# Asymmetric-Selective Polymerization of (*RS*)-$\alpha$-Methylbenzyl Methacrylate with the Cyclohexylmagnesium Chloride–(−)-Sparteine System in Toluene at −78 °C

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ABSTRACT: Asymmetric-selective (or stereoelective) polymerization of (*RS*)-$\alpha$-methylbenzyl methacrylate [(RS)-MBMA] with homogeneous cyclohexylmagnesium chloride (c-HexMgCl)– and bromide (c-HexMgBr)–(−)-sparteine (1/1.2) systems was studied in toluene at −78 °C. The systems polymerized preferentially (*S*)-MBMA over (*R*)-MBMA. The optical purity of the monomer which was polymerized in the early stage of the polymerization was greater than 90% and the optical purity of unreacted monomer was nearly 100% at about 65% polymer yield. This high asymmetric selectivity was ascribed to the unsimultaneous existence of two different active centers. One of them is produced exclusively in the initiation reaction, polymerizes (*S*)-MBMA preferentially, and disappears around 45–65% polymer yields. The other is formed around 45–65% polymer yields and polymerizes only (*R*)-MBMA. The existence of two centers was supported by the studies of optical rotation, molecular weight, and tacticity of the polymer as well as kinetic data.

We have recently found that the highly asymmetric-selective (or stereoelective) polymerization of racemic methacrylates, especially (*RS*)-$\alpha$-methylbenzyl methacrylate [(*RS*)-MBMA], is possible with Grignard reagent–(−)-sparteine systems in toluene at low temperatures.[1–3] For instance, cyclohexylmagnesium chloride (c-HexMgCl)– or bromide (c-HexMgBr)–(−)-sparteine systems initiated the polymerization of (*RS*)-MBMA to form a highly isotactic (*S*) polymer having about 90% optical purity in the early stage of the polymerization, while the unreacted monomer was enriched in (*R*)-antipode whose optical purity was more than 90% at about 60% yield.[1,3] The catalyst systems also polymerized 2,3-epoxypropyl methacrylate (glycidyl methacrylate) stereoelectively to give a highly isotactic polymer.[2] This monomer has an asymmetric carbon at a further remote $\delta$ position from the carbon–carbon double bond in comparison with (*RS*)-MBMA.

In this paper, we describe a detailed investigation of the polymerization of (*R*S)-MBMA with c-HexMgCl– and c-HexMgBr–(−)-sparteine (1/1.2) systems in toluene at −78 °C in order to clarify the polymerization mechanism by these interesting catalyst systems. In addition, the copolymerizations of (*RS*)-MBMA with methyl methacrylate (MMA) or $\alpha,\alpha$-dimethylbenzyl methacrylate by the c-HexMgCl–(−)-sparteine system are also described.

## Experimental Section

**Materials.** The preparations and purifications of the monomer, Grignard reagents, and solvent were previously described.[3] Commercial (−)-sparteine ($[\alpha]^{20}{}_{\mathrm{D}}$ −18.0° in ethanol) was used without purification.

**Polymerization.** The polymerization was carried out in a glass ampule as described previously.[3] Toluene (15 mL), (−)-sparteine (0.24 mmol), and c-HexMgX (0.20 mmol) were mixed at room temperature. After 10 min, the catalyst solution was cooled to −78 °C and then (*RS*)-MBMA (8.0 mmol) was added. The solution must be stirred vigorously in order to dissolve (*RS*)-MBMA as early as possible. The polymerization was terminated by the addition of a small amount of methanol and the polymer was precipitated in methanol. Unreacted monomer was recovered almost quantitatively by distillation after the separation of the polymer by filtration.

The copolymerizations of (*RS*)-MBMA with MMA or $\alpha,\alpha$-dimethylbenzyl methacrylate were carried out in the same way. To the catalyst solution, equimolar amounts of the monomers were added. The polymer was precipitated in methanol.

***Polymerization in the NMR Sample Tube.*** The polymerization was carried out in a dry NMR sample tube of 5-mm diameter under dry nitrogen. (*RS*)-MBMA (~40 mg) and toluene-$d_8$ (0.38 mL) were mixed in the tube and cooled to −78 °C. The c-HexMgCl–(−)-sparteine (1/1.2) (1.0 M) which had previously been prepared in toluene was then added into the monomer solution using a syringe and the tube was sealed. The polymerization was followed with a $^1$H NMR spectrometer (100 MHz) at −78 °C.

**Conversion of Poly(MBMA) to PMMA.** In order to determine the triad tacticity of the polymers, poly(MBMA) and poly(MBMA-*co*-MMA) were treated with hydrogen bromide according to the procedure described previously.[4] In this method only the MBMA unit was transformed into the methacrylic acid unit. The poly(methacrylic acid) and poly(methacrylic acid-*co*-MMA) thus obtained were then converted into PMMA by methylation with diazomethane.

**Measurements.** The measurements of optical rotation, $^1$H NMR spectra, and number-average molecular weight were done in the same manner using the same instruments as shown in the previous paper.[3] The optical purities of the polymer and unreacted MBMA were calculated by dividing $[\alpha]^{20}{}_{\mathrm{D}}$ of the polymer and monomer by $[\alpha]^{20}{}_{\mathrm{D}}$ −125° (toluene) of optically pure isotactic (~100%) poly[(*S*)-MBMA][5] and $[\alpha]^{20}{}_{\mathrm{D}}$ −53.0° (neat) of (*S*)-MBMA,[6] respectively. The problem in calculating the optical purity of polymer was previously described.[3] The specific rotation, $[\alpha]^{20}{}_{\mathrm{D}}$, was represented in the conventional unit, deg cm$^2$/10 g.

## Results

A series of the polymerizations of (*RS*)-MBMA was done with c-HexMgCl- and c-HexMgBr–(−)-sparteine systems in toluene at −78 °C in order to see how the optical purities of the polymer and unreacted monomer change along the reaction. Figure 1 represents the results. The catalyst systems polymerized preferentially (*S*)-MBMA over (*R*)-MBMA. The optical purity of the polymer was greater than 90% in the early stage of the polymerization and about 80% at half reaction. The optical purity of the unreacted monomer was also about 80% at half reaction and reached nearly 100% at about 65% polymer yield.

From the data shown in Figure 1, we calculated the individual conversions of (*S*)- and (*R*)-MBMA at various polymer yields. The results are shown in Figure 2. Up to about 45% polymer yield (*S*)-antipode was predominantly consumed and then the consumption decreased. On the other hand, the consumption of (*R*)-MBMA was very low up to about 45% polymer yield and then was accelerated until about 65% polymer yield.

In Figure 3 is shown the relationship between the polymer yield and the number-average molecular weights of the polymers which were obtained in various polymer yields with the c-HexMgCl–(−)-sparteine system. The molecular weight of the polymer increased up to a 45% yield as the reaction proceeded, where its value was about 70 000 corresponding

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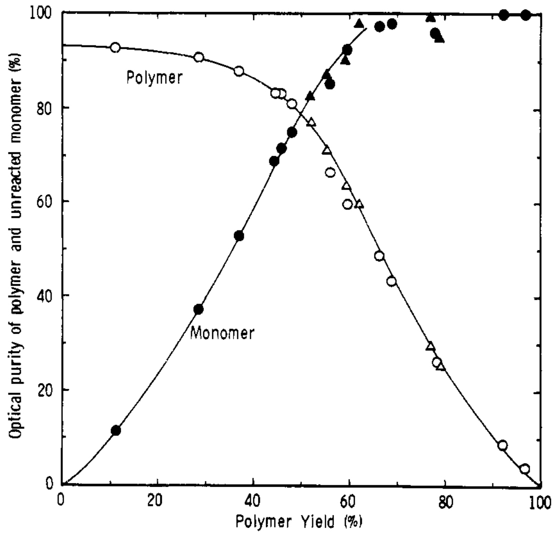

**Figure 1.** Optical purities of the polymer and unreacted monomer obtained in the polymerization of (*RS*)-MBMA by the c-HexMgX-(−)-sparteine (1/1.2) system in toluene at −78 °C: (○) c-HexMgCl; (△) c-HexMgBr.

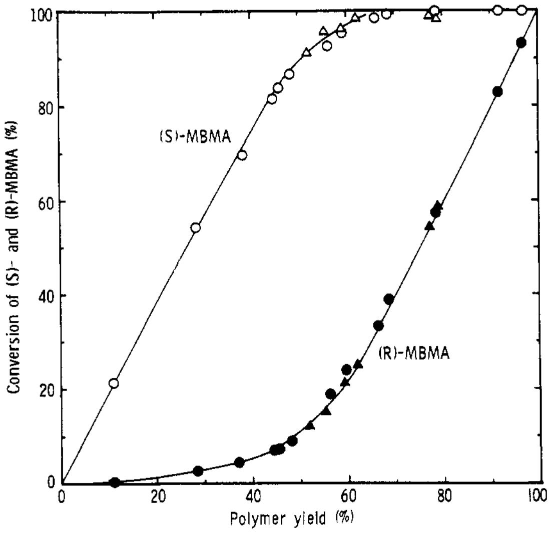

**Figure 2.** Conversion of (*S*)- and (*R*)-MBMA in the polymerization of (*RS*)-MBMA by the c-HexMgX-(−)-sparteine (1/1.2) system in toluene at −78 °C: (○) c-HexMgCl; (△) c-HexMgBr.

to $\overline{DP}$ 350. The molecular weight then decreased steeply to about 40 000 and then increased again to about 80 000.

Table I shows the triad tacticities of the polymers obtained in the polymerization with the c-HexMgCl-(−)-sparteine system. The isotactic content was higher in both the initial and final stages of the polymerization and minimum at about 60% polymer yield.

The rate of the consumption of (*RS*)-MBMA was estimated by the NMR method (Figure 4). Except for a smaller reaction scale and a higher concentration of the catalyst, other reaction conditions were similar to those of the polymerization mentioned above. At −78 °C as shown in Figure 4, the peaks due to the polymer were not observed at all, which facilitated to follow the reaction. This also indicates that the mobility of the polymer is very slow at −78 °C. The decrease of the monomer was followed as the change of the relative ratio of the heights of the peaks, a and b, assigned to the methyl protons attached to the C=C double bond of the monomer and the methyl protons of toluene used as the solvent of the catalyst, respectively. The rates determined in the above method agreed well with those derived from the integration curves to the peaks of the olefinic proton of the monomer and the methyl protons of the toluene. As an example, one of several time–

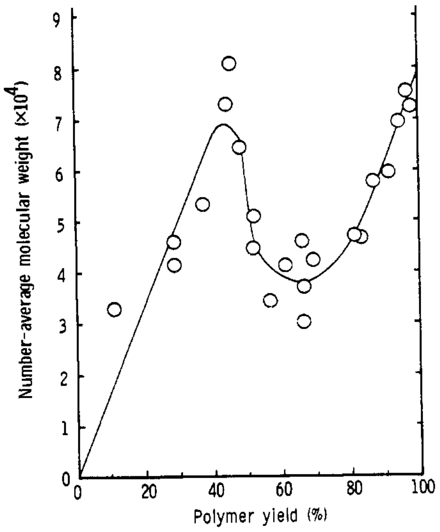

**Figure 3.** Number-average molecular weight of poly(MBMA) obtained by the c-HexMgCl-(−)-sparteine (1/1.2) system in toluene at −78 °C.

**Table I**
**Tacticity of Poly(MBMA) Obtained with the c-HexMgCl-(−)-Sparteine (1/1.2) System in Toluene at −78 °C**

| Yield, % | Opt purity of polym, % | Tacticity, % I | H | S |
|---|---|---|---|---|
| 11.2 | 92.7 | 95.8 | 2.3 | 1.9 |
| 28.4 | 90.6 | 94.9 | 3.0 | 2.1 |
| 44.5 | 83.7 | 91.8 | 5.3 | 3.0 |
| 48.1 | 81.0 | 91.6 | 4.8 | 3.6 |
| 56.1 | 66.7 | 90.5 | 5.9 | 3.6 |
| 66.2 | 49.0 | 89.7 | 6.2 | 4.0 |
| 81.0 | 16.6 | 92.2 | 3.9 | 3.9 |
| 96.7 | 4.0 | 93.5 | 4.4 | 2.1 |
| 98.0 | 1.2 | 94.6 | 3.3 | 2.1 |

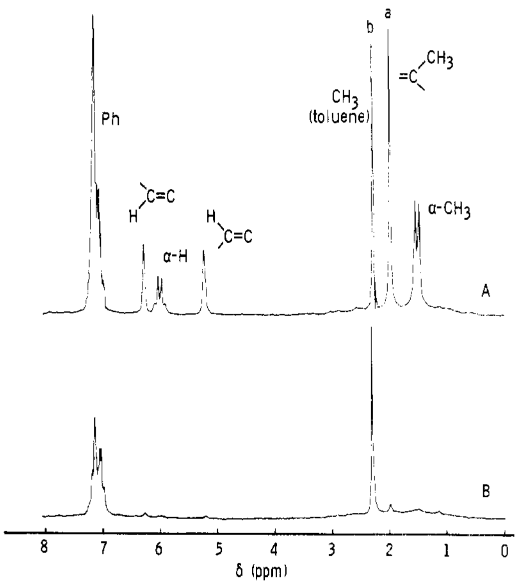

**Figure 4.** $^1H$ NMR spectra of the polymerization system of (*RS*)-MBMA with the c-HexMgCl-(−)-sparteine (1/1.2) system in toluene-$d_8$ at −78 °C: (*RS*)-MBMA (40 mg), c-HexMgCl (0.013 mmol), (−)-sparteine (0.015 mmol), toluene-$d_8$ (0.38 mL), toluene (~0.01 mL). (A) Initial stage of the polymerization; (B) final stage of the polymerization.

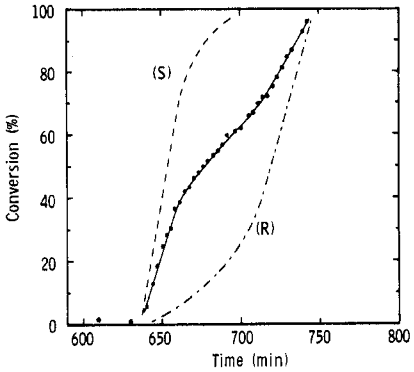

**Figure 5.** Time vs. conversion curve in the polymerization of (*RS*)-MBMA by the c-HexMgCl–(−)-sparteine (1/1.2) system in toluene-$d_8$ at −78 °C: (*RS*)-MBMA (0.21 mmol), c-HexMgCl (0.0087 mmol), toluene-$d_8$ (0.38 mL). (—) Total conversion; (- - -) (*S*)-MBMA; (– – –) (*R*)-MBMA/

conversion curves is represented in Figure 5. Usually we observed an induction period from several minutes to more than 10 h. The reaction pattern was always analogous to that shown in Figure 5 regardless of the length of the induction period. After an induction period, a rapid initiation took place. The reaction rate once slowed down at about 40% total conversion of the monomer and accelerated again at about 70% total conversion. The reaction rate did not go down even at high conversion. This strongly suggests that the reaction proceeds in a coordination mechanism. The reaction rate derived from the first straight plots up to 40% total conversion was about two times greater than that from the second straight plots above 70% total conversion.

When the polymerization was terminated by adding methanol at −78 °C, a considerable amount of cyclohexane was detected in the NMR spectrum. However, when it was terminated with methanol after the reaction mixture had been heated for a long time at 50 °C, we could not observe the formation of cyclohexane. This indicates that only a part, probably 5–10%, of the catalyst was used for the polymerization and the residual catalyst remained unreacted as c-HexMgCl.

The results of the copolymerization of (*RS*)-MBMA ($M_1$) with MMA or α,α-dimethylbenzyl methacrylate ($M_2$) by using the c-HexMgCl–(−)-sparteine system in toluene at −78 °C are shown in Table II. A copolymer was obtained in the former copolymerization but only a homopolymer of MBMA was formed in the latter. Both the copolymer and the homopolymer were highly isotactic.

## Discussion

From the results described above, the most probable reaction mechanism may be expressed as Scheme I. Initiation reaction takes place rapidly to afford an (*S*)-elective center after an induction period passes by. The formation of this center should involve the Grignard reagent–(−)-sparteine complex and probably (*S*)-MBMA. This center polymerizes preferentially (*S*)-MBMA up to about 45% polymer yield. Between 45 and 65% yield, this center completely disappears and during the time a new (*R*)-elective center forms. The (*R*)-elective center polymerizes (*R*)-MBMA exclusively. According to this reaction mechanism, we can well explain the changes of the optical purities (Figures 1 and 2), the number-average molecular weight of the polymers (Figure 3), and kinetic data (Figure 5). The lowering of isotactic content of the polymer around 60% polymer yield may be ascribed to the addition of a small quantity of (*R*)-MBMA to the (*S*)-elective center. This addition may also induce the termination of the (*S*)-center.

**Scheme I**

I. Initiation

c-HexMgCl–(−)-sparteine complex $\xrightarrow{(S)\text{-MBMA}}$ (*S*)-center

II. 0–45%

(*S*)-elective polymerization

III. 45–65%

(*S*)-center $\xrightarrow{\text{terminate}}$ (*S*)-polymer + (*R*)-center

IV. 65%–100%

(*R*)-elective polymerization

Since each of (*S*) and (*R*) centers polymerized about a half of the monomer to form the (*S*) and (*R*) polymers of nearly the same molecular weight (Figure 3), the concentrations of both the centers appear to be close. The results concerning the reaction rates suggest that the concentration ratio of (*S*) to (*R*) center was approximately constant. Consequently, the disappearance of the (*S*) center may be concerned directly with the formation of the (*R*) center. The mechanism about this transformation is not clear at the present time. A simpler mechanism in which two antipodes of the monomer compete in the coordination to the same chiral center and in which the growing chain participates to stereoregulation seems to be unsuitable because this mechanism cannot well explain the change of the molecular weight shown in Figure 3.

The Grignard reagent–(−)-sparteine systems also exhibited a high selectivity toward the monomers in the copolymerization of the methacrylic esters as shown in Table II. A sterically bulky comonomer α,α-dimethylbenzyl methacrylate could not be copolymerized with MBMA, but a smaller comonomer MMA could. The optical purity of the MBMA homopolymer obtained in the copolymerization with α,α-dimethylbenzyl methacrylate was comparable to that of the poly(MBMA) shown in Figure 1. This means that α,α-dimethylbenzyl methacrylate did not affect the polymerization at all and the existence of a methyl group in place of the α-hydrogen of MBMA completely prohibits the coordination of the α,α-dimethylbenzyl methacrylate to an active center. This also suggests that the steric interaction between the α-methyl group of MBMA and the (−)-sparteine moiety may play an

**Table II**
**Copolymerization of (*RS*)-MBMA ($M_1$) with MMA or α,α-Dimethylbenzyl Methacrylate (DMBMA, $M_2$) by the c-HexMgCl–(−)-Sparteine (1/1.2) System in Toluene at −78 °C[a]**

| $M_2$ | $[M_2]_0$/ $[M_1]_0$ | Time, h | Yield, wt % | Conversion of MBMA, % | $[M_2]/[M_1]$ polymer | $[\alpha]^{20}_D$, deg[b] polymer | Tacticity, % I | H | S |
|---|---|---|---|---|---|---|---|---|---|
| MMA | 1.0 | 1 | 50.8 | 56.6 | 0.68 | −35.4[c] | 95 | 3 | 2 |
| DMBMA | 1.0 | 75 | 23.8 | 49.1 | 0 | −94.3 | 92 | 5 | 3 |

[a] $[M_1]_0$ = $[M_2]_0$ 5.26 mmol, c-HexMgCl 0.20 mmol, toluene 15 mL. [b] In toluene. [c] The $[\alpha]^{20}_D$ of unreacted MBMA was +24.4° (optical purity 46.1%).

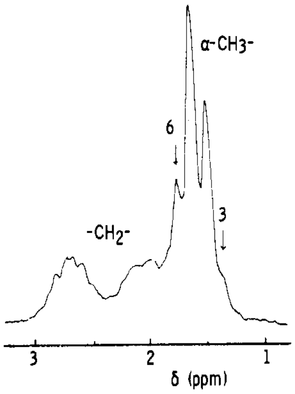

**Figure 6.** $^1$H NMR spectrum of poly(MAA-*co*-MMA) derived from poly(MBMA-*co*-MMA) (100 MHz, 100 °C, pyridine-$d_5$, HMDS).

important role in determining the stereoelection of the polymerization.

The distribution of the monomers in poly(MBMA-*co*-MMA) was investigated from the $^1$H NMR spectrum (Figure 6) of the methacrylic acid (MAA)–MMA copolymer which had been derived from the copolymer by treating with hydrogen bromide. The $^1$H NMR spectrum indicates that the contents of MAA–MAA–MAA (peak 6) and MMA–MMA–MMA (peak 3) triads were very low.[7] Therefore, the copolymer must consist of rather many alternating sequences of MBMA and MMA connected in isotactic manner. The optical purity (46.1%) of the unreacted MBMA was about a half of the purity expected from the data at 56.6% polymer yield in Figure 1. This lower asymmetric selectivity may be due to the fact that both (*S*)- and (*R*)-elective centers were formed by the initiation reaction of the c-HexMgCl–(−)-sparteine system with MMA in addition to the preferential formation of the (*S*)-elective center from the catalyst system and (*S*)-MBMA. The (*S*)- and (*R*)-elective centers probably have the same structure as in the homopolymerization of (*RS*)-MBMA and might form a mixture of an (*S*)-MBMA–MMA copolymer and an (*R*)-MBMA–MMA copolymer of highly isotacticity. Of course, we cannot exclude the possibility that the existence of MMA lowers the selectivity of (*S*)-elective center so that (*R*)-MBMA is incorporated into a polymer chain more easily. In the copolymerization of methacrylates, the interaction between the ester groups is complicated relative to the homopolymerization of methacrylates and hence the preparation of highly stereoregular copolymers was usually difficult.[8] It is therefore an interesting result that a highly isotactic copolymer was formed in the present copolymerization.

As shown in Figures 1 and 2, c-HexMgCl– and c-HexMgBr–(−)-sparteine systems brought about similar results. Using these systems, optically pure (*R*)-MBMA will be obtained in about 35% yield.

## Conclusion

c-HexMgCl– and c-HexMgBr–(−)-sparteine systems were highly asymmetric-selective catalysts for the polymerization of (*RS*)-MBMA. This high selectivity was ascribed to the fact that an (*S*)-elective center having a high selectivity was formed preferentially in the initiation reaction and (*R*)-elective center was formed after more than 80% (*S*)-MBMA had been consumed. Each of the (*S*)- and (*R*)-elective centers yielded different polymer chains. In the copolymerization of MBMA with $\alpha,\alpha$-dimethylbenzyl methacrylate, these centers gave the homopolymer of MBMA having the same optical purity and isotacticity as the above polymerization. However, these centers copolymerized rather alternatingly MBMA with MMA to form an optically active isotactic copolymer.

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# The Effect of Molecular Weight on Triplet Exciton Processes. 2. Poly(2-naphthyl methacrylate)

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ABSTRACT: Delayed fluorescence and phosphorescence of different molecular weight samples of poly(2-naphthyl methacrylate) in matrices of 2-methyltetrahydrofuran at 77 K are reported. The intensity of delayed fluorescence, arising from triplet excitation annihilation, increases with molecular weight, while the phosphorescence intensity and lifetime decrease. The phosphorescence decay is much slower than the delayed fluorescence and neither decay is exponential. The general characteristics of triplet exciton processes on polymers are briefly discussed.

## I. Introduction

In this paper is described the results of studies of the effect of molecular weight on delayed emission for poly(2-naphthyl methacrylate). We will also briefly discuss what seem to be some of the general results of studies of triplet excitons in aryl polymers.

The pioneering work of Fox and Cozzens[1] on poly(1-vinylnaphthalene) (P1VN) demonstrated triplet–triplet annihilation in polymer systems leading to delayed fluorescence. They observed no systematic change of emission with molecular weight and attributed the differences in emission intensity for different molecular weight samples to "end group effects". The molecular weights they reported were very low, corresponding to a degree of polymerization from 16 to 25. Guillet and Somersall[2] prepared 2-naphthyl methacrylate (P2NMA) polymers and observed triplet–triplet annihilation

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