

## Stereochemical effects on the fragmentation in mass spectrometry of stereoregular oligomers of methyl methacrylate

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### SUMMARY

The effects of stereochemical structure of MMA oligomers on the fragmentation during ionization process in electron-impact ionization and chemical ionization mass spectrometry were studied using the oligomers prepared by stereospecific living oligomerization. The MMA oligomers having  $t\text{-C}_4\text{H}_9\text{-}$  group at the left end and methine proton at the right end showed strong tacticity dependence in their fragmentation process. Fragmentation of MMA tetramer having one *head-to-head* linkage in the middle of the chain was also studied.

### INTRODUCTION

Structural investigation of oligomers provides useful and important information on the polymerization mechanism as well as polymer structure<sup>1–17</sup>. Recent advances in NMR spectroscopy have made it possible to determine the precise structures of oligomers including their stereochemistry. We have prepared isotactic oligomers of methyl methacrylate (MMA) by  $t\text{-C}_4\text{H}_9\text{MgBr}$ <sup>18</sup> in toluene and syndiotactic MMA oligomers by  $t\text{-C}_4\text{H}_9\text{Li}/(\text{C}_2\text{H}_5)_3\text{Al}$  ( $\text{Li}/\text{Al}=1/3$ )<sup>19</sup> in toluene. Based on the X-ray analysis of the isotactic trimer<sup>14</sup>, stereochemistry of these oligomers were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy from the left end (initiating end) to the right end (terminating end)<sup>16</sup>. In this work, fragmentation in electron-impact ionization (EI) mass spectra of dimer, trimer and tetramer of MMA with well-defined configurations were studied in regard of stereochemical configurations. Fragmentations of meso and racemic tetramers having *head-to-head* linkage in the middle of the chain were also examined by chemical ionization (CI) mass spectrometry.

### EXPERIMENTAL

Stereospecific oligomerization of MMA in toluene at  $-78^\circ\text{C}$  with  $t\text{-C}_4\text{H}_9\text{MgBr}$ <sup>18</sup> and with  $t\text{-C}_4\text{H}_9\text{Li}/(\text{C}_2\text{H}_5)_3\text{Al}$  ( $\text{Li}/\text{Al}=1/3$  mol/mol)<sup>19</sup>, which gave isotactic and syndiotactic oligomers, respectively. From the oligomer mixture formed with  $t\text{-C}_4\text{H}_9\text{MgBr}$ , meso (*m*) and racemo (*r*) dimers, *mm* trimer (containing 5.7% of *rm* trimer), *mr* trimer, *mmm* and *mmr* tetramers were isolated by successive fractionation with GPC (polystyrene gel with a maximum porosity of 3000,  $\text{CHCl}_3$ ) and HPLC (silica gel, 1-chlorobutane/acetonitrile 96/4 v/v)<sup>16</sup>. The *rr* and *rm* trimers and *rrm* and *rrr* tetramers were similarly obtained from the oligomer mixture prepared with  $t\text{-C}_4\text{H}_9\text{Li}/(\text{C}_2\text{H}_5)_3\text{Al}$ <sup>16</sup>.

MMA tetramer having *head-to-head* linkage in the middle of the chain, 2,4,5,7-tetrakis-(methoxycarbonyl)-2,4,5,7-tetramethyloctane, was obtained as a mixture of meso and racemic isomers, according to the procedure of Caciolli et al.<sup>7</sup>, and the mixture was separated into meso and racemic isomers by recrystallization from 1-chlorobutane.

Electron-impact ionization (EI) and chemical ionization (CI) mass spectra were recorded on a JEOL DX-303HF mass spectrometer. Samples were injected through a gas chromato-

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graph connected to the mass spectrometer. Ionization voltages in the EI and CI experiments were 70 and 200 eV, respectively. The column temperatures were set at 145°C for the dimer, 194°C for the trimer, and 230°C for the tetramer. Each spectrum was obtained as the sum of 10–24 scans. The CI mass spectra were obtained by using ammonia as a reagent gas. The temperature of the ionization chamber was changed from 120 to 150°C. In both types of measurements reproducibility of relative intensities for the peaks discussed in the following was within  $\pm 10\%$ .

## RESULTS AND DISCUSSION

### Stereoregular MMA oligomer

Figure 1 illustrates EI mass spectra of *m* and *r* dimers of MMA having a *t*-C<sub>4</sub>H<sub>9</sub> group at the left end and a methine hydrogen at the right end. Both the spectra show a similar fragmentation patterns. The dimers have four C–C bonds along its main chain, and thus four pairs of fragment ions, which should be formed through the cleavages at these four C–C bonds as indicated in the formula [1], were observed in the spectra. Among the other peaks, for example, the peaks *M/e* = 143 and 243 are the fragments with one and two MMA units, respectively, formed through elimination of the ester CH<sub>3</sub> group; the peaks *M/e* = 128 and 227 are the fragments with one and two MMA units, respectively, formed through elimination of the ester OCH<sub>3</sub> group. Although there are unidentified fragment ions such as *M/e* = 211, 179, and 160, intensities of fragment ions which directly form through main chain cleavages are collected in Table 1. The intensities are normalized as the intensities of *t*-C<sub>4</sub>H<sub>9</sub> ion (*M/e*=57) to be 1.00. The table also includes the relative intensities of the peaks *M/e*=199 and 227, which correspond to the fragments formed through elimination of COOCH<sub>3</sub> and OCH<sub>3</sub>, respectively. All the relative intensities for the *m* and *r* dimers are close to each other; the stereochemical effects on the fragmentation in the EI process are small for the dimers.

Figure 2 shows EI mass spectra of four MMA trimers with different configurations. The trimers have six C–C bonds along its main chain, and six pairs of fragment ions formed through the main-chain cleavages, indicated in the formula [2], were observed in the EI mass spectra. Their peak intensities are collected in Table 2, together with those of [M – COOCH<sub>3</sub>] (*M/e*=299) and [M – OCH<sub>3</sub>] (*M/e*=327). The relative intensities of the latter two fragments are almost the same among the four stereoisomers, indicating no tacticity dependence of the fragmentation of the side group, as in the case of the dimer. Some of the fragment ions formed through main-chain scission, however, showed large dependence of relative intensity on the stereochemical configuration. For example, the intensity of *M/e*=188 (I<sub>188</sub>), the peak of which corresponds to the right-side fragment formed through cleavage at  $\alpha_3$  in formula [2], is greater for the *mr* isomer than for the *mm* isomer; I<sub>188</sub>(*mr*) (3.66) > I<sub>188</sub>(*mm*)(1.89), and also greater for *rr* than for

Table 1 Relative intensity of fragment ions in EI mass spectra of MMA dimers

<i>M/e</i>	<i>m</i>	<i>r</i>
57	1.00	1.00
201	0.63	0.80
71	0.07	0.07
187	0.06	0.07
158	0.35	0.34
101	0.47	0.46
171	0.67	0.74
88	1.22	1.29
199*	1.36	1.49
227**	0.47	0.63

\* [M – COOCH<sub>3</sub>]

\*\* [M – OCH<sub>3</sub>]

(M=parent molecule)

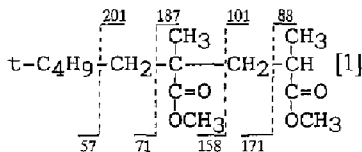


Table 2 Relative intensity of fragment ions in EI mass spectra of MMA trimers

<i>M/e</i>	<i>mm</i>	<i>mr</i>	<i>rm</i>	<i>rr</i>
57	1.00	1.00	1.00	1.00
301	0.63	0.78	0.46	0.48
71	0.12	0.09	0.12	0.12
287	0.43	0.60	0.28	0.29
158	2.62	1.55	2.14	1.23
201	1.35	1.95	1.25	2.38
171	0.15	0.10	0.13	0.14
188	1.89	3.66	2.69	4.17
258	0.98	0.40	1.01	0.28
101	1.15	1.03	0.97	1.00
271	0.27	0.31	0.27	0.26
88	0.33	0.42	0.40	0.47
299*	3.03	2.78	2.78	2.59
327**	1.64	1.48	1.44	1.78

\* [M – COOCH<sub>3</sub>], \*\* [M – OCH<sub>3</sub>]  
(M=parent molecule).

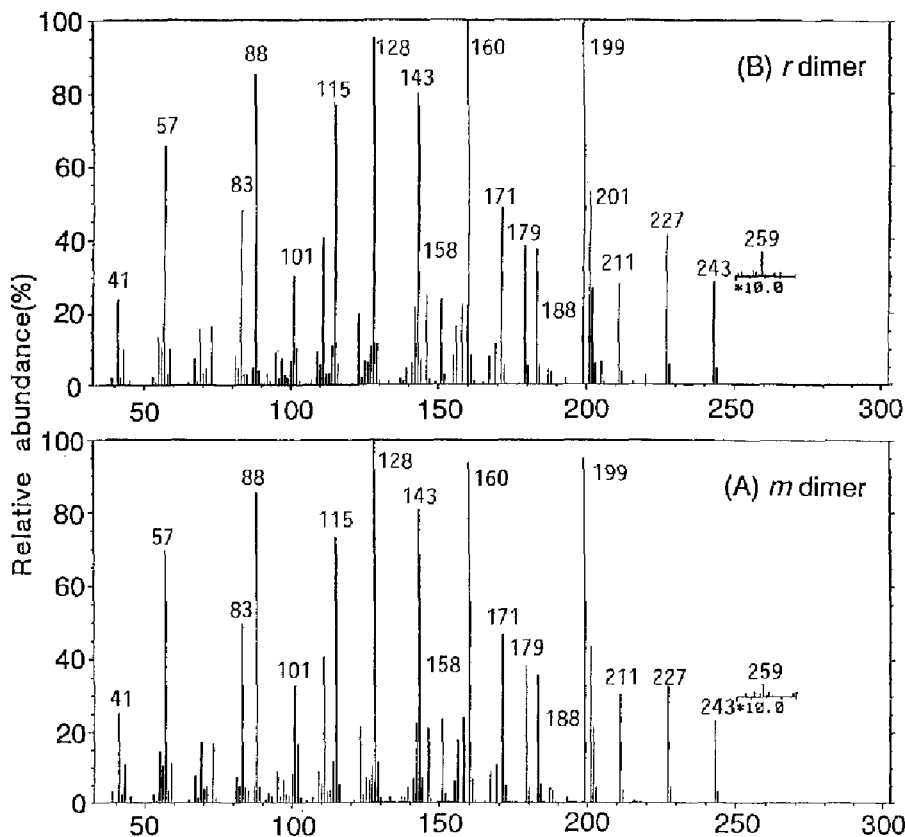
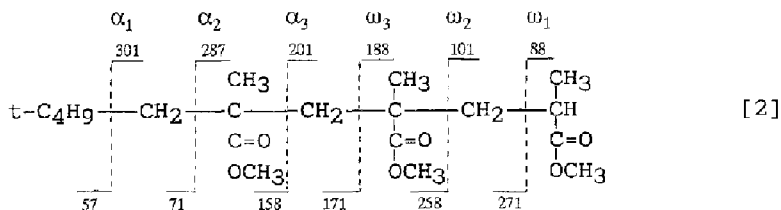


Figure 1 EI mass spectra of (A) *m* and (B) *r* dimers of MMA

$mr$ ;  $I_{188}(rr) (4.17) > I_{188}(rm) (2.69)$ . The intensity of the left-side fragment ion formed through cleavage at  $\omega_2$ ,  $M/e=258$ , also depends on the stereochemical configuration but in an opposite way;  $I_{258}(mm) (0.98) > I_{258}(mr) (0.40)$  and  $I_{258}(rm) (1.01) > I_{258}(rr) (0.28)$ . In both cases, the difference between  $I(mr) > I(rr)$  or that between  $I(mm)$  and  $I(rm)$  is rather small; that is, the intensity ratios are more sensitive to the diad configuration at the right end than to that at the left end.



The relative intensities of fragment ions observed in EI mass spectra of *mmm*, *mmr*, *rrr*, and *rrm* tetramers are listed in Table 3. A similar tacticity dependence of the relative intensities were found for several fragment ions; for the peak  $M/e=188$ ,  $I_{188}(mmr) > I_{188}(mmm)$ , and  $I_{188}(rrr) > I_{188}(rrm)$ ; for the peak  $M/e=258$ ,  $I_{258}(mmm) > I_{258}(mmr)$ , and  $I_{258}(rrm) > I_{258}(rrr)$ . As in the case of the trimer, the right-end diad configuration affects these intensities more

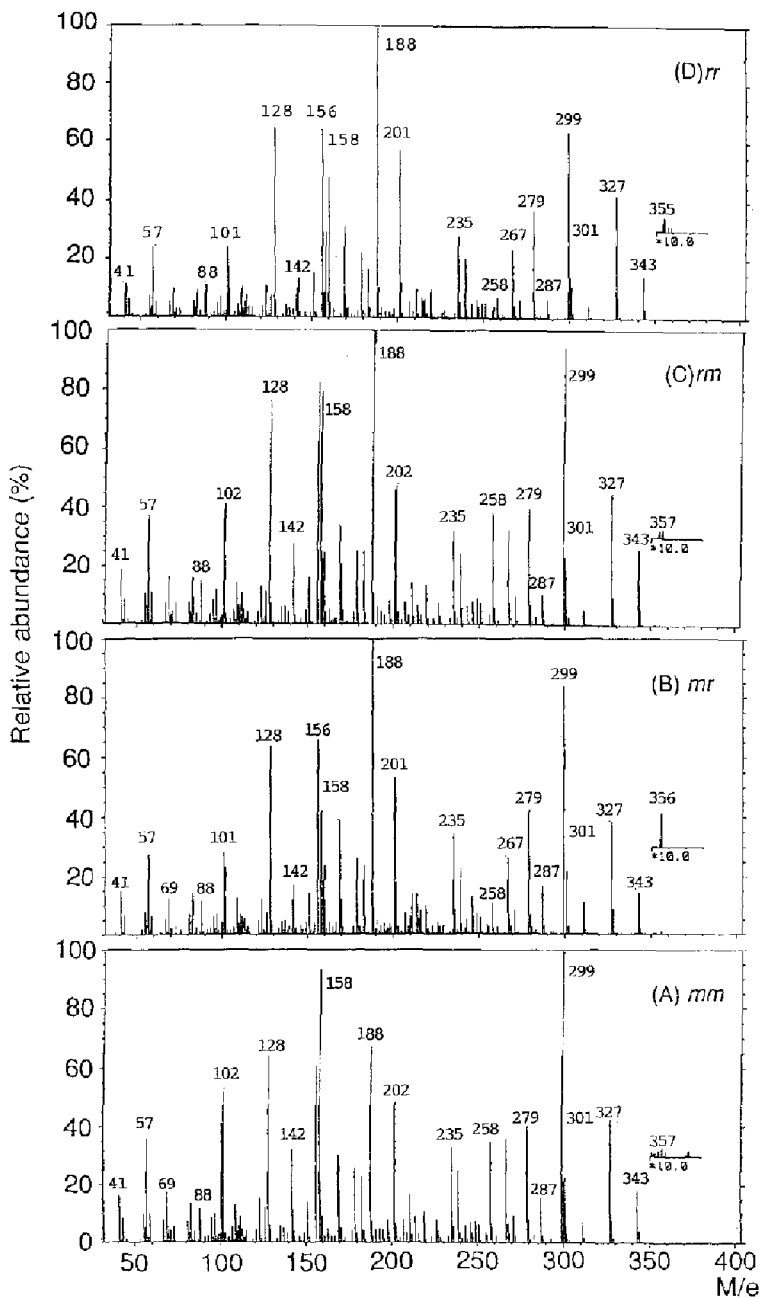


Figure 2 EI mass spectra of (A) *mm*, (B) *mr*, (C) *rm*, and (D) *rr* trimers of MMA

strongly than the configuration at the left end. The relative intensities of the fragment ions for  $[M - \text{COOCH}_3]$  ( $M/e=399$ ) or  $[M - \text{OCH}_3]$  ( $M/e=427$ ) are again quite similar among the four stereoisomers as in the cases of the dimer and trimer.

To evaluate the stability or lability of main-chain C-C bonds in the oligomers in EI process, the relative peak intensities for pairs of fragment ions, formed through bond cleavage at particular positions ( $\alpha_1, \dots, \omega_1$ ) along the main chain, were summed and are listed in Table 4. For example, the bond cleavage at  $\alpha_1$  in the tetramer should produce fragment ions  $M/e=57$  and 401, and thus the sum of the relative intensities for these two fragments,  $I^{\alpha_1} = I_{57} + I_{401}$ , was calculated for each isomer. Similarly,  $I^{\alpha_1}$  for the dimer and trimer are defined as follows:

$$I^{\alpha_1} = I_{57} + I_{201} \text{ (dimer)}$$

$$I^{\alpha_1} = I_{57} + I_{301} \text{ (trimer)}$$

The values of  $I^{\alpha_1}$  and  $I^{\omega_1}$  for all the oligomers examined are little affected by the stereochemistry of the oligomers.  $I^{\omega_2}$  and  $I^{\omega_4}$  for the trimer and tetramer are sensitive to the right-end diad configuration and are larger for  $-m$  ended oligomers than the corresponding  $-r$  ended ones; for the trimers,

$$I^{\omega_2}(mm) > I^{\omega_2}(mr), \text{ and } I^{\omega_2}(rm) > I^{\omega_2}(rr),$$

for the tetramers,

$$I^{\omega_2}(mmmm) > I^{\omega_2}(mmmr), \text{ } I^{\omega_2}(rrrm) > I^{\omega_2}(rrr),$$

$$I^{\omega_4}(mmmm) > I^{\omega_4}(mmmr), \text{ and } I^{\omega_4}(rrrm) > I^{\omega_4}(rrr).$$

$I^{\omega_3}$  and  $I^{\omega_4}$  also showed tacticity dependence but in an opposite way;  $-r$  ended oligomers showed the larger values than  $-m$  ended ones; for the trimers,

$$I^{\omega_3}(mr) > I^{\omega_3}(mm), \text{ and } I^{\omega_3}(rr) > I^{\omega_3}(rm),$$

for the tetramers,

$$I^{\omega_3}(mmmr) > I^{\omega_3}(mmmm), \text{ } I^{\omega_3}(rrr) > I^{\omega_3}(rrrm),$$

$$I^{\omega_4}(mmmr) > I^{\omega_4}(mmmm), \text{ and } I^{\omega_4}(rrr) > I^{\omega_4}(rrrm).$$

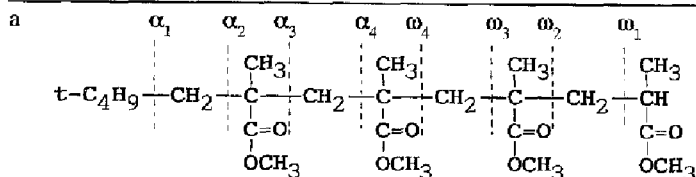
Table 3 Relative intensity of fragment ions in EI mass spectra of MMA tetramers

M/e	mmm	mmr	rrm	rrr
57	1.00	1.00	1.00	1.00
401	0.80	0.75	0.77	0.81
71	0.11	0.10	0.13	0.13
387	0.63	0.58	0.24	0.28
158	1.85	1.42	1.72	1.47
301	1.15	1.23	1.36	1.80
171	0.17	0.16	0.20	0.19
288	0.92	1.32	0.83	1.08
258	2.05	0.77	2.35	1.15
201	0.82	0.41	0.60	0.81
271	0.25	0.35	0.23	0.33
188	3.56	4.75	4.19	5.13
358	0.27	0.10	0.43	0.17
101	0.93	0.93	0.97	0.93
371	0.23	0.18	0.16	0.18
88	0.19	0.28	0.32	0.25
399*	3.06	2.67	2.66	2.73
427**	1.65	1.64	1.94	1.86

\* $[M - \text{COOCH}_3]$ , \*\* $[M - \text{OCH}_3]$   
(M=parent molecule).

Table 4 Sum of relative peak intensities of a pair of fragment ions formed through the main-chain cleavage in the EI mass spectrum of MMA oligomers

Cleavage <sup>a</sup>	Dimer		Trimer				Tetramer			
	m	r	mm	mr	rm	rr	mmm	mmr	rrm	rrr
$\alpha_1$	1.63	1.80	1.63	1.78	1.46	1.48	1.80	1.75	1.77	1.81
$\alpha_2$	0.13	0.14	0.55	0.69	0.40	0.41	0.74	0.68	0.37	0.41
$\alpha_3$			3.97	3.50	3.39	3.61	3.00	2.65	3.08	3.29
$\alpha_4$							1.09	1.48	1.03	1.27
$\omega_4$							2.87	1.18	2.95	1.96
$\omega_3$			2.04	3.76	2.82	4.31	3.81	5.10	4.42	5.46
$\omega_2$	0.82	0.80	2.13	1.43	1.98	1.28	1.20	1.03	1.40	1.10
$\omega_1$	1.89	2.01	0.60	0.73	0.67	0.73	0.42	0.46	0.48	0.43



Thus, the effect of right-end diad configuration on the cleavages at  $\omega_2$  to  $\alpha_4$  along the main chain has an alternating tendency. The effect of the left-end diad configuration is much smaller than that of the right-end configuration. The right-side fragments from the cleavages at  $\alpha_2$ ,  $\alpha_4$ , and  $\omega_3$ , which are the tertiary cations, are always more abundant than the left-side ones, probably due to the instability of the latter primary cations (Tables 2 and 3). In the cleavages at  $\alpha_3$ ,  $\omega_4$ , and  $\omega_2$ , however, the relative amounts of the left- and right-side fragments varied inconsistently. This also demonstrates different features in fragmentations at these two alternate series of cleavage positions ( $\alpha_2$ - $\alpha_4$ - $\omega_3$  and  $\alpha_3$ - $\omega_4$ - $\omega_2$ ).

The  $I^{\alpha 2}$  values for the trimers and tetramers are larger for the oligomers having  $m$  diad sequences at the left end or in the interior sequence;  $I^{\alpha 2}$  values for  $mm$  and  $mr$  trimers are larger than those for  $rm$  and  $rr$  trimers, and  $I^{\alpha 2}$  values for  $mmmm$  and  $mmmr$  tetramers are also larger than those for  $rrm$  and  $rrr$  tetramers.  $I^{\alpha 3}$  depends on the configuration of the trimer and tetramer but has no clear tendency, probably because both the left- and right-end diad configurations influence lability of the cleavage at  $\alpha_3$  in a complicated manner.

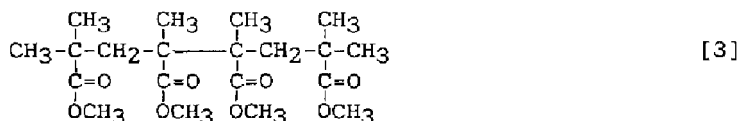
Isotactic PMMA is more flexible than syndiotactic PMMA as observed from NMR relaxation times<sup>20</sup>, and is thermally more stable at least in the range of molecular weight less than  $5 \times 10^4$ <sup>21,22</sup>. The thermal properties seem to be consistent with larger  $I^{\alpha 2}$  and  $I^{\alpha 4}$  values for  $-m$  ended oligomers than those for  $-r$  ended ones, while they are not consistent with  $I^{\alpha 3}$  and  $I^{\alpha 4}$  values. Thus the phenomena are peculiar to the ionization process, which may be complicated by the occurrence of further fragmentations after the main-chain scission, and are not directly related to the lability of bond scission along the main chain.

C-C bond length along the main chain of the  $mm$  trimer was the longest at the linkage  $\alpha_3$  (1.565 Å), as revealed from X-ray single crystal analysis<sup>14</sup>. Among the six  $I$  values for six main-chain C-C bonds, the  $mm$  trimer showed the highest  $I$  value for the bond cleavage at  $\alpha_3$ ,  $I^{\alpha 3}(mm)$ , as seen in Table IV. The results suggest the correlation between bond stability and bond length in the  $mm$  trimer. We have also reported X-ray single crystal analysis of the  $rrm$  tetramer<sup>17</sup>, which does not show alternating tendency in the bond lengths of the main-chain C-C bonds in the crystal. Thus, the alternating tendency in the fragmentation in mass spectrometry of MMA oligomers could not be correlated to bond-length data available at present. As a whole, however, the tacticity dependence of fragmentation in EI mass spectra of the MMA oligomers is evident.

#### Head-to-head tetramer

MMA oligomers with a *head-to-head* linkage have been studied in connection with thermal stability of the *head-to-head* linkage in PMMA<sup>7,13</sup>, the presence of which is considered to lower the thermal stability of radically prepared PMMA.<sup>7,13,23,24</sup>

Fallon *et al.*<sup>7</sup> reported structural analysis of meso and racemic MMA tetramers [3]:



They described that CI mass spectrometry using methane as a reaction gas was effective to detect the molecular ion. We prepared the meso and racemic tetramers and studied the fragmentation in CI mass spectra using ammonia as a reaction gas. Figure 3 shows the CI mass spectra of the tetramers. The peak for  $M+1$  ( $M/e = 403$ ) was observed, accompanying the peak for  $(M+1)+\text{NH}_3$  ( $M/e = 420$ ). Among the several fragment ion peaks, the peak  $M/e=201$ , also accompanying the peak for  $201+\text{NH}_3$  ( $M/e=218$ ), is characteristic because it should form through the bond cleavage at the *head-to-head* linkage<sup>7,19</sup>. The absence of the peaks  $M/e=301$  and  $101$  indicates the location of the *head-to-head* linkage to be the middle of the oligomer chain as depicted by formula [3].

The amount of the fragments with  $M/e=201$  and  $218$  relative to that of the parent ions

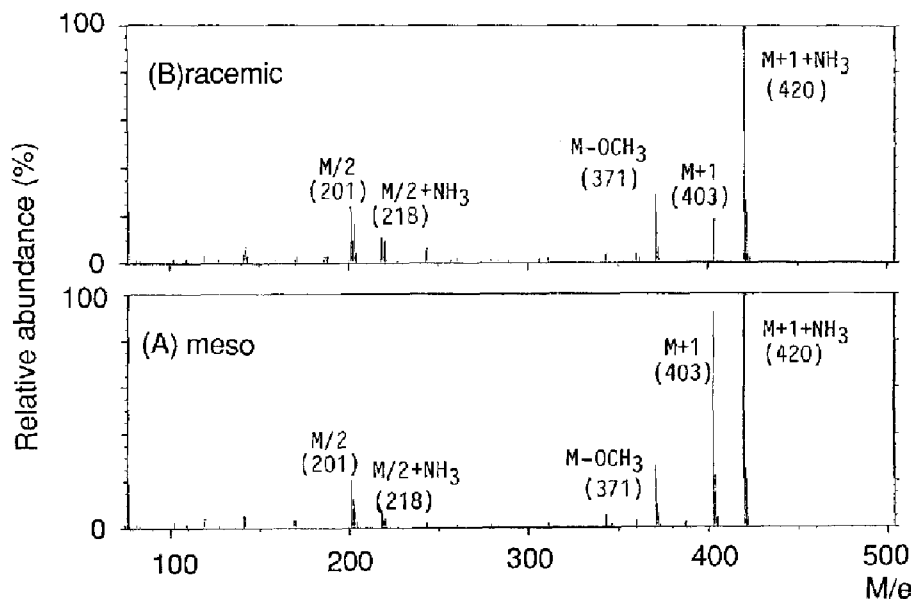


Figure 3 CI mass spectra of (A) meso and (B) racemic tetramers of MMA having head-to-head linkage in the middle of the chain

$M/e=403$  and  $420$  may be regarded as a measure of the stability or lability of the head-to-head linkage in each isomer. The relative intensity ( $R$ ), defined as  $(I_{201} + I_{218}) / (I_{403} + I_{420})$ , was determined for both isomers at various temperatures of ionization chamber, since the expected instability of the head-to-head linkage may not allow one to ignore the thermal effect on the fragmentation during ionization process. The results are plotted in Figure 4 together with total intensity of these four fragment ions. The temperature might not indicate the actual temperature of the sample undergoing ionization. The  $R$  value for the racemic isomer is always larger than that for the

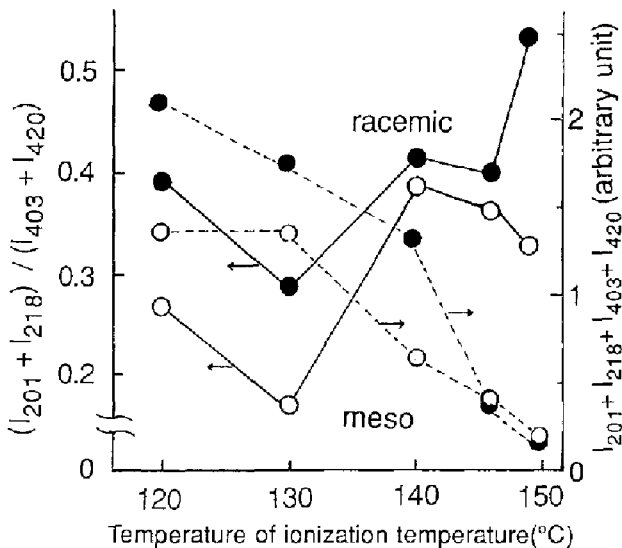


Figure 4 Ratio of relative intensities of the fragment ions,  $(I_{201} + I_{218})$  and  $(I_{403} + I_{420})$ , and the sum of these four ions observed in the CI mass spectra of the meso and racemic head-to-head tetramers of MMA at various ionization temperatures

meso isomer, while the total intensities ( $I_{201} + I_{218} + I_{403} + I_{420}$ ) decreased with an increase of ionization-chamber temperature. Thus, the *head-to-head* linkage in the racemic tetramer has lower stability in the chemical ionization process than that in the meso isomer. When the main chain of the tetramer assumes trans conformation, two ester groups at the *head-to-head* linkage in the racemic isomer occupy the same side of the chain so that the steric hindrance at the *head-to-head* linkage becomes larger than that in the meso isomer. This may be correlated with the difference in the fragmentations in CI mass spectra of these isomers.

The present work showed the effects of stereochemistry of MMA oligomers on the fragmentation during ionization process in EI and CI mass spectrometry. The MMA oligomers having *t*-C<sub>4</sub>H<sub>9</sub> group at the left end and methine hydrogen at the right end showed strong tacticity dependence in their fragmentation in EI mass spectra and, in particular, the effect of the right end configuration is greater than that of the in-chain tacticity. Fragmentation of MMA tetramer with a *head-to-head* linkage is also affected by the stereochemistry at the *head-to-head* linkage. Correlation of these results and other degradation processes such as thermal degradation may be of some interest.

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