Asymmetric Allylation Polymerization of Bis(allylsilane) and Dialdehyde Containing Arylsilane Structure

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Received November 19, 2001
Revised Manuscript Received March 12, 2002

Introduction

There is considerable interest in the development of polymerizations to produce optically active polymers; a variety of approaches have been developed.[1−4] Some of the chiral polymers have found an application to polymeric reagents and catalysts.[5,6] Recently, considerable attention has focused on asymmetric syntheses of chiral polymers with main-chain configurational chirality.[7] Although various chiral polymers have been synthesized and reported to be optically active, determination of the optical purity of the polymers is usually difficult, and in many cases no information on the stereochemical purity is given. We previously[8] found that asymmetric addition of allylsilanes to aldehyde (Sakurai−Hosomi allylation)[9] is a suitable reaction for preparing optically active polymers with main-chain chirality.[10,11] All of the polymers obtained by the asymmetric allylation polymerization were optically active. Model reactions revealed that the asymmetric allylation polymerization proceeded in a stereoselective manner. However, the model reactions show only the initial step of the asymmetric polymerization. This may not be sufficient to fully understand the asymmetric induction and optical purity of the polymers. The most direct procedure to evaluate the optical purity of chiral polymers is to degrade the polymer to chiral repeating units. The stereoisomer ratio of the chiral degraded products can be determined by methods such as chiral GC or HPLC analysis. This procedure, however, requires a very efficient degradation reaction. For this purpose, we have designed arylsilane monomers (**1**−**4**, Scheme 1) that are stable to the Lewis acid catalyst used in the asymmetric polymerization and to the usual workup conditions. After isolation of the optically active polymers, the aryl carbon−silicon bonds in the main chain of the optically active polymer can be easily cleaved by fluoride ion.[12,13] This paper reports the synthesis of the new arylsilane monomers and their polymerization using chiral (acyloxy)borane (CAB) as a catalyst.[14] The resulting optically active polymers were degraded to the chiral homoallyl alcohol repeating units, which were analyzed by HPLC using a chiral stationary phase.

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately before use. Propionitrile was distilled from CaH_2. Commercially available *n*-BuLi (1.6 M in *n*-hexane, Mitsuwa Pure Chemical Co., Ltd.) was used without purification. Tetrabutylammonium fluoride (TBAF) (95+%) was from Aldrich (as a 1.0 M solution in THF). Dichlorodimethylsilane (99+%), dichlorodiethylsilane (99+%), and dichlorodiphenylsilane (99+%) (Shin-Etsu Chemical Co., Ltd.) were used without purification. (2*R*,3*R*)-2-*O*-(2,6-Diisopropoxybenzoyl) tartrate[15] and 3,5-bis(trifluoromethyl)-phenylboric acid[14] were prepared according to the literature procedure. Monomers **1a**,[16] **4**,[16] and **5**[10] were prepared according to the procedures reported in the previous papers.

Measurements. Melting points were determined on a Yanaco micro melting apparatus and were uncorrected. Optical rotations were measured on a JASCO DIP-140 digital polarimeter using a 10 cm thermostated microcell. Both ^{1}H (300 MHz) and ^{13}C (75 MHz) spectra were recorded on Varian Mercury 300 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded with a JEOL JIR-7000 FT-IR spectrometer and were reported in reciprocal centimeters (cm^{-1}). Elemental analyses were performed at the microanalysis center of Kyoto University. HPLC analyses were performed with a JASCO HPLC system composed of a 3-Line Degasser DG-980-50, a HPLC pump PV-980, and a Column oven CO-965, equipped with a chiral column (Chiralpac AD, Daicel) using hexane/propan-2-ol as an eluent (30 °C, flow rate: 0.5 mL/min). A UV detector JASCO UV-975 was used for the peak detection. Size exclusion chromatography (SEC) for the characterization of molecular weight and its distribution was conducted at 40 °C with a JASCO PU-980 as a pump, a JASCO UVDEC-100-III as a UV detector, and Shodex column A-802 and A-803 as columns. The eluent was THF and flow rate was 1.0 mL/min. A molecular weight calibration curve was obtained by using a series of polystyrene standards (Tosoh Co., Japan).

Di(4-formylphenyl)diphenylsilane (1c). 4-Bromobenzaldehyde dimethyl acetal (7.40 g, 32 mmol) was dissolved in THF (120 mL) under nitrogen. *n*-BuLi/hexane solution (1.6 M, 32 mmol, 20 mL) was added slowly at −78 °C over 30 min. After stirring at −78 °C for 1 h, dichlorodiphenylsilane (1.52 mL, 12.5 mmol) was added to the above suspension. The reaction mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and stirred for 12 h. The reaction mixture was quenched with 2 N HCl and extracted with ether. The organic phase was washed with brine and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave the crude product of acetal/aldehyde mixture. Acetic acid (10 mL) and H_2O (3 mL) were added to the mixture and stirred for 3 h at room temperature. The reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted with ether. The combined extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The crude product was purified by column chromatography (hexanes/EtOAc 4:1) to give dialdehyde **1c** in 58% yield (2.85 g, 6.3 mmol) as a white solid; mp 98−100 °C. ^{1}H NMR ($CDCl_3$): δ 10.01 (s, 2H, C*H*O), 7.89 (d, J = 8.0 Hz, 4H, OHC−Ph-*H*), 7.74 (d, J = 8.0 Hz, 4H, OHC−Ph−*H*), 7.56−7.40 (m, 10H, Ph−*H*). ^{13}C NMR ($CDCl_3$): δ 192.7 (C═O), 142.2, 137.5, 137.2, 136.6, 132.4, 130.6, 129.1, and 128.6 (C_{arom}). IR (KBr): 3042, 2829, and 2737 (C−H), 1701 (C═O), 1592 (C═C), 1208, and 815 cm^{-1} (Si−C). Anal. Calcd for $C_{26}H_{20}O_2Si$ (392.5): C, 79.56; H, 5.14. Found: C, 79.52; H, 5.29.

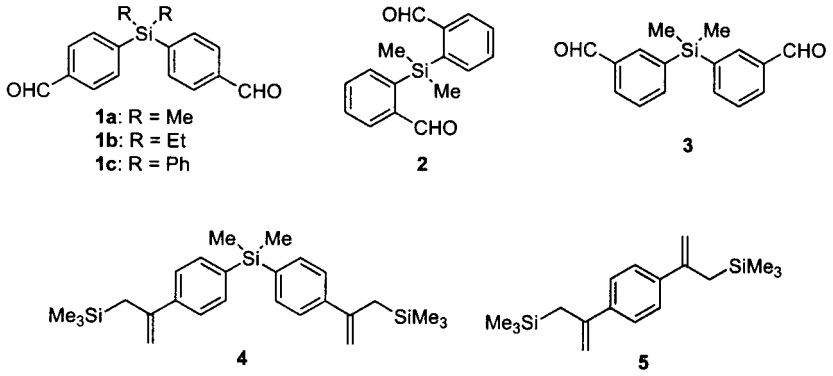
Di(4-formylphenyl)diethylsilane (1b). Yield 62%. Colorless oil. ^{1}H NMR ($CDCl_3$): δ 10.03 (s, 2H, C*H*O), 7.86 (d, J = 8.0 Hz, 4H, Ph-*H*), 7.67 (d, J = 8.0 Hz, 4H, Ph-*H*), 1.16 (q, J = 7.0 Hz 6H, $SiCH_2CH_3$), 1.02 (t, J = 7.0 4H, $SiCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 192.8 (C═O), 144.2, 137.1, 135.6, and 129.0 (C_{arom}), 7.5 (CH_3), 3.7 (CH_2). IR (NaCl): 2956 and 2825 (C−H),1700 (C═O), 1595 (C═C), 1210 and 813 cm^{-1} (Si−C). Anal. Calcd for $C_{18}H_{20}O_2Si$ (296.4): C, 72.93; H, 6.80. Found: C, 72.85; H, 6.88.

Di(2-formylphenyl)dimethylsilane (2). Yield 52%. Colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 9.93 (s, 2H, C*H*O), 7.89−7.54 (m, 8H, Ph−*H*), 0.67 (s, 6H, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ 193.4 (C═O), 141.9, 140.7, 136.5, 133.6, 132.5, and 129.9 (C_{arom}), 0.29 (CH_3). IR (KBr): 3056, 2956, 2837, and 2742 (C−H), 1695 (C═O), 1584 (C═C), 1252 (Si−CH_3), 758 cm^{-1} (Si−C). Anal. Calcd for $C_{16}H_{16}O_2Si$ (268.3): C, 71.60; H, 6.01. Found: C, 71.54; H, 6.01.

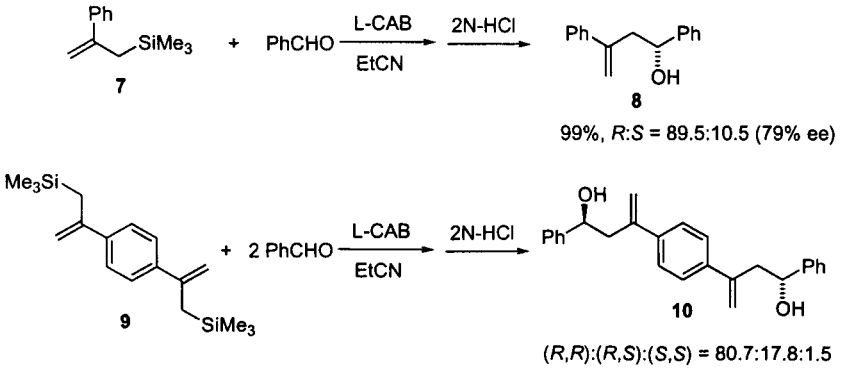
Di(3-formylphenyl)dimethylsilane (3). Yield 52%. Colorless viscous oil. ^{1}H NMR ($CDCl_3$): δ 10.00 (s, 2H, C*H*O), 8.02−

10.1021/ma012023j CCC: $22.00
Published on Web 05/16/2002

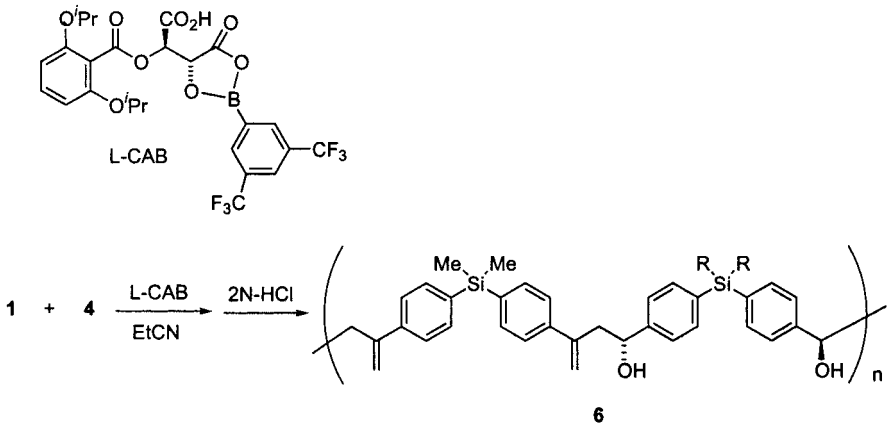
Scheme 1. Monomers for the Asymmetric Allylation Polymerization



Scheme 2. Model Reactions for the Asymmetric Allylation Polymerization[10]



Scheme 3. Asymmetric Allylation Polymerization of Dialdehyde and Bis(allylsilane)



7.51 (m, 8H, Ph-*H*), 0.65 (s, 6H, SiCH_3). ^{13}C NMR ($CDCl_3$): δ 192.9 (C=O), 140.4, 139.1, 136.0, 135.6, 131.0, and 129.0 (C_{arom}), −2.37 (CH_3). IR (KBr): 3051, 2957, and 2817 (C−H), 1696 (C=O), 1584 (C=C), 1257 (Si−CH_3), 814 cm^{-1} (Si−C). Anal. Calcd for $C_{16}H_{16}O_2Si$ (268.3): C, 71.60; H, 6.01. Found: C, 71.07; H, 5.98.

Asymmetric Polymerization of 1c and 4. A dry propionitrile (1 mL) solution of chiral (acyloxy)borane prepared from (2*R*,3*R*)-2-*O*-(2,6-diisopropoxybenzoyl) tartrate (74 mg, 0.2 mmol) and 3,5-bis(trifluoromethyl)phenylboric acid (51 mg, 0.2 mmol) was added to a solution of bis(allylsilane) **4** (219 mg, 0.5 mmol) and dialdehyde **1c** (196 mg, 0.5 mmol) in propionitrile (1 mL) at −78 °C. The mixture was stirred at −78 °C for 12 h and quenched with 2 N HCl (1 mL). The mixture was poured into MeOH/H_2O (2:1), filtered, and dried under vacuum to yield a white solid (305 mg, 89%); M_w = 10 200, M_w/M_n = 2.4, $[\Phi]_{405}$ −1182 (*c* 1.0, THF).[17] ^{1}H NMR ($CDCl_3$): δ 7.55−7.36 (m, 16H, Ph−*H*), 5.47 (s, 2H, C=CH_2), 5.20 (s, 2H, C=CH_2), 4.74 (m, 2H, C*H*OH), 2.90 (m, 4H, CH_2=CCH_2), 2.10 (b, 2H, O*H*), 0.57 (s, 6H, Ph−SiCH_3). ^{13}C NMR ($CDCl_3$): δ 145.6 (*C*=CH_2), 145.1, 141.2, 138.1, 136.9, 136.7, 134.7, 134.5, 129.9, 128.2, 125.9, 125.6, and 125.2 (C_{arom}), 116.5 (C=*C*H_2), 72.3 (CH−OH), 46.1 (CH_2), −2.1 (CH_3).

Degradation of Polymer 6c. The chiral polymer **6c** (100 mg) was dissolved in TBAF/THF solution (1.0 M, 3 mL) and heated at 60 °C for 24 h. The reaction mixture was diluted with ether (50 mL) and washed with 2 N HCl and brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (hexanes/EtOAc 4:1) to give homoallyl alcohol **8** (85%). The enantiomers ratio of 86.9:13.1 (73.8% ee) was determined by HPLC analysis using a chiral stationary phase column (Daicel, Chiralpac AD; hexane/propan-2-ol 30:1; 0.5 mL/min): (*R*)-**8** t_r = 34.1 min; (*S*)-**8** t_r = 38.2 min.

Results and Discussion

The dialdehydes **1**−**3** were prepared by coupling a lithiated benzaldehyde dimethylacetal with dichlorosilane, followed by deprotection of the acetal moiety. All of these monomers were readily prepared in high purity.

Table 1. Repetitive Asymmetric Addition of Bis(allylsilane) with Dialdehyde[a]

			chiral polymer				degradation product	
entry	dialdehyde	bis(allylsilane)	yield (%)	M_w[b]	M_w/M_n[b]	$[\Phi]_{405}$[c]	**10** (*R*,*R*):(*R*,*S*):(*S*,*S*)	**8** *R*:*S*
1[d]	**1a**	**4**	95	57 000	6.9	−990		86.1:13.9
2	**1b**	**4**	83	28 800	4.8	−1050		81.6:18.4
3	**1c**	**4**	89	10 200	2.4	−1182		86.9:13.1
4	**2**	**4**	0					
5	**3**	**4**	95	35 000	5.6	−528		85.0:15.0
6	**1a**	**5**	92	27 400	5.6	−1034	75.5:22.6:1.9	86.8:13.2[g]
7[e]	**1a**	**5**	94	34 200	7.8	+1146	2.1:23.2:74.7	13.7:86.3[g]
8[f]	**1a**	**5**	93	10 800	3.6	−693	63.7:31.6:4.7	79.5:20.5[g]
9	**1b**	**5**	95	33 000	8.0	−942	72.1:23.1:4.8	83.7:16.3[g]
10	**1c**	**5**	95	9 600	3.2	−908	74.3:23.7:2.0	86.2:13.8[g]

[a] Asymmetric polymerization was performed in propionitrile using L-CAB at −78 °C for 12 h, unless otherwise stated. [b] Determined by SEC calibration using polystyrene standards in THF solution. [c] Molar rotation value measure in THF.[17] [d] See ref 12. [e] D-CAB was used. [f] At −20 °C. [g] *R*:*S* ratio calculated from the stereoisomers distribution of the degradation product **10**.

We have reported the enantioselective addition of allylsilane to aldehyde in the presence of chiral (acyloxy)borane (CAB) as a model reaction of asymmetric allylation polymerization.[10] For example, *β*-phenylallylsilane (**7**) reacted with benzaldehyde in the presence of L-CAB at −78 °C to produce the corresponding *R*-homoallyl alcohol in quantitative conversion with 79% ee (Scheme 2).[10] Thus, we have examined asymmetric polymerization of bis(allylsilane)s and dialdehydes containing arylsilane structure. The polymerization using CAB occurred smoothly in propionitrile at −78 °C to yield the optically active polymers in high yield (Scheme 3). Introduction of a silyl group into the monomers improved their solubility at low temperature. The asymmetric polymerization must be performed at lower temperature to attain higher asymmetric induction. The resulting optically active polymers were then treated with terabutylammonium fluoride (TBAF) in THF to give the corresponding chiral repeating units. A reference experiment of TBAF treatment on the enantioenriched homoallyl alcohol proved that this process caused no racemization. Degradation of **6** led to **8**, which was then analyzed by chiral HPLC to determine the enantioselectivity. The enantiomers ratios are listed in Table 1. In most cases, the asymmetric induction degrees were over 70% ee (*R*/*S* > 85/15), which are similar to that of the model reaction. Ortho-substituted dialdehyde **2** resulted in no detectable reaction under the same reaction conditions due to its steric congestion (entry 4). Even when bis(allylsilane) **5** without Si−phenyl linkage was used as a monomer, the use of silicon-containing dialdehyde yielded chiral polymers that could be degraded to the chiral repeating units of **10**. From the stereoisomers distribution of **10**, the *R*/*S* ratios of the stereogenic centers in the chiral polymer main chain were calculated (entries 6−10). Stereoselectivities similar to those obtained from **4** and dialdehydes were attained in the case of polymerization of **5** and **1**. Phenyl substituent in the monomer **1** resulted in somewhat lower enantioselectivity (entries 2 and 9). Polymerization at −20 °C gave lower selectivity than that at −78 °C as expected (entry 8).

In conclusion, arylsilane monomers were prepared, which were soluble even at the low temperature used for the asymmetric allylation polymerization. Optically active polymers containing aryl carbon−silicon linkages in the main chain were obtained. These chiral polymers were easily degraded by treatment with TBAF to the chiral repeating units. The *R*/*S* ratio was determined by chiral HPLC analysis of the degraded product. This method may be applicable to other types of asymmetric synthesis polymerizations and to the evaluation of asymmetric induction.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

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MA012023J