

# Enantioface Differentiation by Chiral Polymers Containing Dimethylaminobornyl Moieties

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## SYNOPSIS

Chiral monomers *cis,endo*-3-dimethylamino-2-bornyl methacrylate (DABM) and *N,N*-dimethyl[*cis,endo*-2-(2-vinyloxy-ethoxy)-3-bornyl]amine (DVEBA) were synthesized from (+)-camphor. The homopolymerization of both DABM and DVEBA, and the copolymerization of both chiral monomers with achiral methylmethacrylate (MMA) and styrene (St) were carried out with 2,2-azobisisobutyronitrile (AIBN) in various organic solvents. Effects of temperature, solvents, reagent molar ratio and reaction time on the polymerizations were studied. Dependences of the feeding concentration and reaction conditions on the specific rotation of the chiral copolymers were investigated. Enantioface differentiation by using the chiral polymers having dimethylaminobornyl moieties synthesized in this investigation were investigated. Effects of temperature and solvent on the asymmetric induction were also studied. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Synthesis of chiral compounds from achiral reagents always yields the racemic modification. This is simply one aspect of the more general rule: optically inactive reactants yield optically inactive products. Optically active compounds, however, can be induced in the presence of chiral catalyst. A large number of studies have been done to produce optically active compounds by asymmetric induction. Homogeneous low molecular weight models often have the advantages of giving high stereoselectivity. Also, every molecule of the catalyst is available to the reactants. In most cases, however, the asymmetric source is expensive and the preparation of asymmetric catalysts is so troublesome that it becomes desirable to use the catalyst repeatedly. This leads to the preparation of polymeric chiral catalysts.

Many studies have been reported on the synthesis of chiral compounds containing bornane groups derived from (+)-camphor. There have been a few

investigations on the synthesis of chiral polymers containing bornane moieties, especially of chiral monomers derived directly from (+)-camphor.

During the course of our investigations on the synthesis of both monomers and polymers containing the (+)-bornane group, it was found that polymers with pendant chiral bornyl groups are effective for asymmetric induction reactions. In connection with the studies on the catalytic functionality of the polymers having bornyl groups, the synthesis and polymerization of new chiral monomers, *cis,endo*-3-dimethylamino-2-bornyl methacrylate (DABM) and *N,N*-dimethyl-[*cis,endo*-2-(2-vinyloxy-ethoxy)-3-bornyl]amine (DVEBA) were studied.

In this article, the optically active DABM and DVEBA were synthesized, homopolymerized, and copolymerized with methyl methacrylate (MMA) or styrene (St). Effects of temperature, solvents, and reaction time on the specific rotation of the chiral polymers and/or copolymers were discussed. Application of the chiral polymers on the asymmetric induction of chiral alcohols from the addition of the *n*-butyllithium to aldehydes was investigated. Effects of temperature and solvent on the asymmetric induction were also studied.

## EXPERIMENTAL

### Measurements

IR were recorded on a Jasco IR-810 grating IR spectrophotometer. NMR spectra were recorded on a Bruker-100 high-resolution spectrophotometer. Optical rotations were measured at 30°C using a Jasco DIP-360 automatic digital polarimeter with readings to  $\pm 0.001^\circ$ . Elemental analyses were calculated with a Heraeus CHN-O rapidelemental analyzer.

### 3-Hydroxyiminobornane-2-one (1)

(+)-Camphor (9.5 g) in dry ether (100 mL) was added to sodium (1.6 g), which was cooled with an ice bath. 4-Methylpentyl nitrile (7.8 g) was then added dropwise to the stirred solution, the temperature being kept below 5°C. An orange-yellow color was formed during the reaction. After the mixture had been stirred for 2 h, water (50 mL) was added carefully. The aqueous layer was extracted with ether to remove unreacted (+)-camphor and then neutralized with acetic acid while cooling with an ice bath to yield a yellow product. The yellow crystalline solid was filtered and then recrystallized from methanol · m.p. 153°C.  $[\alpha]_D = 179.1$  ( $c = 2.2$  mg/mL in  $\text{CHCl}_3$ )  $\text{C}_{10}\text{H}_{15}\text{NO}_2$  (181.2) Calc. C 66.27 H 8.34 N 7.73  
Found C 66.24-H 8.12-N 7.70

### *cis*,Endo-3-Amino-2-bornanol (2)

The procedure employed was that reported by Chittenden and Cooper. The structure was identified by the H-NMR and IR analyses.  
 $\text{C}_{10}\text{H}_{19}\text{NO}$  (169.1) Calc. C 71.02 H 11.24 N 8.28  
Found C 71.12-H 11.20 N 8.25

### *cis*,Endo-3-Dimethylamino-2-bornanol (3)

Methyl iodide (5.8 g) in dry ether was added dropwise to the stirred solution of 3-amino-2-bornanol (2) (7.2 g) in dry ether, the temperature being kept below 5°C. After completion of the addition, the mixture was stirred at low temperature for 2 h, and then stirred at room temperature for further 4 h. The resulting product was washed with water until neutral, dried over magnesium sulfate, and evaporated to leave a pale-yellow oil that was distilled; b.p. 105°C/4.5 torr  $\text{C}_{12}\text{H}_{23}\text{NO}$  (197.3) Calc. C 73.04 H 11.75 N 7.10  
Found C 73.08-H 11.59 N 7.21

### *cis*,Endo-3-Dimethylamino-2-bornyl methacrylate (4)

A mixture of 3-dimethylamino-2-bornanol (3) (8.2 g), methacrylic acid (4.5 g), and *p*-toluenesulfonic acid (1.5 g) was heated in 100 mL of benzene at 100°C in the presence of hydroquinone (3.0 g). Water, liberated during the reaction, was removed by a Dean-Stark apparatus for 20 h. After completion of the reaction, the resulting mixture was washed with dilute aqueous sodium hydrogen carbonate solution and then with water. The oily layer was separated, dried over anhydrous magnesium sulfate, and distilled in vacuum to yield the product; b.p. 93°C/1 torr. Yield: 63%.

IR (neat): 1710, 1740  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).

$\text{C}_{16}\text{H}_{27}\text{NO}_2$  (265.4) Calc. C 72.41 H 10.26 N 5.28  
Found C 72.37 H 10.21 N 5.26

### *N,N*-Dimethyl- [*cis*,endo-2-(2-vinyloxyethoxy)-3-bornyl]amine (6)

To 8 g of (3) in dry ether solution (30 mL) was added excess amount of sodium hydride (1.2 g) at room temperature, and stirred for 10 h. The reaction mixture was then reacted with 5.0 g of 2-chloroethyl vinyl ether (5) (from Waco Chemical Industries, Ltd.) at room temperature for 24 h. After the reaction, the excess amount of sodium hydride remained was decomposed by adding water. Ether and water were removed by a rotatory evaporator to afford the crude product, which was distilled in vacuum to afford pure (6); b.p. 107°C/1 torr.  
Yield: 75%. IR (neat): 1630  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$ ).  
 $\text{C}_{16}\text{H}_{29}\text{NO}_2$  (267.16) Calc. C 71.93 H 10.85 N 5.24  
Found C 71.91 H 10.82 N 5.28

### Polymerization of the Chiral Monomers

Chiral polymers were prepared in various solvents. The monomer, solvents, and AIBN (2,2-azobisisobutyronitrile) were added in the above order into a polymerization tube, which was degassed in vacuum by using a freeze-thaw technique, and then sealed off. After a certain polymerization time, the tube was opened and the mixture was poured into a large excess of methanol to precipitate the chiral polymers. The crude polymers were purified by reprecipitation using benzene/methanol as nonsolvents. The conversion was calculated by gravimetry. Copolymerization of chiral monomers with achiral comonomers of methylmethacrylate (MMA) and styrene (St) were carried out in various solvent for a certain polymerization time. The results of the

**Table I** Polymerization of Chiral Monomers DABM (4) and DVEBA (6)<sup>a</sup>

Entry	Feed Monomer	Solvent	Conditions T/°C (t/h)	Conversion in Percent	$[\alpha]_D^{30}$ ( $\text{cg} \cdot \text{mL}^{-1}$ ) <sup>b</sup>
1	DABM	Benzene	60 (3)	60.2	+25.3 (2.62)
2		Benzene	60 (5)	71.5	+25.2 (2.17)
3		Chloroform	60 (3)	47.5	+22.5 (3.25)
4		Chloroform	60 (5)	62.7	+22.8 (3.14)
5		Toluene	60 (3)	53.7	+24.7 (3.14)
6		Toluene	60 (5)	65.2	+25.1 (3.23)
7	DVEBA	Benzene	60 (3)	64.7	+18.6 (1.67)
8		Benzene	50 (4)	62.9	+18.8 (2.14)
9		Chloroform	60 (3)	52.3	+18.7 (2.52)
10		Chloroform	60 (5)	75.1	+17.9 (2.15)
11		Toluene	60 (3)	59.8	+18.7 (2.75)
12		Toluene	60 (5)	78.1	+19.1 (2.65)

<sup>a</sup>  $[M] = 1.3 \text{ mol/dm}^3$ ;  $[AIBN] = 9.5 \text{ mmol/dm}^3$ .<sup>b</sup> Concentration, in benzene.

homopolymerization and the copolymerization are shown in Table I and Table II.

### Asymmetric Induction

Butyllithium was added to a dry THF solution (50 mL) of chiral polymer (1.6 mmol of chiral units) (1.6 mmol, 15 wt % in hexane) at 0°C under a nitrogen atmosphere. After stirring for 1 h, the reaction mixture was cooled (or heated) to a given temperature for 10 h with stirring, and the aldehyde (1 mmol in dry THF) was added to it, which was then stirred for additional 10 h. The reaction mixture was treated with 2N HCl, and THF was distilled off. The aqueous layer that resulted was extracted several times with ether. The combined ether solution was washed with water, dried over anhydrous mag-

nesium sulfate, and the organic phase was then concentrated. The resulting oily product was pored into a large excess of methanol to precipitate the chiral polymer. After the chiral polymer was filtered off, the clear solution was then concentrated. Pure product was isolated using a silica gel column, and purified subsequently by bulb-to-bulb distillation, and was identified by IR and NMR analyses. The optical purity was calculated using the measured optical rotation. Reaction involving air sensitive compounds were carried out under inert atmosphere.

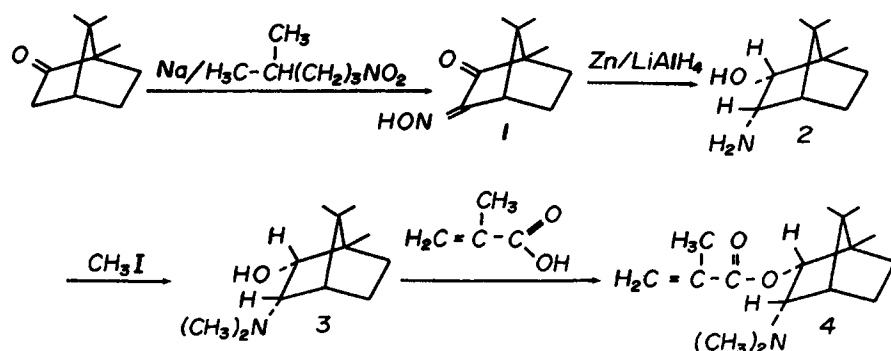
### Recovery of the Chiral Polymers

After the reaction, the linear polymers were recovered by the following procedures: after extraction, the ether layer was washed with water, dried over

**Table II** Copolymerization of DABM and DVEBA With Various Conditions<sup>a</sup>

Entry	Feed Monomer (mol %)	Comonomer	Conversion <sup>b</sup>	Content of Chiral Monomer <sup>c</sup>	$[\alpha]_D^{30}$ ( $\text{cg} \cdot \text{mL}^{-1}$ ) <sup>d</sup>	$M_w^e$ ( $\times 10^{-4}$ )
1	DABM (100)	—	46.2	100	+25.3 (2.57)	6.8
2	(45)	MMA	79.1	19	+12.8 (3.71)	9.2
3	(35)	St	58.7	12	+10.2 (3.12)	7.4
4	DVEBA (100)	—	49.5	100	+18.3 (2.16)	8.6
5	(40)	MMA	76.2	22	+8.7 (2.42)	12.3
6	(20)	St	62.1	14	+5.3 (3.27)	9.8

<sup>a</sup> At 60°C in benzene, with 1 wt % AIBN for 6 h.<sup>b</sup> (Weight of polymer/total weight of monomer)  $\times 100\%$ .<sup>c</sup> Evaluated by elemental analysis, in %.<sup>d</sup> Concentration, in benzene.<sup>e</sup> Molecular weight, evaluated by GPC.



Scheme 1

anhydrous magnesium sulfate, and the ether was then concentrated. The oily residue was poured into a large excess of methanol to precipitate the linear chiral polymer, which was then recovered by filtration leading to a recovery higher than 95%.

## RESULTS AND DISCUSSION

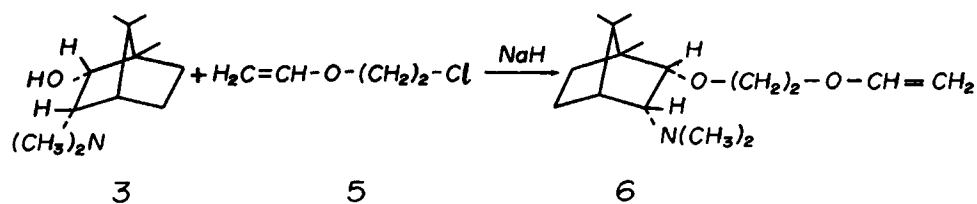
Chiral monomers *cis,endo*-3-dimethylamino-2-bornyl methacrylate (DABM) and *N,N*-dimethyl [*cis,endo*-2-(2-vinyloxy-ethoxy)-3-bornyl]amine (DVEBA) were synthesized from (+)-camphor as shown in Scheme 1 and Scheme 2. 3-Hydroxyiminobornane-2-one (1) was synthesized from (+)-camphor by sodium and methylpentyl nitrile, was reduced to *cis,endo*-3-amino-2-bornanol (2), which was treated with methyl iodide and then methacrylic acid to yield the chiral monomer *cis,endo*-3-dimethylamino-2-bornyl methacrylate (4). The reaction of the *cis,endo*-3-dimethyl amino-2-bornanol (3) and chloroethyl vinyl ether (5) leading to the product of the chiral monomer *N,N*-dimethyl- [*cis,endo*-2-(2-vinyloxyethoxy)-3-bornyl]amine (6). Structures of the synthesized compounds shown in Scheme 1 and Scheme 2 were all confirmed by elemental analysis, H-NMR, and IR spectroscopy. The H-NMR signal of the exo-hydro-

gen in positions 2 and 3 of the compound (2) showed the same chemical shift as those described in the literature.

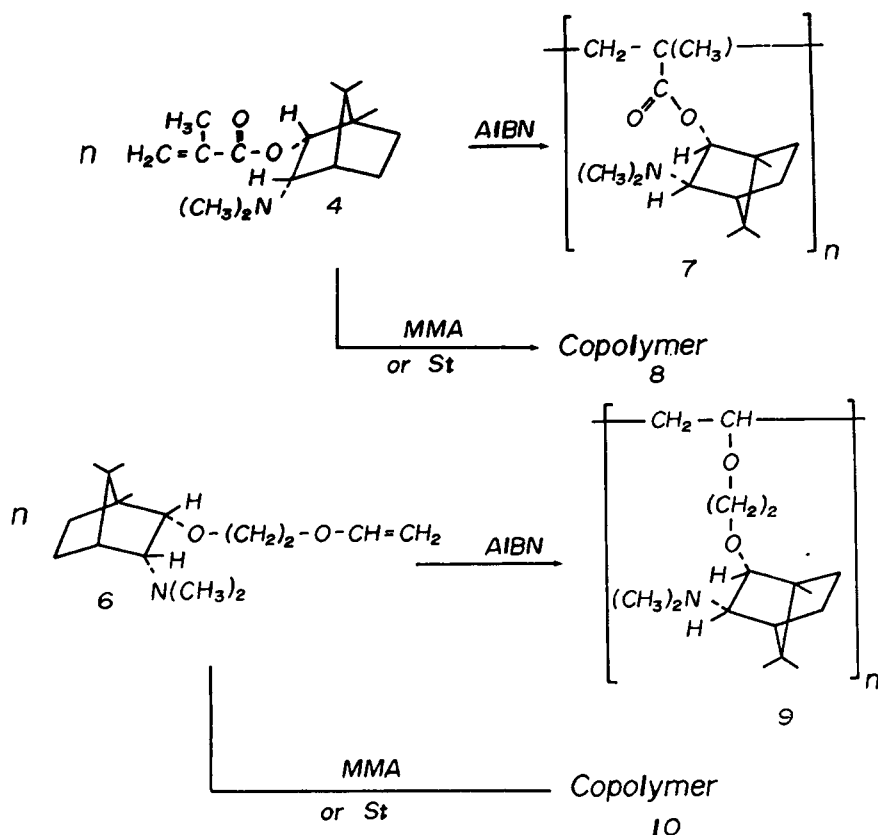
The free radical polymerization of the chiral monomers *cis,endo*-3-dimethylamino-2-bornyl methacrylate (4) and/or *N,N*-dimethyl- [*cis,endo*-2-(2-vinyloxyethoxy)-3-bornyl]amine (6) were carried out in various solvent for a certain polymerization time. Optical rotation of the chiral polymers was determined at 30°C in benzene. As can be seen in Table I, the conversion is affected by reaction temperature, solvent, and reaction time, as it was observed for the polymerization of (+)-bornyl methacrylate. In case of the chiral polymers 7 and 9, however, the optical rotation does not seem to be affected by the solvent and/or reaction conditions.

To study the steric hindrance on the chiral polymers, the copolymerization of both chiral polymers with the achiral monomers of methylmethacrylate (MMA) and Styrene (St) were carried out at 60°C for 6 h. The results are summarized in Table II. Copolymers that were synthesized were confirmed by NMR and IR spectroscopy, and the compositions of the chiral polymers were calculated from the values of elemental analyses.

As shown in Tables I and II, conversions and the molecular weight of the copolymers are higher than those of the homopolymers. This result suggests that a suitable low steric hindrance comonomer might be used as a spacer to decrease the steric hin-

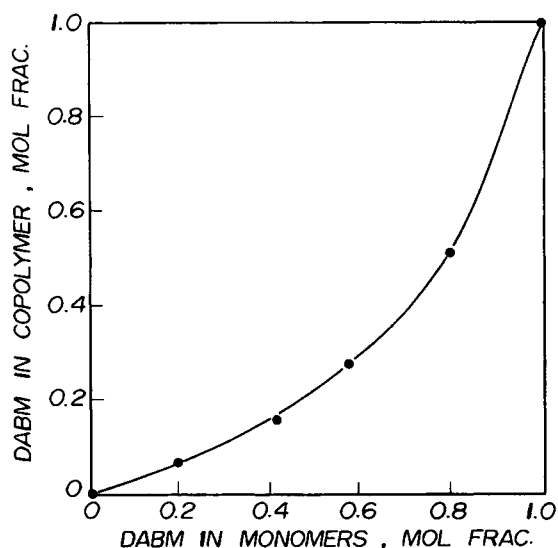


Scheme 2



drance between the DABM and/or DVEBA unit (Scheme 3).

The monomer feed dependence, temperature, and time effects on the copolymerization of DABM with MMA were investigated, and the results are sum-

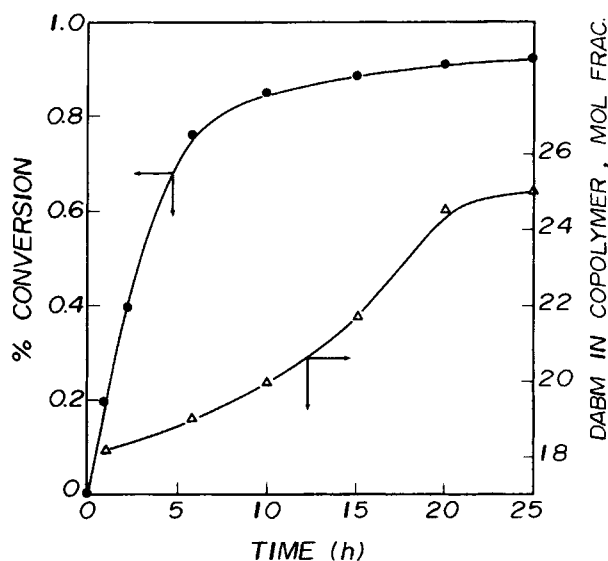


**Figure 1** Composition curve for poly(DABM-co-MMA). In benzene at 60°C for 6 h.

marized in Figures 1, 2, and 3. As can be seen in the figures, the polymer conversion increased with increasing the reaction time and/or temperature. It was found that the specific rotation of the copolymer increased with increasing the chiral DABM and/or DVEBA unit contained in the copolymer, which was dependent on the feeding concentration and reaction conditions.

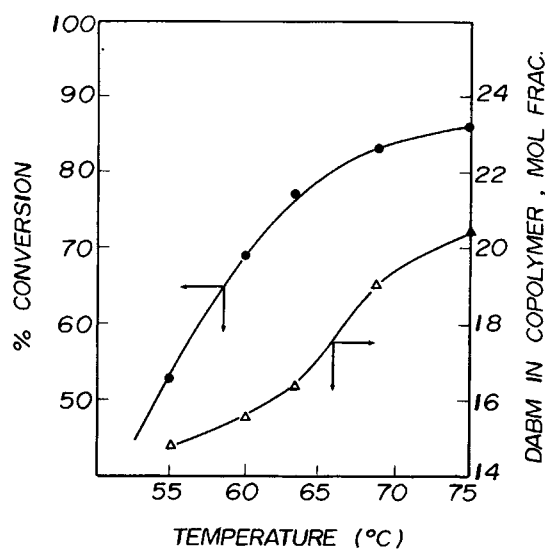
To investigate the catalytic effect of the chiral polymers on the asymmetric induction, the asymmetric addition of *n*-butyllithium to aldehydes was carried out in the presence of chiral polymers (Scheme 4). Table III shows the results of the asymmetric induction of *n*-butyllithium with various aldehydes in the presence of chiral polymers 7 and/or 9 as catalyst. Generally, decreasing the reaction temperature leads to higher enantioselectivity; however, with some low molecular weight models this leads to a decrease of the yield. For asymmetric addition in the presence of a polymer, the enantiomeric excess was found to increase with the reaction temperature to a optimum value. The highest enantiomeric excess (54.9%) was achieved at 0°C with chiral polymer 9 as catalyst.

To investigate the temperature effect, the reaction



**Figure 2** Time effect on the copolymerization of DABM with MMA. Feed monomers: mol % of DABM = 45, AIBN = 1 wt % of total monomers, in benzene at 60°C; (●) % conversion; (Δ) DABM in copolymer mol fraction.

was carried out in THF with chiral polymer 7 as catalyst. As can be seen in Table IV, the enantiomeric excess was found to increase with the reaction temperature. The highest enantiomeric excess (35.9%) was achieved at 10°C. At higher reaction temperatures the enantiomeric excess appears to



**Figure 3** Temperature effect on the copolymerization of DABM and MMA. Feed monomer: mol % of DABM = 40, AIBN = 1 wt % of total monomers, in benzene for 4 h; (●) % conversion; (Δ) DABM in copolymer mol fraction.

decrease. This result may suggest that the complex formed during the reaction is unstable at higher temperatures.

At higher temperatures, the polymer chain may expand and, thus, provide space to form complexes with ligands. Thus, each optically active site of the

**Table III** Results of Asymmetric Addition of *n*-Butyllithium to Aldehydes Using Chiral Polymers as Catalyst<sup>a</sup>

Entry	Aldehydes	Chiral Polymer	Temp. (°C)	Yield <sup>b</sup> (%)	Products	
					$[\alpha]_D^{20}$ ( $\text{cg} \cdot \text{mL}^{-1}$ ) <sup>c</sup>	e.e.%
1	$\text{C}_6\text{H}_5\text{CHO}$	7	20	62	+10.17 (6.12)	32.5 (R) <sup>d</sup>
2			10	59	+10.70 (4.81)	34.2 (R)
3			0	56	+11.17 (4.76)	35.7 (R)
4			20	62	+14.49 (4.12)	46.3 (R)
5			10	45	+16.02 (5.34)	51.2 (R)
6			0	58	+17.12 (6.12)	54.7 (R)
7			20	58	+10.27 (5.12)	32.8 (R) <sup>e</sup>
8	$\text{C}_6\text{H}_{11}\text{CHO}$	9	0	45	+17.18 (4.22)	54.9 (R) <sup>e</sup>
9			10	69	+4.52 (4.21)	35.9 (R) <sup>f</sup>
10			10	73	+9.71 (5.76)	35.2 (R) <sup>g</sup>

<sup>a</sup> Mole ratio of aldehyde/BuLi/polymer = 1/1.2/1.5.

<sup>b</sup> Isolated chemical yield.

<sup>c</sup> Concentration, in benzene.

<sup>d</sup> Enantiomeric excess, based on  $[\alpha]_D = +31.3$  ( $c = 3 \text{ cg} \cdot \text{mL}^{-1}$ , in benzene).

<sup>e</sup> By recovered chiral polymer.

<sup>f</sup> Based on  $[\alpha]_D(\text{neat}) +12.6$ .

<sup>g</sup> Based on  $[\alpha]_D(\text{neat}) +27.6$ .

**Table IV** Temperature Effect on the Asymmetric Addition of *n*-Butyllithium to Aldehydes<sup>a</sup>

Entry	Aldehydes	Temp. (°C)	Yield <sup>b</sup> (%)	Products	
				$[\alpha]_D^{30}$ (cg · ml <sup>-1</sup> ) <sup>c</sup>	e.e.%
1	C <sub>6</sub> H <sub>5</sub> CHO	30	68	+9.42 (4.21)	30.1 (R)
2		20	62	+10.17 (6.12)	32.5 (R)
3		10	59	+10.70 (4.81)	34.2 (R)
4		0	54	+11.17 (4.76)	35.7 (R)
5		-10	47	+9.64 (4.20)	30.8 (R)
6		-20	40	+8.29 (3.86)	26.5 (R)
7		20	75	+4.12 (3.69)	32.7 (R)
8	C <sub>6</sub> H <sub>11</sub> CHO	10	69	+4.52 (4.21)	35.9 (R)
9		0	65	+4.14 (3.67)	32.9 (R)
10		-10	54	+3.81 (3.92)	30.2 (R)
11		-20	48	+3.60 (4.18)	28.6 (R)

<sup>a</sup> Chiral polymer 7 was used.

<sup>b</sup> Isolated chemical yield.

<sup>c</sup> Concentration, in benzene.

<sup>d</sup> Enantiomeric excess, based on  $[\alpha]_D = +31.3$

<sup>e</sup> Based on  $[\alpha]_D(\text{neat}) = +12.6$ .

chiral catalyst is more accessible to the reactants, and the asymmetric induction occurs effectively within the polymeric chiral environment. At higher temperatures, however, the stability of the complex tends to decrease. At lower temperatures, a greater number of reactions may occur under achiral environment without effective chiral induction of the chiral catalyst.

Solvent effect on the asymmetric addition was also investigated. The reactions were carried out in various solvents using chiral polymer 7 as the chiral catalyst. As can be seen in Table V, the low-polarity benzene seems to be a more suitable solvent for the asymmetric induction. The polar site of the chiral polymer might be solvated by the polar solvent that decrease the chiral environment. Reaction temperatures also affect the solubility of the polymer; 20°C is more suitable for benzene in this system.

Generally, the immobilization of the asymmetric

catalysts frequently lowers the optical yields in comparison to those obtained in the homogeneous low molecular weight system. The reaction is not specified in detail, but the inefficiency is presumed to be related to the steric crowding and/or to the reaction environment in the polymer resin phase. The configuration of the products was determined by comparing the sign of rotation described in the literature. A schematic juxtaposition responsible for the enantioselectivity is shown in Scheme 5. Some coordination complex might be formed during the asymmetric addition that gave a relatively low optical yield, different from the case of low molecular weight models in which a more stable complex is considered.

The polymeric catalyst can be recovered quantitatively by a simple filtration technique and could be reused for the further asymmetric addition without causing a decrease in enantiomeric excess.

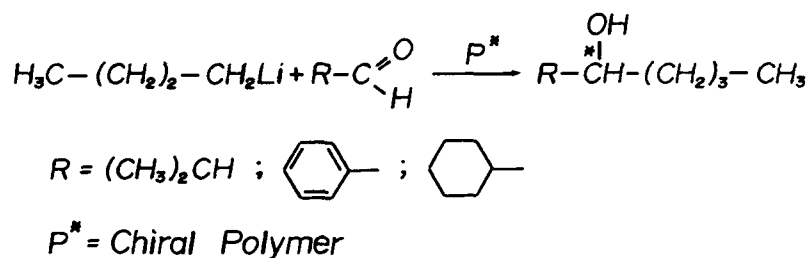
**Scheme 4**

Table V Solvent Effects on the Asymmetric Addition of *n*-Butyllithium to Aldehydes<sup>a</sup>

Entry	Aldehydes	Solvent	Temp. (°C)	Yield <sup>b</sup> (%)	Products	
					$[\alpha]_D^{30}$ ( $\text{cg} \cdot \text{ml}^{-1}$ ) <sup>c</sup>	e.e.%
1	C <sub>6</sub> H <sub>5</sub> CHO	THF	10	59	+10.70 (4.81)	34.2 (R) <sup>d</sup>
2		THF	0	56	+11.17 (4.76)	35.7 (R)
3		Benzene	10	28	+8.83 (3.65)	28.2 (R)
4		Benzene	20	47	+13.05 (3.87)	41.7 (R)
5		Ether	10	62	+14.34 (2.96)	45.8 (R)
6		DMSO	30	45	+4.01 (3.51)	12.8 (R)
7		THF	10	69	+4.52 (4.21)	35.9 (R) <sup>e</sup>
8	C <sub>6</sub> H <sub>11</sub> CHO	THF	0	65	+4.14 (3.67)	32.9 (R)
9		Benzene	20	45	+5.44 (4.12)	43.2 (R)
10		Ether	10	65	+6.14 (4.17)	48.7 (R)
11		DMSO	30	47	+1.78 (3.85)	14.1 (R)
12		THF	10	72	+4.54 (3.22)	36.0 (R) <sup>f</sup>
13		Benzene	20	52	+5.47 (4.51)	43.4 (R) <sup>g</sup>

<sup>a</sup> Chiral polymer 7 was used.

<sup>b</sup> Isolated chemical yield.

<sup>c</sup> Concentration, in benzene.

<sup>d</sup> Enantiomeric excess, based on  $[\alpha]_D = +31.3$

<sup>e</sup> Based on  $[\alpha]_D(\text{neat}) = +12.6$ .

<sup>f</sup> By recovered chiral polymer in entry 7.

<sup>g</sup> By recovered chiral polymer in entry 9.

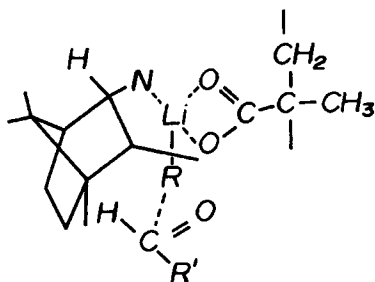
## CONCLUSION

Chiral monomers *cis,endo*-3-dimethylamino-2-bornyl methacrylate (DABM) and *N,N*-dimethyl [*cis,endo*-2-(2-vinyloxy-ethoxy)-3-bornyl]amine (DVEBA) were synthesized from (+)-camphor. The homopolymerization of both DABM and DVEBA, and the copolymerization of both chiral monomers with achiral methylmethacrylate (MMA) and styrene (St) were carried out with 2,2-azobisisobutyronitrile (AIBN) in various organic solvents. The conversion of the polymerization is affected by reaction temperature, solvent, and reaction time. It was found that the chiral polymers

synthesized in this investigation are effective for the enantioface differentiation. The enantiomeric excess was found to increase with the reaction temperature. The highest enantiomeric excess (35.9%) was achieved at 10°C. Solvent polarity was also found to affect the asymmetric induction, low-polarity benzene seems to be more suitable for the system. The chiral polymer can be reused without causing a decrease in enantiomeric excess.

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Scheme 5



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