

Catalysts

Asymmetric Selection Polymerization of (RS)- α -Methylbenzyl Methacrylate with Axially Chiral Catalysts Prepared from Grignard Reagents and Biphenyl Derivates

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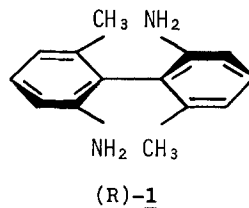
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SUMMARY

Asymmetric selection (stereoselection) polymerization of racemic α -methylbenzyl methacrylate (MBMA) was investigated by using axially dissymmetric catalysts in toluene. The catalysts of binary system, which were prepared *in situ* from optically pure 2,2'-diamino-6,6'-dimethylbiphenyl (1) or its N-methylated derivatives and Grignard reagents (RMgX). The selection depended upon not only the kinds of the amines and RMgX but also the molar ratios. Among the catalysts examined, cyclohexylmagnesium bromide (cHexMgBr) - (R)-1 [1.5/1.0 molar ratio] system gave the best selection and it polymerized (S)-monomer preferentially over (R)-antipode.

INTRODUCTION

Asymmetric selection polymerizations of racemic monomers have been reported by many investigators since early in 1960s, however, no satisfactory selection has been achieved till recently. In 1977 Okamoto and Yuki have succeeded in the highly stereoselective polymerization of (RS)-MBMA using (-)-sparteine - Grignard reagent catalyst (1). Since then many of the detailed papers have been published by them (*e.g.*, 2). These works have prompted us to examine the same polymerization with a new binary catalyst formed from optically pure 1 and cHexMgBr, and fortunately our catalyst has been found to be also quite useful for this object.



The catalyst employed here has a Mg-N bond, which is similar to that used by Joh *et al.* in the stereospecific polymerization of methyl methacrylate (MMA) (3). Concerning the utilization of axially dissymmetric compound as chiral component of catalyst for such an asymmetric polymerization, only paper by S epulchre and Spassky has been published up to date (4). They reported that (RS)-alkylthiirane was polymerized in a high selection with optically pure 2,2'-dihydroxy-1,1'-binaphthyl - diethylzinc catalyst.

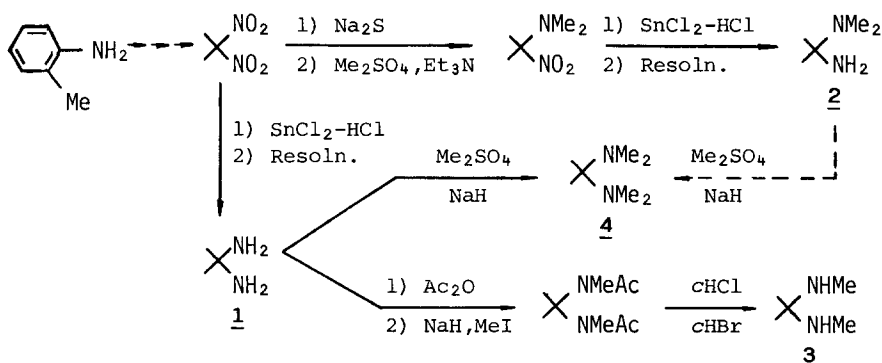
In this article we describe a study of the asymmetric selection polymerization of (RS)-MBMA from the following points of view: (a) molar ratio in the reaction of 1 or its N-methylated derivatives with cHexMgBr; (b) effect of the catalysts formed in the various molar ratios on the polymerization; (c) temperature effect; (d) effect of the catalysts formed by various combinations between the amines and RMgX on the polymerization.

EXPERIMENTAL

Materials

MBMA was prepared from (RS)- α -methylbenzyl alcohol and purified according to the method of Okamoto (2); bp 52°C (0.04 mmHg). Grignard reagents were prepared from the corresponding halides and magnesium in ether by the ordinary procedure, and standardized prior to use for the polymerization. Diethylmagnesium (Et_2Mg) was prepared according to the literature (5) and used as ethereal solution. Toluene was purified in a usual manner, mixed with a small amount of butyllithium in toluene, and redistilled under high vacuum just before use.

Preparation of Optically Pure Aminobiphenyl Derivatives (1-4)



Scheme 1

Amines 1-4 were prepared *via* procedures shown in Scheme 1. Optical resolutions of 1 and 2 were conducted with the help of tartaric acid, where the natural occurring acid led to the crystallization of the (R)-configurational amine salts in EtOH. The maximum rotation and absolute configuration of enantiomeric 1 have been established (6). From this were deduced these properties for the enantiomers of 3 and 4 derived from 1. The absolute configuration of the enantiomeric 2 was determined from the chemical correlation between (R)-(+)-4 and (+)-2 through N,N-dimethylation. The optical purities of 2 and 3 were confirmed by ^1H NMR spectra (CDCl_3) in the presence of $\text{Eu}(\text{TFC})_3$. The amines except 1 were new compounds and their structures were consistent with IR, ^1H NMR, and mass spectral data and elemental analyses.

(S)-1: mp 159–160°C; $[\alpha]_{\text{D}}^{25} -51.0^\circ$ (*c* 1.02, EtOH).

(RS)-2: mp 74.5–75.5°C (benzene); IR (KBr) 3420, 3340, 2760 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.92, 1.98, (ss, 6H, ArCH₃), 2.54 (s, 6H, NCH₃), 3.44 (br, 2H, NH₂), 6.5–7.3 (m, 6H, ArH); MS (75 eV) *m/e* 240. Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.92; H, 8.47; N, 11.54.

(S)-2: mp 70.5–71.5°C (EtOH); $[\alpha]_{\text{D}}^{25} +41.0^\circ$ (*c* 1.01, EtOH).

(RS)-3: mp 106–107°C (EtOH); IR (KBr) 3460, 2790 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.88 (s, 6H, ArCH₃), 2.72 (s, 6H, NCH₃), 3.2 (br, 2H, NH), 6.5–7.3 (m, 6H, ArH); MS (75eV) *m/e* 240. Anal. calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 80.09; H, 8.41; N, 11.90.

(S)-3: mp 64.5–65.5°C (EtOH); $[\alpha]_{\text{D}}^{25} -53.2^\circ$ (*c* 0.50, EtOH).

(RS)-4: bp 135–140°C (0.2 mmHg); IR (neat) 2760 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.97 (s, 6H, ArCH₃), 2.44 (s, 12H, NCH₃), 6.85–7.3 (m, 6H, ArH);

MS (75ev) m/e 268. Anal. Calcd for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 80.85; H, 9.21; N, 10.54.
 (S)-4: mp 43.5-44.5°C (MeOH); $[\alpha]_D^{25}$ -16.3° (*c* 0.50, EtOH).

Polymerization

A typical procedure is illustrated. A glass ampoule containing a biphenyl derivative (0.18 mmol) was evacuated and filled with dry nitrogen. Toluene (10 ml) was charged into the ampoule and the solid biphenyl was dissolved. To the solution was added cHexMgBr (0.27 mmol) in ether and allowed to react for 30 minutes at room temperature. The homogeneous catalyst solution was cooled at -30°C and then the monomer (5.34 mmol) was added. The polymerization reaction was done at this temperature unless otherwise specified, and terminated by the addition of a small amount of methanol. The polymer was precipitated and separated by filtration. Unreacted monomer was recovered by distillation (GLPC purity, >98%), after the removal of inorganic materials and solvents from the filtrate. And the methanol-soluble oligomeric part was less than 2% yield.

The dominant configurations and optical purities of the polymer and unreacted monomer were determined from their optical rotations on the basis of the reported values (2): optical pure isotactic (~100%) poly[(S)-MBMA], $[\alpha]_D^{20}$ -125° (*c* 2, toluene); (S)-MBMA, $[\alpha]_D^{20}$ -53° (neat). The triad tacticity of the poly(MBMA) was determined by ¹H NMR spectrum of poly(MMA) derived from the original polymer (7,8).

RESULTS AND DISCUSSION

Molar Ratio in the Reaction of Diaminobiphenyls with cHexMgBr

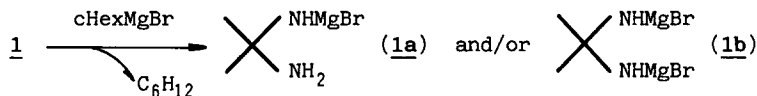
Table 1 Molar Ratio in the Reaction of Chiral Aminobiphenyls with cHexMgBr in Toluene for 30 Minutes ^{a)}

Amine	[cHexMgBr]/ [Amine]	Temp. °C	[C ₆ H ₁₂] ^{b)} / [Amine]
(R)-1	1.5	25	1.48
(R)-1	2.0	-30	1.91
(R)-1	3.0	25	2.10
(R)-1	3.0	-30	2.02
(R)-1	4.0	-30	2.14
(S)-2	1.0	25	0.95
(S)-2	3.0	25	1.08
(S)-3	1.5	25	1.41
(S)-3	3.0	25	2.18
(S)-4	1.0	25	0.02

a) The reaction was quenched by the addition of a toluene solution of I₂. b) Determined by GLPC; internal standard, methylcyclohexane.

The reaction of each of diaminobiphenyl derivatives 1-4 with cHexMgBr was investigated in terms of the molar ratio. When an ethereal solution of cHexMgBr allows to mix with each of the amines 1-3, the amino hydrogen is replaced by MgBr with the release of cyclohexane. The amount of cyclohexane can be measured by the method of GLPC after the conversion of remaining cHexMgBr into cyclohexyliodide, since it has been known that RMgX is able to be converted quantitatively to RI by the addition of excess I₂ (9). From the results shown in Table 1, it is obvious that the primary and secondary amino groups of the biphenyls reacted with an equimolar cHexMgBr at 25 and -30°C, whereas the tertiary amino group did not. On the other hand, it has been known that aniline can react with EtMgBr in 1:2 molar

ratio (10), however, the primary amino groups of 1 and 2 reacted with only an equimolar *c*HexMgBr even in its excess. On the basis of the above findings, the reaction of 1 with *c*HexMgBr is believed to give mono- and/or bis-bromomagnesium amide(s) of 1 (1a and 1b, respectively) depending on the molar ratio as follows:



Effect of cHexMgBr/(R)-1 Molar Ratio on the Polymerization

The effect of the 1 catalysts, which were prepared from 1 and *c*HexMgBr in various molar ratios, on the polymerization of (RS)-MBMA was examined in toluene at -30°C . As shown in Table 2, all the catalysts formed at the ratio between 1.0 and 2.0 showed to be highly effective for the aimed polymerization. And there were no substantial differences between the catalytic action of (R)-1a and that of 1b with respect to the selection. The catalyst derived from (R)-1 selected (S)-monomer preferentially over (R)-one. The polymers obtained at lower conversion were found to be consisted of nearly 90% of (S)-monomer unit. Furthermore, it was found also that these polymers had quantitatively isotactic microstructures. When the ratio was changed to less than unity, or to more than two, the selection as well as the stereoregularity of the polymer decreased. The catalyst formed at the ratio of 2.5 is considered to be a mixture of 1b and unreacted *c*HexMgBr. At -78°C , the monomer seems to have reacted exclusively with the *c*HexMgBr on the basis of the fact shown later. When this catalyst system was used for the polymerization at this temperature, the *c*HexMgBr showed no selectivity even in the presence of 1b. Therefore, each of them could polymerize the monomer concurrently at -30°C , resulting in a small lowering of the overall selection together with a decrease in the isotacticity. In the case of the catalyst having the ratio of 0.5, it is noteworthy that considerable decreases in both the optical purity and regularity of the polymer were found. This catalyst system should be an equimolar mixture of (R)-1a and unreacted (R)-1. Since 1a was found to be an efficient species as mentioned above, the remaining 1 is considered to prevent the desirable reaction.

Table 2 Effect of *c*HexMgBr/(R)-1 Molar Ratio on the Polymerization of (RS)-MBMA in Toluene at -30°C

Run no.	[<i>c</i> HexMgBr]/[(R)-1]	Time min.	Yield %	[α] _D ²⁵ (OP) of polymer	Tacticity, %		
					I	H	S
1	0.5	125	38.1	-23.6 (18.9)	43	26	31
2	1.0	40	12.7	-109.6 (87.7)	100		
3	1.5	55	20.7	-110.6 (88.5)	100		
4	2.0	49	15.2	-108.0 (86.4)	100		
5	2.5	9	26.8	-79.0 (63.4)	90	7	3
6 a)	2.5	(18h)	12.6	0	—		

a) Polymerization temperature, -78°C .

Temperature Effect

The polymerization was examined with *c*HexMgBr - (R)-1 (1.5/1.0) catalyst at different temperatures. The results are summarized in Table 3. As usual, the optical purity of the polymer increased with lowering the react-

Table 3 Effect of Temperature on the Polymerization of (RS)-MBMA with cHexMgBr/(R)-1 (1.5/1.0) Catalyst in Toluene

Temp. °C	Time min.	[cHexMgBr]/ [MBMA] ₀ , mol%	Yield %	[α] _D ²⁵ (OP) of polymer
20	22	3.0	21.7	-81.0 (64.8)
0	23	3.0	41.3	-90.3 (72.2)
-20	60	5.0	32.4	-98.7 (79.0)
-30	90	3.0	20.0	-104.0 (83.2)
-30 ^{a)}	44	6.0	19.9	-108.0 (86.4)
-30 ^{b)}	40	5.0	32.6	-108.0 (86.4)
-40	135	6.0	8.6	-101.3 (81.0)
-50	(9h)	5.0	21.2	-100.0 (80.0)
-78	(12h)	6.0	0	—

a,b) The catalysts were prepared at 50 and -30°C, respectively.

tion temperature until -30°C. Below this, however, the selection rather decreased. A retardation of the polymerization was remarkable at lower temperature than -30°C, and no detectable amounts of polymer were obtained at -78°C in spite of a longer reaction time of 12 hours. When cHexMgBr and (R)-1 were mixed at 50, -30°C and ambient temperature, each of the catalysts showed similar selectivity. This may be interpreted by the fact that the reaction of 1 with cHexMgBr gave the same reactive species independently of the temperature.

Polymerization with Axially Chiral Catalysts

Effect of the variation of the kinds of the aminobiphenyls and Grignard reagents used for the preparation of chiral catalysts on the polymerization was examined. Table 4 shows the results. All of the catalysts yielded polymers, though their optical purities were different from one another in a wide range. The amine 1 gave the best selection. When the enantiomeric catalyst was used, it was observed that the configurational bias of the recovered monomer was reversed as expected. Both the catalysts from 1 and 2 preferred the monomer having the absolute configuration opposed to that of the amines. The catalyst from 3 showed the selection reversed to the above cases, though its selectivity was very low. The catalyst from 4 having two tertiary amino groups did not show any ability for the enantiomer discrimination, and the tacticity of the product polymer was similar to that obtained with cHexMgBr alone. This may be attributed to an impossibility in forming a favourable complex between the amine and cHexMgBr.

All of alkylmagnesium bromides used here brought about high selections in a similar degree independently on the kind of the alkyl groups. This seems to be natural; that is, the alkyl groups were converted to the corresponding alkanes at the formation of the catalyst, thus did not affect the polymerization. Exceptionally PhMgBr - (R)-1 system showed a somewhat lower selection than that by the above systems. From the GLPC analysis of this catalyst solution it was found that a considerable part of the PhMgBr still remained unreacted (about 42%) after the reaction time of 30 minutes. Therefore a lowering of the selection is ascribed to a non-selective polymerization caused concurrently by unreacted PhMgBr.

Effect of halogen of Grignard reagents on the selection were also examined by using cHexMgX - (R)-1 catalysts (X = Cl, Br and I). The chloride gave the catalyst being of poor solubility in toluene and the system became heterogeneous accompanied with fine white solids. The selectivity was found to be in the decreasing order as follows: bromide > chloride > iodide.

Table 4 Polymerization of (RS)-MBMA with Axially Chiral Catalysts in Toluene at -30°C

Amine	RMgX (ratio to amine)	Time min.	Yield %	[α] D^{25} (OP)		Tacticity, %		
				polymer	monomer	I	H	S
(R)-1	cHexMgBr (1.5)	60	30.2	-107.3 (85.8)	+19.8 (37.3)	100		
(S)-1	cHexMgBr (1.5)	60	24.5	+106.7 (84.5)	-15.1 (28.5)	100		
(R)-1	cHexMgCl (1.5) ^{a)}	85	10.8	-80.0 (64.6)	+4.2 (7.9)	85	7	8
(R)-1	cHexMgI (1.5)	50	15.2	-51.8 (41.4)	+4.2 (7.9)	67	23	10
(R)-1	EtMgBr (1.5)	80	14.1	-107.1 (85.7)	n.d.	100		
(R)-1	BuMgBr (1.5)	45	10.1	-105.5 (84.4)	+5.3 (10.0)	100		
(R)-1	PhMgBr (1.5)	60	35.5	-94.6 (75.6)	+22.4 (42.3)	95	2	3
(S)-2	cHexMgBr (0.9)	120	39.3	+9.5 (7.6)	-2.8 (5.3)	81	12	7
(S)-3	cHexMgBr (1.5)	20	44.6	-2.0 (1.6)	+4.8 (9.1)	49	33	18
(S)-4	cHexMgBr (0.9)	5	87.9	0	—	71	13	16
—	^{b)} cHexMgBr	5	71.0	0	—	80	9	11
(R)-1	Et ₂ Mg (0.9) ^{c)}	60	61.6	0	—	14	34	52
(R)-1	Et ₂ Mg (1.9) ^{c)}	60	84.6	0	—	22	30	48

a) The catalyst system was heterogeneous. b) Without any amines.

c) Et₂Mg was used in place of cHexMgBr.

Grignard reagents have been considered to attain Schlenk equilibrium between RMgX and R₂Mg in solution (11). In order to see contributions of the R₂Mg to the asymmetric selection, the polymerization was performed at -30°C using the catalysts from (R)-1 and Et₂Mg in place of the corresponding Grignard reagent. The catalysts showed no selectivity and the polymers were atactic, which indicate that such contribution may be negligible.

Further investigations are currently under way and the results will be published in near future.

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REFERENCES

1. Y.Okamoto, K.Ohta, and H.Yuki, *Chem. Lett.*, **1977**, 617.
2. Y.Okamoto, K.Urakawa, K.Ohta, and H.Yuki, *Macromolecules*, **11**, 719 (1978); Y.Okamoto, K.Ohta, and H.Yuki, *ibid.*, **11**, 724 (1978); Y.Okamoto, K.Suzuki, T.Kitayama, H.Yuki, H.Kageyama, K.Miki, N.Tanaka, and N.Kasai, *J. Am. Chem. Soc.*, **104**, 4618 (1982) and other references cited therein.
3. Y.Joh and Y.Kotake, *Macromolecules*, **3**, 337 (1970).
4. M.Sépulchre and N.Spasky, *Makromol. Chem., Rapid Commun.*, **2**, 261 (1981).
5. W.Strohmeier, *Chem. Ber.*, **88**, 1218 (1965).
6. H.Suda, M.Motoi, M.Fujii, S.Kanoh and H.Yoshida, *Tetrahedron Lett.*, **1979**, 4565.
7. H.Yuki, K.Ohta, K.Uno, and S.Murahashi, *J. Polym. Sci. A-1*, **6**, 329 (1968).
8. F.A.Bovey and G.V.B.Tieres, *J. Polym. Sci.*, **44**, 173 (1960).
9. G.Champetier and R.Kullmann, *Bull. Soc. Chim. France*, **1949**, 693.
10. M.Okubo and S.Ueda, *Bull. Chem. Soc. Jpn.*, **53**, 281 (1980).
11. W.Schlenk and W.Schlenk Jr., *Chem. Ber.*, **62**, 920 (1920).