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Polymer Vol. 36 No. 5, pp. 941-948, 1995
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0032-3861/95/$10.00+0.00

Copolymerization of optically active *N*-(L-menthoxycarbonylmethyl)maleimide with *N*-phenyl- or *N*-benzylmaleimide

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(Received 2 May 1994; revised 18 August 1994)

Optically active *N*-(L-menthoxycarbonylmethyl)maleimide (MGMI; M_1) was radically and anionically copolymerized with *N*-phenylmaleimide (PhMI; M_2) or *N*-benzylmaleimide (BZMI; M_2), in benzene at 60°C and toluene at 0°C, respectively. The monomer reactivity ratios (r_1, r_2) were calculated. In both the radical and anionic copolymerization systems, relationships between the specific rotations and the content (wt%) of MGMI in the copolymers gave a deviation from a straight line connecting 0° with $[\alpha]_D$ of the pure homopolymer. In anionic copolymerizations, there was the possibility of occurrences of an asymmetric induction into the copolymer main chain and an asymmetric perturbation of the side-chain chromophores, judging from the chiroptical properties of model compounds. The circular dichroism (c.d.) spectra of the copolymers obtained with radical and anionic initiators were different. This suggests that the main chains of the respective copolymers contain different conformational structures.

(Keywords: optical activity; maleimide copolymers; c.d. spectroscopy)

INTRODUCTION

In the polymerization of optically active *N*-(L-menthoxycarbonylmethyl)maleimide (MGMI), the specific rotations ($[\alpha]_D$s) were very different between the polymers obtained with different initiators (azobisisobutyronitrile (AIBN), $[\alpha]_D = -56.1$ to -58.1; n-butyllithium (n-BuLi), $[\alpha]_D = -41.1$ to -44.8)[1]. In these polymerization systems, asymmetric induction into the polymer main chain[2] and asymmetric perturbation[3-5] of the chromophores took place, judging from the chiroptical properties of a model compound for poly(MGMI). In fact, a new asymmetric centre (a stereogenic centre) appeared in the repeat units of the optically active *N*-(R-substituted)maleimide (RMI) because of the threo-diisotactic structure of the RMI polymer main chain. Polymerizations of cyclic alkene derivatives can yield two *trans*-openings of the double bond, i.e. (*S*,*S*)- and (*R*,*R*)-chiral centres. If one of these predominates over the other, the polymer that is obtained can be optically active[2]. In the radical copolymerizations of MGMI with styrene (ST) or methyl methacrylate (MMA), the relationship between the content (wt%) of MGMI in the copolymers and the specific rotations gave in practice a slight deviation from a straight line connecting 0° with $[\alpha]_D$ of *the homopolymer*. However, the relationship showed no deviation from a straight line connecting 0° with $[\alpha]_D$ of *the model compound for poly(MGMI)* when the content of MGMI in the copolymer was less than 60 wt%. In addition, there was no asymmetric induction or asymmetric perturbation in the model compound. Accordingly, in the copolymerization of MGMI with ST or MMA, asymmetric induction and asymmetric perturbation could take place only if there was more than 60 wt% of MGMI in the copolymer[1].

Recently, we reported on the polymerizations and copolymerizations of optically active *N*-(α-methylbenzyl)maleimide (MBZMI)[6], *N*-(4-*N'*-(α-methylbenzyl)aminocarbonylphenyl)maleimide (MBPM)[7,8], *N*-(4-*N'*-(α-methylbenzyl)aminocarbonylmethyl)maleimide (MBCM)[9], and *N*-(cholesteroxycarbonylmethyl)maleimide (ChMI)[10]. In these reports we suggested the possibility that a new asymmetric centre (i.e. a stereogenic centre) appeared in the repeat units of the optically active *N*-(R-substituted)maleimide (RMI). In the copolymerizations of the RMI monomers (MBZMI, MBPI, MBCM, and ChMI) with ST or MMA, an asymmetric induction into the copolymer main chain was always observed, regardless of the RMI content in the copolymer. In the homo- and copolymerization systems, an *asymmetric perturbation*[2,3] of the side-chain chromophores should also have been considered.

In this present study, a vinyl type monomer, such as ST or MMA, was not present, but a 1,2-disubstituted cyclic ethylene type monomer, i.e. a *cis*-cyclic alkene, was used as the comonomer of MGMI. The objective of this work is to explore the reactivities and chiroptical properties of the resulting copolymers in the copolymerization of a chiral *cis*-cyclic alkene with an achiral *cis*-cyclic alkene. In this case, both radical and anionic copolymerizations of an optically active MGMI with *N*-phenylmaleimide (PhMI) or *N*-benzylmaleimide (BZMI) were performed in benzene at 60°C and in toluene at 0°C, respectively.

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From the results obtained, the monomer reactivity ratios were determined. Asymmetric induction into the copolymer main chain and asymmetric perturbation of the side-chain chromophores are discussed, based on the specific rotations and c.d. spectroscopy measurements of the copolymers. The polymerization reactivities and chiroptical properties are discussed, and compared with those reported previously for poly(MGMI-*co*-ST)[1], poly(MGMI-*co*-MMA)[1] and other copolymers[6–9] containing the α-methylbenzyl group.

There have been many reports[11–17] including patents (e.g. see ref. 18), on the polymerizations and copolymerizations of RMI monomers. However, only a few investigations on the polymerization of optically active RMI have been made[19–21], except for those from our laboratory. Accordingly, the polymerization reactivities and chiroptical properties of these chiral RMI materials have not yet been properly investigated.

EXPERIMENTAL

Materials

The MGMI monomer was synthesized from maleic anhydride, glycine, and L-menthol, according to the method reported previously[1]. MGMI: total yield = 32%; b.p. 154–155°C/8.5 × 10^{-2} mmHg; $[\alpha]_D = -48.1°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; THF). I.r. (cm^{-1}): 1750 and 1730 (C=O); 1640 (C=C); 1200 and 1170 (OC=O). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 6.68 (s, 2H, CH=CH); 4.70 (m, 1H, O–CH–); 4.20 (s, 2H, N–CH_2CO); 2.18–0.70 (m, 18H, protons in menthyl group). Elemental analysis (%): found, C = 65.30, H = 8.24, N = 4.98; calculated for $C_{16}H_{23}O_4N$, C = 65.51, H = 7.90, N = 4.77.

A model compound of poly(MGMI)[1], namely *N*-(L-menthoxycarbonylmethyl)succinimide (MGSI), was used as a reference in this work. MGSI: 145°C/2 × 10^{-2} mmHg; $[\alpha]_D = -47.6°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; THF).

PhMI and BZMI were synthesized from maleic anhydride and the corresponding amines, according to the usual method of synthesis for RMI compounds[22]: PhMI, m.p. 91.0°C and BZMI, m.p. 70°C.

Other materials

Benzene, tetrahydrofuran (THF), toluene, and other solvents were purified by the usual methods. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallizing twice from chloroform, while commercially available n-butyllithium (n-BuLi), as a solution in hexane, was used without further purification.

Radical and anionic copolymerizations

Radical copolymerization was performed with AIBN as the initiator, in benzene (sealed tube) at 60°C. After polymerization, the polymer solution was poured into a large amount of methanol to precipitate the polymer; the latter was purified by reprecipitation three times from THF/methanol. The polymer was then filtered and dried *in vacuo* at 40°C. The composition of the resulting copolymer was determined from its ^{1}H n.m.r. spectra.

Anionic copolymerization was achieved in toluene at 0°C by using n-BuLi as the catalyst under a nitrogen atmosphere. The polymerization was terminated by adding a few drops of methanol, by using a syringe, after which the solution was poured into a large amount of methanol. The resulting polymer was purified by reprecipitation three times from THF/methanol, and was then filtered and dried *in vacuo* at 40°C.

Measurements

N.m.r. spectra were obtained by using a JEOL JNM-MH-100 spectrometer. D-line specific rotations were measured with a Jasco DIP-140 instrument (Japan Spectroscopic Co.) at 25°C. Optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) spectra ($c = 0.05$–0.1 g dl^{-1}, $l = 1$ mm, THF) were obtained at 25°C by the use of a Jasco J-20C spectrometer (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor. U.v. spectra ($c = 0.01$–0.04 g dl^{-1}, $l = 1$ mm, THF) were obtained with a Shimadzu 200A spectrophotometer. The molecular weights of the copolymers were measured by gel permeation chromatography (g.p.c.), on a Shimadzu LC 3A machine equipped with a data processor, using a u.v.

Table 1 Radical copolymerizations of MGMI (M_1) with PhMI (M_2) or BZMI (M_2) in benzene (6 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polymerization time (h)	Conversion (%)	M_1 in copolymer[b] (mol%)	$\bar{M}_n$[c] ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n$	$[\alpha]_D^{25}$[d] (deg)
1-1	PhMI	10.0	10.0	40.5	10.7	4.8	2.1	−9.2
1-2	PhMI	30.0	10.0	24.5	31.8	4.8	1.9	−21.5
1-3	PhMI	50.0	10.0	20.5	50.8	5.0	1.5	−33.3
1-4	PhMI	70.0	10.0	22.1	70.8	5.3	1.5	−42.3
1-5	PhMI	90.0	10.0	25.8	87.3	5.6	1.6	−50.5
2-1	BZMI	10.1	8.0	29.9	15.2	5.4	2.9	−6.9
2-2	BZMI	30.0	8.0	21.0	40.4	8.3	2.2	−26.6
2-3	BMZI	50.0	8.0	24.9	52.6	11.2	2.1	−33.1
2-4	BZMI	70.0	8.0	24.9	72.4	12.1	2.0	−41.8
2-5	BZMI	89.9	8.0	21.1	89.0	13.9	2.1	−49.9

[a] [AIBN] = 1.0 × 10^{-2} mol l^{-1}; $M_1 + M_2 = 2.0$ g
[b] Determined by ^{1}H n.m.r. spectroscopy
[c] Determined by g.p.c.
[d] Conditions: $c = 1.0$ g dl^{-1}; $l = 10$ cm; THF

detector, THF as the eluent (1.2 ml min^{-1}) and Shimadzu polystyrene gel (HGS-10-15-20-40).

RESULTS AND DISCUSSION

Radical copolymerization of MGMI with PhMI or BZMI

The radical copolymerizations of MGMI (M_1) with PhMI (M_2) or BZMI (M_2) were performed with AIBN in benzene at 60°C. The results are summarized in *Table 1*. The copolymerizations proceeded homogeneously throughout; the resulting copolymers were white powders and optically active. The rates of copolymerization of MGMI with PhMI or BZMI were much smaller than those previously reported for MGMI with ST or MMA. The number-average molecular weights ($\bar{M}_n$s) of the poly(MGMI-*co*-PhMI)s were generally lower than those of the poly(MGMI-*co*-BZMI)s, which were themselves lower than those of the poly(MGMI-*co*-ST) and poly(MGMI-*co*-MMA) materials[1].

The copolymer composition curves of the MGMI–PhMI and MGMI–BZMI systems, as shown in *Figure 1*, both indicated a type of ideal copolymerization along an azeotropic line. The monomer reactivity ratios, r_1 and r_2, determined by both the Integration method[23] and the High Conversion method[24], were as follows: $r_1=0.79$, and $r_2=0.80$ in the MGMI–PhMI system, and $r_1=0.85$, and $r_2=0.48$ in the MGMI–BZMI system.

Anionic copolymerization of MGMI with PhMI or BZMI

The anionic copolymerizations of MGMI (M_1) with PhMI (M_2) or BZMI (M_2) were performed with n-BuLi in toluene at 0°C. The results are summarized in *Table 2*. The copolymerizations proceeded homogeneously throughout; the copolymers obtained were white powders and optically active. The $\bar{M}_n$ values of the poly(MGMI-*co*-PhMI)s were 1.8×10^3 to 2.7×10^3, which were generally similar to those of the poly(MGMI-*co*-BZMI) materials.

The copolymer composition curves of the MGMI-PhMI and MGMI-BZMI systems are shown in *Figure 2*. Each composition curve of the MGMI–PhMI or MGMI–BZMI systems was almost the same as that obtained by the corresponding radical copolymerization method. In both of the radical and anionic systems, the content of BZMI in the polymer was slightly higher than that of PhMI. The monomer reactivity ratios, r_1 and r_2, were as follows: $r_1=0.64$, and $r_2=1.19$ in the MGMI–PhMI system, and $r_1=0.52$, and $r_2=0.71$ in the MGMI–BZMI system.

Chiroptical properties of the copolymers

Figure 3 shows the relationship between the specific rotations and content (wt%) of the monomer unit of MGMI in both radical copolymerization systems. As can be seen from this figure, the specific rotation of poly(MGMI) is different from that of the model compound (MGSI) which means that asymmetric induction and/or asymmetric perturbation has taken place[1]. The specific rotations of a mixture of just poly(MGMI) and poly(PhMI) gave a good linear relationship, as shown in

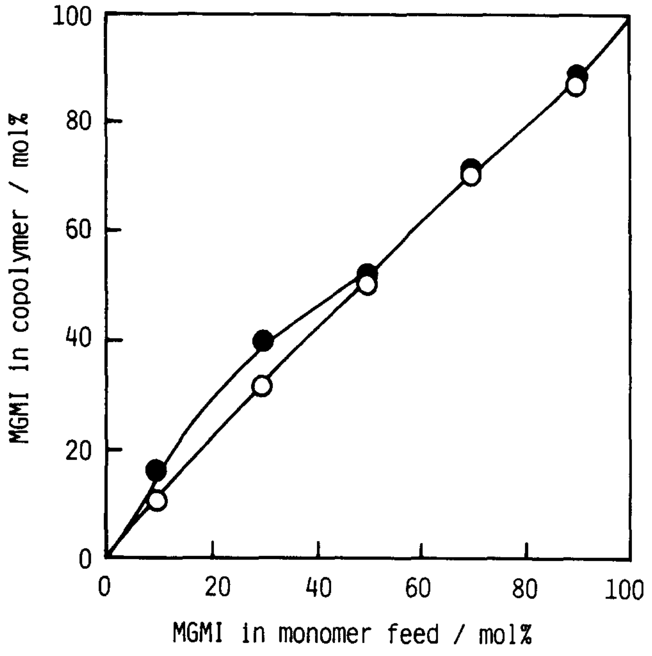


Figure 1 Copolymer composition curves for radical copolymerizations: (○) MGMI–PhMI; (●) MGMI–BZMI systems

Table 2 Anionic copolymerizations of MGMI (M_1) with PhMI (M_2) or BZMI (M_2) in toluene (10 ml) at 0°C[a]

Run	M_2	M_1 in monomer (mol%)	Polymerization time (h)	Conversion (%)	M_1 in copolymer[b] (mol%)	$\bar{M}_n$[c] ($\times10^{-3}$)	$\bar{M}_w/\bar{M}_n$	$[\alpha]^{25}_{D}$[d] (deg)
3-1	PhMI	10.0	20.0	22.2	9.9	7.0	2.7	−3.1
3-2	PhMI	30.0	20.0	21.9	23.4	7.1	2.2	−16.1
3-3	PhMI	50.0	20.0	26.8	38.0	6.8	2.2	−26.2
3-4	PhMI	70.0	20.0	29.9	62.5	6.6	2.1	−35.9
3-5	PhMI	90.0	10.0	28.1	89.6	6.3	1.8	−39.3
4-1	BZMI	10.1	20.0	19.3	10.0	5.8	2.1	−3.2
4-2	BZMI	30.0	20.0	19.2	32.0	5.8	2.9	−13.4
4-3	BMZI	50.0	20.0	24.5	52.7	4.5	2.7	−23.9
4-4	BZMI	69.9	20.0	30.4	66.3	4.5	2.3	−38.9
4-5	BZMI	90.0	10.0	27.8	83.3	3.3	1.8	−43.7

[a] [n-BuLi] = 1.0×10^{-2} mol l^{-1}; $M_1+M_2=2.0$ g
[b] Determined by ^{1}H n.m.r. spectroscopy
[c] Determined by g.p.c.
[d] Conditions: $c=1.0$ g dl^{-1}; $l=10$ cm; THF

Figure 3 (Δ). The absolute values of the specific rotations of the poly(MGMI-*co*-PhMI) materials increased with the content (wt%) of the MGMI unit. However, there was a slight deviation from the straight line connecting 0° with *the specific rotation of pure poly(MGMI)*. A deviation from the straight line connecting 0° with *the specific rotation of the model compound* was observed only when the content of MGMI was more than ~60 wt%. This suggests that asymmetric induction into the copolymer main chain and asymmetric perturbation of the side-chain chromophores appeared as the content of the optically active MGMI unit in the copolymer increased. In the poly(MGMI-*co*-BZMI)s, as shown in *Figure 3*, a similar tendency could be observed. Deviations in the plots for poly(MGMI-*co*-PhMI) and poly(MGMI-*co*-BZMI) were identical to those observed for the poly(MGMI-*co*-ST) and poly(MGMI-*co*-MMA) systems reported previously[1], as shown in *Figure 3* (□, ■). For the radical copolymerizations, the effects of the 1,2-disubstituted cyclic olefins, i.e. RMI, on the chiroptical properties of the MGMI copolymers were found to be similar to those of ST and MMA.

The relationships between the specific rotations and the contents (wt%) of the monomer unit of MGMI in both of the anionic copolymerization systems are shown in *Figure 4*. The absolute values of the specific rotations of poly(MGMI-*co*-PhMI)s increased with an increase in the content of the MGMI unit, and had a slight deviation from the straight line connecting 0° with the specific rotation of poly(MGMI) (□ in *Figure 4*) or MGSI (the model compound for poly(MGMI)) (■ in *Figure 4*). The curves shown in *Figure 4* were different from those obtained for the radical copolymerizations (*Figure 3*). The difference in the deviation among the polymerization systems may result from an excess of the (*R*,*R*-) or (*S*,*S*-) chiral centres in the main chain, i.e. differences in the stereogenic centres, as illustrated in *Scheme 1* (type I). The (*S*,*S*-) or (*R*,*R*-) repeat units, which are formed by

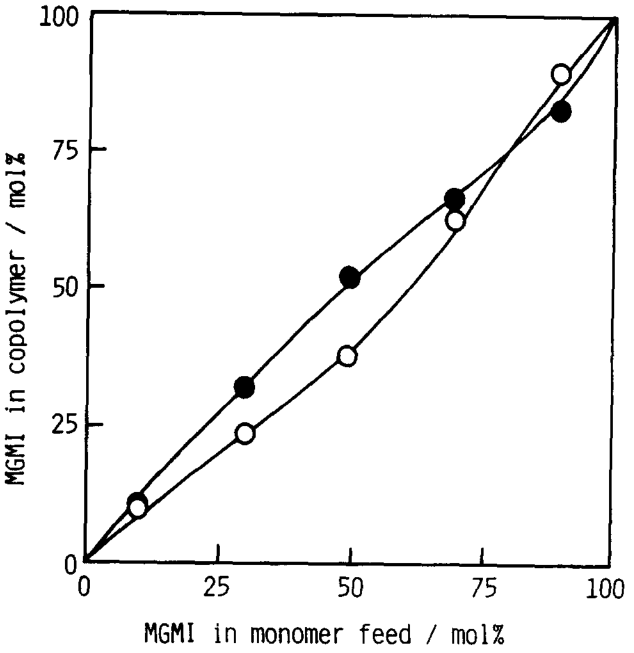


Figure 2 Copolymer composition curves for anionic copolymerizations: (○) MGMI–PhMI; (●) MGMI–BZMI systems

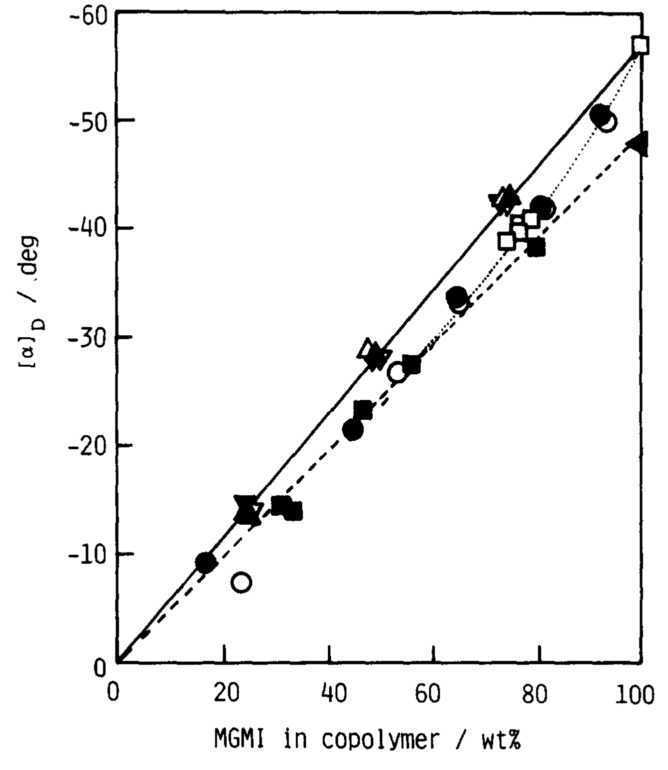


Figure 3 Dependence of the specific rotation $[\alpha]_D^{25}$ on the content (wt%) of MGMI in the various copolymer systems: (●) poly(MGMI-*co*-PhMI)s; (○) poly(MGMI-*co*-BZMI)s; (□) poly(MGMI-*co*-ST)s; (■) poly(MGMI-*co*-MMA)s; (△) a mixture of poly(MGMI) and poly(PhMI); (▲) a mixture of poly(MGMI) and poly(BZMI); (▽) a mixture of poly(MGMI) and poly(ST); (▼) a mixture of poly(MGMI) and poly(MMA); (◀) the model compound for poly(MGMI), MGSI. All polymerizations were carried out by using AIBN in benzene

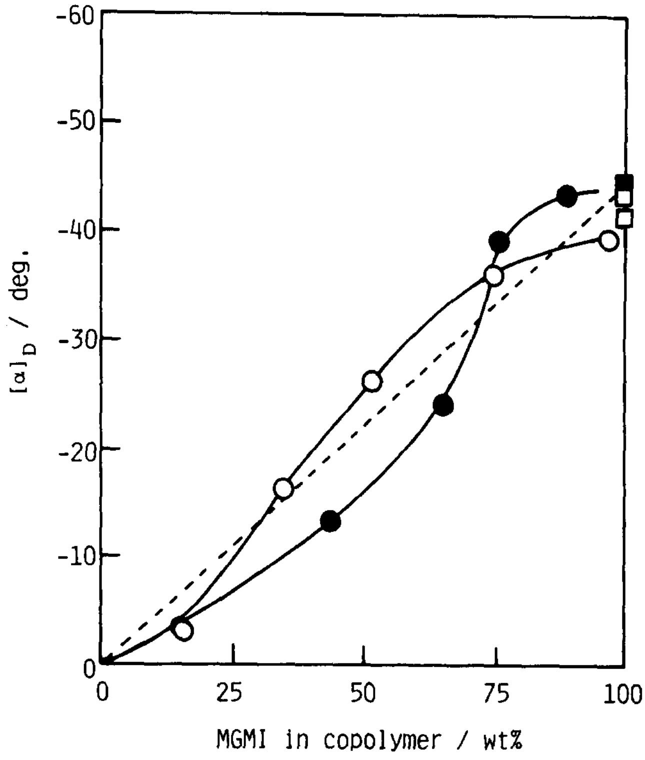
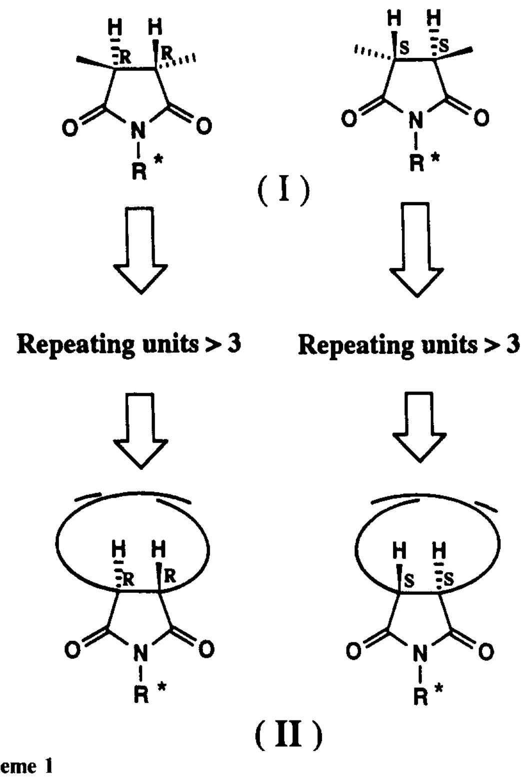


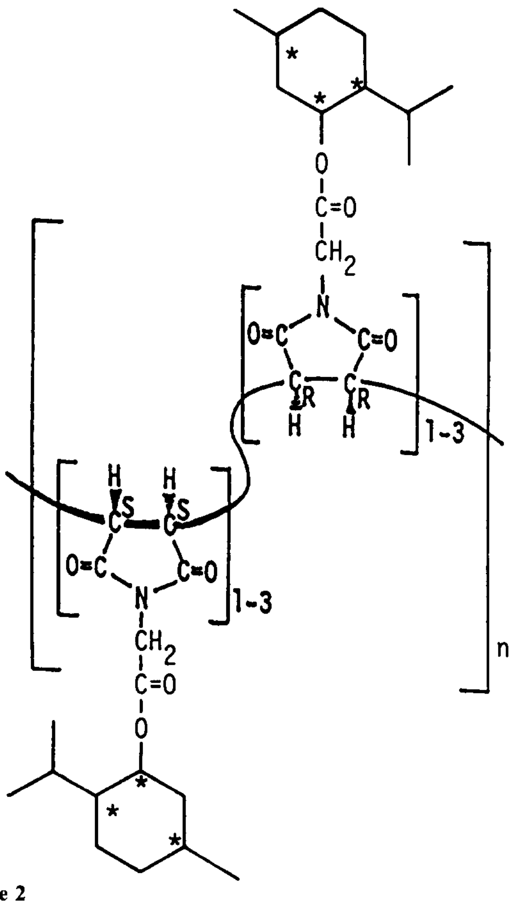
Figure 4 Dependence of the specific rotation $[\alpha]_D^{25}$ on the content (wt%) of MGMI in the various copolymer systems: (○) poly(MGMI-*co*-PhMI)s; (●) poly(MGMI-*co*-BZMI)s; (□) poly(MGMI); (■) the model compound for poly(MGMI), MGSI. All polymerizations were carried out by using n-BuLi in toluene

the threo-diisotactic addition of RMI, can form a helix [*Scheme 1* (type II)]. In this case, both of the stereogenic centres in the main chains and in the chiral side chains can be influenced by the neighbouring chromophores[2-5].

In both of the MGMI–PhMI and MGMI–BZMI systems, the relationship between the specific rotations of the copolymers and the temperature gave straight lines, with very small slopes (the temperature coefficients ($\Delta[\alpha]_D/\Delta T$) = 0.10 to 0.12). Thus, a complete helix is unlikely in the poly(MGMI-*co*-PhMI) and poly(MGMI-*co*-BZMI) systems, and also in the homopolymers[1]. The polymers and copolymers may adopt an almost linear structure, as illustrated in *Scheme 2*, i.e., more than four successive (*S*,*S*-) or (*R*,*R*-) units may not be present. More than a four-unit (*S*,*S*-) or (*R*,*R*-) sequence would produce a helix, as shown in *Scheme 1* (type II). This can be confirmed by inspection of a poly(MGMI) assembled using a ball-and-stick model (HGS model).



Scheme 1



Scheme 2

Figures 5 and *6* show the u.v. and typical c.d. spectra, respectively, of the poly(MGMI-*co*-PhMI) and poly(MGMI-*co*-BZMI) materials obtained by using AIBN.

In a typical c.d. spectrum for poly(MGMI-*co*-PhMI) system, one negative and one positive peak, at ~250 and at a wavelength lower than 215 nm, respectively, were observed. These peaks were due to the $\pi \rightarrow \pi^*$ transition of the phenyl groups in the PhMI units and to the $n \rightarrow \pi^*$

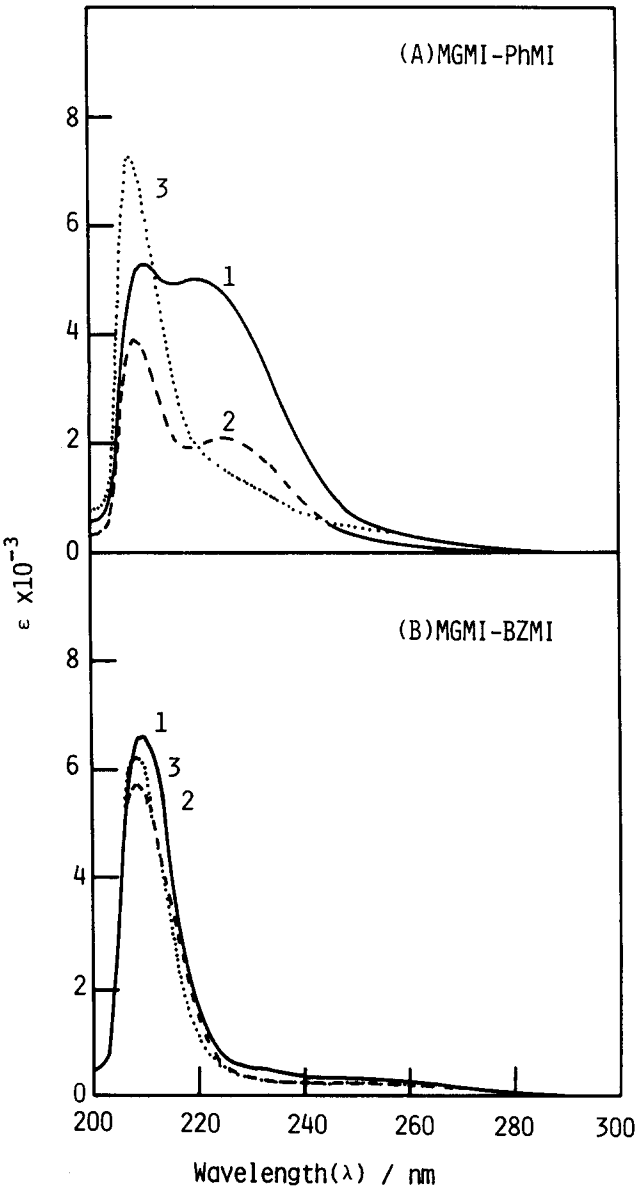


Figure 5 U.v. spectra of the copolymers (c = 0.01–0.04 g dl^{-1}, l = 1 mm, THF). (a) Poly(MGMI-*co*-PhMI)s; (1) run 1-1; (2) run 1-3; (3) run 1-5. (b) Poly(MGMI-*co*-BZMI)s: (1) run 2-1; (2) run 2-3; (3) run 2-5

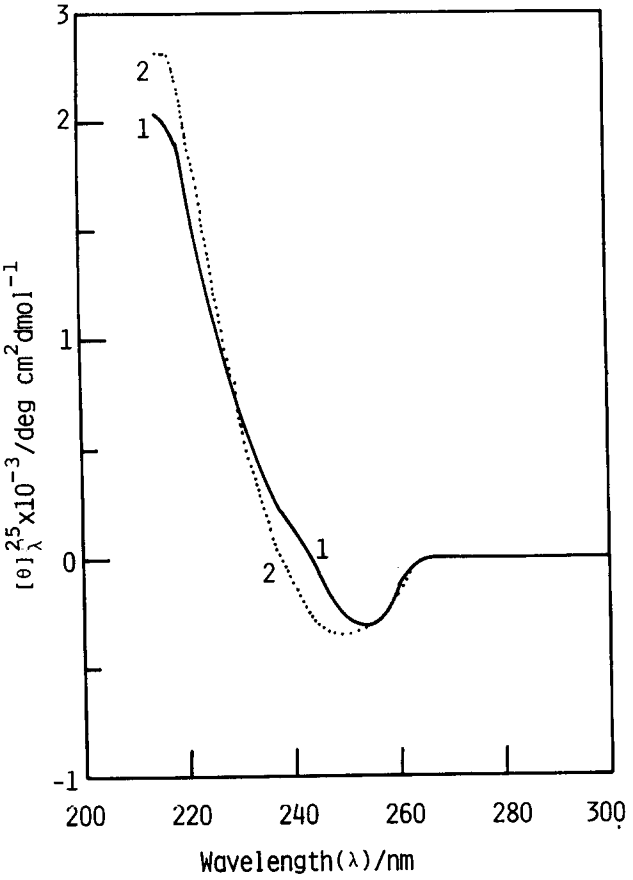


Figure 6 C.d. spectra of the copolymers obtained with AIBN (c=0.05–0.1 g dl^{-1}, l=0.1 mm, THF): (1) poly(MGMI-*co*-PhMI) (run 1-3); (2) poly(MGMI-*co*-BZMI) (run 2-3)

transition of the carbonyl groups in the MGMI and PhMI units, as shown in *Figures 5a* and *6* (curve 1). The c.d. spectra of the poly(MGMI-*co*-BZMI)s obtained using AIBN were similar to those of poly(MGMI-*co*-PhMI) obtained using the same initiator, as exhibited in *Figures 5b* and *6* (curve 2).

In the c.d. spectra of poly(MGMI-*co*-PhMI) obtained with n-BuLi (runs 3-4 and 3-5), as shown in *Figure 7a*, a positive peak appeared at ~260 nm. However, the c.d. peaks of poly(MGMI-*co*-BZMI) obtained with n-BuLi were significantly influenced by the MGMI content of the copolymer, as shown in *Figure 7b*. The u.v. spectra for these copolymers were similar to the corresponding set of curves illustrated in *Figure 5*.

When the u.v. and c.d. spectra in THF are measured at a wavelength lower than 230 nm a solvent effect can be significantly observed. When the c.d. spectra of a RMI containing an ester group as the *N*-substituent were measured in THF using a 1 mm quartz cell, a c.d. peak was observed at 225–220 nm[1,25,26]. Using a 0.1 mm quartz cell, the c.d. peak appears at ~215 nm, i.e. in the region similar to that of λ_{max} in the u.v. spectra. In the c.d. spectra of a RMI containing an amide group, obtained in THF using a 1 mm quartz cell, a c.d. peak was observed in the region 230–225 nm[9]. Using a 0.1 mm quartz cell, the c.d. peak appears in the region 225–220 nm. However, the u.v. peaks appear in the same region.

Figure 8 depicts typical g.p.c. curves for the copolymers obtained with n-BuLi. In general, the copolymers obtained with AIBN and n-BuLi had one peak in their g.p.c. curves, except for curves 2 and 3 shown in

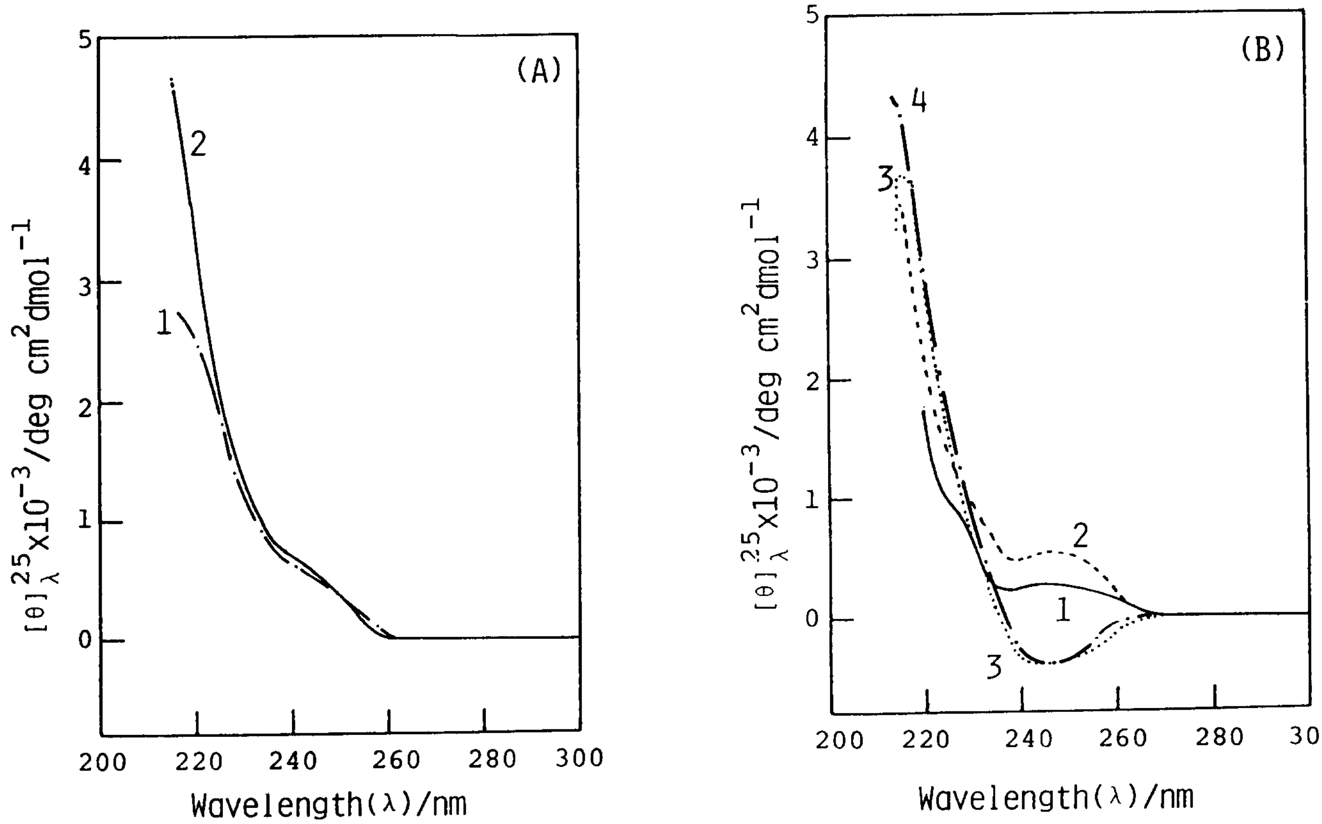


Figure 7 C.d. spectra of the copolymers obtained with n-BuLi (c=0.05–0.1 g dl^{-1}, l=0.1 mm, THF). (a) Poly(MGMI-*co*-PhMI): (1) run 3-4; (2) run 3-5. (b) Poly(MGMI-*co*-BZMI): (1) run 4-2; (2) run 4-3; (3) run 4-4; (4) run 4-5

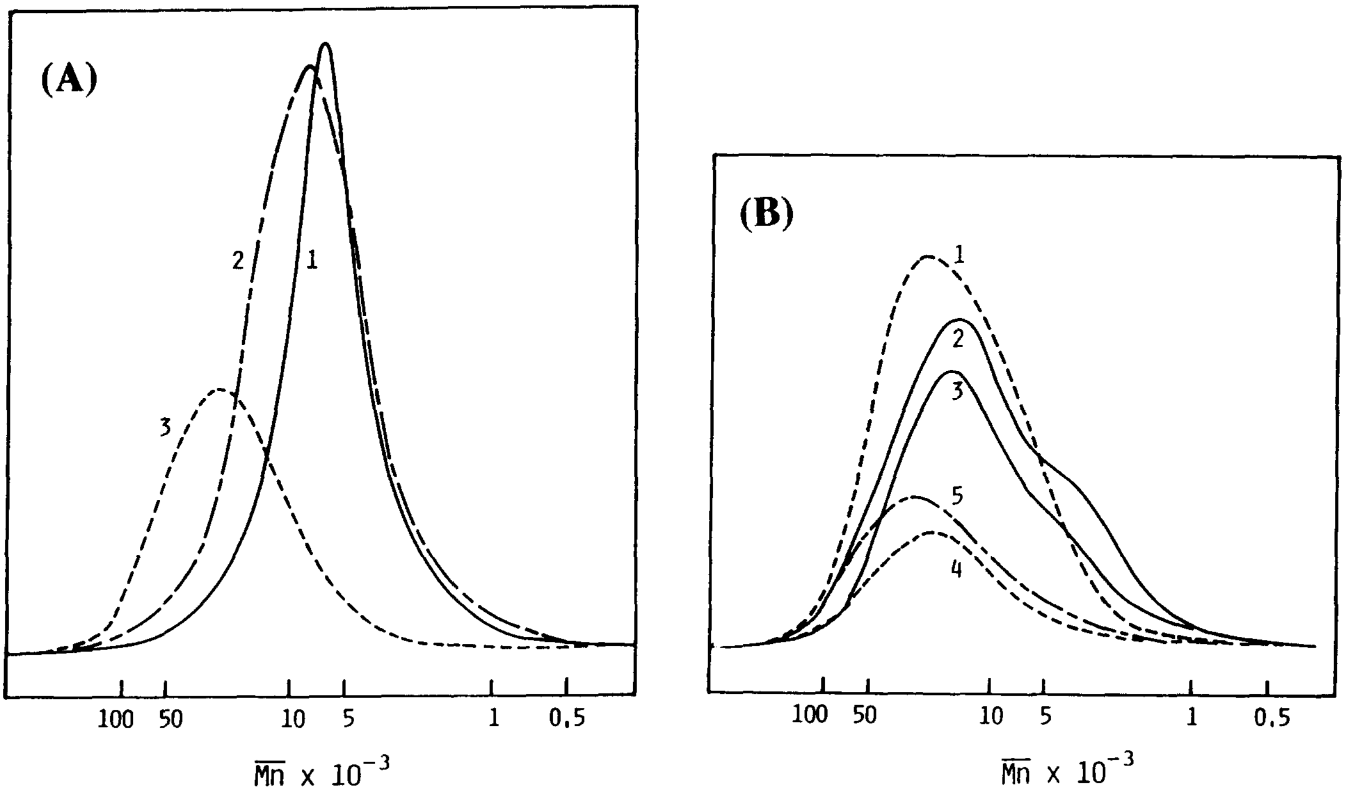


Figure 8 G.p.c. curves for the copolymers. (a) Poly(MGMI-*co*-PhMI)s obtained with: (1) AIBN (run 1-3); (2) n-BuLi (run 3-3); (3) n-BuLi (run 3-5). (b) Poly(MGMI-*co*-BZMI)s obtained with: (1) AIBN (run 2-3); (2) n-BuLi (run 4-2); (3) n-BuLi (run 4-3); (4) n-BuLi (run 4-4); (5) n-BuLi (run 4-5)

Figure 8b. However, the g.p.c. curves of these copolymers (runs 4-2 and 4-3) (see *Table 2*) possessed one large peak, as well as a shoulder at $M_n \sim 4000$.

As can be seen from *Figure 7*, the resulting copolymers gave characteristic c.d. peaks at ~250 nm. This suggests that the chiroptical properties of the copolymers were strongly affected by the comonomers. Asymmetric polymerizations of achiral RMI with n-BuLi-(−)-sparteine gave optically active RMI polymers having relatively high specific rotations (e.g. *N*-(cyclohexyl)maleimide, $[\alpha]_D \sim -40°$)[27,28]. It seemed that this asymmetry was attributed to the formation of stereogenic centres, i.e. threo-diisotactic structures. The c.d. patterns of the resulting RMI polymers indicated a large negative or a positive Cotton effect at ~250 nm[27,28]. In the anionic copolymerizations of MGMI with RMI (PhMI, BZMI), the chiroptical properties may be appreciably influenced by asymmetric induction and asymmetric perturbation, based on the formation of stereogenic centres.

The RMI polymers produced when using radical initiators may contain not only threo-diisotactic, but also syndiotactic structures, as reported by Cubbon[29]. However, in the radical copolymerizations of MGMI with RMI, the resulting copolymers contained less stereogenic centres than the copolymers obtained using n-BuLi. The deviations from linearity in the radical copolymerizations of MGMI with PhMI or BZMI were similar to those of MGMI with ST and MMA, as shown in *Figure 3*. Thus, there were no differences between the vinyl monomers (i.e. ST, MMA) and the 1,2-substituted ethylene type monomers (i.e. PhMI, BZMI) from the viewpoint of asymmetric induction and asymmetric perturbation. In the *N*-(α-methylbenzyl)-maleimide (MBZMI) materials, the deviations were apparently different[30]. The deviations in the MBZMI–PhMI and MBZMI–(*N*-(cyclohexyl)maleimide (CHMI)) systems were much smaller than those of the MBZMI–ST and MBZMI–MMA materials. The difference between the MGMI and MBZMI systems may result from different optically active groups and/or connecting types of chiral group, i.e. ester and amide groups.

CONCLUSIONS

(1) In both radical copolymerizations of MGMI with PhMI and BZMI, the relationship between the specific rotations of the copolymers and the contents of MGMI indicated a small deviation from a straight line connecting 0° with the specific rotation of the pure poly(MGMI) or the model compound for poly(MGMI) when the content of the MGMI unit was more than 60 wt% in the copolymer. The deviation was similar to that observed in the poly(MGMI-*co*-ST) and poly(MGMI-*co*-MMA) systems reported previously.

(2) The deviations could be attributed to an asymmetric induction into the copolymer main chain and an asymmetric perturbation of the side-chain chromophores.

(3) In both of the anionic copolymerizations, considerable deviations from the straight line connecting 0° with the specific rotation of pure poly(MGMI) or the model compound were observed. In this case, the deviations were ascribed to asymmetric induction and asymmetric perturbation.

(4) From the results of the radical copolymerizations of MGMI(M_1) with PhMI(M_2) or BZMI(M_2), the monomer reactivity ratios (r_1, r_2) were determined as follows: $r_1 = 0.79$, and $r_2 = 0.80$ in the MGMI–PhMI

system, and $r_1 = 0.85$ and $r_2 = 0.48$ in the MGMI–BZMI system.

(5) From the results of the anionic copolymerizations of MGMI(M_1) with PhMI(M_2) or BAMI(M_2), the monomer reactivity ratios (r_1, r_2) were determined as follows: $r_1 = 0.64$, and $r_2 = 1.19$ in the MGMI–PhMI system, and $r_1 = 0.52$, and $r_2 = 0.71$ in the MGMI–BZMI system.

ACKNOWLEDGEMENT

We are indebted to Mr M. Momoi for the elemental analysis.

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