

# Tacticity of Methacrylic Copolymers and Their Crosslinked Polymers Studied by Pyrolysis–Gas Chromatography

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**ABSTRACT:** Diad tacticity of methyl methacrylate (MMA) sequences in the copolymers of MMA and various acrylates and their crosslinked polymers was characterized by pyrolysis–gas chromatography (Py-GC) based on the relative peak intensities of the diastereomeric MMA tetramers in the pyrograms. The diad tacticity in the copolymers synthesized at a given temperature proved to be almost consistent with that of corresponding MMA homopolymers (PMMA) prepared under the same conditions. Furthermore, the diad tacticity of PMMAs was also consistent with that of the corresponding crosslinked polymers. These results suggest that the tacticity of MMA sequences in the polymer chains would be dominated by polymerization temperature, independent of the polymerization and crosslinking. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2140–2144, 2000

**Key words:** tacticity; pyrolysis–gas chromatography; poly(methyl methacrylate); polymerization temperature; methacrylic crosslinked polymer

## INTRODUCTION

Methacrylic polymers and their crosslinked polymers are widely used for industrial thermoplastics, including molding materials, sheets, and films. The control of stereoregularity for these polymers is often a requisite to get a specific performance from the polymeric materials. For example, the glass-transition temperature ( $T_g$ ) of methacrylic polymers is known to change as a function of tacticity.<sup>1–2</sup> In 1960 Bovey and Tiers<sup>3</sup> and Nishioka et al.<sup>4</sup> published the first papers to determine the stereoregularity of poly(methyl methacrylate) (PMMA) by means of <sup>1</sup>H-NMR. Their reports triggered many subsequent investi-

gations on the synthesis of various stereoregular PMMAs and their structural characterization.<sup>5–12</sup> However, most NMR studies for methacrylic polymers were concerned with PMMA homopolymers. The NMR studies of methacrylic copolymers have been focused mainly on comonomer sequences, and only a few studies on the stereoregularity of methacrylic copolymers have been reported.<sup>13,14</sup> On the other hand, it is difficult to estimate the stereoregularity of crosslinked polymers by NMR because of their insoluble nature. Therefore, there still exists a need to develop highly sensitive and rapid techniques to characterize the stereoregularity for MMA-related polymers, especially for crosslinked ones.

Recently, pyrolysis–gas chromatography (Py-GC) has been developed as a highly sensitive technique to elucidate microstructures of various vinyl polymers.<sup>15–22</sup> This technique was applied to study the

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**Table I** Polymerization Conditions of MMA-Related Samples

Sample	Monomer Content (%) <sup>a</sup>					Initiator	Polymerization Temp (°C)	Remarks
	MMA	MA	EA	BA	2-EHA			
S-1	100	—	—	—	—	2,2-Azobisisobutyronitrile	40	
S-2	100	—	—	—	—	2,2-Azobisisobutyronitrile	65	
S-3	100	—	—	—	—	Azodi- <i>tert</i> -octane	100	
S-4	100	—	—	—	—	Di- <i>tert</i> -butyl peroxide	145	
S-5	100	—	—	—	—	Di- <i>tert</i> -butyl peroxide	155	
S-6	99.5	0.5	—	—	—	2,2-Azobisisobutyronitrile	40	
S-7	99.5	0.5	—	—	—	2,2-Azobisisobutyronitrile	65	
S-8	96	4	—	—	—	Lauryl peroxide	95	
S-9	85	15	—	—	—	Azodi- <i>tert</i> -octane	100	
S-10	70	30	—	—	—	Azodi- <i>tert</i> -octane	100	
S-11	94	6	—	—	—	Lauryl peroxide	110	
S-12	94	6	—	—	—	Azodi- <i>tert</i> -octane	120	
S-13	99	1	—	—	—	Di- <i>tert</i> -butyl peroxide	160	
S-14	100	—	—	—	—	Azodi- <i>tert</i> -octane	100	crosslinked polymer
S-15	85	15	—	—	—	Azodi- <i>tert</i> -octane	100	crosslinked polymer
S-16	70	30	—	—	—	Azodi- <i>tert</i> -octane	100	crosslinked polymer
S-17	95	—	5	—	—	Lauryl peroxide	95	
S-18	96	—	—	4	—	Azodi <i>tert</i> -octane	95	
S-19	96	—	—	—	4	Azodi- <i>tert</i> -octane	90	

<sup>a</sup> MMA: methyl methacrylate; MA: methyl acrylate; EA: ethyl acrylate; BA: *n*-butyl acrylate; 2-EHA: 2-ethyl hexyl acrylate.

tacticity of vinyl polymers such as polypropylene (PP)<sup>16,17</sup> and polystyrene (PS),<sup>20</sup> where their diastereoisomeric tetramers comprising two asymmetric centers were used to evaluate their average tacticity. However, the stereoisomerization of the diastereoisomers proved to be inherent to some extent during thermal degradation for PP and PS. Recently, the application of Py-GC was extended to determine the tacticity of various stereoregular PMMAs,<sup>22</sup> where it was revealed that no appreciable thermal isomerization occurred during the thermal degradation of PMMA. Therefore, the observed tacticity of PMMA samples by Py-GC was consistent with that obtained by <sup>1</sup>H-NMR. In this study, essentially the same Py-GC technique developed to study the stereoregularity of PMMA was applied to evaluate the tacticity of various MMA copolymers such as MMA-methyl acrylate (MA) copolymers and their crosslinked samples, for which stereoregularity had been difficult to evaluate by NMR.

## EXPERIMENTAL

### Samples

Monomer composition in feed and polymerization temperature of the MMA-related samples used in this work are summarized in Table I. About 0.1% of

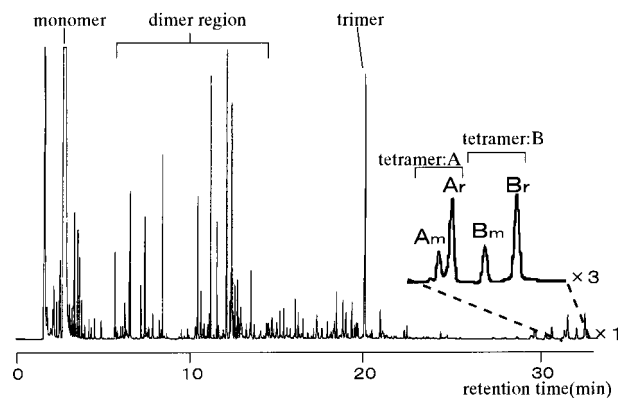
the initiator was used to trigger radical polymerization. For the preparation of crosslinked polymers (S-14, S-15, and S-16), 1% of 1,3-butanediol dimethacrylate was used as the crosslinked agent.

### Tacticity Measurement of PMMAs and MMA-MA Copolymers by <sup>1</sup>H-NMR

The tacticity of linear polymer samples (S-1-S-13) was estimated by <sup>1</sup>H-NMR by use of  $\alpha$ -methyl proton resonances. The measurements of <sup>1</sup>H-NMR spectra were carried out on a JEOL GSX-400 spectrometer at 400 MHz at 120°C. About 20 mg of each sample dissolved in 0.5 mL of DMSO-d<sub>6</sub> was transferred to a Pyrex sample tube of 5 mm o.d. Forty scans of the spectrum were accumulated at a pulse delay of 5.0 s and a flip angle of 45°. The split signals of  $\alpha$ -methyl protons between 0.7 and 1.3 ppm corresponding to the triad sequences (*mm*, *mr*, and *rr*) were used to estimate the tacticity of the polymer samples.<sup>4</sup> Diad tacticity (meso %) (*m* %) was calculated according to the relations  $m = mm + mr/2$  and  $r = rr + mr/2$ , assuming that the stereoregularity of PMMA obeys Bernoullian statistics.<sup>23</sup>

### Py-GC Measurement

The Py-GC measurements were carried out by using an on-line coupling system with a gas chro-



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

matograph (Hewlett Packard, 6890) with a flame ionization detector (FID) and a vertical furnace pyrolyzer (Frontier Lab, single-shot pyrolyzer PY-2010SL). In order to separate the resulting diastereoisomers clearly, a capillary column (Hewlett Packard, HP-5; 30 m  $\times$  0.32 mm i.d., 0.25  $\mu$ m thickness of crosslinked 5% diphenyl/95% dimethyl polysiloxane) was used. About 0.2 mg of the polymer sample was pyrolyzed at 500°C under a flow of carrier gas (He). The pyrolysis products formed in the pyrolyzer were transferred by He carrier gas at a flow rate of 45 mL/min into the separation column through a splitter. The injection port temperature was maintained at 300°C, and the splitter was used with a splitting ratio of 1/30. The column flow was kept at 1.5 mL/min during measurement with an electric pressure controller (EPC). The column temperature was programmed from 40 to 180°C at a rate of 8°C/min and held at 180°C for 2 min, from 180 to 200°C at a rate of 4°C/min and held at 200°C for 2 min, from 200 to 220°C at a rate of 2°C/min and held at 220°C for 10 min, in order to separate the diastereoisomers in MMA tetramers clearly within a shorter period.

## RESULTS AND DISCUSSION

### Tacticity of MMA Sequences in MMA-MA Copolymers

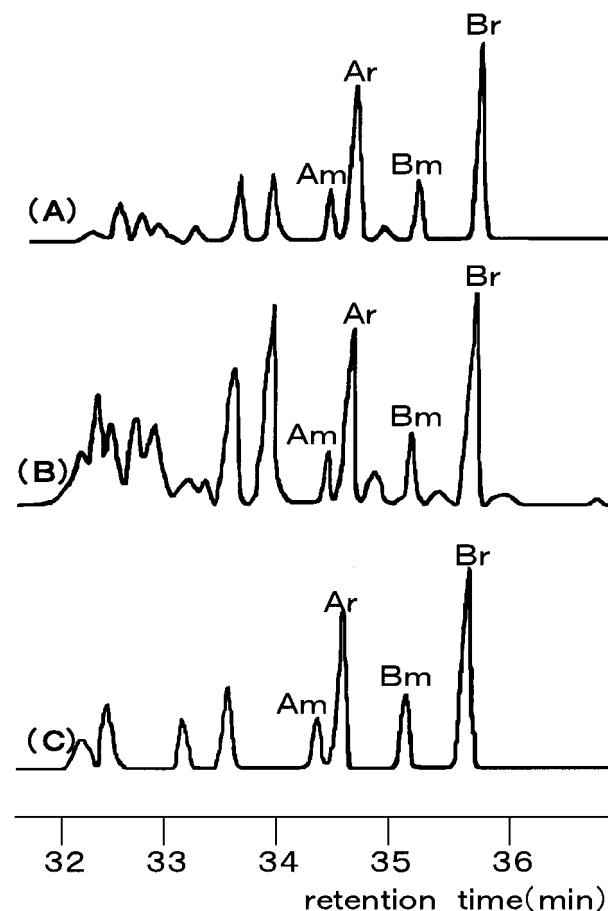
Figure 1 shows the pyrogram of PMMA (S-1) at 500°C together with an expanded partial pyrogram for the tetramer region. As was reported in the previous work,<sup>22</sup> the MMA tetramers consist of two isomers (A and B), each of which has a pair of diastereoisomers (Am and Ar and Bm and Br, respectively) where *m* and *r* designate meso- and

racemo isomers respectively. Thus, the diad tacticity can be directly estimated according to the following relationship for the relative peak intensities of diastereoisomers such as  $I_{Am}$ ,  $I_{Ar}$ ,  $I_{Bm}$ , and  $I_{Br}$ .

$$m\% = (I_{Am} + I_{Bm}) / (I_{Am} + I_{Bm} + I_{Ar} + I_{Br}) \times 100 \quad (1)$$

$$r\% = 100 - m\% \quad (2)$$

The diad tacticity of MMA-MA copolymer was then also determined by Py-GC from the intensities of the diastereomeric MMA tetramers in the observed pyrogram of the copolymer. Figure 2 shows the expanded tetramer regions of the pyrograms for two MMA-MA copolymers with 15% MA (S-9) and 30% MA (S-10) together with that for a PMMA homopolymer (S-3). Although some



**Figure 2** The tetramer region in the pyrogram observed by FID of (a) MMA-MA copolymer with 15% of MA (S-9); (b) MMA-MA copolymer with 30% of MA (S-10); (c) PMMA (S-3).

**Table II Comparison of Diad Tacticity (m%) Values in MMA Sequences of MMA-MA Copolymers Determined by Py-GC and by  $^1\text{H-NMR}$**

Sample	Diad Tacticity (m%)	
	Py-GC	$^1\text{H-NMR}$
S-6	20.5	20.5
S-7	21.8	22.0
S-8	23.7	23.4
S-9	24.4	24.5
S-10	24.6	28.6
S-11	25.1	25.0
S-12	25.8	25.7
S-13	28.6	28.6

additional peaks are observed in the tetramer region of the pyrograms of the copolymer samples [Fig. 2(a,b)], the four diastereomeric tetramers are also clearly separated.

The diad tacticity values for the MMA-MA copolymers thus determined from the relative peak intensities of the diastereomeric MMA tetramers in the pyrograms are summarized in Table II together with those obtained by  $^1\text{H-NMR}$ . The observed diad tacticities by Py-GC are almost consistent with those by  $^1\text{H-NMR}$  except for the sample S-10, which had a higher MA content. Here, the diad tacticity of a higher-MA-content copolymer such as S-10 was difficult to determine accurately by  $^1\text{H-NMR}$  because of insufficient resolution of the observed spectra from the strong effect of MA sequences. On the other hand, the Py-GC technique focuses on only MMA tetramers that are not affected by the presence of the comonomer. Therefore, the MMA sequences in the polymer chains are selectively estimated by Py-GC to give the highly precise determination of the tacticity independent of the comonomer composition.

#### Tacticity of MMA Sequences in the Other Copolymers

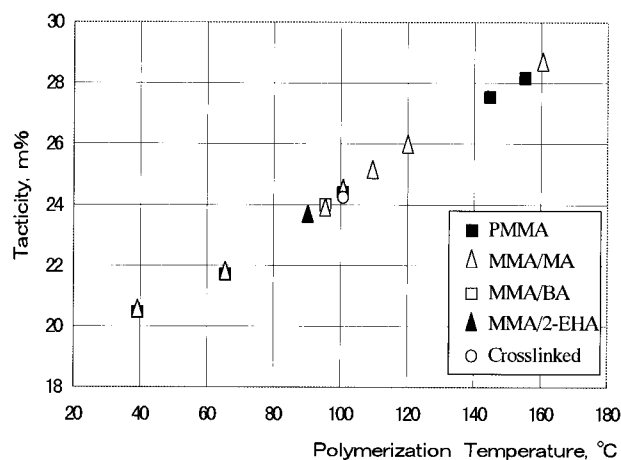
The stereoregularity of the other copolymers such as MMA-ethyl acrylate (EA), MMA-*n*-butyl acrylate (BA) and MMA-2-ethylhexyl acrylate (2-EHA) was also estimated by this technique. The stereoregularity of these copolymers was difficult to estimate by  $^1\text{H-NMR}$  because the peaks from the alkyl group of these comonomers overlapped on  $\alpha$ -methyl proton resonances of MMA sequences. On the other hand, the MMA tetramers

were observed as clearly isolated peaks in the pyrograms of MMA-BA and MMA-2-EHA copolymers to give the precise average tacticities of the copolymers.

In the case of the MMA-EA copolymer, however, the precise estimation of tacticity was not achieved, even by Py-GC, because of peak overlapping of the other products on the MMA tetramers. These overlapped products are probably the tetramers that include one EA unit. In order to improve the resolution of the overlapped peak, an additional study is now currently in progress, using other separation columns with various polarities.

#### Relationship Between Stereoregularity and Polymerization Temperature

Figure 3 shows the relationship between the diad tacticities of all the samples obtained by Py-GC and their polymerization temperatures. The m % values increased almost linearly with increasing polymerization temperature. This suggests that the tacticity of MMA sequences in the methacrylic polymers are strongly dominated by polymerization temperature, independent of the species and compositions of the acrylate comonomers. The observed temperature dependence of tacticity in PMMA has been also reported through NMR study by Bovey et al.<sup>24</sup> In the case of radically polymerized methacrylic polymers, therefore, it is possible to estimate the polymerization temperature of unknown samples to some extent from their tacticities determined by Py-GC.



**Figure 3** Relationship between the tacticity values (m%) obtained by Py-GC and polymerization temperature ( $^{\circ}\text{C}$ ).

**Table III Comparison of Diad Tacticity (m%) for Crosslinked Polymers with those of Linear Polymers Prepared at Same Temperature (100°C)**

Crosslinked Polymer		Linear Polymer		MA Content (%)
Sample	Tacticity (m%)	Sample	Tacticity (m%)	
S-14	24.5	S-3	24.2	—
S-15	24.5	S-9	24.4	15
S-16	24.4	S-10	24.6	30

### Tacticity of MMA Sequences in Crosslinked Polymers

The observed profile of the MMA tetramer region for crosslinked S-15 was similar to that for the linear copolymer with same composition (S-9). No peak overlapping from the crosslinked agent was observed in this region. The diad tacticity values of the crosslinked polymers obtained by Py-GC are summarized in Table III together with those of the linear polymers prepared at the same temperature. No significant differences were observed in the tacticity values among the three crosslinked polymers (S-14–S-16) with various compositions prepared at the same polymerization temperature, 100°C. This result suggests that the tacticity of MMA sequences in the polymer chains of the crosslinked polymers is also dominated by polymerization temperature, independent of the amount of comonomers.

Moreover, it is interesting to note that the estimated diad tacticities are almost the same between the crosslinked polymers and the corresponding linear polymers. This observation suggests that the tacticity of MMA sequences in the polymer chains is also independent of the crosslinking developed with about 1% of 1,3-butanediol dimethacrylate. If the crosslinking density becomes higher, however, the stereoregularity of MMA sequences in the polymer chains may be affected by the crosslinkage. We are going to study the relationship between the wide range of crosslinking density and the diad tacticity of MMA sequences in polymer chains.

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