

A Novel Approach to the Synthesis of Optically Active Poly(β -hydroxy carbonyl)s by Aldol Polymerization Based on Mukaiyama Aldol Reaction

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ABSTRACT: We have synthesized the poly(β -hydroxy ketone)s **1** and poly(β -hydroxy ester)s **2** by means of a novel polyaddition reaction of bis(triethylsilyl enol ether) **5** and bis(triethylsilyl ketene acetal) **7** with various dialdehydes **8–10**, respectively. When chirally modified Lewis acids were used as catalyst for the polyaddition, optically active polymers were obtained.

KEY WORDS Mukaiyama Aldol Reaction / Aldol Polymerization / Bis(triethylsilyl enol ether) / Bis(triethylsilyl ketene acetal) / Lewis Acid / Asymmetric Synthesis Polymerization /

The synthesis of optically active polymers has been the focus of considerable current interest.^{1a} In addition to their potential use as chiral stationary phase in chromatographic separation, chiral polymers have also acquired a growing importance as active components in liquid crystalline formation or construction of supramolecular assembly system, or as molecular recognition materials.^{1a,1b,2} Helix-sense-selective polymerization^{1a} is one of the most developed asymmetric polymerization method to give synthetic optically active polymers.^{3,4} Another approach to the synthesis of optically active polymer is 'asymmetric synthesis polymerization' in which polymerization induces configurational chirality in the main chain.^{1a} In 1960s Natta already studied this kind of polymerization to exhibit polymers having optical activity in several polymerization systems.⁵ More recently, various methodologies to obtain chiral polymers by the asymmetric synthesis polymerization have been developed. Among them the followings are the successful examples of the asymmetric synthesis polymerization; asymmetric alternating copolymerization of α -olefins with carbon monoxide,⁶ asymmetric polyaddition of 1,3-dimercaptobenzene to dibenzylidene acetone,⁷ asymmetric cyclopolymerization of dienes with a chiral catalyst,⁸ and asymmetric anionic polymerization of achiral N-substituted maleimide.⁹

In recent years, highly enantioselective reactions of C-C bond formation have been extensively studied.^{10,11} For example, some Diels-Alder reactions are efficiently catalyzed by chirally modified Lewis acid to give the optically active cyclic adduct in high yield with very high enantioselectivity.¹² Such useful asymmetric C-C bond forming reactions can be applied to the synthesis of optically active polymers through asymmetric polyaddition. An example of such approach to the novel chiral polymer synthesis has been recently demonstrated by us.¹³ Among the asymmetric C-C bond forming reactions, the Mukaiyama aldol reaction is also one of the most important ones and various chiral catalysts have been developed.¹⁴ The Mukaiyama aldol reactions of silyl enol ethers or silyl ketene acetals with aldehydes or ketones are especially valuable transformations which provide efficient access to β -hydroxy carbonyl derivatives.¹⁵ It occurred to us that an intriguing new polymerization might be possible if a repetitive aldol reaction could be realized between bis(silyl enolate)s and dialdehydes. It also seems to be highly possible that the use of chirally modified Lewis acid catalyst would

afford the easy access to the synthesis of optically active poly(β -hydroxy carbonyl)s.

In this paper we report a new strategy for the synthesis of the poly(β -hydroxy carbonyl)s including optically active ones based on the Mukaiyama aldol reaction of bis(silyl enolate)s with dialdehydes. Access to both stable bis(triethylsilyl enol ether) and bis(triethylsilyl ketene acetal) has permitted an investigation of their polyaddition with dialdehydes, the details of which are disclosed herein (Figure 1).

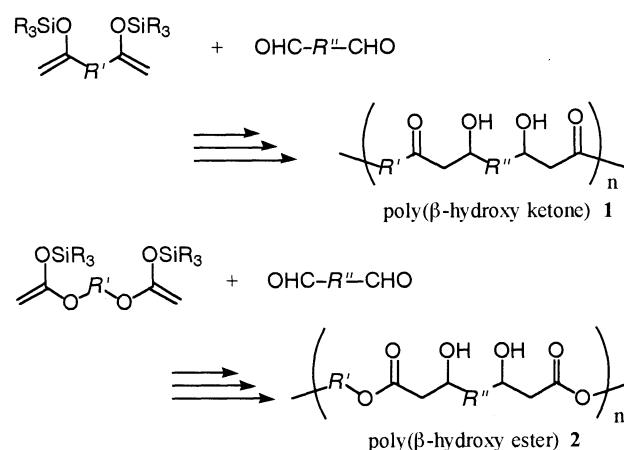


Figure 1. Strategy for the synthesis of poly(β -hydroxy carbonyl)s.

EXPERIMENTAL

General Procedures

Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl, and was freshly distilled just before use. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. All other commercial chemicals were used without further purification. Both ¹H (270 MHz) and ¹³C (67.8 MHz) NMR spectra were recorded on a JEOL JNM-GX270 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. IR spectra were recorded on a JEOL JIR-7000 FT-IR spectrometer as KBr pellets. Melting points were taken on a Yanaco micro melting apparatus and were uncorrected. Optical rotations were taken on a JASCO DIP-140 digital polarimeter using a 10 cm thermostated microcell. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution was conducted at 40°C with JASCO PU-980 as a pump, JASCO UVIDEC-100-III

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as a UV detector and Shodex column KF-806L x 2 as columns. The eluent was THF and flow rate was 1.0 ml min⁻¹. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan).

Materials

Dialdehyde: 10. To a stirred suspension of NaH (0.20 g, 8.33 mmol) in anhydrous THF was added 4-hydroxybenzaldehyde (1.02 g, 8.33 mmol) under nitrogen atmosphere, and the mixture was stirred at 0°C for 1 h. Adipoyl chloride (0.77 g, 4.21 mmol) was then added and stirred for 20 h at room temperature. Then water was slowly added into the resulting mixture. After the organic layer was separated, the residual aqueous layer was extracted twice with ethyl acetate (EtOAc). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated to give the crude solid product, which was washed with hot water. Recrystallization from hexane/EtOAc afforded **10** as a white crystal. (1.50 g, 41% yield) ¹H NMR (δ in ppm from TMS in CDCl₃): 1.90 (br s, 4H), 2.67 (br s, 4H), 7.28 (d, *J* = 8.9 Hz, 4H), 7.93 (d, *J* = 8.3 Hz, 4H), 10.00 (s, 2H); ¹³C NMR: 24.06, 33.89, 122.26, 131.16, 134.02, 155.29, 170.91, 190.78; mp 97—98°C; IR (KBr, cm⁻¹) 2951, 2857, 1756, 1698, 1596, 1374, 1261, 1153, 1008, 922, 857, 508

Dialdehyde: 9. In the same way as described for **10**, this aldehyde was prepared from 4-hydroxybenzaldehyde (7.0 g, 57 mmol), NaH (1.4 g, 57 mmol) and succinoylchloride (2.7 ml, 24.5 mmol). Recrystallization of the crude product from hexane/EtOAc gave **9** (1.6 g, 20%). ¹H NMR (δ in ppm from TMS in CDCl₃): 3.05 (br s, 4H), 7.30 (d, *J* = 8.9 Hz, 4H), 7.93 (d, *J* = 8.3 Hz, 4H), 10.00 (s, 2H); ¹³C NMR: 29.18, 122.23, 131.20, 134.21, 155.13, 170.01, 190.71; mp 90—91°C; IR (KBr, cm⁻¹) 2840, 2746, 1752, 1696, 1596, 1317, 1205, 1136, 924, 834, 794, 675, 508

1,2-bis(2-methyl-1-triethylsiloxy-1-propenyloxy)ethane: 7

A mixture of ethylene glycol dimethacrylate (2.0 g, 10.1 mmol), triethylsilane (2.9 g, 25 mmol) and a catalytic amount of Rh(PPh₃)₃Cl (2 mg) was heated to 60°C and stirred for 5 min. Then fractional distillation under reduced pressure (162—165°C /5 mmHg) gave the title bis(silyl ketene acetal) monomer **7** as a colorless oil (3.4 g, 78% yield). ¹H NMR (δ in ppm from TMS in CDCl₃): 0.73 (q, 12H), 0.99 (t, 18H), 1.54 (s, 6H), 1.58 (s, 6H), 3.87 (s, 4H); ¹³C NMR: 4.9, 6.6, 16.4, 16.9, 67.5, 91.7, 148.4

Aldol polymerization using Sc(OTf)₃

To a solution of dialdehyde **8** (0.41 g, 3.06 mmol) and Sc(OTf)₃ (0.15 g, 0.305 mmol) in dry CH₂Cl₂ (4 ml) was slowly added a CH₂Cl₂ (4 ml) solution of bis(triethylsilyl ketene acetal) **7** (1.32 g, 3.05 mmol) at -5°C. The reaction mixture was allowed to warm to room temperature and stirred for 72 h, and then the solvent was removed *in vacuo*. The obtained polymer was dissolved in THF and precipitated with MeOH/H₂O (7/3). The white precipitate was filtered to give aldol polymer **13a**. Polymer **13a** was dissolved in anhydrous THF and 1.0 M tetrabutylammonium fluoride in THF was added at room temperature. After 3 h of stirring at the same temperature, the reaction mixture was poured into MeOH/H₂O (7/3) containing a small amount of aqueous HCl. White solid was filtered and dried *in vacuo* to give the poly(β-hydroxy ester) **13b**. ¹H-NMR (δ in ppm from TMS in CDCl₃): 0.60—

1.80 (12H -CH₃), 3.40—5.60 (4H -CH(OH)), 6.80—8.20 (4H -C₆H₄-), 9.97—10.16 (0.13H -CHO); IR (KBr, cm⁻¹) 3509, 2978, 1723, 1134

Asymmetric aldol polymerization using chiral (acyloxy) borane (CAB) catalyst 16

To a suspension of monoacylated L-tartaric acid (0.19 g, 0.60 mmol) in CH₂Cl₂ (1 ml) was added borane-dimethylsulfide (Me₂S•BH₃) complex (0.30 ml, 2.0M solution in CH₂Cl₂) at 0°C under N₂. After **16** was formed (1 h), the solution was cooled to -78°C. To this were added a solution of dialdehyde **8** (0.16 g, 1.2 mmol) in CH₂Cl₂ and bis(silyl enol ether) **5** (0.47 g, 1.2 mmol) successively and the mixture was stirred for 72 h. The solvent was removed, and the residue was dissolved in a small amount of THF and the THF solution was poured into MeOH. The precipitated polymer was filtered and dried *in vacuo*. (5% yield)

Asymmetric aldol polymerization using (R)-BINOL-Zn catalyst 17

To a solution of (R)-(+)-1,1'-bi-2-naphthol ((R)-BINOL) (0.23 g, 0.79 mmol) in dry CH₂Cl₂ (3 ml) was added 1.0 M Et₂Zn hexane solution (0.74 mmol) at room temperature under N₂. After stirring for 30 min at ambient temperature, the solvent was removed. Resulting white solid was suspended in CH₂Cl₂ (3 ml) and cooled to -5°C. Then a CH₂Cl₂ solution of terephthaldehyde **8** (0.82 g, 7.77 mmol) and bis(silyl ketene acetal) **7** (3.35 g, 7.77 mmol) were added successively. The resulting mixture was stirred for 60 h at ambient temperature. After removal of the solvent, the THF solution of the crude product was poured into MeOH/water containing a small amount of aqueous HCl. The precipitated polymer was filtered and dried *in vacuo*. (28% yield.)

Asymmetric aldol polymerization using Sc(OTf)₃ and *t*-BuBox 18

To a suspension of Sc(OTf)₃ (0.058 g, 0.117 mmol) and 2,2'-methylenebis[(*S*)-4-*tert*-butyl-2-oxazoline] (*t*-BuBox) (0.037 g, 0.126 mmol) in dry CH₂Cl₂ (1 ml) was added a CH₂Cl₂ solution of dialdehyde **9** (0.344 g, 1.05 mmol) and bis(silyl ketene acetal) **7** successively at -5°C under N₂. The resulting mixture was stirred for 72 h at room temperature. After removal of the solvent, the THF solution was poured into MeOH/water (7:3). The precipitated polymer was filtered and dried *in vacuo*. (13% yield)

Asymmetric aldol polymerization using oxazaborolidinone catalyst 19

To a solution of *N*-sulfonyl-L-valine (0.65 g, 2.4 mmol) in CH₂Cl₂ (2.4 ml) was added Me₂S•BH₃ (2.4 ml, 1.0 M) at ambient temperature. After **19** was formed, the dialdehyde **10** (0.378 g, 1.20 mmol) in CH₂Cl₂ was added at -78°C. Then a solution of bis(silyl ketene acetal) **7** in CH₂Cl₂ (2.4 ml) was added. After 24 h at -78°C, the solvent was removed by evaporation and the crude polymer was dissolved in THF, which was poured into MeOH/buffer solution (pH 6.8) (7/3). The precipitated polymer was filtered and dried *in vacuo*. (62% yield)

RESULTS AND DISCUSSION

The Mukaiyama aldol reaction requires silyl enol ether or silyl ketene acetal as a substrate, which usually - in a number

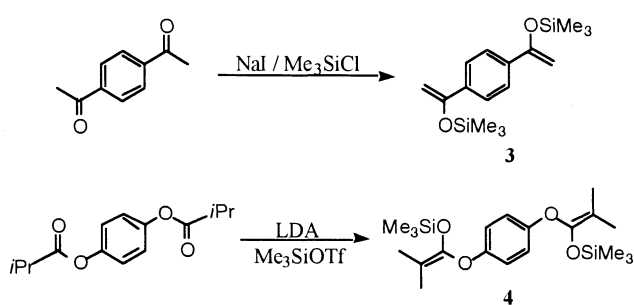


Figure 2. Preparation of bis(trimethylsilyl enol ether) **3** and bis(trimethylsilyl ketene acetal) **4**.

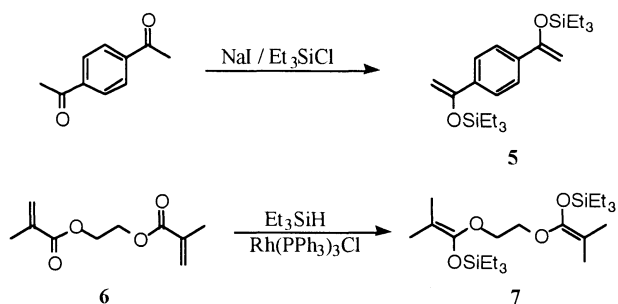


Figure 3. Preparation of bis(triethylsilyl enol ether) **5** and bis(triethylsilyl ketene acetal) **7**.

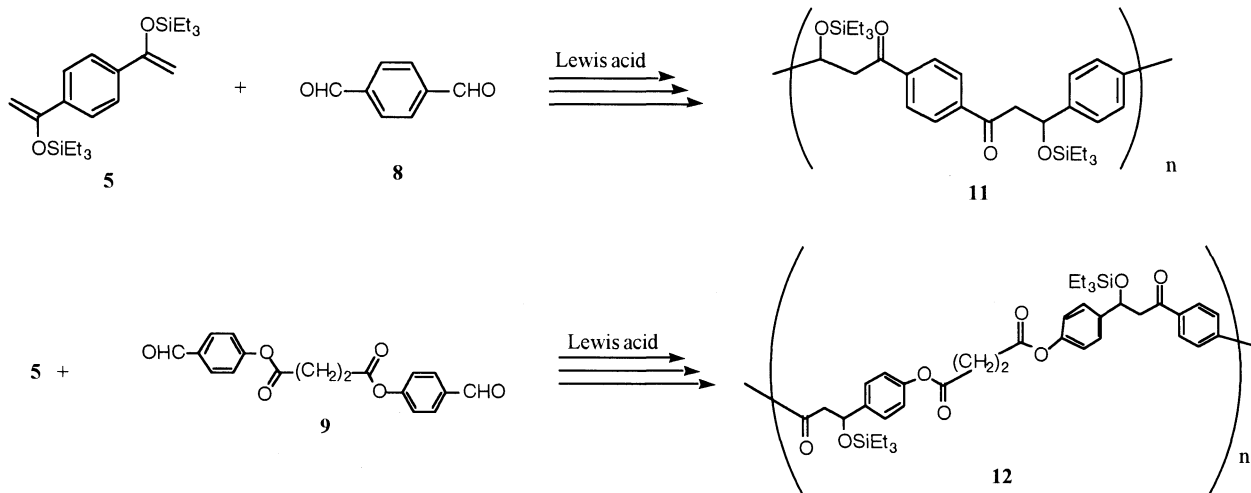


Figure 4. Aldol polymerization of bis(triethylsilyl enol ether) **5** with dialdehydes **8** and **9** in the presence of Lewis acid catalyst.

of cases only prepared *in situ* - serves as a starting material for aldol products. In the case of polymerization, pure monomers of both bis(silyl enolate)s and dialdehydes are indispensable. Initially, we prepared bis(trimethylsilyl enol ether) of 1,4-diacetylbenzene by NaI/Me₃SiCl/CH₃CN method as shown in Figure 2.¹⁶ Unfortunately, the scope of this procedure is restricted by the limited hydrolytic stability of the trimethylsilyl enolate. Bis(enolate) **3** isolated by distillation was always contaminated with nearly 10% of the mono-desilylated compound. Several attempts to purify the monomer were unsuccessful. However, the remarkable ability of triethylsilyl group to stabilize silyl ethers and suppress their tendency to decompose has been well-documented.¹⁷ Monomers of polyaddition reaction always require their high purity in order to obtain high molecular weight of polymers. Thus we synthesized and isolated the bis(triethylsilyl enol ether) as stable, fully characterizable compounds which can be stored for several weeks at -20 °C. The monomer **5** was treated with terephthalaldehyde **8**¹⁹ in the presence of 1 equiv of TiCl₄ in dichloromethane at -78 °C, which is the standard reaction condition used in the Mukaiyama aldol reactions,¹⁸ to produce the corresponding polymer (Figure 4). To our knowledge, this is the first example of aldol polymerization to give the poly(β -hydroxy ketone) which is not easily available by other polymerization methods. The polymerization was accompanied by the formation of insoluble material. THF soluble part was isolated by precipitation into methanol. The results of the aldol polymerization are shown in Table I. The Mukaiyama aldol reaction is normally activated by stoichiometric amounts of Lewis acid, whereas catalytic

activity of rare earth metal triflates has been recently reported.²⁰ When Sc(OTf)₃ was used as a catalyst, repetitive aldol reaction of dialdehyde **8** with **5** occurred to afford **11** in 65% yield (Run 3). Dialdehyde **9** having flexible structure also afforded the corresponding aldol polymer with higher molecular weight (Run 4).

On the other hand, silyl ketene acetals are another important nucleophile of the Mukaiyama aldol reaction. Thus, we prepared bis(silyl ketene acetal) as a monomer for the aldol polymerization. Usual method using LDA/Me₃SiOTf²¹ was attempted for the preparation of bis(trimethylsilyl ketene acetal) **4**. However, the same problem of this monomer instability made it difficult to give the polymer. Hydrosilylation of α,β -unsaturated esters provides an alternative efficient method for the synthesis of silyl ketene acetals.²² We found that this method is well suited for the synthesis of bis(triethylsilyl ketene acetal). Hydrosilylation of bismethacrylate **6** with triethylsilane in the presence of rhodium catalyst afforded **7** in good yield (Figure 3). Also notable is the observation that this silyl ketene acetal can be purified by distillation or even conventional silica gel chromatography without any detectable decomposition. Since the aldol reaction of triethylsilyl derivatives with aldehydes is known to occur smoothly to give the aldols in high yield,²³ we have then attempted to polymerize the bis(triethylsilyl ketene acetal) monomer **7** with dialdehydes (Figure 5). Without Lewis acid catalyst no reaction occurred between **7** and **8**. When neat TiCl₄ was added into a CH₂Cl₂ solution of the monomers, insoluble polymeric material appeared (Table II, Run 1). By contrast, the use of 1.0 M CH₂Cl₂ solution of TiCl₄ as Lewis acid catalyst

Table I. Aldol polymerization of bis(triethylsilyl enol ether) **5** and dialdehydes **8** and **9** in the presence of Lewis acid

Run	Dialdehyde	Lewis acid (equiv)	Temp. ^b °C	Time ^c h	Yield %	<i>Mn</i> ^d	<i>Mw/Mn</i> ^d
1	8	TiCl ₄ ^a (2.0)	-78	12	35	3500	1.79
2	8	Yb(OTf) ₃ (0.1)	-78—20	85	trace	4300	1.23
3	8	Sc(OTf) ₃ (0.1)	-78	26	65	5500	6.08
4	9	Sc(OTf) ₃ (0.1)	-78	9	62	10400	4.40

^aTiCl₄ 1.0 M in CH₂Cl₂ solution was used. ^bReaction temperature ^cReaction time ^dDetermined by GPC calibrated by linear polystyrene standards.

resulted in the formation of the desired aldol polymer **13a**, which was purified by precipitation into methanol/water (7/3). The triethylsilyl group of **13a** was easily eliminated by treatment with tetrabutylammonium fluoride in THF. Instead of TiCl₄, ZnBr₂ is also effective as Lewis acid catalyst for the aldol polymerization of **7** with **8** to give the polymer in high yield.

The Mukaiyama aldol reaction is normally activated by a stoichiometric amount of Lewis acid, whereas a catalytic activity of rare earth metal triflates has been reported.²⁰ In the aldol polymerization of bis(silyl ketene acetal) with dialdehyde, a catalytic amount of rare earth metal triflates could initiate the polymerization to afford the aldol polymer. In the case of Sc(OTf)₃, the reaction temperature must be kept below -5 °C, otherwise insoluble product was yielded. These catalysts are active in the polymerization of **9** with **7**. Dialdehyde **10** having more flexible structure was also polymerized with **7** in the presence of various Lewis acids. BF₃·OEt₂ and Et₂AlCl also served as a catalyst in this system. Although a stoichiometric amount of BF₃·OEt₂ also catalyzed the aldol reaction, the reaction mixture immediately turned to be heterogeneous. A catalytic amount of BF₃·OEt₂ gave the polymer in low yield after long reaction time. The use of a catalytic amount of Sc(OTf)₃ in this monomer combination gave the aldol polymer having higher molecular weight. As can be seen in the results

in Table II, Sc(OTf)₃ is the most suitable catalyst for the aldol polymerization.

The asymmetric Mukaiyama aldol reactions using chiral Lewis acid catalyst have been extensively studied.¹⁴ In our previous studies on the application of Lewis acid catalyzed Diels-Alder reactions to polymer synthesis, we have shown that the chirally modified Lewis acids provide an especially attractive method for the generation of asymmetric carbon atoms in the main chain of the polymers.¹³ It therefore appeared likely that the aldol polymerization in the presence of chiral Lewis acid might afford optically active polymers. Moreover, the above results of aldol polymerization encouraged us to carry out the synthesis of optically active polymers by using a chirally modified Lewis acid catalyst. The results are shown in Table III. For example, Yamamoto has developed chiral (acyloxy)borane (CAB) prepared from tartaric acid derivative and BH₃, which exhibits the high efficiency in the asymmetric aldol reaction of silyl enol ether with aldehyde.²⁴ We have thus used CAB as a chiral catalyst for the asymmetric aldol polymerization of **5** with **8**. Unfortunately, CAB **16** could not be active enough to polymerize these monomers at -78 °C. Raise of the temperature made it possible to obtain the chiral polymer in low yield accompanied with partial decomposition of the catalyst. However the obtained polymer showed optical activity.

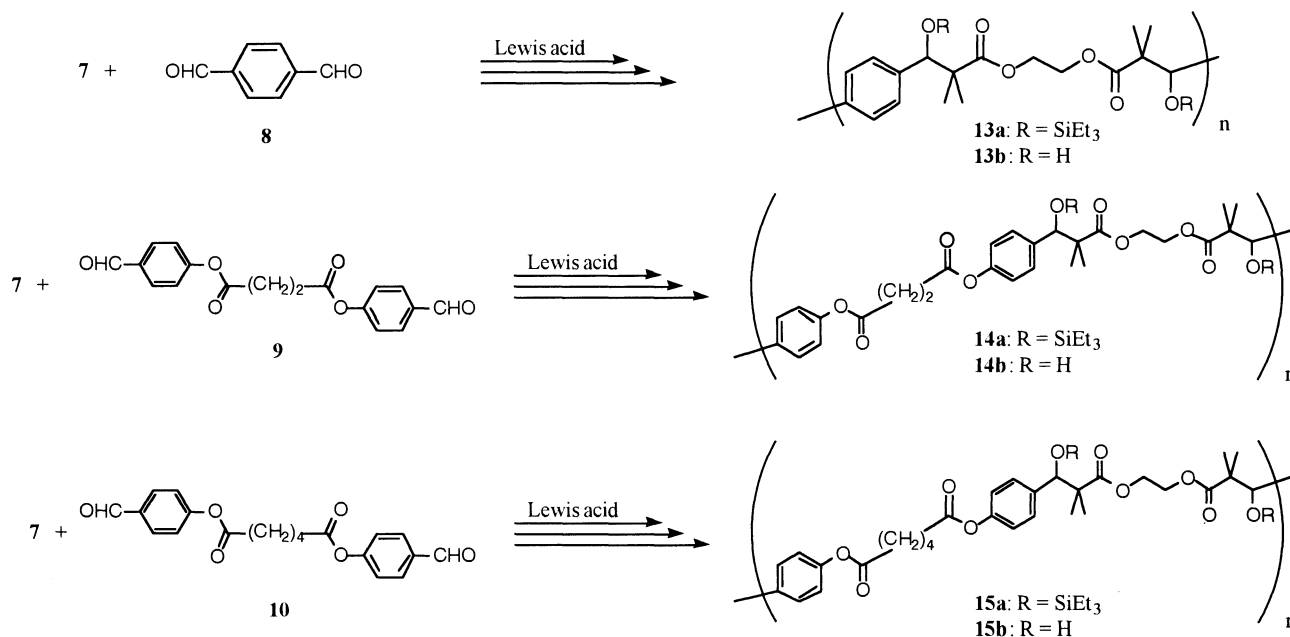
**Figure 5.** Aldol polymerization of bis(triethylsilyl ketene acetal) **7** and dialdehyde **8**, **9** and **10** using Lewis acid catalyst.

Table II. Aldol polymerization of bis(silyl ketene acetal) **7** with dialdehydes **8**, **9** and **10** in CH_2Cl_2

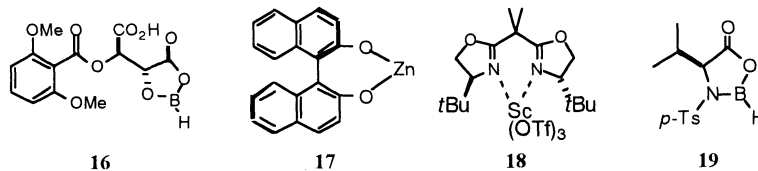
Run	Dialdehyde	Lewis acid	(equiv)	Temp ^c °C	Time ^d h	Yield %	M_n^e	M_w/M_n^e
1	8	TiCl_4^a	(2.0)	-78	4	86	—	—
2	8	TiCl_4^b	(2.0)	-78	4	21	1500	1.60
3	8	ZnBr_2	(2.0)	20	48	84	2800	2.21
4	8	$\text{Yb}(\text{OTf})_3$	(0.2)	20	72	17	2200	1.60
5	8	$\text{Sc}(\text{OTf})_3$	(0.1)	20	72	21	—	—
6	8	$\text{Sc}(\text{OTf})_3$	(0.1)	-5—20	72	40	3800	3.89
7	9	$\text{Yb}(\text{OTf})_3$	(0.2)	-5—20	72	47	2900	4.66
8	9	$\text{Sc}(\text{OTf})_3$	(0.1)	-5—20	72	29	7000	3.29
9	10	TiCl_4^b	(2.0)	-78	4	29	2700	3.27
10	10	ZnBr_2	(2.0)	20	8	47	1800	3.41
11	10	BF_3	(2.0)	-30	5 min. ^f	25	5000	1.80
12	10	BF_3	(0.1)	-20—20	130	19	2100	1.70
13	10	Et_2AlCl	(0.1)	-10—20	48	43	2100	2.28
14	10	$\text{Yb}(\text{OTf})_3$	(0.2)	20	72	15	11300	7.32
15	10	$\text{Sc}(\text{OTf})_3$	(0.1)	-5—20	72	50	55700	2.38

^a Neat TiCl_4 was used. ^b TiCl_4 1.0 M in CH_2Cl_2 solution was used. ^c Reaction temperature ^d Reaction time
^e Determined by GPC calibrated by linear polystyrene standards. ^f Reaction mixture was heterogeneous as soon as BF_3 was added.

Table III. Asymmetric aldol polymerization using chirally modified Lewis acid

Run	Bis(silyl enol ether) or bis(silyl ketene acetal)	Dialdehyde	Chiral Lewis acid (equiv)	Temp. °C	Time h	Yield %	M_n	M_w/M_n	$[\Phi]_D$	$[\Phi]_{435}$
1	5	8	16 (0.5)	-78—20	85	5	1300	1.67	-64	—
2	7	8	17 (0.1)	-5—20	60	28	990	1.55	12	118
3	7	9	18 (0.1)	-5—20	72	13	2700	1.54	11	217
4	7	10	19 (2.0)	-78	24	62	1900	2.21	-49	-47

Lewis acid catalyst:



Silyl ketene acetals also react with aldehyde in enantioselective manner in the presence of chiral Lewis acid. Several useful chiral Lewis acids have been recently developed for this reaction. Kiyooka has reported that *N*-sulfonyloxazaborolidinone efficiently catalyzes the aldol reaction to give the β -hydroxy ester in high yield with high enantioselectivity^{25,26}. We found that enantiopure *N*-sulfonyloxazaborolidinone **19** acted as chiral catalyst for the asymmetric aldol polymerization of **7** with **10** even at -78°C . The aldol polymer having optical activity was again obtained in 62% yield. Since $\text{Sc}(\text{OTf})_3$ showed relatively high efficiency in the aldol polymerization as mentioned above, enantiopure bis(oxazoline) ligand (2,2'-methylenebis[(*S*)-4-*tert*-butyl-2-oxazoline])²⁷ was used as a chiral modifier of $\text{Sc}(\text{OTf})_3$. In the aldol polymerization of **7** with **9**, the chirally modified $\text{Sc}(\text{OTf})_3$ catalyst **18** was used to give the optically active aldol polymer. A Zn based chiral Lewis acid is also effective catalyst for some reactions.²⁸ The chirally modified Zn catalyst **17**, which was easily prepared from ZnEt_2 and (*R*)-1,1'-binaphthol, was used for the asymmetric polymerization of **7** with **8**.

CONCLUSION

We have developed novel polyaddition reactions based on the Mukaiyama aldol reaction of silyl enol ether with aldehydes. As stable and isolable monomers, bis(triethylsilyl enol ether) **5** and bis(triethylsilyl ketene acetal) **7** were prepared. In the presence of Lewis acid catalyst these monomers smoothly reacted with dialdehydes to afford the poly(β -hydroxy carbonyl)s. The asymmetric synthesis polymerization of such monomers with a chirally modified Lewis acid found to be possible to obtain optically active poly(β -hydroxy carbonyl)s having main chain chirality.

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