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HIGHLY ASYMMETRIC SELECTIVE POLYMERIZATION OF (RS)-α-METHYLBENZYL METHACRYLATE BY GRIGNARD REAGENT-(-)-SPARTEINE CATALYST SYSTEMS

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Polymerization of (RS)-α-methylbenzyl methacrylate by Grignard reagent-(-)-sparteine catalyst systems was found to be a highly asymmetric selective process. The catalyst systems polymerized preferentially (S)-monomer over (R)-monomer. At 60-70% yield of the polymer, the optical purity of the unreacted monomer was more than 90%.

It has been demonstrated that the asymmetric selective (or stereoelective) polymerizations of racemic α-olefins by optically active Ziegler-Natta catalysts become increasingly difficult as the distance between the chiral center and vinyl group in the monomer increases.[1,2] The selectivity was rather low even in the monomer having an asymmetric carbon atom in the α-position in relation to a double bond such as 3-methyl-1-pentene and 3,7-dimethyl-1-octene.[3] From the above results, the highly asymmetric selective polymerization of racemic methacrylic ester which has an asymmetric center at γ-position from the vinyl group would not be expected. Actually, almost no selectivity has been observed in the polymerizations of racemic menthyl,[4] α-methylbenzyl,[5,6] and sec-butyl esters.[6] We now wish to report the highly asymmetric selective polymerization of racemic α-methylbenzyl methacrylate (MBMA) by Grignard reagent-(-)-sparteine catalyst systems in toluene at -78°C.

Optically active Grignard reagent, menthylmagnesium chloride (1.0M in ether solution) was prepared from (-)-menthyl chloride;[7] cyclohexylmagnesium chloride (1.40M in ether solution) and cyclohexylmagnesium bromide (1.32M in toluene solution) were obtained from the corresponding halides. Commercial (-)-sparteine (guaranteed grade) was used without further purification after identification by elementary analysis; $[\alpha]_D^{20}$ -18.9° (ethanol, C 4.0g/dl). Purified toluene (15ml) and (-)-sparteine (0.24mmol) were placed in a dry glass ampule under nitrogen. Grignard reagent (0.20mmol) was then added to the solution with a syringe and left for 10 min at room temperature. The catalyst solution thus obtained was cooled to -78°C and (RS)-MBMA (1.52g, 8.0mmol) was added to the solution. The polymerization was terminated by the addition of a trace of methanol and polymer was precipitated in methanol containing a small amount of hydrochloric acid. The unreacted monomer was recovered nearly quantitatively by distillation from the methanol solution after the separation of the polymer by filtration. The amount of the undistilled oligomeric compounds was less than 2%. The optical rotation of the polymer was measured in toluene (C 1.0 ∿ 2.5g/dl) with a Yanagimoto Direct Reading Polarimeter OR-10 using a 5 cm cell at 20°C. Triad tacticity of poly(MBMA) was determined from the NMR spectrum of poly(methyl methacrylate) derived from the polymer.8)

The results of the polymerization are summarized in Table 1. Highly asymmetric selective polymerizations took place regardless of the kind of the Grignard reagents,

Table 1. Polymerization of MBMA by Grignard reagent-(-)-sparteine systems in toluene at -78°C[a]

Run No.	Grignard reagent	Time hr	Polymer				Optical purity of monomer calc.(obs.)[d]	R[e]
			Yield %	$\overline{M}_n$[b] ×10^3	$[\alpha]_D^{20}$ deg	Optical[c] purity,%		
1	CyclohexylMgCl	1.7	11.2	7.2	-115.9	92.7	11.7	29.6
2	CyclohexylMgCl	1.8	28.4		-113.3	90.6	36.0	28.8
3	CyclohexylMgCl	4.0	48.1[f]		-101.3	81.0	75.1	21.3
4	CyclohexylMgCl	2.2	66.0		-55.4	44.3	86.0(90.0)	6.6
5	CyclohexylMgCl	3.7	66.2	36.8	-61.3	49.0	96.0	10.4
6	CyclohexylMgCl	3.0	81.0		-20.7	16.6	70.8(74.2)	2.6
7	CyclohexylMgCl	3.7	82.9	30.4	-19.2	15.4	74.5	4.2
8	CyclohexylMgCl	8.0	98.0[g]		-1.6	1.3	—	—
9	CyclohexylMgBr	3.0	55.3	18.9	-88.6	70.9	87.7	16.5
10	CyclohexylMgBr	50.0	61.8		-74.4	59.5	96.3	14.7
11	CyclohexylMgBr[h]	92.0	77.0		-36.9	29.5	98.8(94.2)	15.4
12	MenthylMgCl[i]	5.0	4.8	43.1	-118.4	94.7	4.7	38.5
13	MenthylMgCl	24.0	24.7		-108.7	87.0	28.5	19.0
14	MenthylMgCl	99.0	55.5	14.3	-88.1	70.5	87.9	16.4

[a] MBMA, 1.52g(8.0mmol); toluene, 15ml; RMgX, 0.20mmol; (-)-sparteine, 0.24mmol.

[b] Number average molecular weight determined by vapor pressure osmometer.

[c] Based on $[\alpha]_D^{20}$ -125°(toluene) for optically pure isotactic(∿100%) poly[(S)-MBMA].9)

[d] On the basis of $[\alpha]_D^{20}$ -53.0(neat) of (S)-MBMA.10)

[e] Calculated using Eq. 1. [f] Triad tacticity, I : H : S = 91.6 : 4.8 : 3.6.

[g] Triad tacticity, I : H : S = 94.6 : 3.3 : 2.1. [h] (-)-Sparteine, 0.30mmol.

[i] (-)-Sparteine, 0.40mmol.

indicating that chiral menthylmagnesium chloride was not a requisite component. In the initial stage of the polymerization (S)-monomer was preferentially consumed to form polymers having optical purity higher than 90%. At 60-70% conversion, the unreacted monomer was enriched in (R)-antipode which optical purity was more than 90%. The observed optical purity of the unreacted monomer accorded with the value calculated from the polymer yield and its optical purity (No. 4, 6, and 11). The data on the polymer yield were scattered because of a long induction period observed in several cases.

The polymer was highly isotactic regardless of the yield and optical purity (No. 3 and 8). The NMR spectrum of the polymer No. 8 which was obtained in 98% yield was very sharp and similar to that of the polymer No. 12 having high optical purity. We have observed that the NMR spectrum of isotactic poly[(RS)-MBMA] obtained by n-BuLi in toluene was much broader than that of poly[(R)-MBMA] of similar isotacticity.11) These results may indicate that there exist only a few bonds connecting (R)-unit with (S)-unit in the polymer. The polymerization appears to be not only a highly asymmetric selective process but also a highly stereoselective process.

The asymmetric selectivity of the polymerization was estimated from R value derived from Eq. 1 which was proposed by Bührer and Elias12) for the polymerization of α-amino acid N-carboxy anhydride.

$$R = \frac{\ln(1 - px - x)}{\ln(1 + px - x)} \qquad (1)$$

where R is a ratio(k_S/k_R) of the rate constants in pseudo first order rate equations, $-d[S]/dt = k_S[S]$ and $-d[R]/dt = k_R[R]$, x is polymer yield, and p is the optical purity of the polymer. Since the R values in the polymerization with cyclohexylmagnesium chloride were not constant, more data seem to be necessary for quantitative discussion on the selectivity. The optical purity of the unreacted monomer was maximum at 60-70% conversion. This implies that the initial (S)-preferred polymerization changes to the (R)-preferred polymerization around this conversion remaining a small amount of (S)-MBMA. On the other hand, (S)-MBMA seems to be almost completely consumed with cyclohexylmagnesium bromide-(-)-sparteine system at about 70% conversion.

In this study (R)-MBMA of highly optical purity was readily obtained in 30-40% yield by Grignard reagent-(-)-sparteine systems. Compared with classical methods, this is an interesting and useful method of optical resolution in respect that a small amount of a chiral compound can resolve a great amount of racemic compounds with good efficiency.

The asymmetric selective polymerization of racemic sec-butyl methacrylate was also investigated with cyclohexylmagnesium chloride-(-)-sparteine catalyst system in toluene at -78°C. The polymer obtained in 19% yield was highly isotactic and showed $[\alpha]_D^{20}$ +5.8° and $[\alpha]_{427}^{20}$ +11.3° (toluene, C 2g/dl), which corresponds that (S)-antipode was preferentially polymerized over (R)-antipode. The optical purity of the polymer was estimated to be about 25% on the basis of the data on optically active poly(sec-butyl methacrylate) reported by Matsuzaki et al.$^{13)}$ Thus, these Grignard reagent-(-)-sparteine systems will be expected to work as highly asymmetric selective catalysts for the polymerizations of other racemic methacrylates.

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