A New Type of Silicon Super Lewis Acids for Polymerization of Silyl Vinyl Ethers

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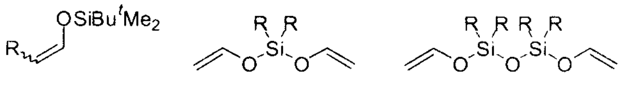
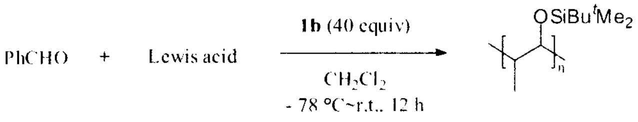
Besides polymerization of vinyl acetates and alkyl vinyl ethers,[1,2] cationic and aldol group transfer polymerizations of silyl vinyl ethers have been reported as alternative synthetic methods that can be employed in the preparation of poly(vinyl alcohol) (PVA) because of the nonaccessibility of the acetaldehyde enolate monomer, regiospecific propagation, and easy conversion to PVA.[3−5] In addition, variation of the silyl groups on the polymer side chain as well as variations in the main chain structure would expand the scope of organosilicon-based macromolecular architecture for surfactants, immobilization of enzymes and proteins, liquid rubbers, etc.[6] The above polymerization technique has been far less studied than the original GTP.[7] To our knowledge, current limitations in aldol group transfer polymerizations include the relatively weak nucleophilicity of silyl vinyl ethers and the small number of Lewis acids that are capable of promoting chain propagation of these Lewis basic monomers without significant termination.[8−10] We have recently discovered a synergistic enhancement of silyl sulfonate esters and sterically encumbered aluminum compounds, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), and methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide)(MABR) on reactivity of the aldol reaction.[11] Herein we report efficient homo- and copolymerization of silyl vinyl monomers **1**−**4** mediated by silicon super Lewis acids consisting of silyl triflates and methylaluminum bis(aryloxide)s (see Chart 1).

Chart 1. Silyl Vinyl Ether Monomers



1a R = H
b R = Me
2 R = Pr^i
3 R = (CH$_2$)$_5$
4 R = Pr^i

Scheme 1. Polymerization of 1b



Lewis acid	yield* (%)	M_n (M_w/M_n)**
Me$_3$SiOTf / MAD	62	5.45 x 10^3 (1.27)
Me$_3$SiOTf / MABR	30	5.05 x 10^3 (1.42)
ZnBr$_2$	<3	- -

* MeOH/acetone insoluble fraction
** Estimated by GPC

An initial polymerization experiment using **1a** was performed in the presence of the above super Lewis acids according to the method reported by Sogah et al.[5] The crystalline polymer was isolated by precipitation in MeOH, and the M_n and M_w/M_n were characterized by GPC. The polymerization data summarized in Table 1 clearly demonstrate that the Me$_3$SiOTf−MAD system, irrespective of temperature, concentration, and monomer/initiator ratio, is highly active although the polymerization data do not show the clear livingness.[12] The system rapidly produces the desired silylated PVA with a range of M_n's (6.7−15.5) × 10^3 and relatively narrow M_w/M_n at higher temperature (entry 10). Better control of M_n and M_w/M_n (entry 1 vs entries 6 and 7) may be ascribed to the higher initiation efficiency of the Me$_3$Si group.[13] Unfortunately, in each case ^{1}H NMR analysis of PVA obtained after cleavage of the silyl ethers using aqueous HF indicated that the polymers are atactic.[14] The reports on polymerizations of internal olefins such as norbornene, crotonate, fumarate esters, etc., are very limited.[15−18] We further examined polymerization of 1-propenyl silyl ether (**1b**) under similar polymerization conditions (see Scheme 1). Earlier works showed that several trialkylsilyl vinyl ethers undergo polymerization in the conventional or aldol-GTP procedure.[19,20] Monomer **1b**, however, does not. For instance, ZnBr$_2$ gave only a trace amount of the corresponding polymer, while our system successfully produced the homopolymer in higher yields and with moderate M_n values (M_{calcd} = 7.00 × 10^3 g mol^{-1}). The broad resonances at 72−78, 43−47, and 10−15 ppm in ^{13}C NMR spectra can be assigned to main-chain carbons of *C*H−O, *C*H−CH$_3$, and *C*H$_3$−CH, respectively. At the initial stage of polymerization of each stereochemically pure **1b**, a mixture of monomer stereoisomers was detected. This indicates

Table 1. Polymerization of 1a in the Presence of R$_3$SiOTf/(ArO)$_2$AlMe Systems[a]

entry	initiator[b]	[**1a**]/[PhCHO]	conditions (°C, h)	polym yield[c] (%)	M_n [d] × 10^{-3}	M_w/M_n [d]
1	MAD/Me$_3$SiOTf/PhCHO	40	−78, 1.5	87	6.7	1.21
2	MAD/Me$_3$SiOTf/PhCHO	100	−78, 2; 25, 10 min[e]	85	10.4	1.39
3[f]	MAD/Me$_3$SiOTf/PhCHO	100	−78, 1; 25, 8[e]	65	7.5	1.21
4[g]	MAD/Me$_3$SiOTf/PhCHO	20	−78, 0.5	91	10.2	1.81
5[g]	MAD/Me$_3$SiOTf/PhCHO	40	−78, 0.5	91	15.5	2.21
6	MAD/^{i}Pr$_3$SiOTf/PhCHO	40	−78, 2; 25, 10 min[e]	80	8.3	2.76
7	MAD/^{t}BuPh$_2$SiOTf/PhCHO	40	−78, 1.5; −50, 1.5[e]	90	11.5	1.73
8	MABR/Me$_3$SiOTf/PhCHO	40	−78, 2.5; 25, 10 min[e]	88	7.6	1.34
9	MABR/Me$_3$SiOTf/PhCHO	100	−78, 2.5; 25, 10 min[e]	88	9.2	1.34
10	MABR/Me$_3$SiOTf/PhCHO	100	−48, 0.5	87	9.3	1.25

[a] Unless otherwise noted, polymerization was conducted in CH$_2$Cl$_2$ under an argon atmosphere; Al Lewis acid/R$_3$SiOTf/PhCHO = 1:1:1 (0.25 mmol); [monomer] = 0.66 M, 5.0−25.0 mmol. [b] MAD: methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide); MABR: methylaluminum bis(4-bromo-2,6-di-*tert*-butylphenoxide). [c] MeOH-insoluble fraction. [d] Estimated by GPC in THF relative to polystyrene. [e] Temperature was raised to complete conversion. [f] [**1a**] = 0.33 M. [g] Toluene was employed as solvent.

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Table 2. Copolymerization of 1a and 1b[a]

entry	**1a**/**1b**	conditions (°C, h)	polym yield[b] g (%)	M_n[c] × 10^{-3}	M_w/M_n[c]	incorporation **1b** in polym (%)[d]
1	67:33	−78, 2; 25, 4	0.53 (63)	4.89	1.14	27
2	50:50	−48, 1; 25, 12	0.37 (45)	5.02	1.12	43
3	33:67	−48, 0.5; 25, 12	0.39 (46)	5.94	1.07	62

[a] Polymerizations were carried out in CH_2Cl_2 solvent (10 mL) under argon atmosphere: MAD, 0.10 mmol; Me_3SiOTf, 0.10 mmol; PhCHO, 0.10 mmol; combined **1a** and **1b**, 5.0 mmol; MAD: methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [b] Yield of MeOH/acetone insoluble fraction. [c] GPC relative to polystyrene in THF. [d] Estimated by ^{13}C NMR measurement.

Table 3. Polymerization of Divinyl Silyl Ethers[a]

entry	monomer	yield[b] (%)	M_n[c] × 10^{-3}	M_w/M_n[c]	*mm*/*mr*/*rr*[d]
1	**2**	73	12.1	10.6	18:61:21
2	**3**	97	6.7	2.27	31:46:23
3	**4**	98	13.4	2.15	26:53:20

[a] All polymerizations were performed in CH_2Cl_2 as follows: PhCHO/MAD/Me_3SiOTf/monomer = 1:1:1:40; conditions: −78 °C for 1 h, then 25 °C for 12 h; MAD: methylaluminum (2,6-di-*tert*-butyl-4-methylphenoxide). [b] Isolated from MeOH. [c] Determined by GPC. Poly(**2**) and poly(**3**) are almost insoluble (<1%) in common organic solvents due to the gelation. [d] Determined by ^1H NMR analysis after conversion to PVA.

that cation-mediated monomer isomerization or polymerization-depolymerization occurs in the system.[21] To extend the scope of our Lewis acid system, we copolymerized **1a** and **1b** with varied monomer ratios (Table 2). In all cases, random copolymers were afforded as white powdery solids. The molar concentration of **1b** in polymer estimated by integral values of CH_3−CH in ^{13}C NMR spectra was slightly less than the initial **1a**/**1b** ratios.

Divinyl ethers **2**−**4** were polymerized in the same manner as described above; the results are listed in Table 3. Precipitation of the polymer from **4** in MeOH gave a powdery solid, whereas **2** and **3** gave gels. ^1H NMR analysis of the polymer from **4** indicated no unreacted vinyl groups. THF soluble fractions from the gels of **2** and **3** were characterized by GPC.[22] These polymers were further treated with 47% HF in H_2O to convert them into PVAs, which appeared to have different tacticities. Interestingly, $mr = 61\%$ (entry 1) is comparable with the heterotact-rich PVA repored by Murahashi.[4]

We, therefore, conclude that the newly developed silicon super Lewis acids can produce a wide variety of silylated PVAs, their analogues, and copolymers, most of which were previously unavailable. Also, the properties of these materials are tunable from crystalline solids to gels, to some extent, depending on the monomer structures.

Supporting Information Available: Experimental procedures and spectroscopic data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Since the polymer with ca. 40 of **1a** unit turned heterogeneous at −78 °C, the polymerization was no longer proceeding with maintaining the temperature. To complete monomer conversion, the polymerization temperature was raised (entries 2, 3, and 6−9). Entry 2 in Table 1 indicates that the observed M_n (10.4×10^3 g mol^{-1}) was deviated from the theoretical value (15.9×10^3 g mol^{-1}).

(13) During the polymerization, scrambling between the trialkylsilyl group of silyl triflates and the *tert*-butyldimethylsilyl group of **1a** is feasible; thus, M_w/M_n is thought to vary depending on the rate of initiation.

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(21) The detailed isomerization mechanism is still unclear.

(22) Poly(**2**) and poly(**3**) were almost insoluble in common organic solvents such as THF, $CHCl_3$, and toluene.

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