes we employed in this study, di(isobutoxy)methylvinylsilane **1** and di(isobutoxy)phenylvinylsilane **2**, with alkyl (meth)acrylates has not been reported. Thus, we investigated copolymerization of **1** and **2** with MMA and *n*-BA to prepare precursor polymers, poly{**1** or **2**-*co*-[alkyl (meth)acrylate]}, which would be transformed into poly{VA-*co*-[alkyl (meth)acrylate]} by oxidative transformation (Scheme 3).



Scheme 3 Radical copolymerization of alkoxyvinylsilane **1** and **2** with MMA and *n*-BA

First of all, we examined radical copolymerization of **1** with MMA using 1,1′-azobis(cyclohexane-1-carbonitrile) (VAZO) as an initiator at 80 °C. For example, bulk copolymerization of **1** with MMA in a feed ratio of [**1**]/[MMA] = 1:1 afforded poly(**1**-*co*-MMA), whose GPC-estimated M_n was 20,600 (based on PMMA standards), in a 22.9% yield after purification by reprecipitation into hexane (run 1 in Table 1). As ^1H NMR spectrum for a representative sample of poly(**1**-*co*-MMA) (run 2 in Table 1) in Fig. 1 demonstrates, the incorporation of the repeating unit derived from **1** was confirmed by the appearance of signals for $SiOCH_2$ at 3.38 ppm and $SiCH_3$ at 0.07 ppm, although the latter would overlap with the signal from contaminating grease. The **1** content in the copolymer can be estimated from the relative signal intensity of $SiOCH_2$ for **1** and OCH_3 for MMA (3.59 ppm) to be 7.8 mol%. The copolymerization with a higher feed ratio of **1** (run 2; [**1**]/[MMA] = 2:1) resulted in the decrease of the copolymer yield with the expected increase of **1** content in the product. The copolymerization with dicumyl peroxide (DCPO) as an initiator exhibited similar behavior, except that the M_n of the products became much higher (runs 3 and 4).

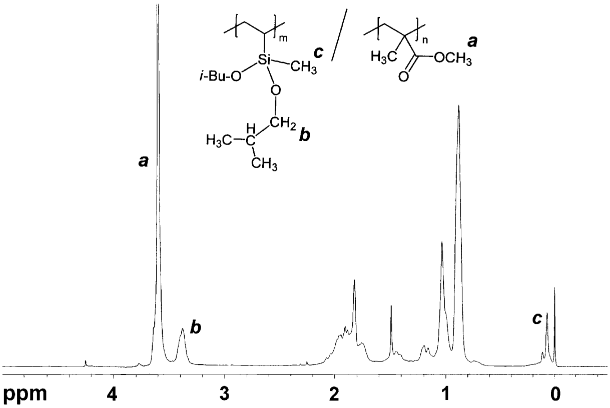


Fig. 1 ^{1}H NMR spectrum of poly(**1**-*co*-MMA) (run 2 in Table 1)

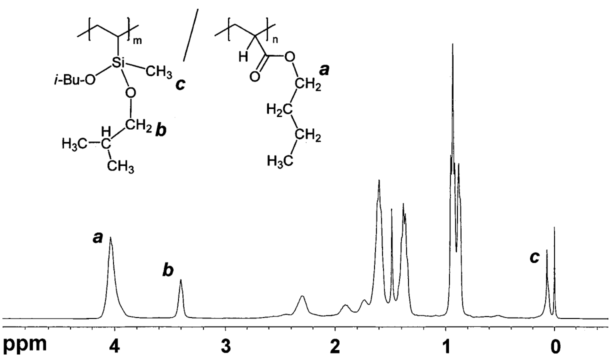


Fig. 2 ^{1}H NMR spectrum of poly(**1**-*co*-*n*-BA) (run 5 in Table 1)

The radical copolymerization behavior of **1** with *n*-BA was somewhat different than that with MMA. As shown in runs 5 and 6 in Table 1, the copolymerizations at 100 and 80 °C with a feed ratio of [**1**]/[*n*-BA] = 1:3 gave copolymers in good yields, and the incorporation of **1** into the products was more efficient than that with MMA, as evidenced by the **1** content of 11–12 mol%. Interesting to note is that the lowering the polymerization temperature brought about drastic increase of M_n of the copolymer, giving a product with $M_n = 254{,}000$ in run 6. On the other hand, copolymerizations with a higher feed ratio of **1** ([**1**]/[*n*-BA] = 1:1) afforded copolymers with lower M_ns (runs 7 and 8), although the **1** content in the products increased as expected. Similar behavior was observed in the copolymerization using DCPO as an initiator, as listed in runs 9 and 10. Figure 2 shows ^{1}H NMR spectrum for poly(**1**-*co*-*n*-BA) (run 5 in Table 1), where the composition can be determined from the peak intensity between OCH_2 signals at 4.04 ppm for *n*-BA and 3.40 ppm for **1**.

Radical copolymerization of di(isobutoxy)phenylvinylsilane 2 with MMA and *n*-BA

Next, di(isobutoxy)phenylvinylsilane **2** was used as a monomer for copolymerization with MMA and *n*-BA. VAZO-initiated copolymerization of **2** with MMA shown in runs 1–4 in Table 2 indicates that yield, M_n, and alkoxyvinylsilane content improved compared to the results of the copolymerization of **1** with MMA under the similar condition, while the similar dependence of these values on the comonomer feed ratio was also observed. The copolymerization with DCPO as an initiator afforded higher molecular weight copolymers as listed in runs 5 and 6.

In the ^{1}H NMR spectrum in Fig. 3 for poly(**2**-*co*-MMA) (run 4 in Table 2), the incorporation of **2** into the product is clearly confirmed by the appearance of SiPh signals at 7.2–7.7 ppm, whose relative intensity ratio to the OCH_3 signal from MMA at 3.59 ppm enables us to estimate the comonomer composition.

On the other hand, copolymerization of **2** with *n*-BA gave relatively low molecular weight copolymers as shown in runs 7–13, although the incorporation of **2** is much more efficient compared to that of **1** under the similar condition. Furthermore, the M_n-increasing effect of lowering the polymerization temperature observed in the case of **1** with *n*-BA was rather moderate in this comonomer combination. As shown in the ^{1}H NMR spectrum of poly(**2**-*co*-*n*-BA) (run 11 in Table 2) in Fig. 4, we can clearly confirm the incorporation of **2** and estimate the composition from the relative signal intensity between the OCH_2 signals at 4.02 ppm for *n*-BA and 3.48 ppm for **2**.

The low incorporation efficiencies of **1** and **2** observed in the copolymerization with MMA and *n*-BA in Tables 1 and 2 agree with the reported copolymerization behavior of alkoxyvinylsilanes with *n*-BA and styrene: r_1 (triethoxyvinylsilane) = 0.086, r_2 (*n*-BA) = 20.0 [9]; r_1 (**1**) = 0.11, r_2 (styrene) = 20.0 [6]. On the other hand, the higher incorporation efficiency of **2** than that of **1** described above indicates that the copolymerization behavior of alkoxyvinylsilanes depends on the substituents on their Si atoms, although we have not succeeded in determining the reactivity ratios for the copolymerizations. The unimodal GPC traces of all the

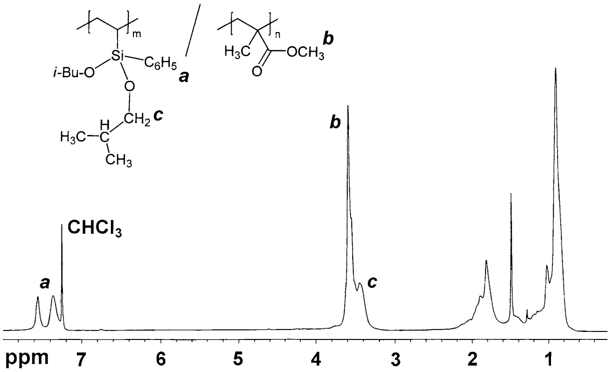


Fig. 3 ^{1}H NMR spectrum of poly(**2**-*co*-MMA) (run 4 in Table 2)

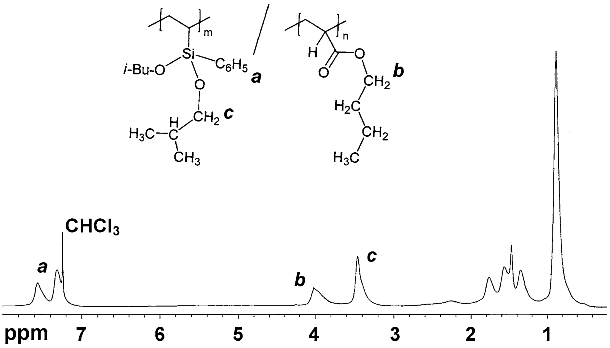


Fig. 4 ^{1}H NMR spectrum of poly(**2**-*co*-*n*-BA) (run 11 in Table 2)

products in Tables 1 and 2 and the radical copolymerization behavior of related alkoxyvinylsilanes in the literatures [6–9] indicate that the products are actually poly(**1** or **2**-*co*-MMA or *n*-BA)s.

Oxidative cleavage of C–Si in poly(1 or 2-*co*-MMA): transformation into poly[(vinyl alcohol)-*co*-MMA]

We have reported that the reaction of poly(**1**-*co*-styrene) with MCPBA in DMF at 60 °C oxidatively cleaved Si–C bonds in the copolymer, affording poly(VA-*co*-styrene) [6, 7]. However, when we tried to cleave the Si–C bonds in poly(**1** or **2**-*co*-*n*-BA) under the same condition employed for poly(**1**-*co*-styrene), the products became insoluble into any solvent. On the other hand, soluble products were obtained by the reaction of poly(**1** or **2**-*co*-MMA) with MCPBA. For example, when poly(**1**-*co*-MMA)s with **1** content = ca. 10 mol% was reacted with MCPBA (5 equiv with respect to **1** repeating unit) in DMF at 120 °C, the $SiOCH_2$ signal completely disappeared in the ^{1}H NMR spectrum of the products, which may suggest the quantitative formation of poly(VA-*co*-MMA). However, disappearance of $SiCH_3$ signal could not be confirmed because the signal overlapped with that from contaminating grease. Accordingly, we cannot rule out the possibility of incomplete oxidation, where SiOH or Si–O–Si group would remain in the polymer structure.

On the other hand, the progress of the oxidative cleavage can be unambiguously confirmed by the disappearance of signals for both $SiOCH_2$ and SiPh in the oxidation of poly(**2**-*co*-MMA). For example, when a poly(**2**-*co*-MMA) sample [$M_n = 42{,}800$, $M_w/M_n = 2.4$ (GPC), **2** content = 9.0 mol%; Fig. 5a] was reacted with MCPBA (10 equiv with respect to **2** repeating unit), poly(VA-*co*-MMA) [$M_n = 34{,}300$, $M_w/M_n = 1.8$ (GPC); Fig. 5b) was obtained in a 47.9% yield. The quantitative progress of the oxidative cleavage was confirmed from the ^{1}H NMR spectra in Fig. 5, where SiPh and $SiOCH_2$ signals of poly(**2**-*co*-MMA) at 7.2–7.7 ppm and 4.02 ppm, respectively, completely disappear after the oxidative transformation, although the signals derived from VA repeating unit could not be identified in the spectrum because of its low incorporation. On the other hand, the transformation did not proceed quantitatively for a poly(**2**-*co*-MMA) sample with

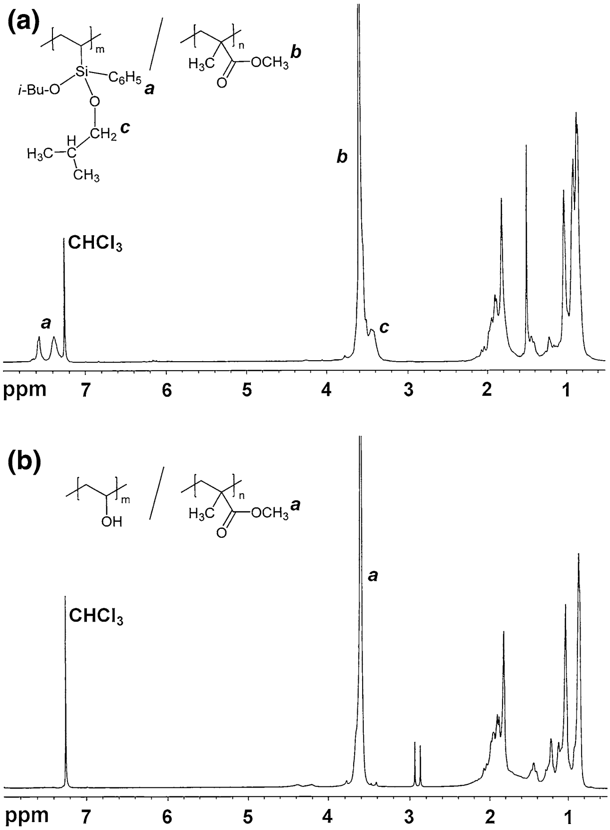
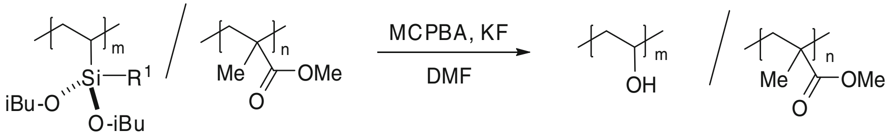


Fig. 5 ^{1}H NMR spectra of poly(**2**-*co*-MMA) (**a**) and poly[(vinyl alcohol)-*co*-MMA] (**b**)

higher **2** content [$M_n = 36{,}400$, $M_w/M_n = 1.6$ (GPC), **2** content = 12.4 mol%) under the same condition, where the ^{1}H NMR estimated conversion of Si–C bond was 80–90% (Scheme 4).



Scheme 4 Preparation of poly[(vinyl alcohol)-*co*-MMA] via oxidative cleavage of Si–C bond in poly(**1** or **2**-*co*-MMA)

Conclusions

We have described radical copolymerization of alkoxyvinylsilanes with MMA and *n*-BA and oxidative cleavage of Si–C bonds in the resulting copolymers to afford poly{VA-*co*-[alkyl (meth)acrylate]}. Although quantitative oxidative cleavage was confirmed only for poly(**2**-*co*-MMA) with low alkoxyvinylsilane content (<10 mol%), we believe that the synthesis of poly(VA-*co*-MMA) is of significance, because the structure cannot be simply obtained by the saponification of poly(VAc-*co*-MMA).

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