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FREE-RADICAL POLYMERIZATION OF MALEIMIDE DERIVATIVES IN THE PRESENCE OF CHIRAL SUBSTANCES

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ABSTRACT

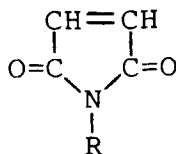
Free-radical homo- and copolymerizations of substituted maleimide derivatives in the presence of chiral substances have been reinvestigated. Optically active copolymers were obtained from the copolymerizations of styrene with *N-t*-butylmaleimide and *N*-phenylcitraconimide. Optically active homopolymers were obtained from *N-t*-butyl-, *N*-isopropyl-, *N*-benzyl-, and *N*- α -phenethylmaleimides, but not from *N-p*-tolyl- and *N*-triphenylmethylmaleimides. The $[\alpha]$ values of poly-*N*-benzylmaleimide increase both with increasing chiral substance concentration and monomer concentration.

INTRODUCTION

Recently, Okamoto et al. [1] reported that a highly optically active polymer is obtained by the anionic polymerization of triphenylmethyl methacrylate (TrMA) with a (-)-sparteine-*n*-BuLi complex as a catalyst. The large optical rotation ($[\alpha]_D^{20} > +250^\circ$) of poly-TrMA is attributed to the helicity of a rigid isotactic poly-TrMA sequence. There have been few reports on successful asymmetric polymerization by free radical initiation. Previous papers showed that optically active copolymers are obtained by the radical copoly-

erization of styrene (St) with maleic anhydride (MAN) [2] and *N*-substituted maleimides [3] and of isobutyl vinyl ether (IBVE) with MAN [4] in the presence of such chiral substances as *l*-menthol (Ment), *N*-(*p*-toluenesulfonyl)-L-proline (Ts-Pro) and *N*-benzyloxycarbonyl-L-proline (Z-Pro).

The present study is concerned with the reinvestigated results of radical homo- and copolymerizations of maleimide derivatives in the presence of chiral substances:



where R = hydrogen (MI), *i*-propyl (*i*-PMI), *t*-butyl (BMI), phenyl (PhMI), *p*-tolyl (*p*-TMI), benzyl (BzMI), α -phenethyl (α -PnMI), β -phenethyl (β -PnMI), and trityl (TrMI).

EXPERIMENTAL

Materials

N-Substituted maleimides were prepared from MAN and corresponding amines by a known method [5]. *N*-Phenylcitraconimide (PhCI) was similarly prepared by the reaction of citraconic anhydride and aniline. *N*-Triphenylmethylmaleimide (TrMI) was synthesized by reacting mercuric maleimide with triphenylmethyl chloride in toluene and was recrystallized from benzene and *n*-hexane. Table 1 lists the melting points, boiling points, and yields of the maleimide derivatives thus obtained.

Fumarates and acrylate were prepared by reacting fumaric acid and acrylic acid with the corresponding alcohols: diisopropyl fumarate (DiPF), bp 63°C/2 torr; dibenzyl fumarate (DBzF), mp 63°C; methyl benzyl fumarate (MBzF), mp 44–45°C; benzyl acrylate (BzA), 95°C/3 torr.

L-Proline derivatives used as the chiral substances were Ts-Pro, Z-Pro, *N*-(α -naphthalenesulfonyl)-L-proline (Nap-Pro), *N*-propionyl-L-proline (Pr-Pro), *N*-ethanesulfonyl-L-proline (Es-Pro), *N*-(α -naphthalenesulfonyl)-L-methyl proline (Nap-MPro) and *N*-propionyl-L-methyl proline (Pr-MPro), which were prepared by the Mukaiyama [6] and Zollinger [7] methods (Table 2).

Ment was commercially available; mp 43°C, $[\alpha]_{\text{D}}^{23} -51.5^\circ$ ($c = 1.0$, CH₃OH). St and *n*-butyl vinyl ether (*n*-BVE) were distilled just before use.

TABLE 1. Properties and Yields of Substituted Maleimide Derivatives (RMI)

RMI	mp, °C	bp, °C/torr	Yield, %
<i>i</i> -PMI	25	65/7.5	33
BMI	—	64/1.5	25
PhMI	88	—	94
<i>p</i> -TMI	150-152	—	49
BzMI	65-67	—	40
α -PnMI	—	115/1.5	55
TrMI	223-227	—	76
PhCI	94	—	40

Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified by the usual method.

Polymerization

The polymerization was carried out in a dry ampule. The prescribed amounts of monomers, chiral substances, initiator, and solvent in a glass ampule were flushed three times with nitrogen, sealed *in vacuo*, and placed in a

TABLE 2. Properties and Yields of L-Proline Derivatives (R-Pro)

R-Pro	mp, °C	bp, °C/torr	$[\alpha]_D^{23}$ (c, methanol)	Yield, %
Ts-Pro	94-99	—	-94.5 (0.8)	88
Z-Pro	67-70	—	-41.5 (0.9)	90
Nap-Pro	126	—	-53.2 (1.0)	70
Pr-Pro	Oil	—	-78.8 (1.1)	95
Es-Pro	89-91	—	-79.0 (2.8)	95
Nap-MPro	—	250/0.5	-52.1 (1.0)	70
Pr-MPro	—	120/1.0	-101.2 (2.1)	70

thermostated incubator. After the intended polymerization time, the ampule was cooled to stop the polymerization and the content was added to a large amount of the precipitant. The polymers were characterized by IR and $^1\text{H-NMR}$ spectral analysis and elemental analysis.

Measurement

Optical rotation was measured with a JASCO DIP-140 in a 10-cm cell. The optical rotatory dispersion (ORD) spectrum was measured with a JASCO J-20 in a 5-cm cell.

RESULTS AND DISCUSSION

Table 3 summarizes the results of radical homo- or copolymerizations of acrylate, fumarates, citraconic anhydride (CAN), and maleimides in the presence of several chiral substances. No optically active polymer was obtained from any of the acrylate and fumarate systems. Similarly, no optically active copolymers were obtained from the St-methyl methacrylate (MMA), St-methacrylic acid (MA), MMA-MA, and MMA-methyl acrylate systems [4]. One possible explanation for this is far higher degrees of freedom of these common vinyl monomers, since an optically active copolymer was obtained from the copolymerization of five-membered MAN and St [2]. However, it was found that optically active copolymers were obtained from the PhCI and BMI systems, but not from the CAN, MI, and PhMI systems. These findings seem to indicate that the nature of the substituents in maleimides, as well as the combination of monomer and chiral substance, may be important for asymmetric induction.

Table 4 shows the results of radical homopolymerizations of several *N*-substituted maleimides in the presence of chiral substances. It is interesting to note that optically active polymers were obtained except for the *p*-TMI and TrMI systems. The resulting optically active polymers were not found to be contaminated with other optically active substances by ^1H -, ^{13}C -NMR, and IR spectral analyses. The $[\alpha]$ value of Polymer 19 was found to vary only little with the nature of the solvent, such as CHCl_3 ($+3.66^\circ$) and THF ($+3.58^\circ$), indicating that the optically active polymer exhibits no helical conformation but an asymmetric center in the polymer chain.

One possible explanation for the observed optical activity is that one of chiral epimeric isomers, (*RR*) or (*SS*), may be involved in the polymer chain, since the (*RS*), (*SR*), (*RRSS*), and (*SSRR*) configurations become achiral *meso*-isomers which should be optically inactive. Thus, the optical activity

TABLE 3. Radical Polymerization of Several Monomers in the Presence of Chiral Substances^a

No.	Monomer		Chiral substance	AIBN, mmol	THF, mL	Temperature, °C	Time, h	Yield, %	$[\alpha]_{400}^{23}$ (c, solvent)
	M ₁ (mmol)	M ₂							
1	BzA (6.3)	—	Ment	0.07	5	50	46	33.7	0
2	BzA (6.3)	—	Ts-Pro	0.06	5	50	46	32.3	0
3	MBzF (3.6)	—	Ment	0.08	5	50	46	1.5	0
4	DiPF (9.8)	<i>n</i> -BVE	Z-Pro	0.17	4	50	17	32.4	0
5	DBzF (15.5)	<i>n</i> -BVE	Z-Pro	0.31	10	50	6	35.7	0
6	CAn (5.4)	St	Ment	0.12	10	45	3	1.8	0
7	CAn (5.4)	St	Z-Pro	0.12	10	45	3	1.1	0
8	MI (5.2)	St	Nap-Pro	0.80	10	60	1	77.0	0
9	PhMI (9.8)	St	Ment	0.02	10	60	2	32.5	0
10	PhCI (3.2)	St	Ment	0.60	10	60	2	26.3	-0.65 (2.0, THF)
11	PhCI (3.2)	St	Z-Pro	0.43	10	60	2	1.7	+2.11 (2.0, THF)
12	PhCI (3.2)	St	Nap-Pro	0.48	10	60	2	1.2	+0.93 (2.0, THF)
13	BMI (17.0)	St	Ment	0.04	10	60	0.5	41.9	+0.36 (2.0, DCE)
14	BMI (8.5)	St	Z-Pro	0.03	10	70	10 ^b	64.4	-1.39 (2.0, THF)

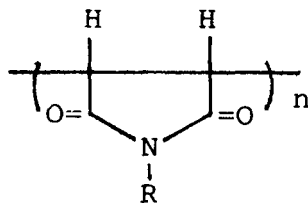
^a[M₁] = [M₂] = [chiral substance].^bminutes.

TABLE 4. Radical Homopolymerization of *N*-Substituted Maleimides in the Presence of Chiral Substances^a

No.	Monomer, mmol	Chiral substance	AIBN, mmol	THF, mL	Temperature, °C	Time, h	Yield, %	<i>R_p</i> , %/h	$[\alpha]_D^{23}$ (c, solvent)
15	<i>p</i> -TMI (8.0)	Z-Pro	0.21	12	50	1	30.0	30.0	0
16	<i>i</i> -PMI (7.2)	Ts-Pro	1.79	10	55	2	27.4	13.7	-0.35 (1.0, THF)
17	BMI (6.5)	Nap-Pro	2.03	10	55	2	32.6	16.3	+0.17 (2.0, THF)
18	BMI (12.0)	Ts-Pro	0.31	10	60	3	55.0	18.3	+0.30 (2.0, THF)
19	BzMI (8.0)	Z-Pro	1.50	5	50	7	10.2	1.5	+3.66 (1.2, CHCl ₃)
20	BzMI (5.0)	Ts-Pro	0.50	5	50	12	33.1	2.8	-1.68 (1.0, CHCl ₃)
21	BzMI (5.0)	Nap-Pro	0.52	5	50	12	20.5	1.7	-1.52 (1.2, CHCl ₃)
22	α -PnMI (8.0)	Ts-Pro	1.70	4	50	6	5.7	1.0	-1.95 (1.1, AcOEt)
23	α -PnMI (8.0)	Z-Pro	2.10	4	50	6	30.0	5.0	+1.83 (2.4, THF)
24	α -PnMI (11.2)	Nap-Pro	3.40	5	50	6	13.6	2.3	-2.83 (1.3, AcOEt)
25	β -PnMI (5.2)	Z-Pro	0.97	5	50	6	25.3	4.2	+2.22 (1.5, THF)
26	TrMI (3.0)	Nap-Pro	0.06	10	50	1	47.1	47.1	0

^a[Monomer] = [chiral substance].

of the polymer is probably caused by partial formation of a chiral center via stereoselective interaction of the monomer or of the propagating radical in the asymmetric surrounding of chiral substances.



-SS-, -RR-, -SR-, -RS-,

-SSRR-, -RRSS-

A question arises: What type of interaction between the chiral substance and the monomer or its radical takes place to cause the asymmetric induction? A hydrogen bonding interaction may be one of the possible factors for asymmetric induction in the *l*-menthol system, since the IR spectra of an equimolar mixture of *l*-menthol and BMI in chloroform showed that the C=O stretching frequency of BMI at 1710 cm^{-1} in the absence of *l*-menthol shifted to a longer wavelength (1720 cm^{-1}).

In proline systems, however, no detectable interaction was observable by IR or UV spectra. Thus, in order to get some information on asymmetric induction for the proline systems, the polymerization of BzMI in the presence of several proline derivatives was carried out (Table 5). Interestingly, optically active polymers were also obtained from esterified prolines which do not have any group of hydrogen bonding ability. Another interesting observation is that the $[\alpha]$ values of poly-BzMI increases with increasing proline concentration for both the Pr-Pro and the Pr-MPro systems, as shown in Fig. 1. Figure 2 shows that the $[\alpha]$ values of polymers increase with increasing monomer concentration for the polymerization of BzMI in the presence of Es-Pro.

These observations seem to indicate that in proline systems the propagating polymer radical, but not the monomer, interacts with the chiral substance, but the details of this are not yet clear.

Monomer + Chiral Substance

Complex

Archiral Polymer

Chiral Polymer

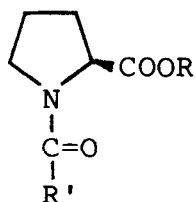
———M•+ Chiral Substance

Complex

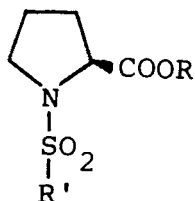
TABLE 5. Radical Homopolymerization of BzMI in the Presence of L-Proline Derivatives (R-Pro) in THF at 50°C^a

No.	R-Pro, mmol	AIBN, mmol	Time, h	Yield, %	$[\alpha]_D^{23}$ (c, CHCl ₃)
27	Pr-Pro (5.0)	0.50	12	22.8	+4.50
28	Pr-MPro (8.0)	0.80	24	10.8	+2.47
29	Z-Pro (8.0)	1.50	7	10.2	+3.66
30	Nap-Pro (5.0)	0.52	12	20.5	-1.52
31	Nap-MPro (3.0)	0.30	12	14.4	-2.22
32	Es-Pro (10.0)	1.00	24	33.7	-1.49

^a[BzMI] = [R-Pro].



Pr-Pro: R = H, R' = C₂H₅
 Pr-MPro: R = CH₃, R' = C₂H₅
 Z-Pro: R = H, R' = OCH₂C₆H₅



Nap-Pro: R = H, R' = C₁₀H₇
 Nap-MPro: R = CH₃, R' = C₁₀H₇
 Es-Pro: R = H, R' = C₂H₅

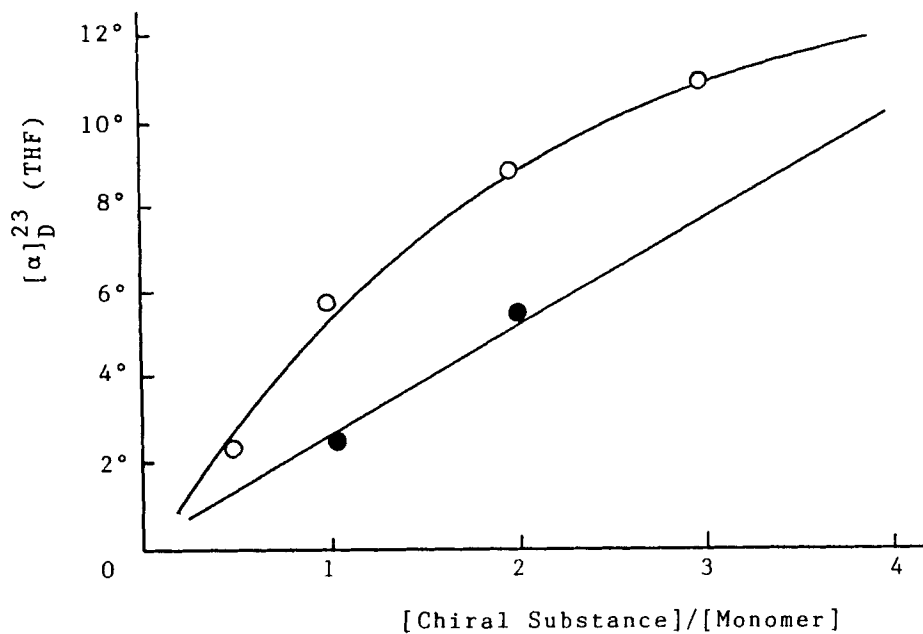


FIG. 1. Relationship between optical rotation of polymer and [chiral substance]/[monomer] ratio. (○) BzMI/Pr-Pro, (●) BzMI/Pr-MPro.

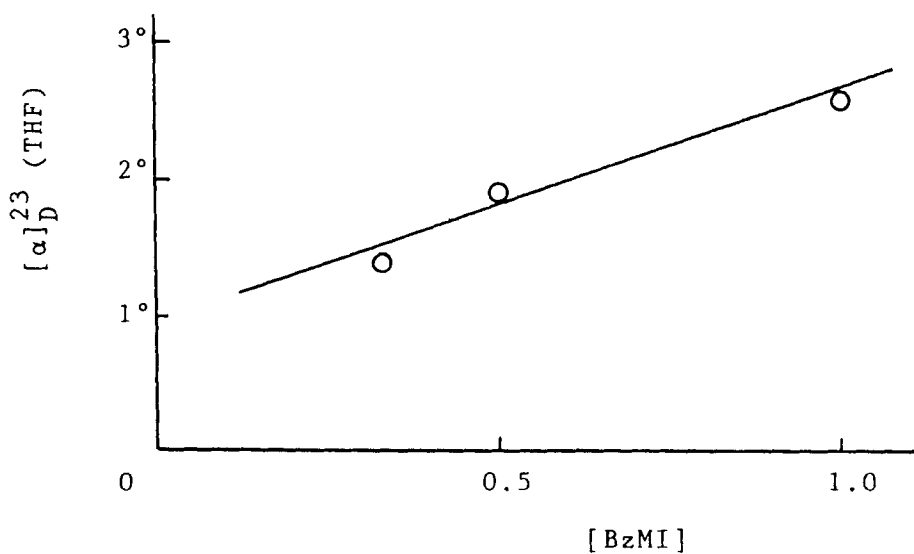


FIG. 2. Relationship between optical rotation of Poly(BzMI) and monomer concentration.

Further investigations on this line are now being conducted in our laboratory, and the results will be reported in the future.

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REFERENCES

- [1] (a) Y. Okamoto, K. Suzuki, K. Hatada, and H. Yuki, *J. Am. Chem. Soc.*, **101**, 4763 (1979). (b) Y. Okamoto, K. Suzuki, and H. Yuki, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3043 (1980).
- [2] H. Fujihara, K. Yamazaki, M. Yoshihara, and T. Maeshima, *J. Polym. Sci., Polym. Lett. Ed.*, **17**, 507 (1981).
- [3] M. Yoshihara, J. Asakura, H. Takahashi, and T. Maeshima, *J. Macromol. Sci.-Chem.*, **A20**, 123 (1983).
- [4] J. Asakura, M. Yoshihara, and T. Maeshima, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1269 (1981).
- [5] (a) L. E. Coleman, J. F. Bork, and H. Dun, *J. Org. Chem.*, **24**, 135 (1959). (b) N. B. Mehta, A. P. Phillips, F. F. Lui, and R. E. Brooks, *Ibid.*, **25**, 1012 (1960).
- [6] M. Asami, H. Ohno, S. Kobayashi, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **51**, 1869 (1978).
- [7] H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta* **42**, 1953 (1959).

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