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Asymmetric-Selective Polymerization of (*RS*)-α-Methylbenzyl Methacrylate

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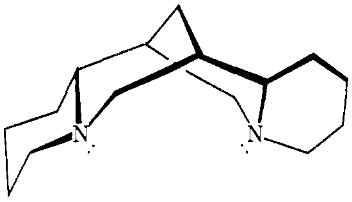
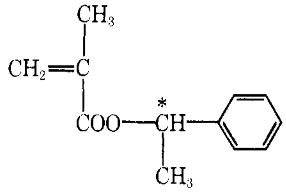
ABSTRACT: The polymerization of (*RS*)-α-methylbenzyl methacrylate [(*RS*)-MBMA] was studied by using diethylmagnesium (Et_2Mg)–chiral alcohol (R^*OH) systems and Grignard reagent–(−)-sparteine systems in toluene. Asymmetric selection was observed in the polymerization with Et_2Mg–R^*OH systems in which the R^* group has heteroatoms like quinine and cinchonine. However, the asymmetric-selective polymerization did not proceed with Et_2Mg–R^*OH systems where the R^* group was hydrocarbon. Grignard reagent–(−)-sparteine systems polymerized preferentially (*S*)-MBMA over (*R*)-MBMA. In the early stage of the polymerization at −78 °C the optical purity of the polymer was about 90%. The asymmetric selectivity was correlated with the tacticity of the resultant polymer; the triad isotacticity of the polymer increased with an increase of the selectivity. The polymerization process could be used as a method of optical resolution.

Asymmetric-selective (or stereoelective)[1] polymerization is of interest and important from many points of view, e.g., preparation of an optically active polymer, optical resolution of a racemic compound, elucidation of the mechanism of stereospecific polymerization, etc. Stereoelective polymerization of cyclic monomers such as epoxide, episulfide, and α-amino acid *N*-carboxylic acid anhydride has been investigated to a considerable extent.[1] On the other hand, the stereoelective polymerization of racemic α-olefins with asymmetric Ziegler–Natta catalysts has been studied by Pino, Ciardelli, and their co-workers who showed that the asymmetric selectivity decreases as the distance between the carbon–carbon double bond and the asymmetric carbon increases.[2–5] The asymmetric selection was not observed in the polymerization of 5-methyl-1-heptene which has an asymmetric carbon at the γ position from the double bond.[5] Recently, Higashimura and Hirokawa have reported the stereoelective cationic polymerization of racemic vinyl ethers by asymmetric catalysts,[6] but the degree of stereoelection in the polymerization seems to be low. From the above results highly asymmetric-selective polymerization of a racemic methacrylic ester would not be expected because the monomer has an asymmetric carbon at the remote γ position with respect to the carbon–carbon double bond. Matsuzaki et al.[7] polymerized (±)-menthyl methacrylate with (−)-amylmagnesium bromide, Solomatina et al.[8] carried out the polymerization of (*RS*)-MBMA with (+)-2-methylbutyllithium and butyllithium–lithium (−)-menthoxide complex, and Ikeda et al.[9] polymerized (*RS*)-MBMA and (*RS*)-*sec*-butyl methacrylate with the triethylaluminum–(−)-sparteine system. However, almost no asymmetric selectivity has been observed in these polymerizations.

Fortunately, we have recently found that the highly asymmetric-selective polymerization of (RS)–MBMA is possible with Grignard reagent–(−)-sparteine systems in toluene at −78 °C.[10] Furthermore, the catalyst systems polymerized stereoelectively (*RS*)-*sec*-butyl methacrylate[10] and 2,3-epoxypropyl methacrylate[11] the later of which has an asymmetric center at the further remote δ position from the carbon–carbon double bond.



(−)-sparteine



MBMA

In the present paper, we describe the detailed investigation on the polymerization of (*RS*)-MBMA by using diethylmagnesium (Et_2Mg)–chiral alcohol systems and Grignard reagent–(−)-sparteine systems.

Experimental Section

Materials. (*RS*)-MBMA was prepared by the reaction of methacryloyl chloride with (*RS*)-α-methylbenzyl alcohol in the presence of triethylamine. The crude monomer was purified by repeated distillation under reduced pressure. Et_2Mg was prepared from ethylmagnesium bromide as diethyl ether solution according to the method of Schlenk.[12] Optically active menthylmagnesium chloride (MentMgCl, 1.0 M) was prepared from (−)-menthyl chloride and magnesium turnings in ether.[13] Other Grignard reagents, cyclohexylmagnesium chloride (c-HexMgCl, 1.40 M) and bromide (c-HexMgBr, 1.32 M), butylmagnesium chloride (*n*-BuMgCl, 1.02 M), and phenylmagnesium bromide (PhMgBr, 1.58 M) were also prepared from corresponding halides in ether. Commercial optically active alcohols, (−)-*cis*-myrtanol ($[\alpha]^{20}_D$ −19.5°, neat), (−)-borneol ($[\alpha]^{20}_D$ −35°, ethanol), (−)-menthol ($[\alpha]^{20}_D$ −50°, ethanol), (−)-2-methylbutanol ($[\alpha]^{23}_D$ −5.8°, neat), (+)-1-*p*-menthen-9-ol ($[\alpha]^{22}_D$ +94°, benzene), strychinine, nicotine, quinine, cinchonine, and cinchonidine were used without further purification after identification by ^1H NMR

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Table I
Polymerization with Et$_2$Mg–Chiral Alcohol Systems in Toluene at −78 °C

Chiral alcohol (R*OH)	Time, h	Yield, %	η_{sp}/C, dL/g	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.)[a] of polymer	Tacticity, %		
					I	H	S
(1*S*:2*R*)-(−)-*cis*-Myrtanol	2.5	19	0.36	−2.7 (2)	7	29	64
(1*S*:2*R*)-(−)-Borneol	2.5	11	0.20	−0.9 (1)			
(1*R*:3*R*:4*S*)-(−)-Menthol	2.5	34	0.26	−1.2 (1)	3	28	69
(*S*)-(−)-2-Methylbutanol	3.0	6		~0			
(+)-1-*p*-Menthen-9-ol	4.0	5		~0			
(−)-Quinine	48	11	0.38	+14.9 (12)	23	26	51
(+)-Cinchonine	144	18	0.64	−21.3 (17)	34	32	34
(−)-Cinchonidine	22	46	1.08	+1.2 (1)	7	19	74
(−)-*cis*-Myrtanol–(−)-sparteine[b]	96	20		−42.9 (34)	39	29	32
(−)-Sparteine							

[a] Optical purity (%). [b] [Myrtanol]/[sparteine] = 1/1.2.

spectroscopy. Commercial (−)-sparteine was employed after identification by elementary analysis and ^{1}H NMR spectroscopy; specific rotation $[\alpha]^{20}_{\mathrm{D}}$ was −18.0° in ethanol (*c* 4.0 g/dL). Toluene was purified in a usual manner, mixed with a small amount of *n*-BuLi, and distilled under high vacuum just before use. Nitrogen was purified by passing through molecular sieves cooled at −78 °C.

Preparation of Catalyst Solution. An Et$_2$Mg–alcohol (1/1) catalyst system was prepared in a dry glass ampule under nitrogen. Toluene (15 mL) and an alcohol (0.20 mmol) were added into the glass ampule by using syringes and the ampule was cooled to 0 °C. Then, Et$_2$Mg (0.20 mmol) was added to the mixture and allowed to react for 10 min. Grignard reagent–(−)-sparteine (1/1.2) catalyst was also prepared in a similar manner as described above. A mixture of (−)-sparteine (0.24 mmol) and Grignard reagent (0.20 mmol) was left for 10 min at room temperature for the formation of a complex.

Polymerization. The above catalyst solutions were usually cooled at −78 °C and then (*RS*)-MBMA (1.52 g, 8.0 mmol) was added with a syringe. The polymerization was terminated by the addition of a few drops of methanol. The polymer was precipitated in 200 mL of methanol containing a small amount of hydrochloric acid. After separation of the polymer by filtration, solvents were evaporated under reduced pressure. The residue was then washed with benzene to separate unreacted MBMA from inorganic compounds and sparteine hydrochloride. The MBMA was isolated almost quantitatively by distillation under high vacuum after removal of benzene. The amount of the undistilled oligomeric compounds was less than 2% of the monomer used for the polymerization.

Conversion of Poly(MBMA) to PMMA. In order to determine the triad tacticity of the polymer, poly(MBMA) was converted to poly(methyl methactylate) (PMMA). Poly(MBMA) was first treated with hydrogen bromide in toluene to convert to poly(methacrylic acid), which was then methylated with diazomethane.[14]

Reduction of Poly(MBMA) with Lithium Aluminum Hydride. Poly(MBMA) (0.60g) having $[\alpha]^{20}_{\mathrm{D}}$ −94.5° (optical purity 75.8%) was dissolved in dry tetrahydrofuran (THF, 25 mL) and then lithium aluminum hydride (0.38 g) was added. After being refluxed for 3 h, the mixture was poured into water (100 mL) containing hydrochloric acid. Insoluble polymer was separated by filtration and the aqueous solution was extracted with ether. The ethereal layer was dried over magnesium sulfate and distilled. It afforded 0.31 g (91%) of α-methylbenzyl alcohol which was pure by the ^{1}H NMR method. The optical rotation of the alcohol was $[\alpha]^{20}_{\mathrm{D}}$ −33.2° which corresponds to 76% optical purity.[14]

Hydrolysis of MBMA with Sodium Hydroxide. (*R*)-MBMA (4.0 g, 21 mmol) with 41.6% optical purity was added into the water–methanol (1:1) mixture (20 mL) containing sodium hydroxide (24 mmol) and the mixture was stirred for 24 h at room temperature. The reaction mixture was extracted with ether and the ethereal layer was dried over magnesium sulfate. After the ether was evaporated, the residue was distilled under vacuum. There was obtained 2.0 g (80%) of (*R*)-α-methylbenzyl alcohol whose $[\alpha]^{20}_{\mathrm{D}}$ (neat) was +17.6° corresponding to 40.2% optical purity.[14]

Measurements. Optical rotation was measured with a Yanagimoto Direct Reading Polarimeter Model OR-10 at 20 °C; the precision of readings was ±0.003°. Specific rotation, $[\alpha]^{20}_{\mathrm{D}}$, was calculated in the conventional unit (deg cm^2/10 g). The rotation of the polymer was determined in toluene (*c* 1–3 g/dL) using a 5-cm cell, and its optical purity was calculated on the basis of $[\alpha]^{20}_{\mathrm{D}}$ −125° (*c* 2, toluene) for optically pure isotactic (~100%) poly[(*S*)-MBMA].[15] The rotation of the undiluted monomer was measured with 0.1–1.0-cm cells and its optical purity was calculated based on $[\alpha]^{20}_{\mathrm{D}}$ −53.0° (neat) of (*S*)-MBMA.[16] The ^{1}H NMR spectrum of PMMA was taken on a JNM-MH-100 (100 MHz) spectrometer in CDCl$_3$ at 60 °C using Me$_4$Si as internal standard. Solution viscosity of the polymer in toluene (*c* 0.5 g/dL) was measured with an Ubbelohde type viscometer at 30.0 °C. The number-average molecular weight of the polymer which had been purified by reprecipitation from a benzene solution into methanol was measured with a Hitachi vapor pressure osmometer Model 117 in benzene at 42 °C. A calibration line was made using benzil as a standard.

Results

Optical Purity of Polymer. In this paper the optical purity of polymerized monomer is denoted as the optical purity of polymer and calculated by dividing $[\alpha]^{20}_{\mathrm{D}}$ of the polymer by $[\alpha]^{20}_{\mathrm{D}}$ 125° of optically pure isotactic (~100%) polymer. This calculation might be questionable because the optical rotation of poly[(*R*)-MBMA] slightly decreased as its isotactic content decreased.[14] On the other hand, the optical purity (α_p) of the polymer can be estimated by using the equation, $\alpha_p = \alpha_m(1 - Y)/Y$ where α_m and Y are the optical purity of unreacted monomer and polymer yield, since no side reaction took place in the present polymerization. In most cases, the optical purities obtained by the above two methods agreed with each other within a few percent errors.

Polymerization with Et$_2$Mg–Chiral Alcohol (1/1) Systems. Table I shows the results of the polymerization of (*RS*)-MBMA with a variety of Et$_2$Mg–chiral alcohol (R*OH) systems in toluene at −78 °C. The R* groups of (−)-*cis*-myrtanol, (−)-borneol, (−)-menthol, (−)-2-methylbutanol, and (+)-1-*p*-menthen-9-ol are hydrocarbons. The systems obtained from these chiral alcohols did not work as efficient asymmetric-selective catalysts. On the other hand, quinine and cinchonine have heteroatoms in their R* groups and the catalysts consisting of them polymerized (*RS*)-MBMA stereoelectively; the former system polymerized preferentially (*R*)-MBMA over (*S*)-MBMA and the latter did (*S*)-MBMA over (*R*)-MBMA. A similar compound cinchonidine, however, was not efficient in terms of the asymmetric selectivity. The addition of a slight excess of (−)-sparteine to Et$_2$Mg–(−)-*cis*-myrtanol system was found to improve strongly the stereoelectivity of the catalyst. The meso dyad content of the polymer formed in the stereoelective polymerization was higher compared with that in the nonstereoelective polymerization. Asymmetric selectivity seems to be correlated with isotactic propagation.

Polymerization with Grignard Reagent–(−)-Sparteine Systems. The polymerization with several different types of asymmetric catalysts was also investigated and the results are summarized in Table II. Asymmetric Grignard reagent MentMgCl itself exhibited a low stereoelectivity. The combination with (−)-nicotine seems to lower the asymmetric selectivity and the combination with strychinine decreased the reactivity of the Grignard reagent. However, the addition of (−)-sparteine to MentMgCl resulted in the formation of a

Table II
Polymerization with Chiral Catalyst Systems in Toluene at −78 °C

Catalyst	Time, h	Yield, %	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.)[a] of polymer	Tacticity, % I	H	S
MentMgCl	7	22	−4.8 (4)[b]	21	30	49
MentMgCl–strychinine(1/1.2)	24	~0				
MentMgCl–(−)-nicotine(1/1.2)	24	51	−2.4 (2)	9	37	54
MentMgCl–(−)-sparteine(1/1.5)	24	16	−108.1 (87)	89	6	5
$\mathrm{Et_2Mg}$–(−)-sparteine(1/1.2)	96	~0				
n-BuLi–(−)-sparteine(1/1.2)	0.2	95	~0	8	33	59

[a] Optical purity (%). [b] $[\alpha]^{20}_{427}$ −9.7°.

Table III
Polymerization with Grignard Reagent–(−)-Sparteine (1/1.2) Systems in Toluene at −78 °C

RMgX[a]	Time, h	Yield, %	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.)[b] of polymer	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.)[b] of monomer
MentMgCl	99.0	55.5	−88.1 (71)	+47.4 (89.4)
c-HexMgCl[c]	2.5	56.1	−83.4 (67)	+46.8 (88.3)
c-HexMgBr	3.0	55.3	−88.6 (71)	+47.3 (89.2)
n-BuMgCl	1.0	52.6	−93.9 (75)	+45.0 (84.8)
PhMgBr	192	0		

[a] Ether solution. [b] Optical purity (%). [c] Toluene solution.

polymer having high (*S*)-MBMA content and isotacticity. The $\mathrm{Et_2Mg}$–(−)-sparteine system did not initiate the polymerization. The *n*-BuLi–(−)-sparteine system showed a very high catalytic activity for the polymerization, but no asymmetric selectivity.

Since the MentMgCl–(−)-sparteine system was found to be a highly asymmetric-selective catalyst, we carried out the polymerization of (*RS*)-MBMA using different Grignard reagents. The results are shown in Table III. Except for PhMgBr, four Grignard reagents, MentMgCl, c-HexMgCl, c-HexMgBr, and n-BuMgCl, brought about similar results. At almost the same yield, the optical purities of the (*S*) polymer and unreacted (*R*) monomer were rather similar. Consequently, the chiral Grignard reagent, MentMgCl, was not a requisite component. The PhMgBr–(−)-sparteine system did not initiate the polymerization at −78 °C.

In order to see the effect of diethyl ether used as the solvent of the Grignard reagents, it was replaced with toluene on a vacuum line. The toluene solutions of MentMgCl and c-HexMgCl thus obtained still contained nearly one equimolar amount of the ether to each Grignard reagent. In Table IV the results of the polymerization with these Grignard reagents are shown together with the results with the same Grignard reagents in ether. It is clear that the ether had little effect on the polymerization in toluene. However, when THF was used as a medium of the polymerization in place of toluene, the asymmetric selectivity of the catalyst greatly decreased.

The polymerization was carried out with the catalyst systems having various ratios of (−)-sparteine to c-HexMgCl at −78 °C. The results are shown in Table V. The asymmetric selection of the polymerization was independent of the [(−)-sparteine]/[c-HexMgCl] ratio, when more than an equivalent amount of (−)-sparteine was employed. We observed a long induction period at [(−)-sparteine]/[c-HexMgCl] = 1.2. In the polymerization of (*RS*)-MBMA with Grignard reagent–(−)-sparteine systems, sometimes there existed a long induction period the reasons for which are not clarified yet.[17]

The effect of the temperature was investigated using the c-HexMgCl–(−)-sparteine (1/1.2) system as a catalyst (Table VI). The optical purities of the polymer and unreacted monomer at the same polymer yield decreased with an increase in the temperature. This indicates that the asymmetric selectivity of the catalyst decreases with the temperature. As previously described, the PhMgBr–(−)-sparteine system did not initiate the polymerization at −78 °C but did at −40 °C. The asymmetric selectivity and stereoregulation of the catalyst, however, were much lower than those of the c-HexMgCl–(−)-sparteine system at the same temperature.

Discussion

Polymerization with $\mathrm{Et_2Mg}$–Chiral Alcohol Systems. It has been reported that alkylmagnesium alkoxides are obtained by the reaction of dialkylmagnesium with alcohols[18]

Table IV
Effect of Solvent of Grignard Reagent in the Polymerization of (*RS*)-MBMA with RMgCl–(−)-Sparteine (1/1.2) Systems in Toluene at −78 °C

RMgCl/solvent	Time, h	Yield, %	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.) of polymer	$[\alpha]^{20}_{\mathrm{D}}$ (O.P.) of monomer
MentMgCl/ether	22	23.2	−106.0 (85)	+12.9 (24.3)
MentMgCl/toluene	24	24.7	−108.7 (87)	+14.4 (27.2)
c-HexMgCl/ether	2.2	66.0[b]	−55.3 (44)	+48.2 (90.9)
c-HexMgCl/toluene	2.8	66.1[c]	−50.1 (40)	+44.9 (84.6)
c-HexMgCl/ether	4.0	91.7	−11.8 (10)	+50.0 (94.3)
c-HexMgCl/ether[a]	2.0	89.7	−0.9 (1)	+2.8 (5.2)

[a] Polymerization medium, THF. [b] Number-average molecular weight ($\overline{M}_{\mathrm{n}}$) of polymer was 46 000. [c] $\overline{M}_{\mathrm{n}}$ = 30 500.

Table V
Effect of (−)-Sparteine/c-HexMgCl Ratio in the Polymerization of (*RS*)-MBMA in Toluene at −78 °C

[(−)-Sparteine]/ [c-HexMgCl][a]	Time, h	Yield, %	$[\alpha]^{20}_D$ (O.P.) of polymer	$[\alpha]^{20}_D$ (O.P.) of monomer
0	1.8	8.9[b]		
0.5	1.8	8.0	−74.4 (59)	+2.9 (5.5)
1.0	1.8	45.5	−101.1 (81)	+36.2 (68.2)
1.2	68.3	44.5	−104.6 (84)	+36.5 (68.9)
1.5	1.8	43.8	−102.9 (82)	+33.7 (63.6)
2.0	1.8	33.6	−105.8 (85)	+23.2 (43.7)

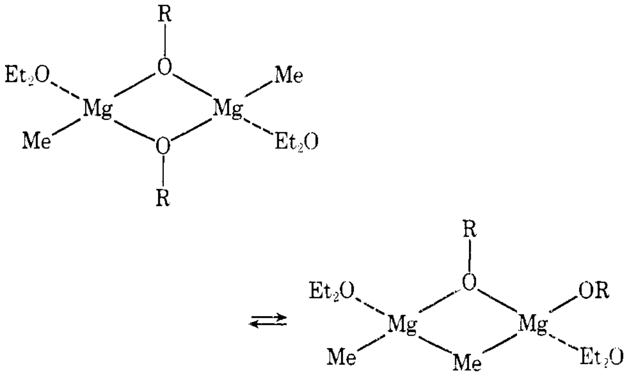
[a] c-HexMgCl 0.20 mmol. [b] I-H-S = 17:43:40.

Table VI
Effect of Temperature in the Polymerization of (*RS*)-MBMA with c-HexMgCl-(−)-Sparteine (1/1.2) System in Toluene

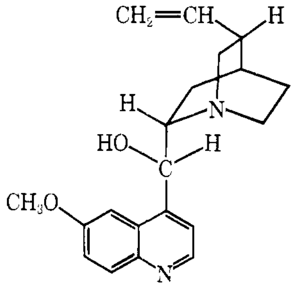
Temp, °C	Time, h	Yield, %	$[\alpha]^{20}_D$ (O.P.) of polymer	$[\alpha]^{20}_D$ (O.P.) of monomer	Tacticity, % I	H	S
−78	1.8	28.4[b]	−113.3 (91)	+18.1 (34.2)	95	3	2
−78	3.5	66.2[c]	−61.3 (49)	+46.8 (88.3)	90	6	4
−40	1.0	28.3	−77.9 (62)	+14.2 (26.8)	80	12	8
0	1.0	73.9	−23.4 (19)	+31.9 (60.2)	53	31	16
+30	1.0	72.8	−7.7 (6)	+11.6 (21.8)	36	39	25
−40[a]	72	22.6	−23.3 (19)	+3.3 (6.2)	33	24	43

[a] PhMgBr was used. [b] $\overline{M}_n$ = 45 800. [c] $\overline{M}_n$ = 37 100.

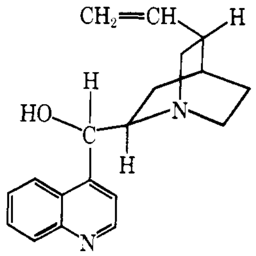
and they exist in associated forms such as dimer, trimer, and tetramer.[18-20] For instance, Nackashi and Ashby reported that $CH_3MgOCPh_2CH_3$ (MeMgOR) in diethyl ether exists as dimers:[20]



If the anionic polymerization of a methacrylic ester is initiated by such an alkylmagnesium alkoxide, the alkoxy group will always be situated near the active center, attaching to magnesium ion, and influence the stereoregulation of the polymerization. Actually we have recently shown that in the polymerization of MMA, the tacticity of the polymer depended on the structure of alkoxides:[21] Et_2Mg-(−)-*cis*-myrtanol and Et_2Mg-(−)-2-methylbutanol systems formed highly isotactic PMMA, while Et_2Mg-(−)-menthol and Et_2Mg-(−)-borneol systems yielded syndiotactic PMMA. Therefore, alkylmagnesium alkoxides obtained from optically active alcohols (R*OH) were expected to work as asymmetric catalysts. The results of the polymerization by chiral alkoxides are shown in Table I. For the polymerization of (*RS*)-MBMA Et_2Mg-(−)-myrtanol and Et_2Mg-(−)-menthol systems were not stereoelective catalysts and yielded syndiotactic polymers of a similar regularity. The systems of Et_2Mg-quinine, cinchonine, and cinchonidine were not stereospecific catalysts for the polymerization of MMA,[21] but two of these systems polymerized (*RS*)-MBMA stereoelectively. The stereoregulation in the polymerization of MMA by these Et_2Mg-chiral alcohol systems was not directly correlated with the asymmetric selectivity of these systems in the polymerization of (*RS*)-MBMA. On the other hand, the stereoregulation in the polymerization of (*RS*)-MBMA by Et_2Mg-alcohol systems seems to be correlated with the asymmetric selectivity. Et_2Mg-quinine and Et_2Mg-cinchonine systems polymerized preferentially (*R*)-MBMA and (*S*)-MBMA, respectively. This difference may be attributed to the configurational difference of these two alkaloids. They differ from one another in the configuration of the carbon attached to a hydroxy group and the carbon adjacent to it. Cinchonidine is a stereoisomer of cinchonine and has the same configuration as quinine. The Et_2Mg-cinchonidine system did not work as an asymmetric-selective catalyst. Based on a molecular model, the coordinations of methoxy oxygen and the nitrogen of a bicyclo ring to magnesium appear to play an important role in determining the stereoelection of the catalysts.



quinine



cinchonine

Polymerization with Grignard Reagent-(−)-Sparteine System. It has been reported that asymmetric selection was not observed in the polymerization of (±)-menthyl methacrylate by (−)-amylmagnesium bromide.[7] In the polymerization of (*RS*)-MBMA with MentMgCl alone (Table II) we obtained a polymer having a low optical rotation which seems to be beyond the rotation arising from only the terminal menthyl group. The MentMgCl prepared from (−)-menthyl chloride has been proved to be configurationally stable and the configurations of three asymmetric carbons are the same as (−)-menthol.[13] The stereoelection might occur only in a few initial addition steps of the monomer to the chiral menthyl group.

Grignard reagent-(−)-sparteine systems were highly asymmetric-selective isotactic catalysts, whereas the *n*-

BuLi–(−)-sparteine system as well as the $AlEt_3$–(−)-sparteine system[9] was a nonasymmetric-selective syndiotactic catalyst. The polymerization with the latter systems seems to follow the Bernoulli statistics. The different catalytic behavior of these systems is very interesting and suggestive. The reactivities of *n*-BuLi[22] and $AlEt_3$[9] were greatly enhanced by the coordination with (−)-sparteine, which probably makes the carbon–metal bond more polar even in a nonpolar hydrocarbon solvent. Such a coordination in the polymerization may increase the reactivity of the polymer anion and make it difficult for the carbonyl groups of the polymer and incoming monomer to coordinate to the counterion. Thus, syndiotactic propagation will be favorable as in radical polymerization.[9,23–26] Our results, however, indicate that if a proper combination of metal cation and ligand is chosen, the complex can control the polymerization more strictly. The size and charge of magnesium ion must be very suitable for the formation of such a complex with (−)-sparteine. In the polymerization with the Grignard reagents, the presence of (−)-sparteine brought about a drastic change from a nonstereospecific polymerization to a highly isotactic polymerization (Tables II and V). Since the polymerizations with Grignard reagent–(−)-sparteine systems sometimes have a long induction period, we cannot compare the reactivities of the Grignard reagents in the presence and absence of (−)-sparteine. However, the side reactions which are often recognized in the polymerization of methacrylates by a Grignard reagent[27] did not take place in the polymerization of (*RS*)-MBMA by the Grignard reagent–(−)-sparteine system, because the polymer was obtained quantitatively after a prolonged polymerization reaction. Judging from the mild reactivity, high stereospecificity, and stereoelectivity, the catalyst system probably has a rigid structure. It must be a 1:1 complex of magnesium ion and (−)-sparteine (Table V) and stable in the presence of diethyl ether but unstable in the presence of a stronger base, THF (Table IV). One of the most probable structures of the propagating species might be octahedral, if the following five or six ligands would coordinate to the magnesium ion: two nitrogen atoms of (−)-sparteine, one halide anion, one polymer anion, one monomer, and probably one carbonyl group of the polymer. The existences of five- and six-coordinated organomagnesium compounds have been proved by the X-ray diffraction technique.[28,29] Such a structure may be unstable at higher temperature, which will lead to lowering the asymmetric selectivity and stereospecificity of the polymerization (Table VI).

The catalytic action of the PhMgBr–(−)-sparteine system differed greatly from other Grignard reagent–(−)-sparteine systems (Tables III and VI). This indicates that the alkyl group of the Grignard reagent is also important, but more data are necessary to clarify this point.

From the optical purities of the polymers obtained in the early stage of the polymerization at −78 °C, the asymmetric selectivity in the present study seems to be highest in the asymmetric-selective polymerizations so far reported including the ring opening polymerizations of cyclic monomers such as propylene oxide,[30] propylene sulfide,[31] and *N*-carboxylic acid anhydride.[32] This high selectivity can be utilized as a preparative method in the optical resolution of (*RS*)-α-methylbenzyl alcohol. Compared with conventional methods, this resolution requires only a catalytic amount of a chiral compound for resolving a great amount of a racemic compound. We could readily obtain (*R*)-α-methylbenzyl alcohol from poly(MBMA) in a good yield without racemization by the reduction with $LiAlH_4$. (*S*)-α-Methylbenzyl alcohol was also recovered from (*S*)-MBMA by hydrolysis with sodium hydroxide. This method will be applicable to other alcohols, if the asymmetric-selective polymerization of their methacrylic esters proceeds.

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