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Asymmetric Allylation Polymerization: Novel Polyaddition of Bis(allylsilane) and Dialdehyde Using Chiral (Acyloxy)borane Catalyst

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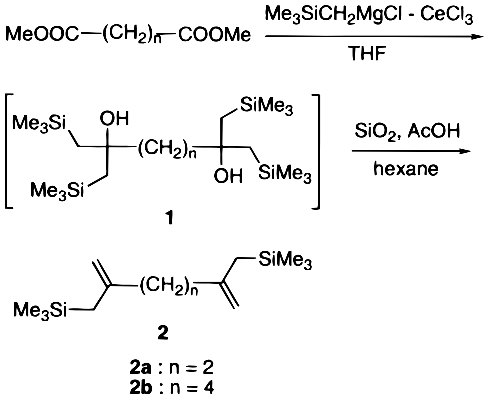
In recent years, optically active synthetic polymers have attracted considerable attention.[1−3] Considerable research effort has focused on the development of efficient synthetic methods for optically active polymers from achiral monomers.[4] Generation of well-controlled configurational chirality in the polymer main chain is highly desired for development of new methodologies for the synthesis of optically active polymers. A number of excellent asymmetric C−C bond formation reactions have appeared.[5] Thus, one of the most promising ways to obtain optically active polymers having main chain chirality is polymerization based on repetitive asymmetric C−C bond forming reactions. Asymmetric polymerizations involving this approach have not been studied extensively.[6] Now we have focused on the nucleophilic addition reaction of allylsilanes to carbonyl compounds, first reported by Hosomi and Sakurai,[11] which is a powerful method for the construction of C−C bonds together with the possibility of creating a new stereogenic center and represents an invaluable tool in organic synthesis. The use of a chiral Lewis acid enabled an optically active homoallylic alcohol structure to be prepared. An interesting new polymerization might be possible if bis(allylsilane)s and dialdehydes could undergo a repetitive allylation reaction. In this communication, we report the first asymmetric polyaddition between bis(allylsilane)s and dialdehydes using Sakurai−Hosomi allylation as a novel methodology for the preparation of a new class of chiral poly(alcohol)s with chirality in the polymer main chain. We propose to term this polymerization “asymmetric allylation polymerization”.

We prepared bis(allylsilane)s **2** and dialdehydes **3**[10] as monomers for the asymmetric allylation polymerization. The cerium mediated conversion of ester to allylsilane[12] was suitable for the synthesis of **2**. Reaction of the diesters with $TMSCH_2MgCl-CeCl_3$, followed by deoxysilylation on silica gel with acetic acid, afforded the desired monomers **2** in high purity as shown in Scheme 1. We first surveyed achiral Lewis acid catalysts for the allylation polymerization of **2b** and **3b**. Although no reaction proceeded without the catalyst, addition of a stoichiometric amount of $TiCl_4$, a well-known catalyst used in addition of allylsilane to aldehyde,[11] to the monomer solution in propionitrile resulted in the formation of a jellylike solid within 15 min. This solid was added into methanol/water (2:1) to precipitate the desired polymer **4** (Table 1, entry 1). This is the first attempt at a polymer synthesis using Sakurai−Hosomi allylation. The resulting polymer structure containing hydroxy and exo methylene groups is unique and may be difficult to prepare by other polymerization methods. Addition of $BF_3 \cdot OEt_2$ to the monomer solution also catalyzed the allylation polymerization of **2b** and **3b** to produce the same polymer (entry 2). Since high catalytic efficiency of $Sc(OTf)_3$ in the Sakurai−Hosomi allylation was reported,[13] we used 10 mol % of $Sc(OTf)_3$ for the allylation polymerization. However, a considerable amount of monomer remained after 24 h at room temperature, and the polymer yield was low (entry 3).

Scheme 1. Preparation of Bis(allylsilane)



One of the most useful and reliable catalysts for the enantioselective allylation of aldehyde is chiral (acyloxy)boranes developed by Yamamoto.[14] Chiral (acyloxy)borane catalyst system exhibits excellent enantioselectivity with high yields in the allylation of aldehyde. Thus, we have applied the chiral (acyloxy)borane catalyst to the asymmetric polymerization of bis(allylsilane) monomers and dialdehydes. Addition of 20 mol % of the chiral (acyloxy)borane **6** to the propionitrile solution of monomers **2a** and **3a** catalyzed the allylation polymerization, and both monomers disappeared in 1 h (Scheme 2). After treatment of the reaction mixture with Bu_4NF/THF, the whole mixture was poured into methanol/water (2:1) to precipitate the corresponding optically active polymer **4**, which exhibited a molar optical rotation of $[\Phi]_{405}$ +35.7° (entry 4). This polymer was soluble in THF, DMSO, and DMF and insoluble in hexane, methanol, and all aqueous solutions. Gel permeation chromatographic analysis of **4** relative to polystyrene gave an average M_n of 4900. Polymerization at lower temperature (−20 °C) produced polymer with a higher molar rotation value ($[\Phi]_{405}$ +145.4°) (entry 5). Other combinations of **2** and **3** were polymerized by asymmetric allylation in the presence of chiral (acyloxy)borane catalyst (entries 6−12). Optically active polymers obtained from **2b** and **3b**[10] showed relatively higher molecular weight (entries 12−17). A molar optical rotation value of +184.7° with molecular weight of 7400 was attained by using the catalyst **6** at −20 °C (entry 14). In comparison with **6**, the dimethoxy derivative **5** yielded a polymer with a somewhat lower molar optical rotation. These results are consistent with Yamamoto’s report that **6** is a more efficient catalyst than **5** for the enantioselective allylation of aldehyde.[14] Enantio-enriched homoallyl alcohols with high ee’s up to 96% ee were obtained when **6** was used at −78 °C.[14] The pentafluorophenyl derivatives of chiral (acyloxy)borane (**7**, **8**) also catalyzed the same polymerization to give optically active polymers (entries 15−17). In all cases, lowering the temperature below −20 °C precipitated the monomer in propionitrile, which hindered the allylation polymerization.

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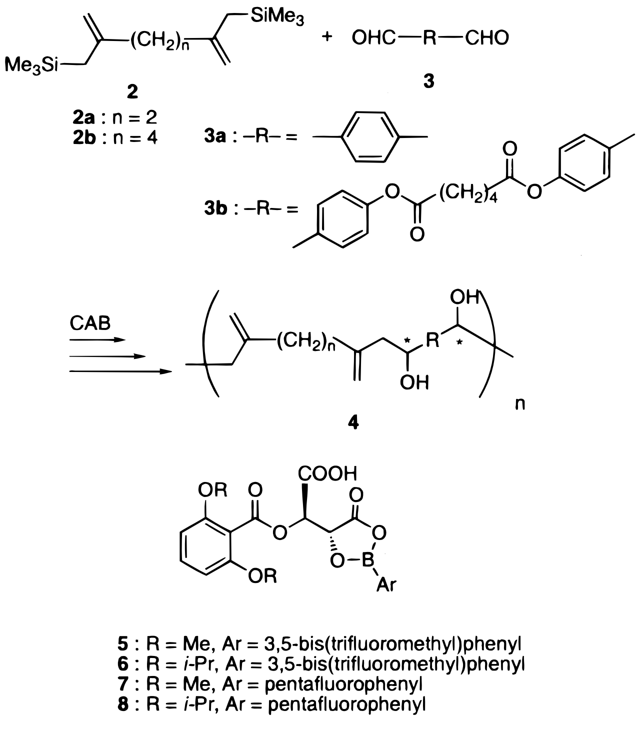
Table 1. Asymmetric Allylation Polymerization of Bis(allylsilane)s with Dialdehydes at Room Temperature in Propionitrile

entry	bis(allylsilane)	dialdehyde	catalyst	time, h	yield,[a] %	M_n[b]	M_w/M_n[b]	$[\Phi]_{405}$,[c] deg
1[d]	**2b**	**3b**	$TiCl_4$	15 min	95	3600	3.78	
2[d]	**2b**	**3b**	$BF_3 \cdot OEt_2$	10 min	80	2400	7.81	
3	**2b**	**3b**	$Sc(OTf)_3$	24	29	3300	1.71	
4	**2a**	**3a**	**6**	1	71	4900	3.34	+35.7
5[e]	**2a**	**3a**	**6**	48	80	4400	2.40	+145.4
6	**2a**	**3b**	**5**	3	89	2200	7.69	+33.0
7	**2a**	**3b**	**6**	1	90	2500	5.05	+91.5
8[e]	**2a**	**3b**	**6**	72	87	4300	3.04	+149.9
9	**2b**	**3a**	**5**	4	86	1800	6.26	+26.1
10	**2b**	**3a**	**6**	1	71	2000	107	+107.1
11[e]	**2b**	**3a**	**6**	26	67	2000	22.5	+118.5
12	**2b**	**3b**	**5**	1	89	5100	4.01	+31.5
13	**2b**	**3b**	**6**	1	92	6800	3.58	+76.4
14[e]	**2b**	**3b**	**6**	72	96	7400	3.07	+184.7
15	**2b**	**3b**	**7**	3	78	5500	11.83	+46.3
16	**2b**	**3b**	**8**	1	82	5400	6.52	+83.7
17[e]	**2b**	**3b**	**8**	4	88	7800	4.53	+168.5

[a] Precipitated in MeOH/H_2O (2:1). [b] Determined by GPC relative to linear polystyrene. [c] Measured in THF. [d] At 0 °C. [e] At −20 °C.

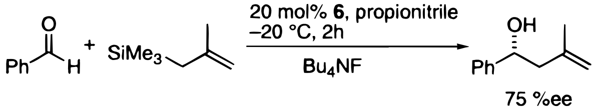
Scheme 2. Asymmetric Allylation Polymerization of Bis(allylsilane) and Dialdehyde Using Chiral (Acyloxy)borane Catalyst



At −20 °C, we have examined the efficiency of **6** as a chiral catalyst in the model reaction as shown in Scheme 3. Benzaldehyde reacted smoothly with methallylsilane in the presence of **6** in propionitrile to give the corresponding homoallylic alcohol having *R* configuration in quantitative yield with 75% ee. This model reaction indicates that asymmetric allylation polymerization with **6** at −20 °C should occur highly stereoselectively. The absolute configuration of the polymers is estimated to be *R*.

In conclusion, we have described the asymmetric allylation polymerization based on Sakurai−Hosomi allylation using chiral (acyloxy)borane catalyst. This is the first reported polymerization using the Sakurai−Hosomi allylation of aldehyde. Chiral (acyloxy)borane **6** is an excellent catalyst for the asymmetric allylation polymerization. Asymmetric allylation polymerization should provide a general strategy for the synthesis of a wide range of new chiral polymers.

Scheme 3. Model Reaction of Benzaldehyde and Methallylsilane Using 6 as Chiral Catalyst at −20 °C



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Supporting Information Available: Details of synthesis, spectral data for compounds **2a** and **2b**, and a procedure for asymmetric polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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