Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Polymerization of Optically Active N-α-Methylbenzylcitraconimide

Tsutomu Oishi[a]; Minoru Fujimoto[a]
[a] Department of Industrial Chemistry, Technical College Yamaguchi University, Ube Yamaguchi, Japan

To cite this Article Oishi, Tsutomu and Fujimoto, Minoru(1986) 'Synthesis and Polymerization of Optically Active N-α-Methylbenzylcitraconimide', Journal of Macromolecular Science, Part A, 23: 5, 619 — 633
To link to this Article: DOI: 10.1080/00222338608058500
URL: http://dx.doi.org/10.1080/00222338608058500

J. MACROMOL. SCI.–CHEM., A23(5), pp. 619-633 (1986)

Synthesis and Polymerization of Optically Active N-α-Methylbenzylcitraconimide

TSUTOMU OISHI and MINORU FUJIMOTO

Department of Industrial Chemistry
Technical College
Yamaguchi University
2557 Tokiwadai, Ube Yamaguchi 755 Japan

ABSTRACT

Optically active N-α-methylbenzylcitraconimide (MBZCI) was prepared from citraconic anhydride and d-α-methylbenzylamine. The polymerizations of MBZCI were carried out with α,α'-azobisisobutyronitrile (AIBN) in several solvents and in bulk. The specific rotations of the polymers were between 48.6 and 56.7°. The number-average molecular weights for the polymers were 1 400 to 1 900. MBZCI was copolymerized with styrene (ST) and methyl methacrylate (MMA) with AIBN in tetrahydrofuran at 50°C to obtain optically active copolymers. The monomer reactivity ratios of MBZCI (M_1) with ST (M_2) and MMA (M_2) were determined as $r_1 = 0.12$, $r_2 = 0.24$ in the MBZCI-ST; $r_1 = 0.23$, $r_2 = 2.38$ in the MBZCI-MMA system. The Q-e values were obtained as $Q_1 = 0.63$, $e_1 = 1.07$. It was found that all the polymers and copolymers showed a strongly negative circular dichroism (CD) peak at about 258 nm. From the results of chirality of the copolymer, it was concluded that induction of asymmetric carbon atoms into the MBZCI-ST copolymer main chain took place.

0022-233X/86/0619$3.50/0

INTRODUCTION

There have been many reports on asymmetric induction copolymerizations of chiral vinyl monomers with achiral α,β-disubstituted vinyl monomers. Schuerch et al. [1, 2] reported that the copolymer of maleic anhydride with (-)-α-methylbenzyl methacrylate or (-)-α-methylbenzyl vinyl ether revealed an optical activity, even after cleavage of the optically active side groups. Their experiment was the first successful synthesis of the asymmetric polymer. Matsuzaki et al. [3] reported on the copolymerization of l-menthyl vinyl ether with maleic anhydride. Sakota et al. [4, 5] reported the photopolymerization of methacryloyl-l-valine methyl ester with maleic anhydride. Lately, Minoura et al. reported on the asymmetric induction copolymerization of l-menthyl vinyl ether with ST [6], N-phenyl maleimide [6], maleic anhydride [7], dimethyl maleate [7], dimethyl fumarate [7], indene [8-11], acenaphthylene [8], and vinyl carbonate [11]. However, there are few investigations on asymmetric induction by radical copolymerizations of chiral α,β-disubstituted vinyl monomers with other achiral vinyl monomers. Radical copolymerizations of (-)-3-menthyl hydrogen maleate with ethyl acrylate [12] or ST [13] were investigated. The radical copolymerization of optically active N-bronyl maleimide [14] with ST and MMA was also reported. Most recently, Minoura et al. [15] reported on asymmetric induction in the radical copolymerization of mono- and di-l-menthyl fumarate with ST.

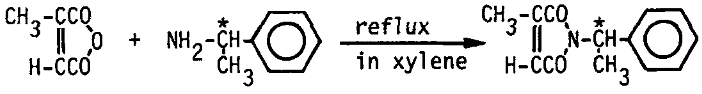
We have also reported the synthesis and polymerization of optically active N-α-methylbenzylmaleimide (MBZMI) [16].

In this article, a novel, optically active N-α-methylbenzylcitraconimide (MBZCI) was synthesized, homopolymerized, and copolymerized with ST and MMA. The monomer reactivity ratios r_1, r_2 were calculated, and the Q_1, e_1 values for MBZCI were also determined. The specific rotation $[\alpha]_D$, optical rotatory dispersion (ORD), and circular dichroism spectra (CD) of these polymers and copolymers were measured. From the results of chirality for the copolymer, the induction of asymmetric carbon atoms in the polymer main chain is discussed.

EXPERIMENTAL

MBZCI Monomer

Optically active MBZCI was prepared from citraconic anhydride and α-methylbenzylamine ($[\alpha]_D$ = +35.9°; bp 181°C/765 torr), as shown in Scheme 1, according to the method of N-substituted maleimide synthesis reported by Coleman et al. [17] with some modification [16]. The crude product was purified by distillation repeatedly; yield 60%;



CAn D-(+)-α-methylbenzylamine MBZCI

bp 111-112°C/2 torr, colorless oil, $[\alpha]_D^{25}$ = +43.0° (THF, c = 1.0%, l = 10 cm), $[\alpha]_D^{25}$ = +49.1° (ethanol (EtOH), c = 1.0%, l = 10 cm), n_D^{25} = 1.5458. IR (neat), wavenumber (cm^{-1}): 2 950, 1 765, 1 700, 1 640, 1 380, 1 360, 850, 690. ^{1}H-NMR, chemical shift, δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 7.05-7.45(m) phenyl; 6.05(m) CH=C; 5.28(q, J = 7.20 Hz) CH–N; 1.88(d, J = 2.00 Hz) CH_3–C=C; 1.74(d, J = 8.02 Hz) CH_3–C–N. Elemental analysis: Found, C = 73.68, H = 6.19, N = 6.55%. Calculated for $C_{13}H_{13}NO_2$, C = 72.54, H = 6.09, N = 6.51%.

Racemic dl-N-α-methylbenzylcitraconimide (dl-MBZCI) was prepared from citraconic anhydride and racemic dl-α-methylbenzylamine by the same method as described above. bp 135-136°C/6 torr, colorless oil, n_D^{25} = 1.5455. IR (neat), wavenumber (cm^{-1}): 2 980, 1 765, 1 700, 1 640, 1 380, 850, 690. ^{1}H-NMR, chemical shift, δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 7.14-7.42(m) phenyl; 6.08(m) CH=C; 5.30(q, J = 7.20 Hz) CH–N; 1.86(d, J = 2.02 Hz) CH_3C=C; 1.72(d, J = 8.00 Hz) CH_3C–N.

Optically active d-N-(methylbenzyl)-α-methylsuccinimide (MBZMSI) was synthesized from α-methylsuccinic anhydride (bp 120-121°C/12 torr) and d-α-methylbenzylamine ($[\alpha]_D^{25}$ = +35.9°, bp 181 °C/175 torr) by the same method as described above. bp 136-137°C/1 torr, colorless oil, $[\alpha]_D^{25}$ = +55.3° (THF, c = 1.3%, l = 10 cm) n_D^{25} = 1.5345. IR (neat), wavenumber (cm^{-1}): 2 950, 1 780, 1 695, 1 385, 1 355, 1 180, 745, 695. ^{1}H-NMR, chemical shift, δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 7.35-7.75(m) phenyl; 5.55(q, J = 7.02 Hz) CH–N; 2.13-3.01(m) CO–CH–CH_2–CO; 1.85(d, J = 8.02 Hz) N–C–CH_3; 1.32(d, J = 6.02 Hz) CH_3–C–CO.

Comonomers and Other Materials

ST and MMA were purified by the usual methods. α,α'-Azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), tetrahydrofuran (THF), benzene, and methanol were purified by the usual methods.

Polymerization and Copolymerization

The radical homopolymerizations of MBZCI monomer in bulk or in solvent were carried out in a sealed-glass tube in the presence of a radical initiator (AIBN or BPO) at 50-90°C. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The polymers were purified several times by reprecipitation from THF-methanol solution.

The radical copolymerizations of MBZCI (M_1) with ST (M_2) or MMA (M_2) were achieved in sealed glass tubes in THF (4 mL) or benzene (4 mL) in the presence of AIBN (1.0×10^{-2} mol/L). After the prescribed time, the product was poured into a large amount of methanol and purified by reprecipitation several times, using THF-methanol solution, and dried in vacuum. The composition of the copolymer was determined from nitrogen analysis.

Measurements

D-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.). ORD and CD spectra were obtained by a Jasco J-20 (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor. UV spectra were measured with a Shimadzu UV-200A spectrophotometer (Shimadzu Co.). The molecular weights of the polymers and copolymers were measured by gel permeation chromatographic (GPC) analysis using the same technique as described in an earlier article [18]. IR and NMR spectra were obtained, and elemental analysis was done, using the same instruments as reported previously [19].

RESULTS AND DISCUSSION

Homopolymerization of MBZCI

Results of the radical homopolymerizations of MBZCI and dl-MBZCI are shown in Table 1. The radical homopolymerizations of MBZCI were carried out in THF under several conditions, giving no appreciable amount of homopolymers. In benzene, however, the polymers were obtained in low yields. MBZCI was homopolymerized in bulk in order to obtain the homopolymer in greater yields. It was thought that in these homopolymerizations, ordinary additional polymerizations took place, judging from results of elemental analysis, IR, and NMR spectra. The number-average molecular weights for the homopolymers were found to be 1 400 to 1 900, which was based on the steric hindrance of the α-methyl group in the maleimide ring. The

TABLE 1. Radical Homopolymerizations of MBZCI and dl-MBZCI[a]

Experiment	Monomer	Polymerization temperature, °C	Yield, %	N analysis, %	M_n	M_w/M_n	$[\alpha]_D^{25}$,[e] degrees	$[\Phi]_D^{25}$[f]	$[\theta]_{258}^{25}$[g]
A-1	MBZCI	50	6.8	6.35	1 900	1.9	52.0	112.0	-730
A-2	MBZCI	70	10.8	6.45	1 400	1.7	48.6	104.6	-840
A-3	MBZCI[b]	90	8.4	6.25	1 700	1.5	51.2	110.1	-830
A-4	MBZCI[c]	50	-	-	-	-	-	-	-
A-5	MBZCI[d]	50	2.7	6.46	1 400	2.1	56.7	121.9	-550
A-6	dl-MBZCI	50	6.8	6.12	1 900	2.2	0	0	0
A-7	dl-MBZCI	70	8.4	6.58	1 800	1.2	0	0	0
A-8	dl-MBZCI[b]	90	8.2	6.05	1 400	1.6	0	0	0
A-9	dl-MBZCI[c]	50	-	-	-	-	-	-	-
A-10	dl-MBZCI[d]	50	1.7	6.40	3 100	1.1	0	0	0

[a] Initiator, AIBN (1% of monomer); polymerization time, 96 h.
[b] Initiator, BPO; polymerization time, 72 h.
[c] Solvent, THF (2 mL); AIBN, 1.0×10^{-2} mol/L.
[d] Solvent, benzene (2 mL); AIBN, 1.0×10^{-2} mol/L.
[e] In THF; c, ~1.0%; l, 10 cm.
[f] $[\Phi] = [\alpha] \times M/100$.
[g] In THF; c, ~0.1%; 1 mm quartz cell.

specific rotation $[\alpha]_D$ and the molar rotation were +48.6 to +56.7 and +104.6 to +121.9, respectively. In addition, the ellipticity in 258 nm was -550 to -840 deg·cm^2/dm. These data are discussed in detail later.

Copolymerization

The results of copolymerizations of MBZCI (M_1) with ST (M_2) and MMA (M_2) are summarized in Tables 2 and 3. Both the copolymerizations were homogeneous throughout. In the ST system, MBZCI content in the copolymer was increased scarcely with increasing the MBZCI concentration in the monomer feed. The number-average molecular weight was decreased from 32 000 to 11 000 in the MBZCI-ST, 24 400 to 1 100 in the MBZCI-MMA system, and the specific rotation, on the contrary, was increased with increasing the MBZCI content in the copolymer.

The copolymer composition curves are shown in Fig. 1. In the MBZCI-ST system, the polymerization was found to be a considerable alternating one. It can be seen from Fig. 1 that the plots of the specific rotation for the copolymer were parallel to the composition curve. The specific rotation $[\alpha]_D$ for N-α-methylbenzyl-α-methylsuccinimide (MBZMSI), which was a low molecular weight model compound of MBZCI homopolymer, was almost in agreement with that of MBZCI homopolymer, as illustrated in Fig. 1. The monomer reactivity ratios (r_1, r_2) and Q, e values were determined, according to the methods reported by Mayo-Lewis [20] and Alfrey-Price [21], respectively. The copolymerization parameters are indicated in Table 4. In the ST system, both the r_1 and r_2 values were smaller than 1, which suggested alternating copolymerization. This character was inferior to that of N-α-methylbenzylmaleimide and N-benzylmaleimide. In the MMA system the r_2 was larger than 1, which indicated the greater possibility that MMA radical could add successively to the MMA monomer. This tendency was also observed in the other maleimide derivatives.

Temperature Dependence of the Specific Rotation and Solvent Effects

It was apparent from Fig. 2 that a linear relationship between the specific rotation and temperature was observed. No helix in the polymer and copolymers is present because the temperature coefficients ($\Delta[\alpha]/\Delta T$) were about -0.1 [16]. When the specific rotation was plotted against the solvent concentration ([THF]/([THF] + [EtOH])), a straight line was observed. This fact supports the lack of a helix in the polymer and copolymer.

TABLE 2. Result of Radical Copolymerizations of MBZCI (M_1) with ST (M_2) in THF at 50°C[a]

Experiment	$[M_1]$, mol%	Conversion, %	N analysis, %	$d[M_1]$, mol%	$M_n \times 10^{-4}$	M_w/M_n	$[\alpha]_D^{25}$,[e] degrees	$[\Phi]_D^{25}$[f]
B-1	21.9	37.4	3.64	38.1	3.20	1.8	19.6	28.7
B-2	39.4	41.7	4.02	43.9	2.72	1.8	22.2	33.9
B-3	49.6	41.4	4.19	46.7	1.37	2.4	24.5	37.9
B-4	60.4	40.0	4.37	49.7	1.92	1.7	26.0	41.4
B-5	75.9	28.3	4.71	56.0	1.10	1.2	30.4	50.6
B-6	50.1[b]	48.4	4.17	46.3	1.32	13.6	24.2	37.7
B-7	49.8[c]	65.6	4.16	46.2	1.48	13.0	23.6	36.6
B-8	50.0[d]	48.1	4.15	46.0	0.68	2.0	20.1	31.2

[a] [AIBN], 1.0×10^{-2} mol/L; THF, 4 mL; polymerization time, 48 h; $M_1 + M_2 = 2.0$ g.

[b] $M_1 + M_2 = 4.0$ g.

[c] Benzene, 4 mL; $M_1 + M_2 = 4.0$ g; polymerization time, 70 h.

[d] Photopolymerization at 35°C.

[e] In THF; c, 1.0%; l, 10 cm.

[f] $[\Phi] = [\alpha] \times m/100$, $m = N_1M_1 + N_2M_2$; deg·cm²/dmol.

TABLE 3. Result of Radical Copolymerizations of MBZCI (M_1) with MMA (M_2) in THF at 50°C[a]

Experiment	$[M_1]$, mol%	Conversion, %	N analysis, %	$d[M_1]$, mol%	$M_n \times 10^{-3}$	M_w/M_n	$[\alpha]_D^{25}$,[e] degrees	$[\Phi]_D^{25}$[f]
C-1	20.3	54.5	1.08	8.4	24.4	1.8	13.1	14.4
C-2	41.0	33.9	2.21	19.3	11.3	1.3	23.2	28.4
C-3	49.7	27.8	2.60	23.6	7.1	1.4	25.4	32.0
C-4	60.1	17.3	3.17	30.6	9.6	1.2	31.5	42.6
C-5	80.1	2.9	4.64	53.6	1.1	12.7	44.7	72.3
C-6	50.5[b]	34.6	2.66	24.3	7.2	13.1	26.0	33.3
C-7	50.3[c]	39.7	2.58	23.4	6.6	12.4	22.7	28.8
C-8	50.3[d]	24.8	2.60	23.6	6.3	2.8	23.5	30.6

[a] [AIBN], 1.0×10^{-2} mol/L; THF, 4 mL; polymerization time, 48 h; $M_1 + M_2 = 2.0$ g.

[b] $M_1 + M_2 = 4.0$ g.

[c] Benzene, 4 mL; $M_1 + M_2 = 4.0$ g; polymerization time, 70 h.

[d] Photopolymerization at 35°C.

[e] In THF; c, 1.0%; l, 10 cm.

[f] $[\Phi] = [\alpha] \times m/100$, $m = N_1M_1 + N_2M_2$; deg·cm²/dmol.

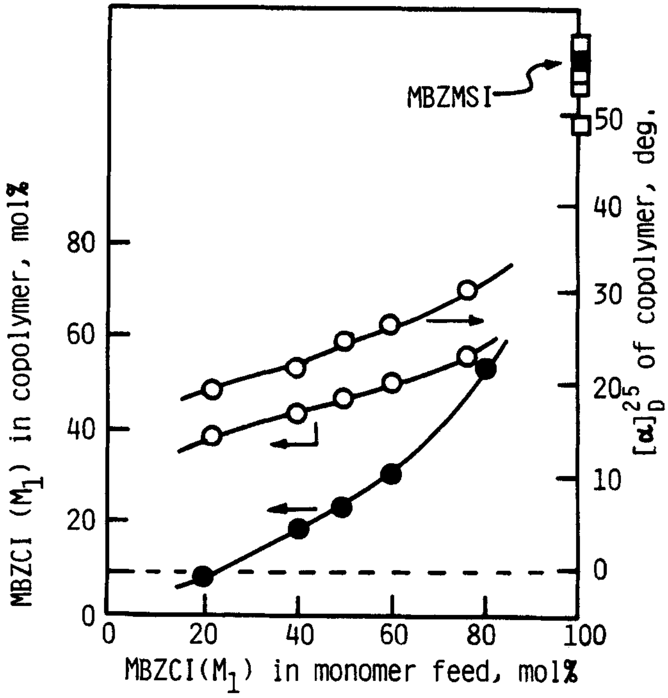


FIG. 1. Composition curves of the copolymers, (○) MBZCI-ST and (●) MBZCI-MMA, and correlation between MBZCI (mol%) in the monomer feed and $[\alpha]_D$ of the copolymer.

CD Spectra

As illustrated in Fig. 3, at the MBZCI monomer the negative Cotton effect was detected at about 300 nm based on the $n \rightarrow \pi^*$ transition of the carbonyl group in the maleimide ring. A strongly negative CD peak at 260 nm was observed in the following order: MBZCI-MMA copolymer < MBZCI homopolymer < MBZCI-ST copolymer. The mean residue ellipticity $[\theta]$ for N-α-methylbenzyl-α-methylsuccinimide (MBZMSI) was -400, as shown in Fig. 3.

Correlations between the molar rotation $[\Phi]$ or the mean residue ellipticity $[\theta]$ and MBZCI content in the copolymer are shown in Fig. 4. The molar rotation of MBZCI-MMA copolymer increased proportionally with an increase of the content of the optically active MBZCI unit, as shown in Fig. 4. Judging from this linear relation, the optical activity of MBZCI-MMA copolymer was attributed exclusively to the optically active MBZCI residue in the side chain. The molar rotation of

TABLE 4. Monomer Reactivity Ratios (r_1, r_2) for MBZCI (M_1) and ST (M_2) or MMA (M_2), and Q_1, e_1 Values for MBZCI

M_1	M_2	r_1[a]	r_2[a]	Q_1[b]	e_1[b]	Refs.
MBZCI	ST	0.12	0.24	0.91	1.09	-
MBZCI	MMA	0.23	2.83	0.34	1.04	-
MBZMI[c]	ST	0.027	0.094	1.50	1.64	16
MBZMI[c]	MMA	0.15	1.54	0.78	1.60	16
BZMI[d]	ST	0.02	0.04	2.94	1.87	22
BZMI[d]	MMA	0.14	1.54	0.79	1.63	22
BZCI[e]	ST	0.0	0.24	0.80	1.26	23
BZCI[e]	MMA	0.0	2.41			23

[a] Calculated according to the method of Mayo and Lewis.

[b] Calculated by assuming that Q_2 and e_2 values for ST and MMA were 1.0, -0.8 and 0.74, 0.40, respectively.

[c] N-α-Methylbenzylmaleimide.

[d] N-Benzylmaleimide.

[e] N-Benzylcitraconimide.

MBZCI-ST also increased with an increase of the optically active MBZCI unit content, as shown in Fig. 4. However, a deviation from linearity was detected, which was ascribed to the influence of the induced Cotton effects caused not only by the d-α-methylbenzyl group but also by new asymmetric carbons introduced in the copolymer main chain. Our several attempts to remove the optically active α-methylbenzyl group from the polymer and copolymer were unsuccessful. The conclusion described above, however, was supported by the fact that our experimental results were consistent with those reported by Kurokawa et al. [6]. That is, they reported that $[\alpha]_D$ of l-menthyl vinyl ether (l-MVE)-N-phenyl maleimide (N-PMI) copolymer increased with an increase of the content of the optically active l-MVE unit, but a deviation from linearity was observed. They concluded that this deviation was due to the introduction of a new carbon in the copolymer main chain from the ether cleavage reaction of l-MVE-N-PMI copolymer [6].

In addition, a linear correlation between the mean residue ellipticity [θ] of MBZCI-MMA copolymer and the content of the optically active MBZCI unit was observed. This suggests that chirality of MBZCI-MMA copolymer is due only to the optically active MBZCI residue in the side chain. On the other hand, plots of the ellipticity

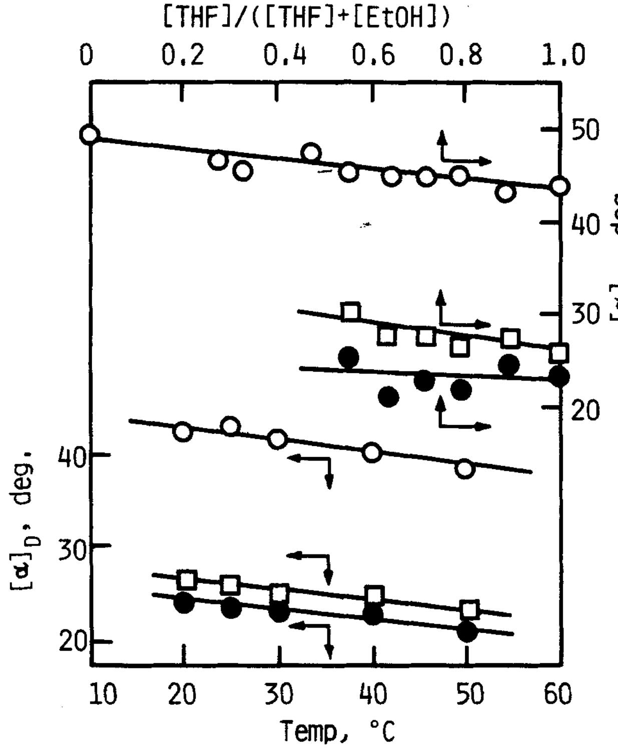


FIG. 2. Temperature dependence and solvent effect on the specific rotation ($[\alpha]_D$, c = ~1%; THF, l = 10 cm) of (○) MBZCI monomer, (●) MBZCI-ST (Experiment B-3), and (□) MBZCI-MMA (Experiment C-3).

[θ] of MBZCI-ST copolymer versus the MBZCI unit content gave a curve which had a maximum absolute value of ellipticity in 50 mol% of the MBZCI content. This also indicates that asymmetric induction took place in the copolymer backbone and might be associated with alternating copolymerization.

Judging from the fact that 1) the CD peak of MBZCI homopolymer was considerably stronger than that of N-α-methylbenzyl-α-methylsuccinimide (MBZMSI), which was a low molecular weight model compound of MBZCI homopolymer, as shown in Fig. 4; 2) and the number-average molecular weight of MBZCI homopolymer was small, with the carbon atoms in the backbone in the neighborhood of an initiator introduced by asymmetric induction, as illustrated in Scheme 2(a).

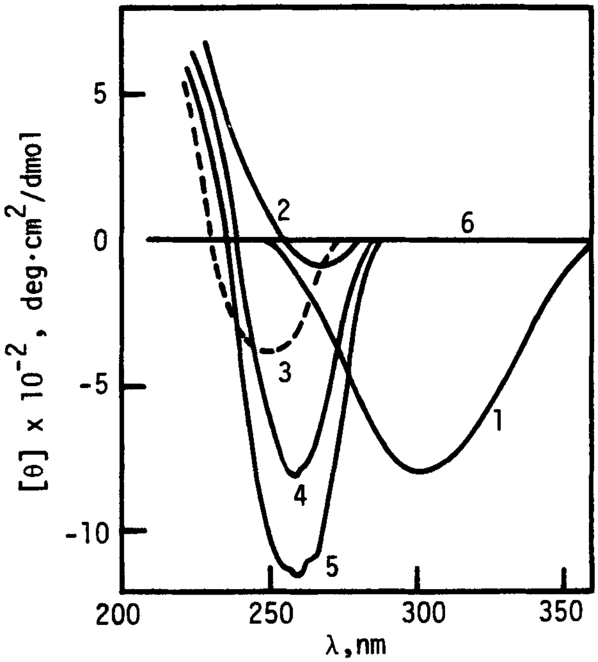


FIG. 3. CD spectra for MBZCI monomer and polymers (in THF, 1 mm quartz cell): (1) MBZCI monomer, (2) MBZCI-MMA, (3) MBZMSI, (4) MBZCI homopolymer, (5) MBZCI-ST, (6) dl-MBZCI monomer and polymer.

CONCLUSION

(1) Optically active N-α-methylbenzylcitraconimide (MBZCI) was polymerized using a radical initiator to obtain chiral polymers. The specific rotations of the homopolymers obtained were +48.6 to +56.7°. The number-average molecular weight for the homopolymers were between 1 400 and 1 900.

(2) The monomer reactivity ratios r_1, r_2 and Q_1, e_1 values obtained were: MBZCI (M_1)-ST (M_2): $r_1 = 0.12$, $r_2 = 0.24$, $Q_1 = 0.91$, $e_1 = 1.09$; MBZCI (M_1)-MMA (M_2): $r_1 = 0.23$, $r_2 = 2.83$, $Q_1 = 0.34$, $e_1 = 1.04$. The number-average molecular weight for the MBZCI-ST and MBZCI-MMA copolymers were 32 000 to 11 000 ($M_w/M_n = 1.2$ to 2.4) and 24 400 to 1 100 ($M_w/M_n = 1.2$ to 12.7), respectively.

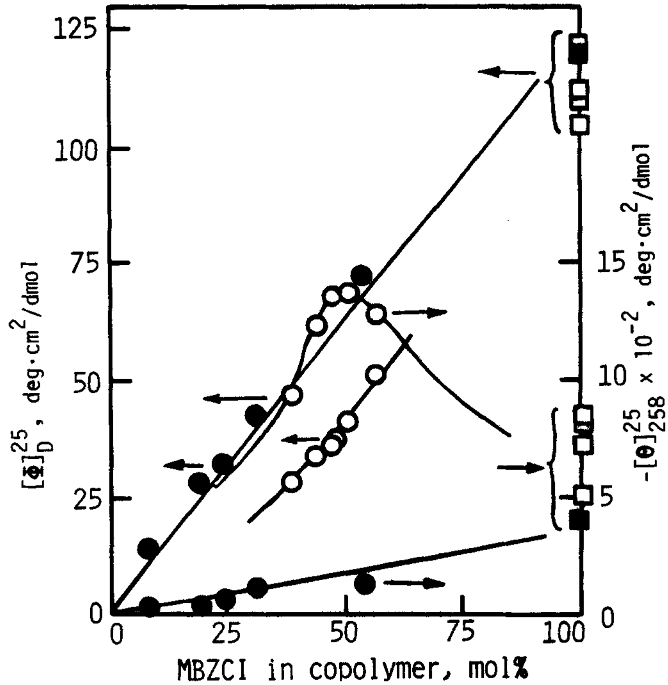
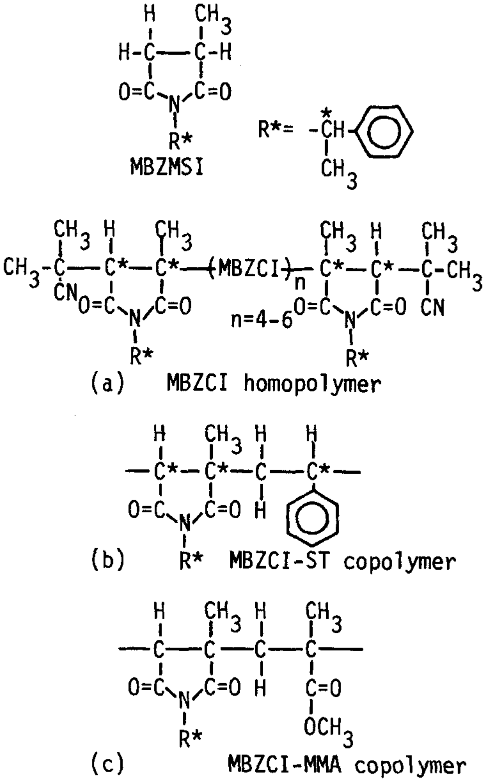


FIG. 4. Correlations between the molar rotation [Φ] in THF at 25°C or the mean residue ellipticity [θ] and [MBZCI] (mol%) in copolymers: (○) MBZCI-ST, (●) MBZCI-MMA, (□) MBZCI homopolymer, (■) MBZMSI.

(3) Attempts to cleave the optically active α-methylbenzyl group from the polymer and the copolymer main chain were unsuccessful. In the MBZCI-ST copolymer, however, the asymmetric carbon atoms were introduced in the copolymer main chain under the influence of an optically active α-methylbenzyl group, as shown in Scheme 2(b). This is because these copolymers were almost alternating copolymers as judged by the monomer reactivity ratios. In the MBZCI-MMA copolymer, asymmetric induction scarcely took place.



SCHEME 2.

ACKNOWLEDGMENT

The authors are very indebted to Mr M. Momoi for carrying out the elemental analysis.

REFERENCES

[1] N. Beredjick and C. Schuerch, J. Am. Chem. Soc., 80, 1933 (1958).
[2] G. J. Schmitt and C. Schuerch, J. Polym. Sci., 45, 313 (1960).
[3] K. Matsuzaki and T. Sugimoto, Makromol. Chem., 164, 127 (1973).
[4] N. Sakota, K. Kishibe, S. Shimada, and Y. Minoura, J. Polym. Sci., Polym. Chem. Ed., 12, 1782 (1974).

[5] K. Nishihara, A. Suzuoka, and N. Sakota, Ibid., 11, 2315 (1973).
[6] M. Kurokawa, T. Doiuchi, H. Yamaguchi, and Y. Minoura, Ibid., 16, 129 (1978).
[7] M. Kurokawa, Y. Minoura, Ibid., 17, 473 (1979).
[8] M. Kurokawa, H. Yamaguchi, and Y. Minoura, Ibid., 17, 485 (1979).
[9] M. Kurokawa, H. Yamaguchi, and Y. Minoura, Ibid., 17, 2441 (1979).
[10] M. Kurokawa, H. Yamaguchi, and Y. Minoura, Ibid., 17, 2253 (1979).
[11] M. Kurokawa and Y. Minoura, Ibid., 17, 3297 (1979).
[12] M. Kurokawa and Y. Minoura, Makromol. Chem., 181, 293 (1980).
[13] C. S. Marvel, R. L. Frank, J. Am. Chem. Soc., 64, 1675 (1942).
[14] H. Yamaguchi and Y. Minoura, J. Polym. Sci., Part A-1, 8, 1467 (1970).
[15] M. Kurokawa, H. Yamaguchi, and Y. Minoura, Makromol. Chem., 183, 115 (1982).
[16] T. Oishi and M. Fujimoto, J. Polym. Sci., Polym. Chem. Ed., 22, 2789 (1984).
[17] L. E. Coleman Jr., F. F. Bork, and H. Dunn Jr., J. Org. Chem., 24, 145 (1959).
[18] T. Oishi, M. Fujimoto, and T. Kimura, J. Polym. Sci., Polym. Chem. Ed., 20, 2999 (1982).
[19] T. Oishi and M. Fujimoto, Ibid., 20, 2727 (1982).
[20] F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc., 66, 1594 (1944).
[21] T. Alfrey Jr. and C. C. Price, J. Polym. Sci., 2, 101 (1947).
[22] T. Oishi and T. Kimura, Kobunshi Ronbunshu, 33, 685 (1976).
[23] T. Oishi, Polym. J., 13, 65 (1981).

Received February 14, 1985