Conformational Analysis of Methacrylates by IR and ^{1}H NMR Spectroscopies

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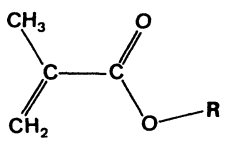
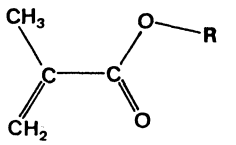
The molecular structures of α-methylbenzyl methacrylate, 1,2-diphenylethyl methacrylate, α-*t*-butylbenzyl methacrylate, 1,2,2,2-tetraphenylethyl methacrylate, diphenylmethyl methacrylate, and 1,1-diphenylethyl methacrylate in solution were investigated by means of IR spectroscopy and ^{1}H NMR spectroscopy using a lanthanoid-induced chemical shift (LIS) reagent [Eu(fod)$_3$] by reference to X-ray analysis data. The preferred conformation between the C=C double bond and the C=O group was estimated to be s-cis in solution. The conformation of ester groups of α-substituted benzyl methacrylates in toluene depended upon the α-substituent and the temperature. On the basis of structural data, the mechanism of the highly enantiomer-selective polymerization of racemic methacrylates with a (−)-sparteine-Grignard reagent complex is discussed.

(−)-Sparteine (Sp)-Grignard reagent complexes are effective initiators in the enantiomer-selective (asymmetric-selective or stereoelective) polymerization of racemic α-monosubstituted benzyl methacrylates such as α-methylbenzyl methacrylate (MBMA),[1,2] α-ethylbenzyl methacrylate (EBMA),[3] α-isopropylbenzyl methacrylate (iPrBMA),[3] 1,2-diphenylethyl methacrylate (DPEMA-1,2),[4] and α-*t*-butylbenzyl methacrylate (*t*-BBMA).[3] For example, in the polymerization of racemic MBMA with a cyclohexylmagnesium bromide (*c*-HexMgBr)-Sp complex in toluene at −78 °C, the polymer obtained in the early stage of the polymerization was rich in (*S*)-antipode whose optical purity was as high as 93%; the monomer recovered at about 65% conversion was almost optically pure.[2] (S)-Selective polymerization was also achieved for EBMA, iPrBMA, and DPEMA-1,2. However, for *t*-BBMA (*R*)-enantiomer was polymerized preferentially over (*S*)-enantiomer.[3] It has been pointed out that this reverse enantiomer selection of *t*-BBMA and other methacrylates may be caused by the difference in conformation of the monomers.[3] Recently, we also found that (*S*)-antipode of 1,2,2,2-tetraphenylethyl methacrylate (TrBMA) was polymerized preferentially with rather low enantiomer selectivity.[5] Among these monomers, DPEMA-1,2, *t*-BBMA, and TrBMA gave crystals suitable for X-ray diffraction study. The results of X-ray analyses have already been reported and the mechanism of the enantiomer-selective polymerization has been discussed on the basis of the determined molecular structures.[6] X-Ray structure analyses were also achieved on some achiral methacrylates, diphenylmethyl methacrylate (DPMMA),[7] 1,1-diphenylethyl methacrylate (DPEMA-1,1),[8] triphenylmethyl methacrylate (TrMA),[8] and diphenyl-2-pyridylmethyl methacrylate (D2PyMA)[9] which show interesting phenomena in the stereospecific polymerization with anionic and radical initiators.[10-12]

One of the problems concerning the molecular structures of methacrylates is the conformation between the C=C double bond and the C=O group: that is, whether it is s-trans or s-cis. This, especially on



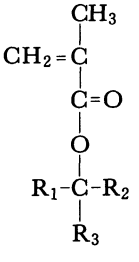
s-trans



s-cis

methyl methacrylate (MMA), has been studied by several methods. However, the results obtained are not always consistent with one another. It has been found that the molecules of DPMMA, DPEMA-1,2, and D2PyMA have the s-trans form in crystal.[6,7,9] This is consistent with the results of an electron diffraction study,[13] molecular polarizability measurements[14] and an ab initio MO calculation of MMA.[15] On the other hand, DPEMA-1,1, TrMA, and TrBMA exist as the s-cis form in crystal.[6,8] This agrees with the results of the ^{1}H NMR study of molecular complexes of MMA and Lewis acids,[16] and the conformational analysis of MMA by a lanthanoid-induced chemical shift (LIS) reagent.[17]

The present work was undertaken in order to obtain more detailed information on the conformation of DPMMA, MBMA, DPEMA-1,2, DPEMA-1,1, TrMA, and TrBMA, in solution by IR spectroscopy and ^{1}H NMR spectroscopy with an LIS reagent. The results helped us to understand the mechanism of the



	R_1	R_2	R_3
MBMA	H	CH_3	Ph
DPEMA-1,2	H	CH_2-Ph	Ph
t-BBMA	H	*t*-Bu	Ph
TrBMA	H	$C(Ph)_3$	Ph
DPMMA	H	Ph	Ph
DPEMA-1,1	CH_3	Ph	Ph
TrMA	Ph	Ph	Ph

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enantiomer-selective polymerization of the racemic methacrylates with the (−)-Sp-Grignard reagent system in toluene.

Experimental

Materials. All methacrylates used in this study were synthesized and characterized according to our previous work.

An NMR shift reagent $Eu(fod)_3$ (Nakarai Chemical Co.) was used without further purification.

Measurements. IR spectra of the methacrylates were measured with a JASCO IR-810 spectrophotometer in KBr pellets and in CCl_4 or toluene with a 50-μm NaCl cell at room temperature. The wavenumbers were calibrated using a polystyrene film. The ^1H NMR spectra were recorded on a JNM MH-100 or JNM FX-100 (100 MHz) instrument in toluene-d_8; tetramethylsilane (TMS) was used as an internal standard.

LIS Measurements. The lanthanoid-induced chemical shifts were measured with $Eu(fod)_3$ in toluene-d_8 at 35 and −40 °C. The concentration of the methacrylates was 0.5 mol l^{-1} and the molar ratio of [$Eu(fod)_3$]/[Methacrylate]([Ld]/[M]) was changed in a range of 0—0.30.

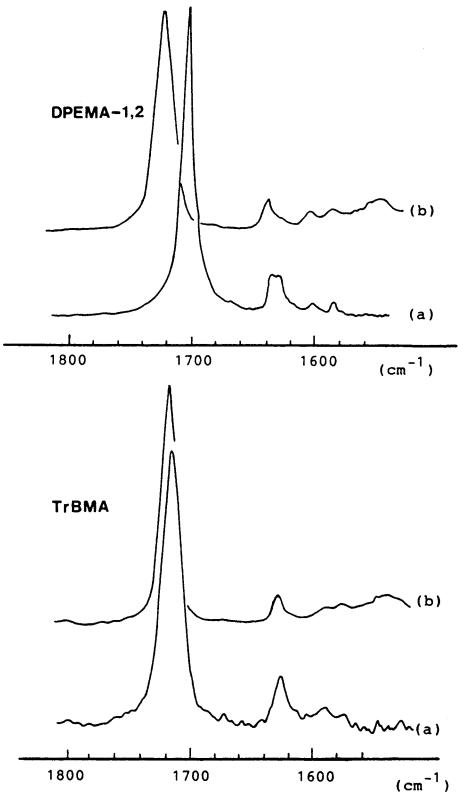


Fig. 1. IR spectra of C=O and C=C bands of DPEMA-1,2 and TrBMA in KBr (a) and in CCl_4 (b).

Results and Discussion

IR Spectra of Methacrylates. It has been well-known that IR spectroscopy differentiates the s-cis and s-trans conformations of α,β-unsaturated ketones and there exist some relatively simple rules in the relationship between the conformation (s-cis or s-trans) and the C=O and C=C bands of α,β-unsaturated ketones;[18,19] (1) there is a greater frequency separation between the C=O and C=C stretching bands of the s-cis form than the s-trans form, (2) the ratio of the band intensities of the C=O to the C=C stretching vibrations is considerably larger for the s-trans than the s-cis. However, so far, no such rules have been reported for α,β-unsaturated esters. The molecular structures of the methacrylates used in this study have already been determined by X-ray analysis. This promoted us to investigate the relationships between the conformation and the C=O and C=C bands of methacrylates in both crystal and solution by IR spectroscopy.

Figure 1 shows the IR spectra of DPEMA-1,2 and TrBMA in KBr pellets (a) and in CCl_4 solutions (b). The former methacrylate has the s-trans form and the latter the s-cis form in crystal according to X-ray diffraction studies. DPEMA-1,2 had a C=O band of 1702.5 cm^{-1} in KBr and its frequency moved by 20.2 cm^{-1} to 1722.7 cm^{-1} in a CCl_4 solution. TrBMA showed a C=O band at 1714.2 cm^{-1} in KBr and it only slightly shifted to 1719.0 cm^{-1} that was similar to the frequency of the C=O band of DPEMA-1,2 in a CCl_4 solution. The C=C bands appeared at ca. 1635 cm^{-1} in both KBr and CCl_4. These results strongly suggest that the conformation of DPEMA-1,2 changes from the s-trans in a crystalline solid to the s-cis in solution and TrBMA exists as the s-cis form both in a solid state and in a CCl_4 solution. Similar results were also obtained for other methacrylates (Table 1). The C=O band of

Table 1. Frequencies of C=O and C=C Bands of α-Substituted Benzyl Methacrylates

Monomer	R_1	R_2	Crystal structure[a]	ν(KBr)/cm^{-1}		ν(CCl_4)/cm^{-1}		$\Delta\nu_{C=O}$[b]	$\Delta\nu_{C=C}$[b]
				C=O	C=C	C=O	C=C	cm^{-1}	cm^{-1}
DPMMA	Ph	H	s-trans	1707.8	1636.0	1722.8	1637.8	15.0	1.8
DPEMA-1,2	Bz	H	s-trans	1702.5	1635.0	1722.7	1637.4	20.2	2.4
						(1721.4	1636.4	18.9	1.4)[c]
DPEMA-1,1	Ph	CH_3	s-cis	1721.4	1635.3	1724.0	1636.3	2.6	1.0
TrMA	Ph	Ph	s-cis	1725.9 (1718.8)[d]	1635.3	1727.6	1637.6	1.7	2.3
TrBMA	$C(Ph)_3$	Ph	s-cis	1714.2	1634.7	1719.0	1636.7	4.8	2.0

a) Conformation between C=O and C=C in crystal determined by X-ray diffraction study. b) Frequency difference in CCl_4 and KBr. c) In parenthesis are shown the frequencies in toluene solution. d) Shoulder.

Table 2. Chemical Shifts and $Eu(fod)_3$ Induced Shifts of Methacrylates in Toluene-d_8[a)]

		DPMMA		MBMA		DPEMA-1,2		*t*-BBMA		TrBMA	
		35 °C	−40 °C	35 °C	−40 °C	35 °C	−40 °C	35 °C	−40 °C	35 °C	−40 °C
Ha	δ[b)]	5.20	5.13	5.20	5.13	5.25	5.11	5.30	5.11	5.08	5.09
	$\Delta\delta$[c)]	4.00	6.44	3.64	6.44	3.25	5.34	2.47	4.80	2.78	4.55
	$\Delta\delta_{rel}$[d)]	0.64	0.66	0.72	0.59	0.64	0.57	0.62	0.61	0.58	0.58
	$\Delta\delta_{cal}$[e)]	3.49	6.43	3.29	6.27	2.88	5.16	2.18	4.86	2.37	4.32
Hb	δ[b)]	6.18	6.19	6.09	6.15	6.14	6.12	6.22	6.11	5.95	6.10
	$\Delta\delta$[c)]	8.30	16.07	7.69	14.97	7.25	13.33	5.58	10.71	6.50	9.30
	$\Delta\delta_{rel}$[d)]	1.32	1.66	1.53	1.37	1.44	1.43	1.40	1.32	1.35	1.19
	$\Delta\delta_{cal}$[e)]	8.29	16.01	7.78	14.98	7.45	13.35	5.82	10.69	6.37	9.47
Hc	δ[b)]	7.10	7.10	5.93	5.91	6.16	6.06	5.72	5.61	7.66	7.88
	$\Delta\delta$[c)]	16.40	22.04	12.10	19.00	14.07	17.09	12.03	15.30	14.17	12.50
	$\Delta\delta_{rel}$[d)]	2.61	2.27	2.40	1.74	2.79	1.83	3.62	1.83	2.94	1.60
	$\Delta\delta_{cal}$[e)]	16.35	22.06	12.05	19.04	13.91	17.09	11.79	15.28	14.13	12.60
CH_3	δ[b)]	1.80	1.75	1.80	1.77	1.79	1.70	1.85	1.76	1.68	1.67
	$\Delta\delta$[c)]	6.28	9.71	5.05	10.91	5.05	9.32	3.99	8.30	4.82	7.80
	$\Delta\delta_{rel}$[d)]	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	$\Delta\delta_{cal}$[e)]	6.67	9.76	5.29	10.92	5.37	9.40	4.45	8.32	5.26	7.56
Δ(Hb−Ha)		0.98	1.06	0.89	1.02	0.89	1.01	0.92	1.00	0.87	1.01

a) Concentration of methacrylates=0.5 (mol l^{-1}). b) Chemical shift in toluene-d_8. c) Molar induced shift by $Eu(fod)_3$. d) Relative induced shift based on CH_3 resonance. e) Molar induced shift calculated for the structure giving the minimum AF value.

another s-trans methacrylate, DPMMA also shifted to a higher frequency in solution (from 1707.8 to 1722.8 cm^{-1}) but those of other s-cis methacrylates were little changed in a CCl_4 solution. The higher frequency shift of the C=O band of DPEMA-1,2 was also observed in a toluene solution (Table 1). These results are quite consistent with those of α,β-unsaturated ketones as mentioned above. However, the C=C band frequency and the ratio of the band intensities of the C=O to C=C stretching vibrations do not seem to be closely related to the conformation.

Conformational Analysis with LIS Reagent. The observed molar LISs were obtained from the line slopes of the plots of induced chemical shifts versus [Ld]/[M] ratios. The plots for DPEMA-1,2 is shown in Fig. 2 as an example. In all cases, good straight lines were obtained in the plots. The chemical shifts (δ) and molar LISs ($\Delta\delta$) are summarized in Table 2.

The molar LIS is the change in chemical shift caused by complexation with an equimolar lanthanoid shift reagent, being expressed by the McConnell and Robertson equation (Eq. 1):[20)]

$$\mathrm{LIS}(\Delta\delta) = K(3\cos^2 X - 1)/r^3, \quad (1)$$

where X is the O(2)-Ld-H internuclear angle (O(2) is the carbonyl oxygen in an ester group, see Fig. 3), r is the corresponding Ld-H distance and K is the pseudo-contact constant which refers to the magnitude of the induced magnetic dipole of a lanthanide ion. The most probable conformation of a methacrylate can be chosen by comparing the observed $\Delta\delta$ with the calculated molar LIS for a set of conformers.

The LIS simulation processes were worked-up according to the method reported by Montaudo et al.[21)] The structure of the complex of a methacrylate and $Eu(fod)_3$ in solution is shown in Fig. 3, where R is the Eu-O(2) distance (2.0—3.0 Å at 0.1 Å intervals), ϕ the Eu-O(2)-C(1) angle (120—180° at 5° intervals), ω the torsion angle of Eu-O(2)-C(1)-C(2) about the O(2)-C(1) bond (0—360° at 10° intervals) and θ the torsion angle of Hc-C(5)-O(1)-C(1) about the C(5)-O(1) (0—360° at 10° intervals). The conformation between the C=C and the C=O group was fixed to be

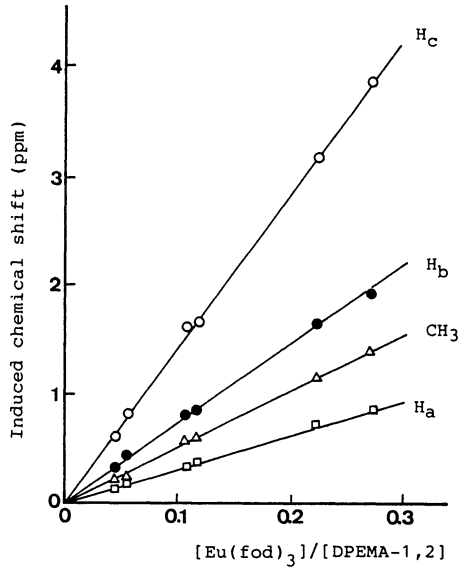


Fig. 2. The plots of induced shifts vs. molar ratio [$Eu(fod)_3$]/[DPEMA-1,2] in toluene-d_8 at 35 °C; assignment of protons are shown in Fig. 2.

s-cis or s-trans. It has been confirmed that esters coordinate to a Eu ion at the carbonyl rather than the ether oxygen.[22] The structural data of a methacrylate are also shown in Fig. 3 which is depicted according to the molecular structures of methacrylates determined by X-ray analysis. However, two assumptions are involved; (1) methacrylate (CH_2=C(CH_3)-COOC) has a planar structure, (2) all bond angles in the methacryloyl group are 120°. These two assumptions seem reasonable for the LIS simulation process since the differences from the actual molecular structures determined by X-ray analysis are very little.

A computer simulation was performed according to the method reported by Montaudo et al.[21] The calculated LISs for a given set of R, ϕ, ω, θ values (i.e., for each Eu and Hc spatial location) were obtained. Evaluation of the difference between the observed and calculated LISs was carried out by using the agreement factor (AF) which is defined by the following equation (Eq. 2):[23]

$$AF = \sqrt{\frac{(LIS_{obsd} - LIS_{calcd})^2}{(LIS_{obsd})^2}} \qquad (2)$$

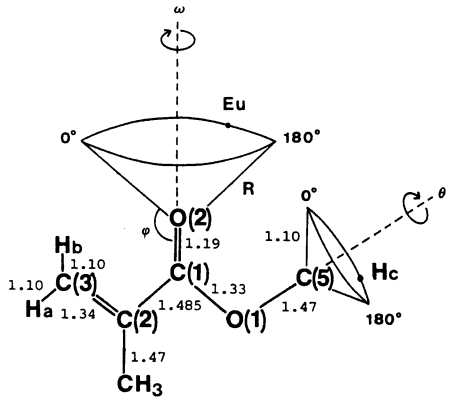
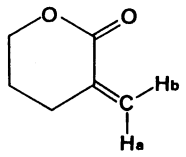


Fig. 3. Structure of the Eu(fod)$_3$-methacrylate complex.

The conformer giving the minimum value of AF is assumed the most likely molecular geometry of a complex (Tables 2 and 3).

It has been pointed out that in the NMR of α,β-unsaturated ketones or esters, the C=O group causes the deshielding of β-methylene protons when the C=O and C=C are in s-cis position.[19,24] This deshielding effect of the C=O is considered to induce a significant difference of chemical shifts of the two methylene protons on β-carbon atom due to much closer position of one of methylene protons to the other (see Fig. 3). This effect is amplified by employing aromatic solvents. The differences of chemical shifts δ (Hb—Ha) observed for the β-methylene of all the methacrylates used in this study were in a range of 0.87—0.98 ppm at 35 °C and 1.00—1.06 ppm at −40 °C in toluene-d_8 (Table 2). These values are much greater than that of 0.19 ppm of s-trans alkyl vinyl ketone calculated by Naito et al.[25] and rather similar to 0.80 ppm for the s-cis form. The δ (Hb—Ha) value (0.83 ppm) of α-methylene-δ-valerolactone (MVL),[26] which exists only



MVL

in s-cis form, is nearly equal to those of the methacrylates. These results also indicate that the C=C and C=O groups of the methacrylates are likely to be in the s-cis position in toluene, although DPMMA and DPEMA-1,2 take the s-trans position in crystals.

The results of conformational analyses of the methacrylates by LIS are collected in Tables 2 and 3. The observed and calculated LISs at 35 and −40 °C are shown in Table 2, and the molecular geometry of the Eu(fod)$_3$ complexes giving the minimum AF values are listed in Table 3. The best agreement between experimental and calculated LISs i.e., the minimum agree-

Table 3. Summary of the Conformation of Methacrylates

Monomer	Temp	R	ϕ	ω	θ	K	AF	C(1)-C(2)		O(1)-C(5)[b]
	°C	Å	°	°	°		%	I[a]	II[b]	A or B
DPMMA	35	2.3	170	−30, 30	0	866	3.3	s-trans	s-cis	A
	−40	2.4	175	−30, 30	−20, 20	1295	0.3		s-cis	A
MBMA	35	2.3	175	−30, 30	0	672	2.8	—	s-cis	A
	−40	2.3	170	−50, 50	−40, 50	1405	0.6	—	s-cis	B
DPEMA-1,2	35	2.4	170	0	0	730	3.3	s-trans	s-cis	A
	−40	2.4	170	−20, 20	−50, 50	1274	0.8		s-cis	B
t-BBMA	35	2.4	165	−40, 40	0	614	4.5	s-trans	s-cis	A
	−40	2.2	175	−30, 30	−30, 30	1010	0.3	and s-cis	s-cis	B
TrBMA	35	2.4	165	−30, 30	0	730	3.7	s-cis	s-cis	A
	−40	2.2	175	−10, 10	−40, 40	921	2.1		s-cis	B

a) Conformation in crystal determined by X-ray analysis. b) Conformation in toluene-d_8, see Fig. 4.

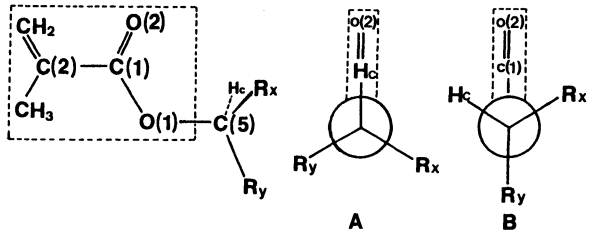


Fig. 4. Conformers of methacrylate.

Table 4. Molar Induced Shifts ($\Delta\delta$, ppm) of Two Groups (R and Ph) on the Asymmetric Carbon of Methacrylates[a)]

	MBMA		DPEMA-1,2		*t*-BBMA	
	35 °C	−40 °C	35 °C	−40 °C	35 °C	−40 °C
R[b)]	3.95	7.69	4.13	5.79	2.20	2.70
Ph[c)]	2.91	4.99	1.88 3.55	2.20[d)] 4.42[d)]	3.98	4.80

a) In toluene-d_8, concentration of methacrylates=0.5 (mol l^{-1}). b) R are methyl, methylene, and *t*-butyl groups on the asymmetric carbon atoms of MBMA, DPEMA-1,2, and *t*-BBMA, respectively. c) Ortho proton of phenyl group. d) Two phenyl groups were observed separately.

ment factor, was always observed in the s-cis form. The s-trans form gave much greater agreement factors. The results in Tables 2 and 3 also indicates that the hydrogen atom (Hc) attached to the asymmetric carbon atom of the all methacrylates exists on the methacryloyl plane containing the C=C double bond and C=O group at 35 °C as shown in Fig. 4(A) and its position is rather similar to that determined by X-ray analysis. However, at −40 °C, the minimum agreement factor (AF) values for most methacrylates were obtained for the conformer in which Hc was at the gauche position to the methacryloyl plane as depicted in Fig. 4(B). DPMMA showed little conformational change at −40 °C, probably because of the symmetrical structure of the ester group.

We also presumed the positions of the other two groups attached to the asymmetric carbon atom by comparing the LISs at 35 and −40 °C (Table 4). In MBMA, the difference of LISs of the methyl group at two temperatures was larger than that of the ortho protons of the phenyl group. The same was true in DPEMA-1,2; the LIS change of the methylene group in benzyl group is also larger than those of the ortho protons of the phenyl groups, which seem to indicate that at −40 °C, the largest phenyl group attached to the asymmetric carbon atom occupy the position remote from the carbonyl group and the other groups are in staggered positions on either side of the ester carbonyl (see Fig. 5(a)). This was also supported by the fact that the Hc resonances of MBMA and DPEMA-1,2 did not shift downfield at −40 °C as large as Ha and Hb. On the other hand, in *t*-BBMA, the difference of LISs of the largest *t*-butyl group at 35 and −40 °C was nearly equal to that of the phenyl group and the LIS values of the *t*-butyl group were smaller than those of the ortho protons of the phenyl group. These results indicate that in *t*-BBMA the largest *t*-butyl group may occupy a position remote from the carbonyl group; the other groups, hydrogen and phenyl, may be in a staggered position as illustrated in Fig. 5(b). However, the deviation of Hc from the methacryloyl plane in *t*-BBMA at −40 °C seems to be smaller than that of MBMA and DPEMA-1,2, and the conformation may be analogous to that determined by X-ray analysis. It seemed to be difficult to estimate the positions of the two groups attached to the asymmetric carbon atom of TrBMA in a similar manner. Therefore, we assumed that the bulkyl triphenylmethyl group occupies a position remote from the carbonyl and other two, hydrogen and phenyl, groups were in a staggered position as in *t*-BBMA (Fig. 5(c)). This conformation has been observed in crystal although the deviation of Hc is smaller in crystal.

Mechanism of the Enantiomer-Selective Polymerization. Previously, we demonstrated that the enantiomer-selective polymerization of racemic methacrylates with Grignard reagent-Sp complexes in toluene at −78 °C proceeded in a coordination mechanism; that is, a monomer always coordinates to an active center before being incorporated into a polymer chain end.[2,3)] The enantiomer selection may be controlled by two main interations. One is the interation between the ester group of a monomer and Sp, and the other is the interaction between the ester group of a monomer and the growing chain end. The hydrogen on the asymmetric carbon atom of the ester group is important in order to avoid any steric hindrance when the monomer, probably, its carbonyl group coordinates to the magnesium (Mg) counterion in the active center because the Sp-Grignard reagent complexes can not polymerize α,α-dimethylbenzyl methacrylate which has no hydrogen atom on the asymmetric carbon.[2)] Figure 5 shows the schematical structures of active centers in the enantiomer-selective polymerization of MBMA (a), *t*-BBMA (b), and TrBMA (c) which have (*S*), (*R*), and (*S*) configurations, respectively. Their molecular structures are illustrated on the basis of the results obtained in this study.

In the case of (*S*)-MBMA, the large phenyl group occupies a position remote from the carbonyl group and other two smaller hydrogen and methyl group are in a staggered position. This conformation is analogous to those proposed for α-keto esters by Prelog.[27)] The close position of the hydrogen on asymmetric carbon to (−)-sparteine makes it easy for the monomer to coordinate to Mg and to add to the growing end. However, in (*R*)-MBMA, the position of the hydrogen and methyl group is reversed, and the methyl group appears to hit (−)-sparteine moiety upon the coordination to Mg in the same way as shown in Fig. 5(a).

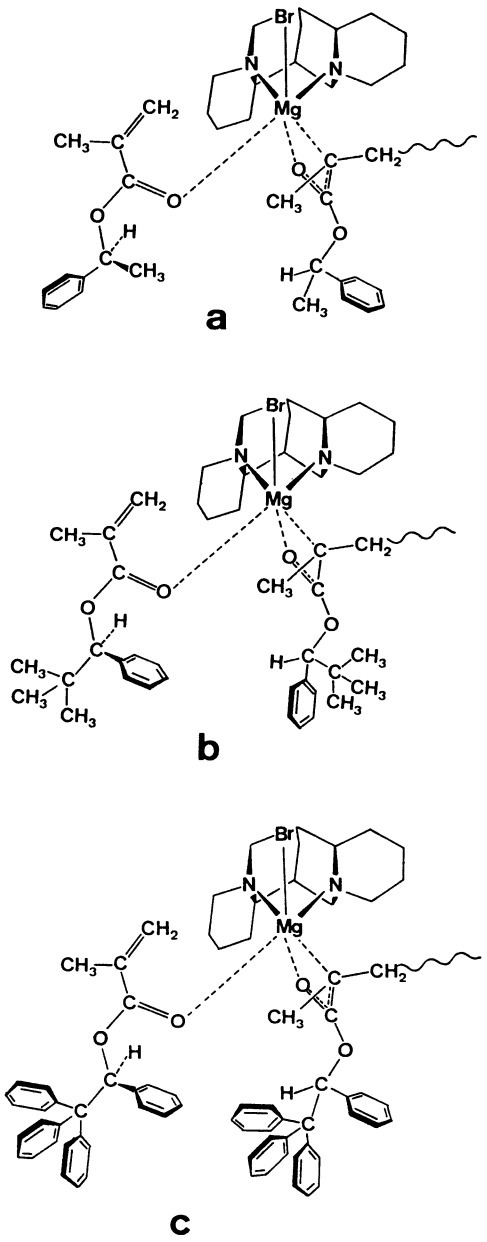


Fig. 5. Schematical structures of active centers in the enantiomer-selective polymerization of MBMA (a), *t*-BBMA (b), and TrBMA (c).

Hence, (*S*)-MBMA may be more reactive than (*R*)-MBMA. The structure of the active center, where the positions of the growing chain end and monomer are those in Fig. 5, may be favorable because the left-hand side of (−)-sparteine in Fig. 5 is more sterically hindered than the right-hand side of (−)-sparteine according to the molecular structure of Sp-ethylmagnesium bromide complex obtained by X-ray analysis, then the bulky growing chain end appears to occupy the right-hand side.[28]

In other monomers having smaller alkyl groups than phenyl on asymmetric carbon atom like EBMA, iPrBMA, and DPEMA-1,2, their conformation is probably similar to that as shown in Fig. 5(a) and (*S*) enantiomers are expected more reactive for the same reason discussed regarding MBMA.

However, when the alkyl group is larger than the phenyl group, like a *t*-butyl group, an enantiomer with the conformation shown in Fig. 5(b) must be preferable. Again, the hydrogen on the asymmetric carbon plays an important role to avoid any steric hindrance in the coordination process of the monomer to the Mg cation. Therefore, the reactive enantiomer must be the (*R*) isomer as observed in the polymerization of *t*-BBMA. In the case of TrBMA, we can also rationally explain that the preferable enantiomer is the (*S*) isomer, as shown in Fig. 5(c), where the phenyl group and hydrogen occupy staggered positions, as in *t*-BBMA and the bulky triphenylmethyl group exists at trans position to carbonyl group. Since the relative positions of the phenyl group to the triphenylmethyl group in the Cahn-Ingold-Prelog system is reversed to that of phenyl to the *t*-butyl group in *t*-BBMA, the (*S*)-isomer is favored for the enantiomer-selective polymerization of TrBMA.

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