Anionic Copolymerization of (S)- or (RS)- α -Methylbenzyl Methacrylate and Methyl Methacrylate

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ABSTRACT: Anionic copolymerizations of (S)- or (RS)- α -methylbenzyl methacrylate (MBMA, M_1) and methyl methacrylate (MMA, M_2) were carried out by butyllithium in toluene and in tetrahydrofuran (THF) at -78°C . The monomer reactivity ratios were $r_1=0.78$ and $r_2=1.68$ in toluene and $r_1=1.52$ and $r_2=2.04$ in THF, where (S)- and (RS)-MBMAs showed the same reactivity in the same solvent. The isotacticity of poly[(RS)-MBMA] obtained in toluene was lower than that of poly[(S)-MBMA], while the copolymer of (RS)-MBMA and MMA showed an isotacticity nearly equal to that of the corresponding copolymer of (S)-MBMA and MMA. The copolymers obtained in THF were syndiotactic. The values of σ_{12} and σ_{21} , the probabilities of forming a *meso* dyad between M_1 or M_2 chain end and M_2 or M_1 monomer, were calculated assuming the terminal model statistics for the copolymerization in THF. The copolymers of (S)-MBMA and MMA showed negative optical rotations having absolute values slightly higher than those calculated from the rotation of poly[(S)-MBMA].

KEY WORDS Anionic Copolymerization / (S)- α -Methylbenzyl Methacrylate / (RS)- α -Methylbenzyl Methacrylate / Methyl Methacrylate / Butyllithium / Monomer Reactivity Ratios / Stereoregularity / Optical Rotation / Circular Dichroism Spectra /

A number of papers have been published on the polymerization of optically active methacrylates and have described the relationships between the optical activity and the stereoregularity of these polymers. However, there have only been a few reports on the copolymerizations of optically active methacrylates with other vinyl monomers.¹⁻⁶ Arcus and West¹ have reported the radical copolymerization of (+)-1,3-dimethylbutyl methacrylate and methyl methacrylate (MMA), mentioning the contribution of MMA units to the optical activity of the copolymer. Matsuzaki, *et al.*,² have studied the anionic copolymerization of (–)-menthyl methacrylate and the (+)-isomer. Yuki and co-workers³ have investigated the copolymerization of (R)- α -methylbenzyl methacrylate [(R)-MBMA] with (S)-antipode. In both cases, approximately linear relationships were observed between the optical rotations and the contents of excess antipode in the copolymers. Majumdar, *et al.*,⁴ have reported that the alternating copolymer of

(–)-menthyl methacrylate and styrene showed a weak negative circular dichroism band assignable to the 1L_b electronic transition of the phenyl ring. Chiellini and co-workers⁵ prepared the copolymer of (–)-menthyl methacrylate and *N*-vinylcarbazole. Recently, we reported that a copolymer obtained from (S)-MBMA and trityl methacrylate has a largely positive rotatory power attributable to one screw sense of a helical conformation of isotactic sequences of trityl methacrylate units.⁶

In this work, the copolymerization of (S)-MBMA and MMA was carried out by butyllithium (BuLi) in toluene and in tetrahydrofuran (THF) at -78°C , and comparison is made with the copolymerization of (RS)-MBMA and MMA.

EXPERIMENTAL

Materials

(S)-MBMA was prepared from methacryloyl chloride and (S)- α -methylbenzyl alcohol (α_{D}^{20}

−8.85 deg (neat, $l=2$ cm)), obtained by the optical resolution of (*RS*)- α -methylbenzyl hydrogen phthalate.³ bp 50.2–50.5°C/0.15 mmHg. $[\alpha]_{589}^{20}$ −5.30 deg cm²/g* (neat).

(*RS*)-MBMA was prepared from the racemic alcohol and methacryloyl chloride.

MMA was purified in the usual way and stored over CaH₂. It was redistilled under vacuum just before use.

Toluene was purified and dried over sodium. Before use it was mixed with a small amount of BuLi in toluene and redistilled under high vacuum.

THF was refluxed over CaH₂ and was redistilled over LiAlH₄ under high vacuum.

BuLi was prepared in heptane or in toluene according to Ziegler's method⁷ from butyl chloride and metallic lithium under an argon atmosphere.

Nitrogen and argon were purified by being passed through a column packed with type 4A molecular sieves cooled at −78°C.

Polymerization

A glass ampoule equipped with a three-way stopcock was flame-dried while being evacuated, and filled with dry nitrogen. The monomers and the solvent were introduced into the ampoule with hypodermic syringes. The polymerization was initiated by adding the catalyst to the monomer solution at −78°C. The reaction was brought to a stop by adding a small amount of methanol, and the polymer was precipitated by pouring the reaction mixture into a large amount of methanol. The polymer was collected by filtration, washed several times with methanol, and dried *in vacuo* at 60°C.

Conversion of Poly (MBMA-co-MMA) to PMMA

MBMA units in poly(MBMA-co-MMA) were selectively converted to methacrylic acid (MAA) units by a reaction with hydrogen bromide in toluene solution.³ The poly(MAA-co-MMA) thus obtained was methylated with diazomethane in benzene–diethyl ether solution. The triad tacticity of the original copolymer was determined from the ¹H NMR spectrum of the derived PMMA.⁸

* In this paper, c.g.s. units are used to represent specific rotation and specific ellipticity. These give values 10 times lower than the conventional specific quantities (deg cm³/g dm).

Measurements

¹H NMR spectra were measured with a JNM-MH-100 spectrometer at 100 MHz. The spectra of poly(MBMA-co-MMA) and PMMA were obtained at 60°C using tetramethylsilane as an internal standard in CCl₄ and CDCl₃, respectively.

Optical rotations at 589 nm were measured on a Yanagimoto OR-10 polarimeter at 20°C. The concentration of polymer solution in toluene was about 0.02 g/ml and a cell of 5 cm in width was used. The precision of the reading was ± 0.003 deg.

The circular dichroism (CD) spectrum was taken on a polymer solution in THF (1–3 mg/ml) using a JASCO J-40 spectrometer equipped with a computerizing data processor. The spectrum obtained was the average of 16 separate scans between 200 and 260 nm using a cell with a path length of 0.1 mm and also an average of 8 scans between 240 and 300 nm using a 1 cm cell.

RESULTS

The result of the copolymerization of (*S*)-MBMA (M₁) and MMA (M₂) by BuLi in toluene and in THF at −78°C are shown in Tables I and II, respectively. The content of the (*S*)-MBMA unit in the copolymer was determined from the ¹H NMR spectrum. In the spectrum the methoxy resonance of the MMA unit in the copolymer was much broader than that of PMMA; the peak gradually shifted downfield with an increasing fraction of MMA. These results indicate that the distribution of the monomers in the copolymer is more or less random. A similar spectral change was also observed in the copolymerization of MMA and benzyl methacrylate.^{9,10} In Figure 1 the composition of the initial copolymer obtained at the conversion below 12.5% was plotted against the composition of the monomer mixture in feed. The monomer reactivity ratios in the copolymerization of (*RS*)-MBMA and MMA have already been determined as $r_1=0.78$, $r_2=1.68$ in toluene and $r_1=1.52$, $r_2=2.04$ in THF.⁹⁻¹¹ The copolymer composition curves based on these r_1 and r_2 values are shown in the Figure. The experimental points seem to fit the curves well, suggesting that (*S*)-MBMA has the same reactivity as that of the racemic monomer in the copolymerization with

Table I. Anionic copolymerization of (*S*)-MBMA(M_1) and MMA (M_2) by BuLi in toluene at -78°C^a

M_1/M_1+M_2 , mol/mol	Time, hr	Yield, wt %	m_1/m_1+m_2 , mol/mol	$[\alpha]_{589}^{20}$, deg cm ² /g	$[\alpha]_{\text{calcd}}^{20}$, deg cm ² /g	Tacticity, %		
						<i>I</i>	<i>H</i>	<i>S</i>
1.00	48	90.6	1.00	-11.77	-11.77	79.4	16.6	4.0
0.80 ^b	3	0.1	0.76	—	—	—	—	—
0.80	25	30.5	0.79	-10.38	-10.33	81.5	14.6	3.9
0.65 ^b	6	10.5	0.58	-8.49	-8.52	71.4	20.7	7.9
0.50 ^c	16	12.5	0.40	-7.34	-6.58	68.4	23.5	8.1
0.20 ^c	2	1.2	0.14	—	—	—	—	—
0.20 ^c	6	5.7	0.16	—	—	—	—	—
0.20	16	44.9	0.18	-3.94	-3.46	69.4	19.7	10.9

^a M_1+M_2 , 10 mmol; toluene, 20 ml; BuLi, 0.50 mmol.^b BuLi, 0.40 mmol.^c BuLi, 0.33 mmol.**Table II.** Anionic copolymerization of (*S*)-MBMA(M_1) and MMA (M_2) by BuLi in THF at -78°C^a

M_1/M_1+M_2 , mol/mol	Time, hr	Yield, wt %	m_1/m_1+m_2 , mol/mol	$[\alpha]_{589}^{20}$, deg cm ² /g	$[\alpha]_{\text{calcd}}^{20}$, deg cm ² /g	Tacticity, %		
						<i>I</i>	<i>H</i>	<i>S</i>
1.00 ^b	0.05	6.0	1.00	—	—	8.2	29.1	62.7
1.00	48	93.0	1.00	-10.38	-10.38	11.5	28.4	60.1
0.80	6	61.5	0.80	-9.97	-9.17	8.2	29.8	62.0
0.79 ^b	0.17	4.1	0.81	-10.15	-9.24	6.9	32.0	61.1
0.50	14	58.4	0.50	-7.98	-6.80	5.7	31.6	62.7
0.48 ^b	0.33	2.7	0.45	-7.43	-6.32	5.4	30.9	63.7
0.20	0.11	12.5	0.11	-3.03	-1.97	6.0	40.1	53.7

^a M_1+M_2 , 10 mmol; THF, 20 ml; BuLi, 0.50 mmol.^b BuLi, 0.25 mmol. **Figure 1.** Copolymer composition curves for the anionic copolymerization of (*S*)- or (*RS*)-MBMA (M_1) and MMA (M_2): $\circ$, M_1 , (*S*)-MBMA (in toluene); $\bullet$, M_1 , (*S*)-MBMA (in THF).

MMA in toluene as well as in THF.

The copolymerization of (*RS*)-MBMA and MMA was carried out in toluene for 24 hr. The tacticity of the copolymer was determined in order to compare the tacticity with that of the copolymer of (*S*)-MBMA and MMA. The results are shown in Table III. The dependence of the stereoregularity of poly[(*S*)-MBMA-*co*-MMA] and poly[(*RS*)-MBMA-*co*-MMA] prepared in toluene upon the copolymer composition is shown in Figure 2. The isotacticity of the homopolymers was in the order of poly[(*S*)-MBMA] > PMMA > poly[(*RS*)-MBMA]. The stereoregularity of poly[(*S*)-MBMA-*co*-MMA] rich in the (*S*)-MBMA unit was nearly equal to that of the poly[(*S*)-MBMA], while the copolymer containing less than 60 mol% of the (*S*)-MBMA unit showed the same tacticity as that of PMMA. On the other hand,

Table III. Anionic copolymerization of (*RS*)-MBMA (M_1) and MMA (M_2) by BuLi in toluene at -78°C^a

M_1/M_1+M_2 , mol/mol	Yield, wt %	m_1/m_1+m_2 , mol/mol	Tacticity, %		
			<i>I</i>	<i>H</i>	<i>S</i>
1.00	86.4	1.00	56.2	34.6	9.2
0.83	33.8	0.80	70.0	23.3	6.7
0.69	35.9	0.63	71.7	22.1	6.2
0.48	58.4	0.43	72.3	19.8	7.9
0.29	73.6	0.26	70.1	21.6	8.3
0.14	86.0	0.13	69.1	24.7	6.2

^a M_1+M_2 , 10 mmol; toluene, 20 ml; BuLi, 0.33 mmol; time, 24 hr.

Figure 2. Tacticity of poly[(*S*)- or (*RS*)-MBMA-*co*-MMA] obtained by BuLi in toluene at -78°C : $\circ$, poly[(*S*)-MBMA-*co*-MMA]; $\bullet$, poly[(*RS*)-MBMA-*co*-MMA].

the isotacticity of poly[(*RS*)-MBMA-*co*-MMA] was considerably higher than that of poly[(*RS*)-MBMA] and also close to that of PMMA.

In Figure 3 are shown the triad tacticities of the copolymers of (*S*)- or (*RS*)-MBMA with MMA obtained in THF. Both poly[(*S*)-MBMA-*co*-MMA] and poly[(*RS*)-MBMA-*co*-MMA] were syndiotactic and their tacticities were similar to each other. The syndiotacticity decreased slightly with an increase in the content of MMA unit in the copolymer.

As shown in Tables I and II, each poly[(*S*)-MBMA-*co*-MMA] had a larger optical rotation in the absolute value than that calculated for the mixture of the homopolymers having the same composition as the copolymer. Figure 4 shows the relationship between the optical rotation and

Figure 3. Tacticity of poly[(*S*)- or (*RS*)-MBMA-*co*-MMA] obtained by BuLi in THF at -78°C : $\circ$, poly[(*S*)-MBMA-*co*-MMA]; $\bullet$, poly[(*RS*)-MBMA-*co*-MMA]. Solid lines; calculated from $r_1=1.52$, $r_2=2.04$, $\sigma_{11}=0.20$, $\sigma_{22}=0.25$, and $\sigma_{12}=\sigma_{21}=0.22$.

the weight fraction of the (*S*)-MBMA unit in the copolymer.

DISCUSSION

In a previous work,³ a higher isotacticity of the polymer was found for the polymerization of (*R*)-MBMA in toluene than for that of (*RS*)-MBMA. Similar results were reported by Matsuzaki, *et al.*, on poly[($-$)-menthyl methacrylate] and poly[($\pm$)-menthyl methacrylate] prepared by LiAlH_4 or phenylmagnesium bromide.² A helical conformation of the growing polymer chain was postulated in the stereospecific polymerization of MMA by BuLi in nonpolar medium.¹² It has also been suggested that the chain-end anion, the penultimate MMA unit in the chain, and the lithium cation may form a rigid structure at the growing chain end which favors the isotactic placement of an incoming monomer.^{13,14} In the homopolymerization of optically active MBMA in toluene, the isotacticity of the polymer was higher than that of PMMA. The growing chain in this polymerization may take a more rigid conformation since the size of the ester group of MBMA is larger than that of MMA. In the polymerization of racemic MBMA, which is actually a copolymerization of the equimolar amount of (*R*)- and (*S*)-isomers, the polymer of the lower stereore-

gularity was obtained. This indicates that the steric interaction between the optical antipodes, one of which being the ester group of the monomer unit at the growing chain end and the other, that of the incoming monomer, is less favorable to the formation of isotactic placement than the interaction between (*R*)-methylbenzyl groups and *vice versa*.

As shown in Figure 2, the copolymer of (*S*)-MBMA with 20 mol% of MMA showed a tacticity similar to that of the homopolymer of (*S*)-MBMA, indicating that the formation of the helical conformation of the growing chain was not interrupted by the occasional addition of MMA of small size. However, a more frequent insertion of MMA in the copolymer chain seems to bring about a decrease in the steric interaction between the ester groups in neighboring (*S*)-MBMA units resulting in a decrease in the isotacticity of poly[(*S*)-MBMA-*co*-MMA] to the same level as the isotacticity of PMMA.

The copolymers of (*RS*)-MBMA and MMA also showed similar stereoregularity to PMMA, and accordingly, to most of the poly[(*S*)-MBMA-*co*-MMA]s. These results indicate that the steric interaction between (*R*)-MBMA and MMA and between (*S*)-MBMA and MMA is nearly equal to that between MMA and MMA. The steric interaction between (*R*)-monomers or (*S*)-monomers should be more favorable to isotactic addition and that between (*R*)- and (*S*)-MBMAs, less favorable. However, the fact that the incorporation of only 20 mol% of MMA units into the copolymer are enough to improve the stereoregularity of poly[(*RS*)-MBMA-*co*-MMA] suggests another role played by MMA in the stereoregulation of the copolymerization. That is, the presence of a MMA unit in the neighbor of (*R*)- or (*S*)-MBMA chain end may reduce the steric interaction and thus favor the isotactic addition between that end and the incoming monomer.

As for the copolymerization in THF, not only the monomer reactivity ratios but also the stereoregularity of the copolymer (Figure 3) were equal between the racemic monomer—MMA and (*S*)-monomer—MMA systems. Among the configurational parameters σ_{ij} , the probability that M_j monomer will add in the isotactic configuration to a growing polymer chain ending in an M_i unit, the values of σ_{12} and σ_{21} can be calculated

from the data of monomer reactivity ratios and triad tacticities of the homopolymers and copolymers, if terminal model statistics prevail in the copolymerization.¹⁵ This has been applied in the copolymerization of MMA and trityl methacrylate in THF.^{16,17} In the present work, we also have assumed terminal model statistics and calculated the coisotactic parameters, $\sigma_{12}=\sigma_{21}$, to be 0.22 by using $r_1=1.52$, $r_2=2.04$, $\sigma_{11}=0.20$, and $\sigma_{22}=0.25$. It was found that the values calculated from these data (solid lines in Figure 3) agreed well with the observed triad tacticity of poly(MBMA-*co*-MMA)s.

The optical rotation of isotactic poly[(*S*)-MBMA] is larger than the rotation of syndiotactic poly[(*S*)-MBMA], which is nearly equal to the rotation of the monomeric analog, (*S*)-methylbenzyl pivalate ($[\alpha]_{589}^{20} -10.32$ deg cm²/g, toluene). The difference is small but distinguishable. In Figure 5 are shown the CD spectra of THF solutions of isotactic and syndiotactic poly[(*S*)-MBMA]s. The spectra of the polymers were similar in shape to each other but a negative peak at about 215 nm of the isotactic polymer was larger than the corresponding peak of the syndiotactic one. These results indicate that the conformation is different between the isotactic and syndiotactic poly[(*S*)-MBMA]s in solution. It is generally considered that an isotactic polymer takes a helical conformation while a syndiotactic

Figure 4. Relationship between the optical rotation at 589 nm and the weight fraction of (*S*)-MBMA unit in poly[(*S*)-MBMA-*co*-MMA]: O, obtained in toluene; ●, obtained in THF.

polymer a zig-zag conformation. The negative rotation of the isotactic poly[(*S*)-MBMA] being larger than that of the syndiotactic one owes to the isotactic helix preferential in the one screw sense. Such a chiral conformation taken on by the isotactic polymer has also proposed for the optically active poly- α -olefins.¹⁸

As shown in Figure 4, the specific rotation of the syndiotactic copolymer of (*S*)-MBMA and MMA obtained in THF is concave downward and deviates from the rotation (the broken line) evaluated for the homopolymer mixture having the same composition as the copolymer. These results indicate that the optical rotation of the syndiotactic copolymer is enhanced by the incorporation of MMA unit. On the other hand, the specific rotation of the isotactic copolymer obtained in toluene seemed close to the straight line (the chain line) calculated from the specific rotation of the isotactic homopolymer of (*S*)-MBMA. In the copolymerization of (*S*)-MBMA and MMA in toluene, the product was not a mixture of the homopolymers but a rather random copolymer, judging from the ¹H NMR spectroscopy and the monomer reactivity ratios. Therefore, the isotactic (*S*)-MBMA sequence in the copolymer becomes shorter by the insertion of the MMA unit and the specific rotation of (*S*)-MBMA unit in the isotactic copolymer may be similar to that in the syndiotactic polymer. From this point of view, the optical rotation of the isotactic copolymer is possibly enhanced by the incorporation of the MMA unit similarly in the case of the syndiotactic copolymer. The enhancement of the specific rotation of the copolymer is attributable to some chiral conformation of the MMA unit induced by a neighboring (*S*)-MBMA unit, regardless of the stereoregularity and the sequence distribution of the copolymer.

The CD spectroscopy of the copolymer was investigated in order to obtain information about the contribution of the MMA unit in the copolymer to the optical activity. The CD spectrum of an isotactic poly[(*S*)-MBMA-co-MMA] is shown in Figure 5. The specific ellipticity at each wavelength was nearly equal to the product of the corresponding ellipticity of the syndiotactic poly[(*S*)-MBMA] and the weight fraction of the (*S*)-MBMA unit in the copolymer, indicating that the contribution of the MMA unit to the CD bands

Figure 5. CD spectra of (1) isotactic and (2) syndiotactic poly[(*S*)-MBMA]s, and (3) poly[(*S*)-MBMA-co-MMA] ($m_1/m_1 + m_2 = 0.58$ mol/mol) obtained in toluene.

in the measured region was not detectable. It was found that in the poly[(*−*)-menthyl methacrylate] obtained by BuLi in THF at -78°C the CD band assignable to the ester carbonyl group was small (the maximum of the specific ellipticity at 219 nm was $+129 \text{ deg cm}^2/\text{g}$, in THF).¹⁹ The reason as to why this difference could not be detected may be due to the very small CD band based on the $n \rightarrow \pi^*$ transition of the carbonyl chromophore of MMA unit in the copolymer.

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