

## STEREOELECTIVE RADICAL COPOLYMERIZATION OF (*RS*)- $\alpha$ -METHYLBENZYL VINYL ETHER WITH (*S*)-(-)- OR (*R*)-(+)-*N*-( $\alpha$ -METHYLBENZYL)MALEIMIDE

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**Abstract**—Racemic  $\alpha$ -methylbenzyl vinyl ether was copolymerized with optically active (*S*)-(-)- or (*R*)-(+)-*N*-( $\alpha$ -methylbenzyl)maleimide using 2,2'-azobisisobutyronitrile in order to examine the possibility of stereoelective radical polymerization of vinyl-type racemic monomers. The resulting copolymers were found to have almost alternating sequences of the two kinds of monomeric units. The non-polymerized  $\alpha$ -methylbenzyl vinyl ether, recovered from the copolymerization system, showed an optical activity of opposite sign to the optically active comonomer used, indicating clearly that the copolymerization process is stereoelective. It was confirmed that  $\alpha$ -methylbenzyl vinyl ether preferentially incorporated in the copolymer has the same absolute configuration as the optically active *N*-substituted maleimide.

### INTRODUCTION

A "stereoelective" (or "asymmetric-selective") polymerization is a process in which preferential polymerization of either of the enantiomorphous monomers from the mixture occurs to form an optically active polymer; the unreacted monomer is consequently enriched in the opposite antipode. Ever since Inoue *et al.* [1] reported a preparation of an optically active polymer from racemic propylene oxide with a diethylzinc/*d*-borneol system, a variety of stereoelective ring-opening polymerizations have been made with racemic oxiranes [2-5], thiiranes [2-6],  $\alpha$ -amino acid *N*-carboxy anhydrides [2, 7] and  $\beta$ -propiolactones [5, 8-10] by use of chiral catalysts.

Many kinds of racemic vinyl-type compounds were also polymerized stereoelectively under stereochemical control by chiral organometallic catalysts to give optically active polymers with asymmetric centres in their lateral chains. Pino *et al.* observed stereoelection phenomena in coordinated anionic polymerization of racemic  $\alpha$ -olefins in the presence of chiral Ziegler-Natta-type catalysts; for example, racemic 3-methyl-1-pentene [11], 3,7-dimethyl-1-octene [11], and 4-methyl-1-hexene [12] were polymerized by using a (+)-bis[(*S*)-2-methylbutyl]zinc/TiCl<sub>4</sub> catalytic system. Higashimura and Hirokawa [13] elucidated a stereoelective cationic polymerization of racemic *cis*-1-methylpropyl propenyl ether by (-)-menthoxyaluminum dichloride, giving rise to a polymer with a positive optical activity. Recently, Okamoto *et al.* have studied a highly stereoelective polymerization of racemic methacrylic [14, 15] and acrylic [16] esters by using Grignard reagent/(-)-sparteine systems. These stereoelective polymerizations were generally interpreted in terms of the predominance of one type of monomeric enantiomer at the chiral catalytic site; the configuration of the chiral ligand of the catalyst governs the configuration of the enantiomer preferentially incorporated in the polymer chain.

On the other hand, stereoelection of racemic

monomers was also observed in copolymerization with chiral comonomers, using stereospecific catalysts. Racemic 3,7-dimethyl-1-octene and 3-methyl-1-pentene were copolymerized, respectively, with (*S*)-3-methyl-1-pentene and (*R*)-3,7-dimethyl-1-octene in the presence of TiCl<sub>4</sub>/Zn(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> or TiCl<sub>4</sub>/Al(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> catalyst by Ciardelli *et al.* [17], who proved that the copolymerization is stereoselective [18] and also stereoelective. Similarly, cationic copolymerization of racemic 1-methylpropyl vinyl ether with (*S*)- or (*R*)-1-phenylethyl vinyl ether was demonstrated by Chiellini [19] to be stereoselective and stereoelective in the presence of a heterogeneous catalyst, Al(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>.

No study has been reported on stereoelective radical polymerization but it is of great interest whether such a process can occur. In principle, stereoelection cannot be expected in radical polymerization of racemic monomers initiated by chiral radical initiators. Even if a chiral primary radical is able to differentiate between enantiomorphous monomers in the initiation step of the polymerization, the ability should decrease rapidly as propagation proceeds. Hence, the concentration of growing radical chain end composed of an (*R*)-monomeric unit would be statistically equal to that composed of an (*S*)-monomeric unit. Some asymmetric control at the growing active site is needed for attainment of stereoelective radical polymerization as well as in the case of stereoelective ionic polymerization noted above.

Utilization of chiral comonomers instead of chiral radical initiators, however, may solve the problem of stereoelective radical polymerization of racemic monomers. If a growing radical chain end composed of a chiral monomeric unit differentiates between enantiomorphous monomers, a stereoelective radical copolymerization must be achieved. We have attempted alternating copolymerization of a pair of electron-rich racemic monomer and electron-deficient chiral monomer. In the present investigation, stereoelective radical copolymerization of racemic  $\alpha$ -methylbenzyl vinyl ether with (*S*)-(-)- or (*R*)-(+)-*N*-( $\alpha$ -methyl-

benzyl)maleide was studied using 2,2'-azobisisobutyronitrile (AIBN) as initiator.

## EXPERIMENTAL

### Materials

**Racemic  $\alpha$ -methylbenzyl vinyl ether.** The monomer was prepared by a vinyl transesterification [20]. A mixture of racemic  $\alpha$ -methylbenzyl alcohol and a large excess of isobutyl vinyl ether was refluxed for 48 hr in the presence of a small amount of mercuric acetate as catalyst. After removal of the volatile materials, the residue was fractionated by distillation under reduced pressure, followed by distillation over Na metal through a 30 cm packed column, b.p. 71–72°/13 Torr (lit. [21] 70–73°/14 Torr);  $d_4^{20}$  0.9477. I.R. (neat)  $\nu$ ,  $\text{cm}^{-1}$ : 700, 760, 1500, 1600 (Ph); 1380, 1460 ( $\text{CH}_3$ ); 1640 ( $\text{C}=\text{C}$ ); 1200 ( $=\text{C}-\text{O}-\text{C}$ ). U.V. (in methanol)  $\lambda_{\text{max}}$  ( $\epsilon$ ): 264 (140); 258 (190); 252 (166); 203 (shoulder, 15,700). Anal. calcd (%) for  $\text{C}_{10}\text{H}_{12}\text{O}$ : C 81.04; H 8.16. Found: C 80.91; H 8.10.

**(S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide (3).** An ethereal solution of (S)-(-)- $\alpha$ -methylbenzylamine (1),  $[\alpha]_D^{25}$  -39.7° (neat), 98.5% e.e. [23], was added dropwise to a cold solution of the stoichiometric amount of maleic anhydride in dry ether with stirring to precipitate a white powder of (S)-(-)-N-( $\alpha$ -methylbenzyl)maleamic acid (2), which was filtered, washed with ether, dried *in vacuo*, and used in the next step without purification, m.p. 120–121°;  $[\alpha]_D^{25}$  -213.9° ( $c$  = 12.5 g/dl, methanol).

The maleamic acid (2) was dehydrated to cyclize by applying the procedure used in the preparation of *N*-substituted maleimides [24, 25]. A mixture of 136 g of 2, 100 g of anhydrous sodium acetate, and 900 ml of acetic anhydride was heated on an oil bath at 90° for 20 hr with stirring. During the reaction, the mixture turned dark brown. After cooling, the mixture was treated with a large amount of ice-cold water to separate a black tar in the lower layer. The crude product was washed with cold water and purified by reduced pressure distillation to give (S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide (3) as viscous and colourless liquid in 68% yield (85 g) based on the maleamic acid, b.p. 125–126°/2 Torr; m.p. 23°;  $d_4^{25}$  1.161;  $[\alpha]_D^{25}$  -69.2° (neat). I.R. (neat)  $\nu$ ,  $\text{cm}^{-1}$ : 700, 760, 1500, 1600 (Ph); 1370, 1460 ( $\text{CH}_3$ ); 1710 ( $\text{C}=\text{O}$ ). U.V. (in methanol)  $\lambda_{\text{max}}$  ( $\epsilon$ ): 297 (560); 263 (426); 258 (438); 251 (409); 210 (17,800). Anal. calcd (%) for  $\text{C}_{12}\text{H}_{11}\text{NO}_2$ : C 71.63; H 5.51; N 6.96. Found: C 71.40; H 5.47; N 6.88.

**(R)-(+)-N-( $\alpha$ -methylbenzyl)maleimide.** This monomer was prepared from (R)-(+)- $\alpha$ -methylbenzylamine,  $[\alpha]_D^{25}$  +39.5° (neat), 97.3% e.e. [26], and maleic anhydride in the same manner as above. Physical properties of this compound were identical with those of the (S)-(-)-isomer except for specific rotation,  $[\alpha]_D^{25}$  +71.8° (neat).

### Procedures

The copolymerization was carried out in a sealed glass ampoule in a thermostated water bath for a prescribed time. The system was treated with a large amount of ether to precipitate the copolymer. It was necessary to mince the copolymer to extract the nonpolymerized monomer mixture. The copolymer was purified by reprecipitation from a tetrahydrofuran solution with a large excess of methanol and the precipitated copolymer was filtered and dried *in vacuo*.

The ether-extract was concentrated and the nonpolymerized  $\alpha$ -methylbenzyl vinyl ether was recovered by distillation at reduced pressure in the presence of 1,1-diphenyl-2-picrylhydrazyl (DPPH) as a polymerization inhibitor. The recovered  $\alpha$ -methylbenzyl vinyl ether was polymerized by  $\text{BF}_3 \cdot \text{OEt}_2$  in toluene at -78°.

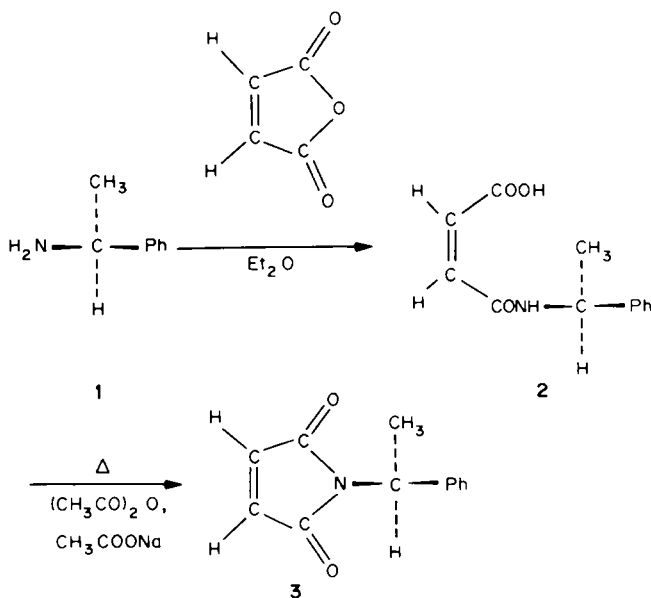
### Measurements

Viscosity measurement of the copolymers was performed in tetrahydrofuran at  $30 \pm 0.1^\circ$  using an Ubbelohde-type viscometer. I.R. spectra were measured with a Jasco IRA-2 spectrophotometer, using KBr plates. U.V. spectra were taken on a Hitachi 200-10 spectrophotometer, using a pair of 10 mm quartz cells. Specific rotation,  $[\alpha]_D$ , was measured with a Jasco DIP-4 polarimeter. Optical rotatory dispersion (ORD) spectra were recorded on a Jasco J-20 automatic recording spectropolarimeter with a 10 mm quartz cell.

## RESULTS AND DISCUSSION

### Copolymerization of racemic $\alpha$ -methylbenzyl vinyl ether ( $M_1$ ) with (S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide ( $M_2$ )

The copolymerization was performed with various molar ratios  $M_1$  to  $M_2$  at 30° for 48 hr in the presence of AIBN as initiator. The copolymerization proceeded homogeneously. Every copolymer isolated was soluble in benzene, toluene, benzonitrile, anisole,



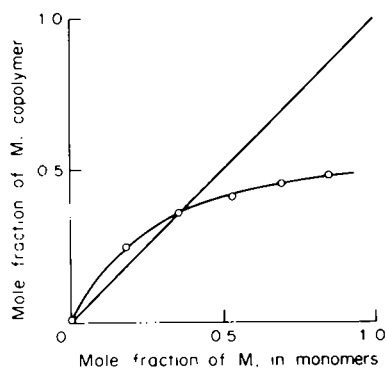


Fig. 1. Monomer-copolymer composition diagram.  $M_1$  = (RS)- $\alpha$ -methylbenzyl vinyl ether.  $M_2$  = (S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide.

1,4-dioxane, THF, and cyclohexanone, was swollen in acetone and acetonitrile, and insoluble in methanol, *n*-hexane, cyclohexane and diethyl ether. The intrinsic viscosities of the copolymers fell in the range of 0.84 to 1.18 dl/g in THF at 30°.

The monomer-copolymer composition diagram is illustrated in Fig. 1. The mole fraction of  $M_1$  in the copolymers lie in the range of 0.24–0.48. According to the method of Fineman–Ross, the monomer reactivity ratios,  $r_1$  and  $r_2$ , were determined as 0.005 and 0.48, respectively. The compositions of the copolymers and the monomer reactivity ratios are consistent with the fact that  $M_2$  was homopolymerized, whereas  $M_1$  was not homopolymerized by radical initiation. Although the compositions of the copolymers were affected by the monomer composition, every copolymer was rich in  $M_2$  and the copolymerization seems to proceed alternately to some extent, especially for higher ratios  $M_1/M_2$ .

#### Stereoselection of (RS)- $\alpha$ -methylbenzyl vinyl ether

Racemic  $\alpha$ -methylbenzyl vinyl ether ( $M_1$ ) was copolymerized with (S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide ( $M_2$ ) with different molar ratios of the monomers at 30° in the presence of AIBN. The copolymerization conditions and the results are summarized in Table I.

The nonpolymerized  $M_1$ , recovered from the system, showed slight optical activity of opposite sign to that of the optically active comonomer. The ORD measurement for the recovered  $M_1$  gave a positive or negative plain spectrum in the wavelength region above 300 nm. The recovered  $M_1$  (run S-3) was polymerized by cationic initiation with  $\text{BF}_3 \cdot \text{OEt}_2$  to give a polymer with a positive optical activity. These findings indicate that the copolymerization is stereoselective and that (S)-(-)- and (R)-(+)- $M_2$  copolymerize preferentially with (S)-(-)- and (R)-(+)- $M_1$ , respectively. Thus,  $M_2$  copolymerizes preferentially with the enantiomer of  $M_1$  having the same chirality as  $M_2$ . In addition, in the copolymerization of benzyl vinyl ether, an achiral monomer, with (S)-(-)- $M_2$ , the recovered benzyl vinyl ether was optically inactive (runs S-11, S-12), implying that the vinyl ethers were freed of  $M_2$ , an optically active and high boiling comonomer, by the distillation.

Table I. Copolymerization of vinyl ethers ( $M_1$ ) with optically active N-( $\alpha$ -methylbenzyl)maleimides ( $M_2$ )<sup>a</sup>

Run no.	$M_1$ (mmol)		$M_2$ (mmol)		Molar ratio ( $M_1/M_2$ )	Time (day)	Yield (g)	$[\eta]$ (dl/g)	Mole fraction of $M_1$	Copolymer					Nonpolymerised $M_1$					
	MBVE†	BVE‡	(S)-(–)	(R)-(+)						$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{35}$	$[\alpha]_D^{40}$	$[\alpha]_D^{45}$	$[\alpha]_D^{25}$	$[\alpha]_D^{30}$	$[\alpha]_D^{35}$	$[\alpha]_D^{40}$	$[\alpha]_D^{45}$	
S-1	19.21		17.33		1.11	5	2.125	1.38	0.41	–32.3	–32.3	+1.03	+0.29	+0.29						
S-2	25.61		11.55		2.21	5	2.437	1.41	0.46	–33.1	–33.1	+0.78	+0.22	+0.22						
S-3	25.61		11.55		2.21	7	3.705	1.24	0.46	33.3	33.3	+1.21	+0.34	+0.34						
S-4	32.02		5.78		5.54	5	1.802	1.01	0.48	34.0	34.0	+0.36	+0.10	+0.10						
R-1	25.61			11.55	2.21	5	2.141	1.25	0.46	+33.2	+33.2	–0.69	–0.18	–0.18						
R-2	25.61			11.55	2.21	7	3.365	1.16	0.46	+33.6	+33.6	–1.02	–0.28	–0.28						
S-11		28.99	11.55		2.51	3	1.074	0.85	0.42	–39.0	–39.0	0.00	0.00	0.00						
S-12		28.99	11.55		2.51	5	3.327	0.89	0.43	–39.0	–39.0	0.00	0.00	0.00						

<sup>a</sup>Temperature = 30 ± 0.1°, AIBN = 10 mg (0.061 mmol). †MBVE = racemic  $\alpha$ -methylbenzyl vinyl ether.

‡BVE = benzyl vinyl ether. §Measured in THF at 30°. ||Measured in THF at 25°,  $c = 5.0 \text{ g dl}^{-1}$ .

¶Measured at 25°, neat. \*\* $[\alpha]_D$  of poly- $M_1$  (recovered) prepared by cationic initiation, measured in THF at 25°,  $c = 35.3 \text{ g dl}^{-1}$ .

Table 2. Effect of temperature on the copolymerization of (RS)- $\alpha$ -methylbenzyl vinyl ether ( $M_1$ ) with (S)-(-)-N-( $\alpha$ -methylbenzyl)maleimide ( $M_2$ )<sup>a</sup>

Run no.	Temperature (°C)	Polymerization time	Yield (g)	[ $\eta$ ] <sup>b</sup> (dl/g)	Copolymer		Nonpolymerized $M_1$		
					[ $\alpha$ ] <sub>D</sub> <sup>c</sup>	Mole fraction of $M_1$ <sup>d</sup>	Conversion of $M_1$ <sup>e</sup> (%)	[ $\alpha$ ] <sub>D</sub> <sup>f</sup>	% e.e. <sup>g</sup>
S-21	70	20 min	2.166	0.45	-30.9	0.42	19.9	+0.40	0.21
S-22		30 min	2.925	0.41	-30.9	0.42	26.9	+0.54	0.28
S-23		40 min	3.117	0.41	30.9	0.42	28.6	+0.57	0.28
S-24	50	5 hr	1.723	0.89	32.0	0.43	16.2	+0.43	0.22
S-25		7.5 hr	2.888	0.85	32.0	0.43	27.2	+0.71	0.37
S-26		10 hr	3.391	0.80	32.0	0.44	32.8	+0.84	0.44
S-27	30	4 day	1.687	1.34	33.1	0.45	16.7	+0.53	0.28
S-28		6 day	3.193	1.27	33.1	0.46	32.4	+1.04	0.54
S-29		8 day	3.724	1.24	-33.3	0.46	37.8	+1.21	0.63
S-30	0	28 day	0.172			0.47	1.7		
S-31		130 day	0.774	2.13	-34.4	0.47	8.0	+0.32	0.16
S-32		6 hr††	1.568			0.47	16.3	+0.68	0.33

<sup>a</sup>  $M_1$  = 3.791 g (25.61 mmol);  $M_2$  = 2.322 g (11.55 mmol); molar ratio,  $M_1/M_2$  = 2.21; AIBN = 10 mg (0.061 mmol).<sup>b</sup> Measured in THF at 30°C; <sup>c</sup> Measured in THF at 25°C;  $c$  = 5.0 g/dl; <sup>d</sup> Determined by elemental analysis; <sup>e</sup> Calculated from mole fraction; <sup>f</sup> Measured at 25°C, neat.<sup>g</sup> Calculated from the reported specific rotation value of the (S)-(-)-isomer, [ $\alpha$ ]<sub>D</sub> = -54.2°; † Irradiated with a 300 W Hg-lamp, distance 5 cm.

The stereoelectivity in the copolymerization of the racemic monomer with the optically active comonomer should vary with polymerization conditions. The effect of polymerization temperature on the stereoelection was studied at 0, 30, 50 and 70°C with the same contents. Table 2 shows the conditions and the results. The mole fraction of  $M_1$  in the copolymers was in the range of 0.42 to 0.47, slightly increasing with decrease in polymerization temperature. The specific rotation value of the copolymers was almost constant irrespective of the conversion but not of the polymerization temperature. In spite of the decreasing in (S)-(-)- $M_2$  monomeric unit, i.e. increasing in  $M_1$ , specific rotation value of the copolymer was increased in negative sense by decreasing polymerization temperature. It is premature, however, to infer that the increase in specific rotation is attributable to a higher optical purity of  $M_1$  monomeric unit incorporated in the copolymer produced at a lower temperature. As can be seen from runs S-1 to S-4 (Table 1), in which the copolymerization was performed at 30°C with different molar ratios of the monomers, specific rotation of the resulting copolymers was increased in a negative sense with decrease in proportion of (S)-(-)- $M_2$  in the copolymer. The higher the degree of alternation of the two monomeric units, the greater becomes the specific rotation of the copolymer. In fact, specific rotation of poly[(S)-(-)- $M_2$ ] was [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -7.5 ( $c$  = 10.3 g/dl, THF), much lower in absolute value than those of the copolymers. The specific rotation value of the copolymer seems to depend largely on the sequence of the two monomeric units.

The optical purity of  $M_1$  monomeric unit in the copolymer, i.e. stereoelectivity, must be exactly reflected in the optical purity of the nonpolymerized  $M_1$  recovered by distillation. Figure 2 shows the variations of optical activity of the nonpolymerized  $M_1$  with polymerization temperature and with con-

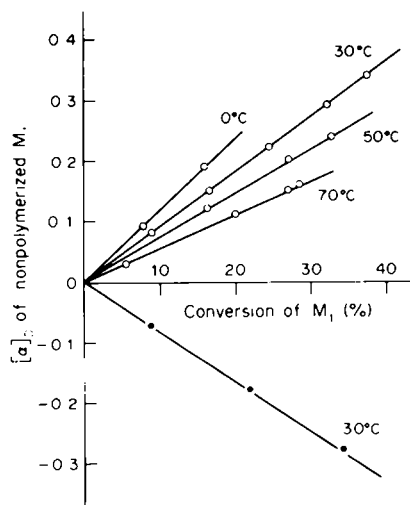


Fig. 2. Plots of [ $\alpha$ ]<sub>D</sub> of nonpolymerized  $M_1$  vs conversion of  $M_1$  in the copolymerization of  $M_1$  with (S)-(-)- $M_2$  (○) or (R)-(+)- $M_2$  (●) at various temperatures.  $M_1$  = (RS)- $\alpha$ -methylbenzyl vinyl ether; 3.791 g (25.61 mmol).  $M_2$  = optically active N-( $\alpha$ -methylbenzyl)maleimide; 2.322 g (11.55 mmol). AIBN; 10 mg (0.061 mmol).

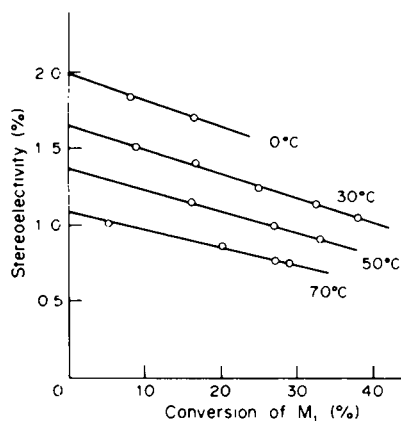


Fig. 3. Variation of overall stereoelectivity with conversion of  $M_1$  in the copolymerization of  $M_1$  with  $M_2$  at various temperatures.  $M_1$  = (*RS*)- $\alpha$ -methylbenzyl vinyl ether: 3.791 g (25.61 mmol).  $M_2$  = (*S*)-(-)-*N*-( $\alpha$ -methylbenzyl)-maleimide: 2.322 g (11.55 mmol). AIBN: 10 mg (0.061 mmol).

version of  $M_1$  in the copolymerization. The conversion of  $M_1$  is given by the following equation.

$$\begin{aligned} \% \text{ conversion of } M_1 &= \frac{148x}{148x + 201(1-x)} \\ &\times \frac{\text{weight of copolymer}}{\text{weight of initial } M_1} \times 100 \end{aligned} \quad (1)$$

where  $x$  denotes mole fraction of  $M_1$  in the copolymer. The specific rotation of the nonpolymerized  $M_1$  was almost proportional to the conversion of  $M_1$ . It is apparent that the slope of the straight line is decreased with increase in polymerization temperature, indicating that the stereoelectivity is higher at a lower temperature. The lowering in stereoelectivity with polymerization temperature is reasonable, comparing with temperature dependency of optical yield in general asymmetric organic reactions [27].

The driving force of the stereoselective phenomenon observed in the copolymerization can be regarded as the enantiomer-selection ability of the chiral  $M_2$  radical site upon the enantiomeric monomers. The overall stereoelectivity in the copolymerization is calculated from the conversion of  $M_1$  and optical purity of the nonpolymerized  $M_1$ , using equation (2).

$$\begin{aligned} \% \text{ stereoelectivity}_{(\text{overall})} &= \% \text{ e.e. of } M_1 \text{ in copolymer} \\ &= \frac{(100 - \% \text{ conversion of } M_1)}{\% \text{ conversion of } M_1} \\ &\times \% \text{ e.e. of nonpolymerized } M_1 \end{aligned} \quad (2)$$

The relationships between the overall stereoelectivity and the conversion of  $M_1$  are shown in Fig. 3. The decrease in stereoelectivity with the conversion of  $M_1$  may be due to a significant lowering in the concentration of (*S*)-(-)- $M_1$  at the micro-environment around the active radical site, accompanying the progress of stereoelection. The stereoelectivity is

higher at a lower temperature at the same conversion. At 70°, the stereoelectivity was reduced to about one-half that at 0° at every conversion. From the approximately linear relationship between the stereoelectivity and the conversion of  $M_1$ , the stereoelectivity in the initial stage of the copolymerization is evaluated by extrapolation to be about 2% at 0°.

## CONCLUSIONS

A stereoelection phenomenon was observed in "radical" copolymerization of (*RS*)- $\alpha$ -methylbenzyl vinyl ether with (*S*)-(-)- or (*R*)-(+)-*N*-( $\alpha$ -methylbenzyl)maleimide. Although the degree of stereoelection of the racemic monomer was not high, the optical activity of the nonpolymerized  $\alpha$ -methylbenzyl vinyl ether was of opposite sign to that of the optically active comonomer, clearly indicating that the copolymerization is stereoselective. The degree of stereoelection was the same as those reported for stereoselective copolymerizations by stereospecific catalysts [17, 19] in which the catalytic complex plays an important role in the stereoelection and the stereoselection of enantiomeric monomers in the transition state. It is noticeable that stereoelection occurs in the copolymerization by a "radical" mechanism, in which no counter ion is present around the propagating active site. The stereoelection is, therefore, due only to the enantiomer-selection ability of the propagating active site of the chiral *N*-( $\alpha$ -methylbenzyl)-maleimide radical upon (*S*)-(-)- and (*R*)-(+)- $\alpha$ -methylbenzyl vinyl ethers.

The chiral centre of the optically active *N*-( $\alpha$ -methylbenzyl)maleimide is situated in the  $\gamma$ -position with respect to the double bond. The cyclic structure of the maleimide ring, however, may overcome the problem of being far from the double bond, generally disadvantageous [18] for stereoelection. Thus, because of the rigidity of the molecular structure, the chirality of the *N*- $\alpha$ -methylbenzyl group may produce effective stereoelection in the copolymerization. Hence, the racemic monomer would be differentiated by the maleimide radical with chiral *N*- $\alpha$ -methylbenzyl group.

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