Macromolecules **1997,** *30,* 4891−4896

Stereoregularity of Poly(methyl methacrylate)s Studied by Pyrolysis−Gas Chromatography/Mass Spectroscopy

Taihei Nonobe and Shin Tsuge*

Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Hajime Ohtani

Center of Integrated Research in Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Tatsuki Kitayama and Koichi Hatada

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received October 21, 1996; Revised Manuscript Received June 17, 1997[⊗]

ABSTRACT: The stereoregularity of poly(methyl methacrylate) (PMMA) prepared by various methods was characterized by pyrolysis−gas chromatography/mass spectroscopy (Py-GC/MS) at 500 °C under He carrier gas. The diad tacticity determined from the relative peak intensities of the diastereomeric tetramers in the pyrograms was consistent with that obtained by ^{1}H NMR, suggesting that no appreciable thermal isomerization occurred during the pyrolysis. The thermal degradation mechanisms to yield the diastereomeric tetramers from PMMA without isomerization were discussed, with the possibility of estimating the triad tacticity of PMMA from the distribution of diastereomeric pentamers.

Introduction

The stereochemical structure of vinyl polymers is known to affect their properties. Detailed examination of tacticity for a given polymer also often provides significant information on the stereochemistry of the associated polymerization reactions. In 1960 Bovey and Tiers[1] and Nishioka et al.[2] published the first papers to determine the stereoregularity of poly(methyl methacrylate) (PMMA) by means of ^{1}H NMR. This triggered many subsequent investigations on the synthesis of various stereoregular PMMA's and their structural characterization.[3−22] The stereoregularity of PMMA's can be varied from highly isotactic to highly syndiotactic configurations by controlling polymerization conditions such as initiators, solvents, temperature, etc. Although ^{1}H NMR and ^{13}C NMR have been most extensively utilized to study the stereoregularity of PMMA's, there are still discrepancies between the proposed polymerization mechanisms and the observed stereospecific configurations of the resulting PMMA's.[4,15,18,19] Therefore, there is still a need to develop sensitive and rapid techniques to characterize the stereoregularity of PMMA's.

Table 1. PMMA Samples

	polymerization conditions							
	initiator/		tacticity,[c] %			tacticity,[c] %		
sample	solvent/temp, °C	M_n	mm	mr	rr	m	r	ref
S-1	*t*-BuLi/Et$_3$Al(1/3)/ toluene/−78	23 000[a]	0.5	10.2	89.3	5.6	94.4	20
S-2	benzoyl peroxide/ toluene/100	17 000[b]	3.5	41.1	55.4	24.0	76.0	24
S-3	BuLi/toluene/−78	79 000[a]	76.2	13.2	10.5	82.8	17.1	
S-4	*t*-BuMgBr/ toluene/−60	21 000[a]	96.6	1.2	2.2	97.2	2.8	13

[a] Number-average molecular weight determined by ^{1}H NMR on the basis of relative intensities of the methyl protons in the *tert*-butyl end group. [b] Number-average molecular weight determined by SEC. [c] Determined by ^{1}H NMR.

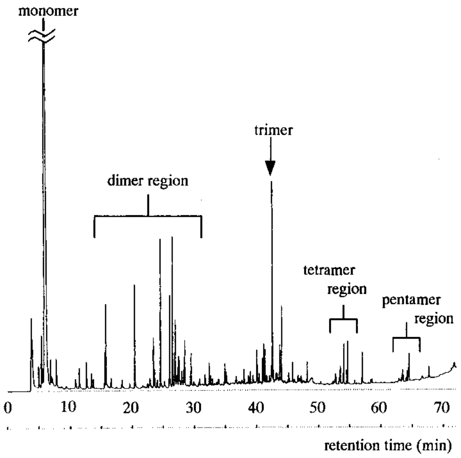


Figure 1. Pyrogram of S-2 at 500 °C observed by FID.

Recently, pyrolysis−gas chromatography (Py-GC) has been utilized as a highly sensitive technique to elucidate microstructures of PMMA's.[23−28] In these studies, however, the end groups in the polymer chains have been mostly determined. If the tacticity of vinyl polymers is to be determined by Py-GC, diastereoisomers larger than tetramers which comprise at least two asymmetric centers have to be separately observed in the pyrograms. Therefore, the early application of Py-GC to the study of the tacticity was limited to vinyl polymers consisting of relatively smaller monomer units such as polypropylene (PP).[29,30] Recently, Py-GC has been extended to characterize the stereoregularity of various stereoregular polystyrene (PS) samples by use of fused-silica and deactivated metal capillary columns with temperature programming up to 390 °C.[31] In these Py-GC studies,[29−31] however, it was proved that stereoisomerization of the degradation products occurred to some extent during the thermal degradation of PP and PS. Therefore, the relative intensities of the diastereo-

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

S0024-9297(96)01541-0 CCC: $14.00

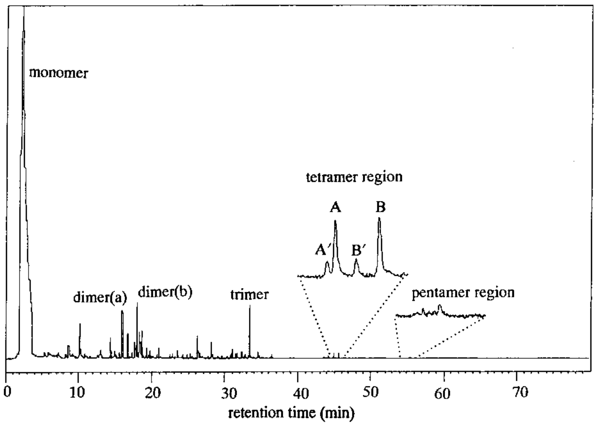


Figure 2. Pyrogram of S-2 observed in total ion monitor by CI mode MS.

meric tetramers observed in the pyrograms of the PP and PS samples were not completely consistent with the diad concentrations determined by ^{1}H NMR.

In this work, basically the same Py-GC technique developed to study the tacticity of PS[31] was applied to determine the tacticity of various stereoregular PMMA samples by separating the associated diastereomeric tetramers identified by a directly coupled Py-GC/MS system. The observed stereoregularity of the PMMA samples was then shown to be consistent with that obtained by ^{1}H NMR, suggesting that no appreciable stereoisomerization of the degradation products occurs during the pyrolysis of PMMA. The associated degradation mechanisms of PMMA were also discussed.

Experimental Section

Samples. Four PMMA samples (S-1−S-4) prepared by different synthetic methods are summarized in Table 1 together with their M_n values and tacticity values determined by ^{1}H NMR.

Tacticity Measurements of PMMA's by ^{1}H NMR. The tacticity of PMMA samples (S-1−S-4) was estimated by 500-MHz ^{1}H NMR by use of the α-methyl proton resonances. The measurements of ^{1}H-NMR spectra were carried out on a Varian VXR500 spectrometer at 500 MHz at 60 °C. About 5 mg of each sample dissolved in 1 mL of benzene-d_6, which was used to avoid the spectral interference of the terminal groups such as *tert*-butyl groups, was transferred to a Pyrex sample tube of 5-mm o.d. Two hundred scans of the spectrum were accumulated at a pulse delay of 1.216 s and a flip angle of 45°. The split signals of α-methyl protons between 1.2 and 1.7 ppm corresponding to the triad sequences (mm, mr, and rr) were used to estimate the tacticity of the PMMA samples. The relative peak intensities of the α-methyl proton signals were measured by the cut-and-weigh method. The tacticity values thus obtained are shown in Table 1 together with the average tacticity values calculated according to the relations m = mm + mr/2 and r = rr + mr/2.

As expected from the polymerization conditions, S-1 prepared with *t*-BuLi/Et$_3$Al in toluene at −78 °C is highly syndiotactic, S-2 radically polymerized with benzoyl peroxide in toluene at 100 °C is relatively syndiotactic rich, S-3 anionically polymerized with BuLi in toluene at −78 °C is relatively isotactic rich, and S-4 anionically polymerized with *t*-BuMgBr in toluene at −60 °C has extremely high isotacticity.

Py-GC Measurement. The Py-GC system utilized in this work is almost the same as that described previously.[30] The Py-GC measurements were carried out by using a gas chromatograph (Hewlett-Packard, 5890 Series-II) equipped with a flame ionization detector (FID). In order to separate the resulting diastereoisomers as well as possible, a deactivated metal capillary column (Frontier Lab, Ultra Alloy-1; 50 m × 0.25 mm i.d., 0.15 μm thickness of cross-linked polydimethylsiloxane) was used. About 400 μg of the sample was pyrolyzed under a flow of carrier gas (He) by using a vertical furnace pyrolyzer (Frontier Lab, Single-shot Pyrolyzer PY-2010SL). The optimum pyrolysis temperature of 500 °C to attain reproducible and higher intensity of the diastereo-

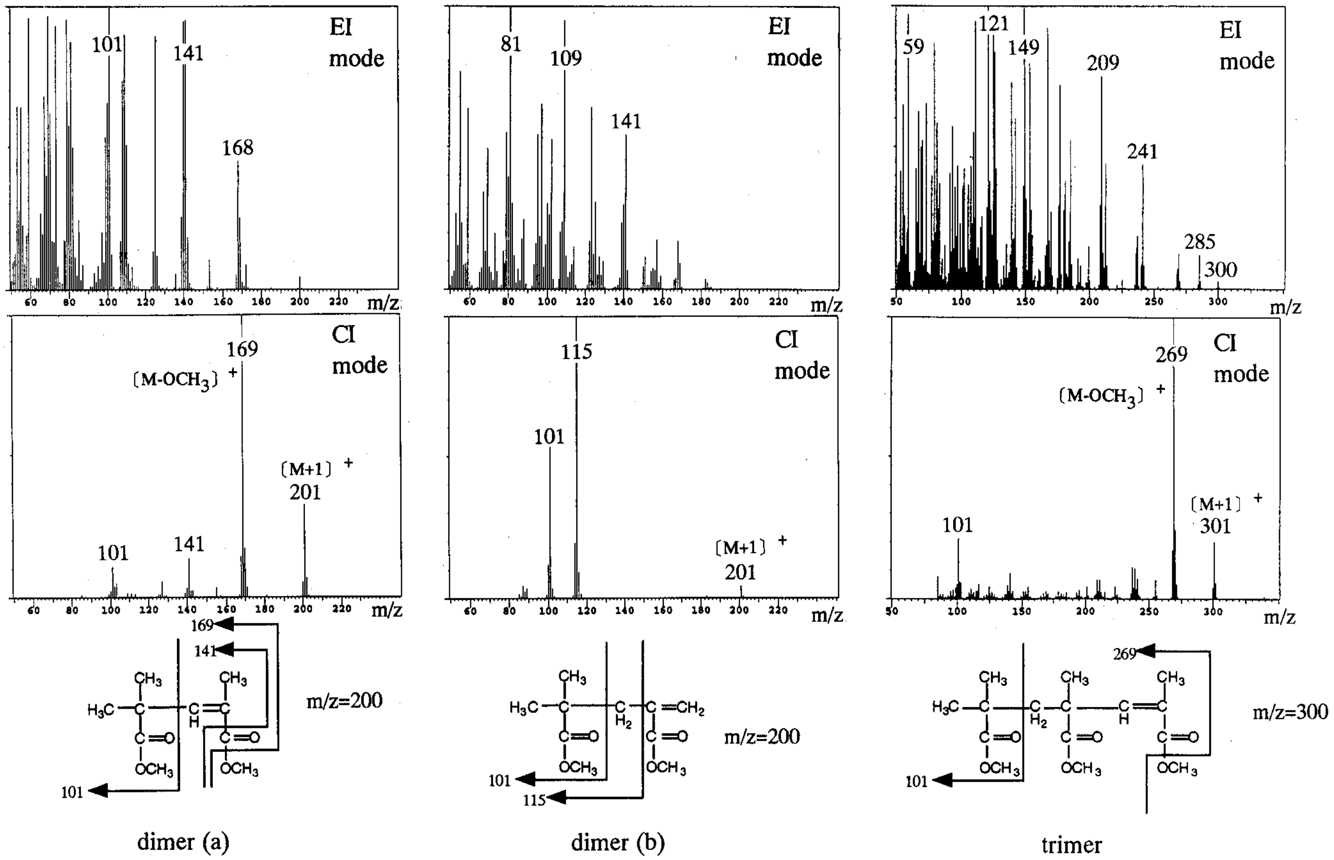


Figure 3. EI and CI mass spectra of dimers and trimer and their expected structures.

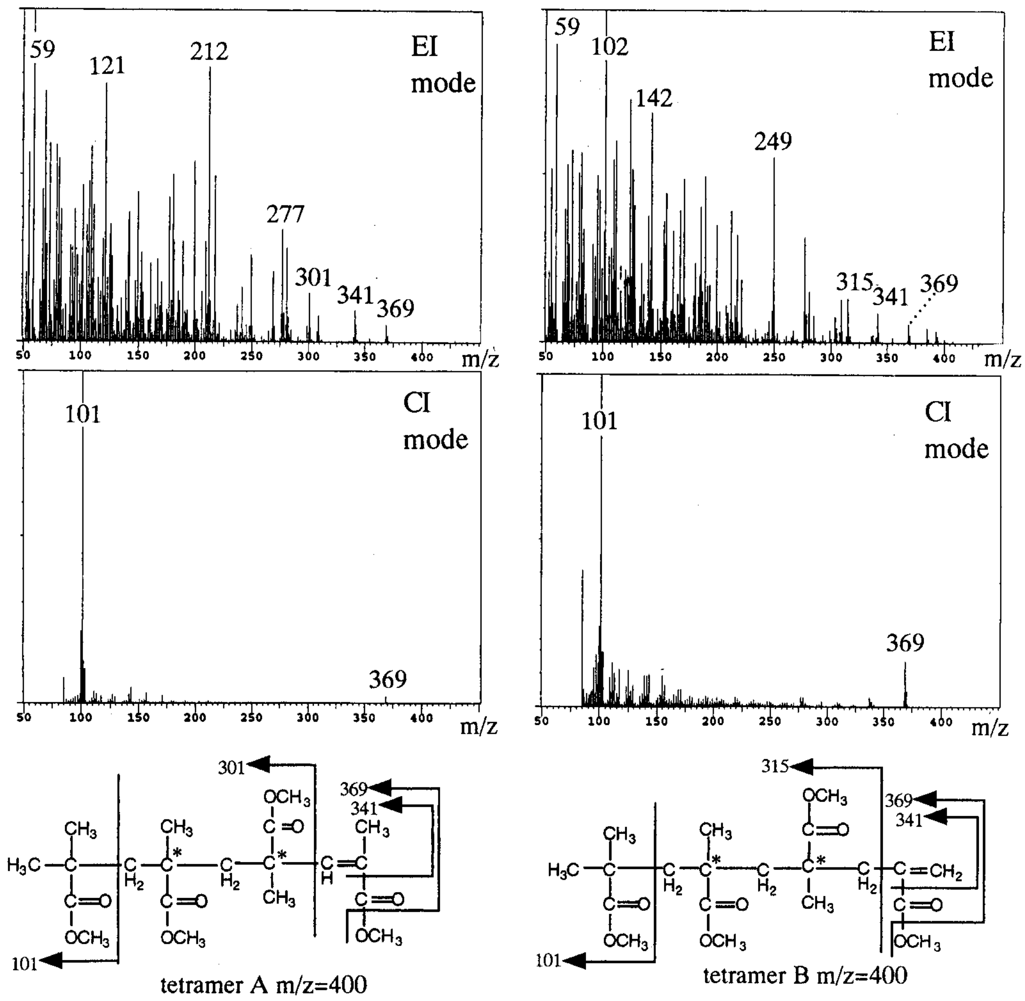


Figure 4. EI and CI mass spectra of tetramers and their expected structures.

isomers was empirically determined after examining various temperatures between 350 and 650 °C. The pyrolysis products formed in the pyrolyzer were transferred by He carrier gas at a rate of 50 mL/min and introduced into the separation column through a splitter with a splitting ratio of 1/50 at the column head pressure of 200 kPa. The column temperature was programmed from 50 to 340 °C at a rate of 4 °C/min and held at 340 °C for 30 min.

Py-GC/MS Measurement. Identification of the diastereoisomers in the pyrograms of PMMA samples was carried out mostly by Py-GC/MS measurements. The Py-GC/MS system was composed of a gas chromatograph−mass spectrometer (GC/MS) system (JEOL, Automass System II) equipped with the same type pyrolyzer mentioned above. Both electron impact (EI) at 70 eV at 250 °C and chemical ionization (CI) at 180 °C by use of isobutane as the reagent gas were used. A fused-silica capillary column (H.P. Ultra-1, 25 m × 0.2 mm i.d., 0.33 μm thickness of polydimethylsiloxane) operated at the head pressure of 140 kPa was used. About 1 mg of a sample was pyrolyzed at 500 °C under a flow of carrier gas (He). The resulting pyrolysis products were transferred by a flow of He carrier gas at 50 mL/min and introduced into each separation column through a splitter with a splitting ratio of 1/50. The column temperature was programmed from 50 to 280 °C at a rate of 4 °C/min and held at 280 °C for 30 min.

Results and Discussion

Identification of Diastereomeric Tetramers in the Pyrograms of PMMA. Figure 1 shows a typical program of PMMA (S-2) at 500 °C observed by FID. The main peak is due to the monomer (about 96%) because PMMA is easily depolymerized at elevated temperatures.[23−28] On the pyrogram recorded with higher sensitivity, however, one can clearly recognize the tetramers (about 0.1%) and even the pentamers (about 0.03%) as well as the dimers and the trimers. Among these fragment clusters, the tetramers and the pentamers should contain at least two (m and r) and four (mm, mr, rm and rr) diastereoisomers since they have two and three asymmetric centers in the molecules, respectively. Then, the chemical structures of the diastereoisomers in the tetramer region were estimated from EI and CI mass spectra of the tetramers observed by Py-GC/MS in comparison with those of the dimers and the trimers.

Figure 2 shows a typical pyrogram of a PMMA sample (S-2) observed in the total ion monitor (TIM) by the Py-GC/MS system in the CI mode. In order to elucidate the possible common positions of the double bonds among the pyrolysis products, the EI and CI spectra for the two representative dimer peaks at ca. 16 min (a) and at ca. 18 min (b) and the main trimer peak at ca. 33 min were compared in detail. The molecular formula of the dimers (a) and (b) and the trimer have been reported as $C_{10}H_{18}O_4$ (MW = 200) and $C_{15}H_{27}O_6$ (MW = 300), respectively, while most of the satellite dimeric products around the dimers (a) and (b) have MW = 186 or 214 rather than MW = 200.[25,27] Figure 3 shows the mass spectra for the dimers (a) and (b) and the trimer. In the corresponding CI spectra, we can clearly observe $[M + 1]^+$ at $m/z = 201$ for the both dimers and at $m/z = 301$ for the trimer. The trimer structure is confirmed as that shown in the figure on the basis of the formation mechanism discussed later in Scheme 2. Also, the main dimer structures with MW = 200 should be those shown

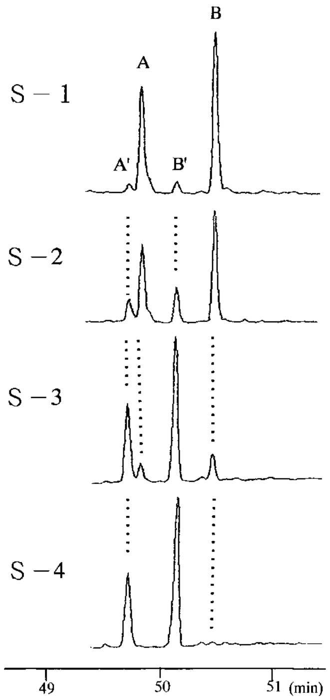


Figure 5. Expanded pyrograms of PMMA samples in the tetramer region.

Table 2. Comparison of the Diad Tacticity (%) of PMMAs As Determined by Py-GC and ^{1}H NMR

	Py-GC					
	from A peaks		from B peaks		^{1}H NMR	
sample	m	r	m	r	m	r
S-1	7.3	92.7	7.4	92.6	5.6	94.4
S-2	21.3	78.7	24.1	75.9	24.0	76.0
S-3	79.7	20.3	81.8	18.2	82.8	17.1
S-4	98.5	1.5	97.3	2.7	97.2	2.8

in the figure. Furthermore, according to the characteristic fragments, especially the prominent $[M - OCH_3]^+$ peak observed as the base peak in the CI mass spectra, we can estimate that the dimer (a) and the trimer should have the same terminals illustrated at the bottom of the figure.

Figure 4 shows the EI and CI spectra corresponding to the two strong peaks for tetramer A at ca. 45 min and tetramer B at about 46 min in the pyrogram of Figure 2. Although the expected quasi-molecular ions are not observed even in the CI spectra, the common ions at $m/z = 369$ can be attributed to $[M - OCH_3]^+$. Thus, both A and B should have the same molecular weight (MW = 400). Furthermore, in the EI spectra, the teramer A shows a fairly strong peak at $m/z = 301$, while B exhibits a prominent peak at $m/z = 315$. The possible bond cleavages are shown at the bottom of the figure together with the possible structures for the isomers. In this case, the relationship between the retention times and the position of the double bonds for the tetramers is also consistent with that for the dimers. Additionally the small satellite peaks (A′ and B′) appearing a little smaller retention times than those of the main tetramers (A and B) observed in the expanded pyrogram (Figure 2) showed exactly the same mass spectra for A and A′ and for B and B′, suggesting that they are stereoisomers, respectively.

Determination of Tacticity in PMMA by Py-GC. As mentioned in the introduction, the stereoregularity of vinyl polymers should be reflected in the fragments larger than tetramers which contain more than two asymmetric centers. Figure 5 shows the expanded partial pyrograms of the tetramer region for the PMMA samples (S-1−S-4). By comparing the pyrogram for the highly syndiotactic S-1 with that for the highly isotactic S-4, it is apparent that the diastereoisomers with the meso configuration (m) always appear at smaller retention times than those with the racemic configuration (r). Here, it is interesting to note that this retention order

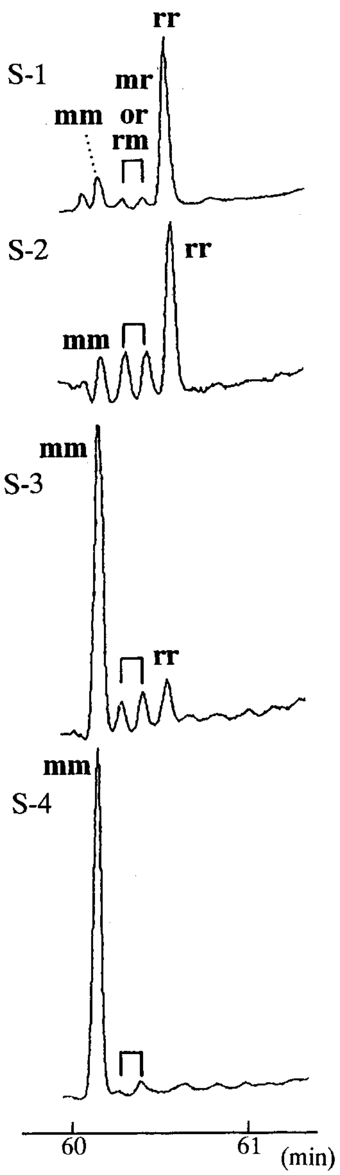
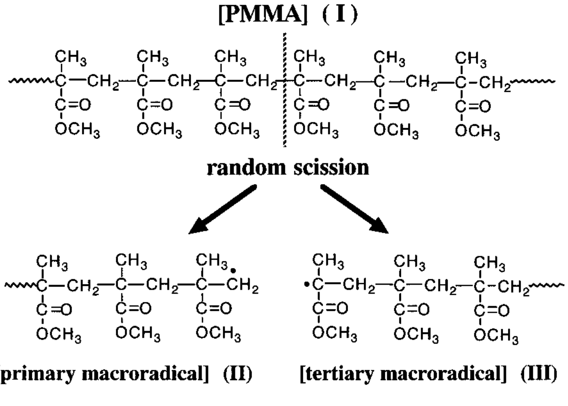
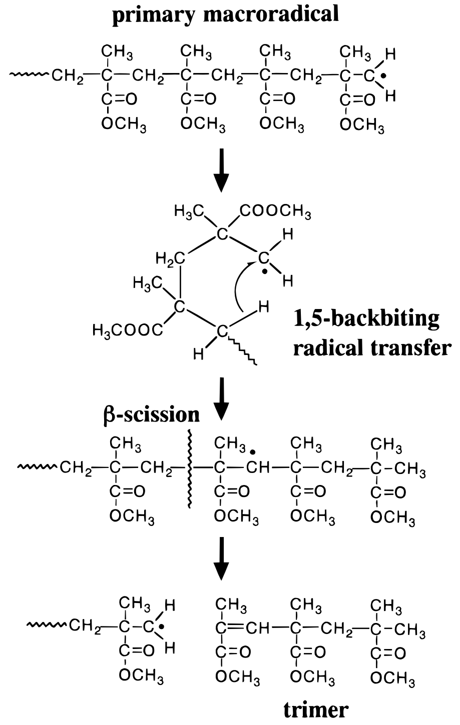


Figure 6. Expanded pyrograms of PMMA samples in the pentamer region.

Scheme 1. Initial Thermal Degradation Step of PMMA To Yield Primary and Tertiary Macroradicals



Scheme 2. Formation Mechanism of Trimer through 1,5-Radical Transfer from Primary Macroradical



for the diastereoisomers for PMMA is the same as in PP and the reverse of that in PS, probably because of the contribution of the steric hindrance of phenyl groups in styrene units causing the higher boiling point of the meso isomers.[31]

Table 3. Comparison of the Triad Tacticity (%) of PMMAs As Determined by Py-GC and ^{1}H NMR

	Py-GC[a]			^{1}H NMR		
sample	mm	mr+rm	rr	mm	mr	rr
S-1	14.0	7.5	78.6	0.5	10.2	89.3
S-2	13.6	30.3	56.1	3.5	41.1	55.4
S-3	74.0	15.6	10.4	76.2	13.1	10.5
S-4	92.5	4.7	2.7	96.6	1.2	2.2

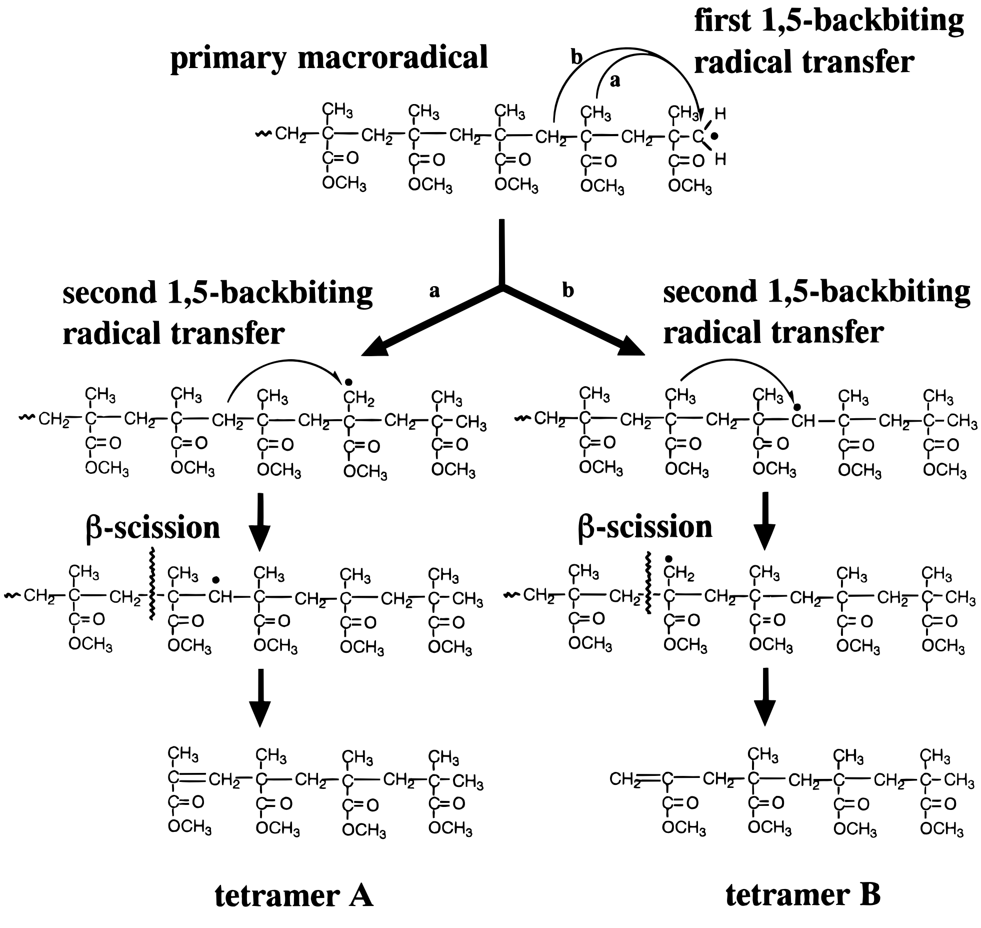
[a] Determined by relative peak intensities for pentamer.

Provided that these diastereoisomers reflect the original stereoregularity of the PMMA samples, we can estimate the diad tacticity from the relative peak intensities of A′(m) and A(r) or B′(m) and B(r). The diad tacticity values thus determined are summarized in Table 2 together with the reference values obtained by ^{1}H NMR. Here, fairly good reproducibility of the measurement by Py-GC as CV = 2.0% was obtained for seven repeated runs with S-3.

The observed diad tacticity values by use of either tetramer pair, A and A′ or B and B′, are in fairly good agreement with those by ^{1}H NMR. This fact suggests that no appreciable thermal isomerization accompanies the thermal degradation of PMMA to the tetramers. Moreover, the observed tacticity values by Py-GC were almost independent of the pyrolysis temperatures between 400 and 600 °C. This is quite different from the behavior of PP and PS where the thermal isomerization was inevitable in the formation of their tetramers.[29−31]

Finally we tried to assign the pentamers appearing between 61 and 62 min in the pyrogram observed by FID (Figure 2). Figure 6 shows the expanded partial pyrograms of the pentamer region for the PMMA samples (S-1−S-4). Theoretically the pentamers should have at least four diastereoisomers, mm, mr, rm, and rr, reflecting the triad sequences of the original polymer chains. As expected, in this region we can recognize

Scheme 3. Formation Mechanism of Tetramers from Primary Macroradical



four peaks for which the CI mass spectra are exactly the same with the relative intensities varying with the tacticity of the samples. From a comparison of these data with those obtained by ^{1}H NMR, these four peaks can be empirically assigned as mm, mr (or rm), rm (or mr), and rr components, in the order of retention time.

As in the estimation of the diad tacticity, the triad tacticity was estimated from the relative peak intensities of these four peaks. The results for the PMMA samples are summarized in Table 3 together with the values obtained by ^{1}H NMR. Although for the isotactic S-3 and S-4, fairly good agreement with that obtained by ^{1}H NMR is observed, for the syndiotactic S-1 and S-2, there is fairly large discrepancy.

Provided that the contribution of the thermal isomerization are negligible during the formation of the pentamers as in the case for the tetramers, the above observations suggest that there is some peak overlap especially in the mm related peaks and/or that the diastereomeric pentamer peaks other than the four peaks used in this trial might be hidden in the pyrograms. In order to resolve this uncertainty, additional pyrograms measured under different separation conditions, e.g., using another separation column with different polarity, should be considered.

Mechanisms of Thermal Degradation to Yield Diastereomeric Tetramers from PMMA. When the pyrolysis reaction of PMMA (I) is initiated by random scission, both primary (II) and tertiary macroradicals (III) are formed as in Scheme 1. Although both macroradicals (II and III) mostly depolymerize to monomer, some dimers, trimers, tetramers, pentamers, etc. are also formed to a lesser extent mainly through 1,5-radical transfer(s) of the primary radical (II) followed by β-scission since 1,5-radical transfer(s) cannot occur for the tertiary macroradicals (III).

The reason why the main trimer peak consists of only one component is easily explained by Scheme 2, where the trimer is exclusively formed through 1,5-radical transfer of the primary macroradical (II) at the fifth methylene carbon followed by β-scission, since 1,5-radical transfer of the primary macroradical (II) at the fifth methyl carbon followed by β-scission yields only a dimer at best. When double back-biting occurs through 1,5- and then 5,9-radical transfers of the primary macroradical (II) at the fifth and the ninth methylene carbons, the pentamers consisting of only one chemical structure are formed in a similar manner as the trimer formation although they comprise the associated diastereoisomers (Scheme 2). On the other hand, in the tetramers, two kinds of position isomers [A (or A′) and B (or B′)] can be formed depending on the paths of the double back-bitings followed by β-scission as shown in Scheme 3. In path (a), the first back-biting occurs at the fifth methyl carbon of the primary macroradical (II) and the second 1,5-radical transfer at the seventh methylene carbon followed by β-scission to yield the tetramer A (or A′), while in path (b), the first back-biting occurs at the fifth methylene carbon and the second 1,5-radical transfer does at the ninth methyl carbon followed by β-scission to yield the tetramer B (or B′). In both paths, there is no chance for the thermal isomerization since the associated radical transfers always occur only at methyl and methylene carbons. In the cases of the thermal degradation of PP and PS, however, the corresponding double back-bitings followed by β-scission to yield their tetramers occur mostly at asymmetric methine carbons resulting in some thermal isomerization.[29−31]

Acknowledgment. This research was financially supported by Grant-in-Aid for Scientific Research (A) (07555262 and 09305056) and (B) (09555262) from the Ministry of Education, Science, Sports and Culture, Japan, and by the Grant “Research for the Future” Program of the Japan Society for the Promotion of Science (JSPS-RFTF, 96R11601). H.O. gratefully acknowledges financial support by a grant from the Mazda Foundation.

References and Notes

(1) Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* **1960**, *44*, 173.
(2) Nishioka, A.; Watanabe, H.; Yamaguchi, I.; Shimizu, H. *J. Polym. Sci.* **1960**, *45*, 232.
(3) Ramey, K. C.; Messick, J. *J. Polym. Sci. A-2* **1966**, *4*, 155.
(4) Reinmoller, M.; Fox, T. G. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1966**, *7*, 999.
(5) Abe, H.; Imai, K.; Matsumoto, M. *J. Polym. Sci., C* **1968**, *23*, 469.
(6) Johnson, L. F.; Heatley, F.; Bovey, F. A. *Macromolecules* **1970**, *3*, 175.
(7) Lando, J. R.; Semen, J.; Farmer, B. *Macromolecules* **1970**, *3*, 524.
(8) Inoue, Y.; Nishioka, A.; Chujo, R. *Polym. J.* **1971**, *4*, 535.
(9) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(10) Chapman, A. J.; Billingham, N. C. *Eur. Polym. J.* **1980**, *16*, 21.
(11) Allen, P. E. M.; Mair, C. *Eur. Polym. J.* **1984**, *20*, 697.
(12) Hatada, K.; Nakanishi, H.; Ute, K.; Kitayama, T. *Polym. J.* **1986**, *18*, 581.
(13) Hatada, K.; Ute, K.; Tanaka, Y.; Okamoto, Y.; Kitaytama, T. *Polym. J.* **1986**, *18*, 1037.
(14) Sugai, S.; Nitta, K.; Toyama, Y.; Ohno, N. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 47.
(15) Moad, G.; Solomon, D. H.; Spurling, T. H.; Johns, S. R.; Willing, R. I. *Aust. J. Chem.* **1986**, *39*, 43.
(16) Hatada, K.; Ute, K.; Tanaka, K.; Imanari, M.; Fujii, M. *Polym. J.* **1987**, *19*, 425.
(17) Ferguson, R. C.; Ovenall, D. W. *Macromolecules* **1987**, *20*, 1254.
(18) Chujo, R.; Hatada, K.; Kitamaru, R.; Kitayama, T.; Sato, H.; Tanaka, Y. *Polym. J.* **1987**, *19*, 413.
(19) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189.
(20) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem., Suppl.* **1989**, *15*, 167.
(21) Kitayama, T.; Masuda, E.; Yamaguchi, M.; Nishiura, T.; Hatada, K. *Polym. J.* **1992**, *8*, 817.
(22) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 719.
(23) Ohtani, H.; Ishiguro, S.; Tanaka, M.; Tsuge, S. *Polym. J.* **1989**, *21*, 41.
(24) Ohtani, H.; Tanaka, M.; Tsuge, S. *J. Anal. Appl. Pyrolysis* **1989**, *15*, 167.
(25) Ohtani, H.; Tanaka, M.; Tsuge, S. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1196.
(26) Ohtani, H.; Luo, Y. F.; Nakashima, Y.; Tsukahara, Y.; Tsuge, S. *Anal. Chem.* **1994**, *66*, 1438.
(27) Ito, Y.; Tsuge, S.; Ohtani, H.; Wakabayashi, S.; Atarashi, J.; Kawamura, T. *Macromolecules* **1996**, *29*, 4516.
(28) Ohtani, H.; Takehana, Y.; Tsuge, S. *Macromolecules* **1997**, *30*, 2542.
(29) Sugimura, Y.; Nagaya, T.; Tsuge, S.; Murata, T.; Takeda, T. *Macromolecules* **1980**, *13*, 928.
(30) Ohtani, H.; Tsuge, S.; Ogawa, T.; Elias, H.-G. *Macromolecules* **1984**, *17*, 465.
(31) Nonobe, T.; Ohtani, H.; Usami, T.; Mori, T.; Fukumori, H.; Hirata, Y.; Tsuge, S. *J. Anal. Appl. Pyrolysis* **1995**, *33*, 121.

MA9615415