

# Microstructure of the Copolymers of Methyl Methacrylate with Other Methacrylates Obtained by Radical and Anionic Copolymerizations in Tetrahydrofuran

HEIMEI YUKI, YOSHIO OKAMOTO, YOSHIKI SHIMADA, KOJI OHTA,  
and KOICHI HATADA, *Department of Chemistry, Faculty of Engineering  
Science, Osaka University, Toyonaka, Osaka 560, Japan*

## Synopsis

Monomer reactivity ratios  $r_1$  and  $r_2$  were determined in the copolymerizations of methyl methacrylate (MMA,  $M_1$ ) with 1,1-diphenylethyl (DPEMA),  $\alpha,\alpha$ -dimethylbenzyl (DMBMA), *tert*-butyl (*t*-BuMA), diphenylmethyl (DPMMA), phenyl (PhMA), and 1-naphthyl (NpMA) methacrylates ( $M_2$ ) in tetrahydrofuran (THF) by azobisisobutyronitrile (AIBN) at 60°C and butyllithium (*n*-BuLi) at -78°C. The reactivities of the monomers were explained in terms of the polar effect of the ester groups in both copolymerizations. All the copolymers isolated in low yields were converted to PMMA either directly or by copoly(MMA-methacrylic acid) to determine the triad tacticities of the copolymers. Coisotactic parameters  $\sigma_{12}$  and  $\sigma_{21}$  were determined by assuming the terminal model statistics. The  $\sigma_{12}$  values always accorded to the  $\sigma_{21}$  values within experimental error, and in radical copolymerizations they were between isotactic parameters  $\sigma_{11}$  and  $\sigma_{22}$  of the homopolymerizations of MMA and  $M_2$  monomers. In anionic copolymerizations, however, the  $\sigma_{12} = \sigma_{21}$  values varied, depending on the  $M_2$  monomers. In copolymerization with DPEMA the values were less than both  $\sigma_{11}$  and  $\sigma_{22}$ ; with DMBMA they were between  $\sigma_{11}$  and  $\sigma_{22}$ , with DPMMA, nearly equal to  $\sigma_{11}$ , and with PhMA and NpMA, greater than both  $\sigma_{11}$  and  $\sigma_{22}$ . The application of these parameters to copolymerizations performed at high conversion was also investigated.

## INTRODUCTION

Many studies have been done on the stereospecific polymerizations of methyl and other methacrylates. Only a few articles, however, on the stereoregulation in the copolymerizations of methacrylates have been published. Recently we reported the reactivities of monomers and the tacticities of copolymers in the anionic copolymerizations of various methacrylates.<sup>1,2</sup> We also reported briefly on the compositional and configurational analysis of the copolymer of MMA with trityl methacrylate (TrMA) obtained with *n*-BuLi in THF at -78°C and determined configurational parameters  $\sigma_{ij}$ :  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{12}$ , and  $\sigma_{21}$  (ref. 3). The  $\sigma_{ij}$  is the probability of generating a *meso*-dyad when a new monomer unit  $M_j$  is formed at the  $M_i$  end of a growing chain, if terminal model statistics prevail in the copolymerization.

In this article we describe the analysis of the  $\sigma_{ij}$  in the radical and anionic copolymerizations that use MMA and other methacrylates as  $M_1$  and  $M_2$  monomers. The  $M_2$  monomers were as follows: 1,1-diphenylethyl (DPEMA),  $\alpha,\alpha$ -dimethylbenzyl (DMBMA), *tert*-butyl (*t*-BuMA), diphenylmethyl (DPMMA), phenyl (PhMA), and 1-naphthyl (NpMA) methacrylates. The copolymerizations were carried out in THF with AIBN at 60°C and with *n*-BuLi at -78°C.

The monomer reactivity ratios  $r_1$  and  $r_2$  were determined by the Fineman–Ross method. The initial copolymers obtained in these experiments were converted to PMMA to determine the triad tacticities. Using the data of the reactivity ratios and tacticities, we evaluated the  $\sigma_{ij}$  values according to the method proposed by Klesper and Gronski.<sup>4,5</sup>

## EXPERIMENTAL

### Materials

The preparations and purifications of DPEMA,<sup>6</sup> DMBMA,<sup>7</sup> and DPMMA<sup>8</sup> have been reported. PhMA and NpMA were prepared by the reaction of methacryloyl chloride with phenol and 1-naphthol, respectively. PhMA was purified by distillation, bp 47°C/0.15 mm Hg, NpMA, by recrystallization from benzene solution, mp 95.5–96.5°C. Commercial MMA and *t*-BuMA were purified in the usual manner, dried over calcium hydride, and distilled under vacuum before use. Purified THF was stored over lithium aluminum hydride from which it was distilled just before use. *n*-BuLi was synthesized in heptane from butyl chloride and metallic lithium under an argon atmosphere. AIBN was purified by recrystallization from ethanol.

### Polymerization

The copolymerization was carried out in a glass ampule under nitrogen that had been dried by passing through molecular sieves 4A cooled at dry-ice temperature. The detailed method of copolymerization was described in an earlier article.<sup>1</sup> The copolymers were precipitated in a large amount of methanol and isolated by filtration. Because the homopolymer and copolymer of *t*-BuMA were partly soluble in methanol, the polymers were isolated by evaporation of the solvent and unreacted monomers under vacuum after separation of lithium compounds. The polymers thus obtained contained oligomeric compounds.

The copolymer composition was determined from <sup>1</sup>H-NMR spectra of the copolymers. Monomer reactivity ratios  $r_1$  and  $r_2$  were calculated by the least-squares method, using the Fineman–Ross equation, and confidence limits were calculated at 90% confidence coefficient.

### Conversion of Copolymers to PMMA

Copolymers of MMA with DPEMA, DMBMA, and *t*-BuMA were hydrolyzed by refluxing in methanol containing a small amount of hydrochloric acid. After the solvent was evaporated the residue was washed with ether. Copoly(MMA–MAA) thus obtained was dried *in vacuo*. Copoly(MMA–DPMMA) was converted to copoly(MMA–MAA) by reaction with hydrogen bromide in toluene. This method has been applied to the conversion of poly( $\alpha$ -methylbenzyl methacrylate) to poly(MAA).<sup>9</sup> In these procedures only  $M_2$  monomers were transformed into MAA units to give copoly(MMA–MAA)s quantitatively except for copoly(MMA–*t*-BuMA). The oligomeric compounds, that existed in copoly(MMA–*t*-BuMA) were excluded when they were washed with ether after hydrolysis with hydrochloric acid. Copoly(MMA–MAA)s were then converted to PMMA by methylation with diazomethane.

Copoly(MMA-PhMA) and copoly(MMA-NpMA) were directly converted into PMMA by treating the copolymers with an excess of sodium methoxide (28% solution in methanol) in dimethyl sulfoxide.<sup>10</sup> The polymer was precipitated in water and confirmed as PMMA by a <sup>1</sup>H-NMR spectrum and elementary analysis.

### <sup>1</sup>H-NMR Spectrum

The <sup>1</sup>H-NMR spectra were taken with a JNM-MH-100 (100 MHz) spectrometer. The spectra of the monomers were measured on 0.5-mole/liter solutions in carbon tetrachloride at 35°C with TMS as an internal standard.

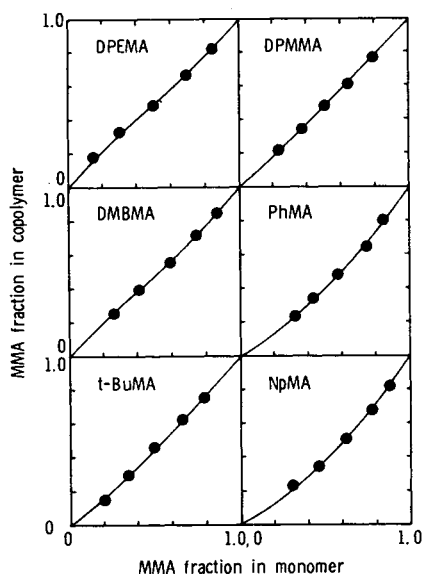


Fig. 1. Copolymer composition curves for radical copolymerizations of MMA ( $M_1$ ) with DPEMA, DMBMA, *t*-BuMA, DPMMA, PhMA, and NpMA ( $M_2$ ) with AIBN in THF at 60°C ( $[M_1]_0 + [M_2]_0 = 7.5$  mmole; [AIBN], 0.075 mmole; THF, 7.5 ml).

TABLE I  
Monomer Reactivity Ratios

$M_2$	Radical copolymerization		Anionic copolymerization	
	$r_1$	$r_2$	$r_1$	$r_2$
DPEMA	$0.72 \pm 0.03$	$0.77 \pm 0.10$	$1.13 \pm 0.35$	$1.62 \pm 1.00$
DMBMA	$0.81 \pm 0.02$	$0.92 \pm 0.08$	$1.52 \pm 0.25$	$1.49 \pm 0.34$
<i>t</i> -BuMA	$0.96 \pm 0.09$	$1.35 \pm 0.19$	$6.95 \pm 0.98$	$0.09 \pm 0.10$
DPMMA	$0.81 \pm 0.03$	$1.07 \pm 0.08$	$1.15 \pm 0.29$	$1.77 \pm 0.83$
PhMA	$0.66 \pm 0.03$	$1.55 \pm 0.14$	$0.19 \pm 0.00$	$29.2 \pm 10.9$
NpMA	$0.61 \pm 0.03$	$1.52 \pm 0.16$	$0.06 \pm 0.00$	$36.4 \pm 16.0$
TrMA	$0.89 \pm 0.17^a$	$0.33 \pm 0.07^a$	$0.62 \pm 0.08^b$	$0.62 \pm 0.32^b$

<sup>a</sup> Reference 12.

<sup>b</sup> Reference 3.

## RESULTS

Determination of Coisotactic Parameters  $\sigma_{12}$  and  $\sigma_{21}$ 

It has been shown that the coisotactic parameters  $\sigma_{12}$  and  $\sigma_{21}$  can be evaluated from the data of the monomer reactivity ratios  $r_1$  and  $r_2$  and the triad tacticities of the copolymers and the respective homopolymers if terminal model statistics prevail in the copolymerization<sup>4,5</sup>; for example, six different isotactic triads [eq. (1)] exist in the copolymer of  $M_1$  and  $M_2$ , and the summation of the contents of these six triads should be equal to the isotactic content determined from derived PMMA:

$$I = I(M_1M_1M_1) + I(M_1M_2M_1) + I(M_1M_1M_2^+) + I(M_1M_2M_2^+) + I(M_2M_1M_2) + I(M_2M_2M_2) \quad (1)$$

where  $I$  represents the probability of finding the isotactic triad of the sequences in parentheses and the superscript + indicates that the triad consists of forward and reverse forms. Each  $I$  is evaluated in terms of the conditional parameters for sequence distribution,  $P_{ij}$ :  $P_{12}$  and  $P_{21}$ , and the configurational parameters  $\sigma_{ij}$ :  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{12}$ , and  $\sigma_{21}$ . The  $P_{ij}$  is the probability of finding the  $M_j$  unit as the neighbor of the  $M_i$  unit and can be calculated from monomer reactivity ratios  $r_1$  and  $r_2$  (ref. 11). The  $\sigma_{11}$  and  $\sigma_{22}$  are obtainable from dyad or triad contents of the corresponding homopolymers, and  $\sigma_{12}$  and  $\sigma_{21}$  can be estimated by a trial-and-error method by comparing the calculated triad contents with the experimental values.

## Radical Copolymerization

To determine the monomer reactivity ratios  $r_1$  and  $r_2$  the copolymerizations were carried out at various feed ratios of monomers in THF at 60°C by using AIBN as initiator. The copolymers were obtained in about 10 wt% yield. The results of the copolymerizations are illustrated as copolymer composition curves in Figure 1. The  $r_1$  and  $r_2$  values calculated from the results are collected in Table I. The reactivities of the monomers seem to depend on the polar effect of ester groups.

The copolymers as well as  $M_2$  homopolymers obtained by the same radical polymerization were converted to PMMA. The triad tacticities of the polymers were determined from <sup>1</sup>H-NMR spectra of the PMMA and are summarized in Figure 2. Generally, isotactic ( $I$ ), heterotactic ( $H$ ), and syndiotactic ( $S$ ) contents of the copolymers lay between the corresponding contents of the  $M_1$  (MMA) and  $M_2$  homopolymers and changed linearly with copolymer composition.

The parameters  $\sigma_{ij}$ :  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{12}$ , and  $\sigma_{21}$  are collected in Table II with the data of the copolymerization of MMA with TrMA reported by Yamada and Tanaka.<sup>12</sup> The  $\sigma_{12}$  value always agreed with the  $\sigma_{21}$  value and satisfied the relationship  $\sigma_{12} = \sigma_{21} = (\sigma_{11}\sigma_{22})^{1/2}$ . The lines shown in Figure 2 were obtained theoretically by using the parameters  $\sigma_{ij}$  in Table II and are in fair agreement with experimental values.

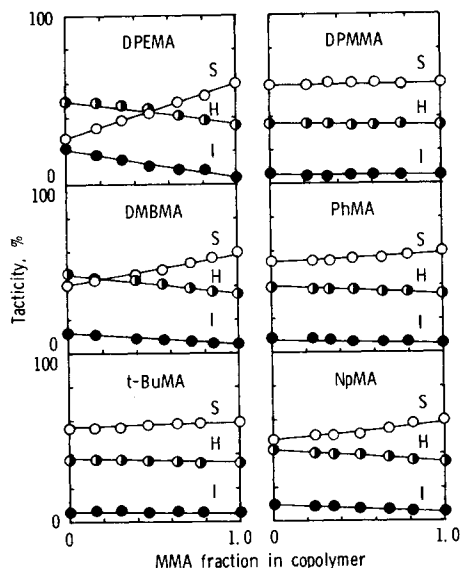


Fig. 2. Triad tacticities of the copolymers isolated in the copolymerizations shown in Fig. 1.

TABLE II  
Coisotactic Parameters

$M_2$	Radical copolymerization			Anionic copolymerization		
	$\sigma_{22}$	$\sigma_{12} = \sigma_{21}$	$\sigma_{11}$	$\sigma_{22}$	$\sigma_{12} = \sigma_{21}$	$\sigma_{11}$
DPEMA	0.47	0.32	0.23	0.42	0.17	0.25
DMBMA	0.36	0.30	0.23	0.20	0.22	0.25
<i>t</i> -BuMA	0.25	0.24	0.23	0.40	0.26	0.25
DPMMA	0.24	0.23	0.23	0.10	0.27	0.25
PhMA	0.27	0.25	0.23	0.21	0.50	0.25
NpMA	0.31	0.27	0.23	0.20	0.34	0.25
TrMA	0.71 <sup>a</sup>	0.43 <sup>a</sup>	0.24 <sup>a</sup>	0.94 <sup>b</sup>	0.25 <sup>b</sup>	0.25 <sup>b</sup>

<sup>a</sup> Reference 12.

<sup>b</sup> Reference 3.

### Anionic Copolymerization

The anionic copolymerizations were carried out at various feed monomer compositions with *n*-BuLi in THF at  $-78^\circ\text{C}$ . In most cases the polymer yields were in the range of 5–15 wt%. The copolymer composition curves are illustrated in Figure 3. The monomer reactivity ratios obtained from these results are summarized in Table I. The reliability of the data seems to be lower than that of the radical copolymerizations, but it is clear that the difference in reactivities among the monomers is much greater in comparison with radical copolymerizations.

The triad tacticities of the copolymers obtained in the above copolymerizations are shown in Figure 4 and the coisotactic parameters are summarized in Table II. The  $\sigma_{12}$  values again agreed with the  $\sigma_{21}$  values. They did not, however, always exist between  $\sigma_{11}$  and  $\sigma_{22}$ . Only in the copolymerization of MMA with DMBMA was the relationship  $\sigma_{12} = \sigma_{21} = (\sigma_{11}\sigma_{22})^{1/2}$  held. The  $\sigma_{12} = \sigma_{21}$  values were nearly equal to  $\sigma_{11}$  values in the copolymerizations with *t*-BuMA and

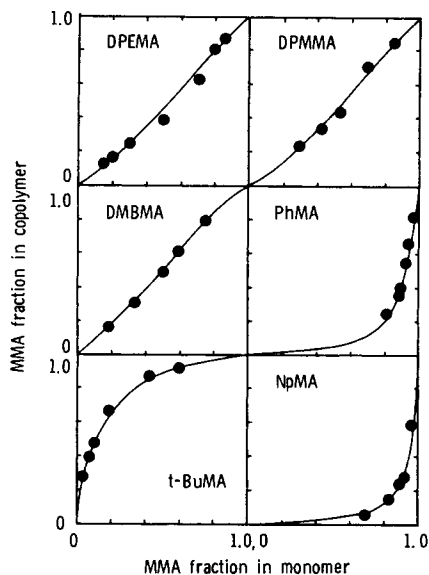


Fig. 3. Copolymer composition curves for anionic copolymerizations of MMA ( $M_1$ ) with DPEMA, DMBMA,  $t$ -BuMA, DPMMA, PhMA, and NpMA ( $M_2$ ) with  $n$ -BuLi in THF at  $-78^\circ\text{C}$  ( $[M_1]_0 + [M_2]_0 = 7.5$  mmole;  $[n\text{-BuLi}]_0, 0.15$  mmole; THF, 7.5 ml).

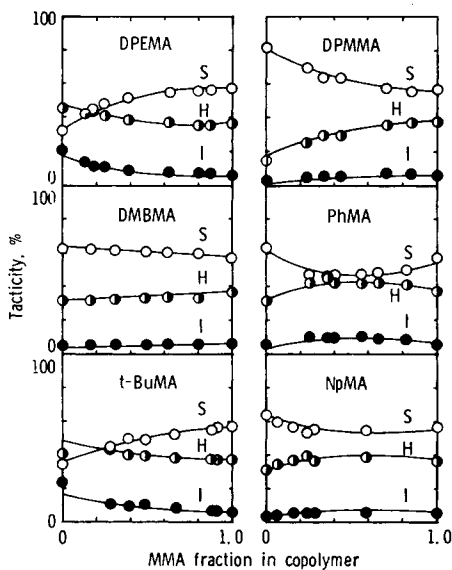


Fig. 4. Triad tacticities of the copolymers isolated in the copolymerizations shown in Fig. 3.

DPMMA. A similar relationship has been observed in the copolymerization of MMA with TrMA as shown in Table II.<sup>3</sup> The  $\sigma_{12} = \sigma_{21}$  values in the copolymerization with DPEMA were less than those of  $\sigma_{11}$  and  $\sigma_{22}$ . The curves in Figure 4 were obtained by using the  $\sigma_{ij}$  values in Table II. The homopolymerization of  $t$ -BuMA did not obey the terminal model at all, with the result that a large deviation developed between the observed and calculated values. In this polymerization  $\sigma_{22}$  value was tentatively elucidated from the syndiotactic triad content.

## DISCUSSION

## Reactivity of Monomer

The relative reactivities of methacrylates toward MMA radical or anion can be estimated from the value of  $1/r_1$ . The order of reactivity of the monomers was  $\text{NpMA} > \text{PhMA} > \text{DPEMA} > \text{DPMMA} > \text{DMBMA} > t\text{-BuMA} \geq \text{MMA}$  in the radical copolymerizations and  $\text{NpMA} > \text{PhMA} > \text{MMA} > \text{DPEMA} \geq \text{DPMMA} > \text{DMBMA} > t\text{-BuMA}$  in the anionic. Except for the reactivity of MMA, the order of relative reactivity in the radical copolymerizations agrees with that in the anionic, which suggests that the radical and anionic active centers of MMA more readily attack the monomer with an electron withdrawing group. In an earlier study<sup>1</sup> we found that the plots of  $\log(1/r_1)$  against  $^1\text{H}_a$  (*cis*-to-carbonyl group) chemical shifts of methacrylates show good linearity. The same plots appear in Figure 5. Again, good linearities were found for the data of the radical and anionic copolymerizations. As the  $^1\text{H}_a$  chemical shift increased (or moved downfield side) the reactivity of the  $M_2$  monomers increased. Because the  $^1\text{H}_a$  chemical shift can be related to the electron density on the carbon-carbon double bond,<sup>1</sup> it is probable that the reactivity of the monomers depends mainly on the electron density on the double bond. Judging from the nature of the active species, the polar effect of the ester groups will be more pronounced in the anionic than in the radical copolymerizations. This was actually observed in the results shown in Figure 5.

## Stereoregulation in Copolymerization

In the radical polymerization the isotacticity of the polymers ( $\sigma_{22}$  value in Table II) seems to increase with an increase in the bulk of the ester groups. Matsuzaki and co-workers have investigated the correlation between the tacticities of many polymethacrylates and the bulkiness of their ester groups and found that the syndiotacticity of the polymers decreases as the size of the ester groups increases.<sup>13</sup> The coisotactic parameters  $\sigma_{12} = \sigma_{21}$  were nearly equal to the geometric mean  $(\sigma_{11}\sigma_{22})^{1/2}$  of  $\sigma_{11}$  and  $\sigma_{22}$  (Table II). This probably means that the stereoregulation of the copolymerization is controlled mainly by the bulk of the ester groups.

On the other hand, the stereoregulation of anionic copolymerizations is not

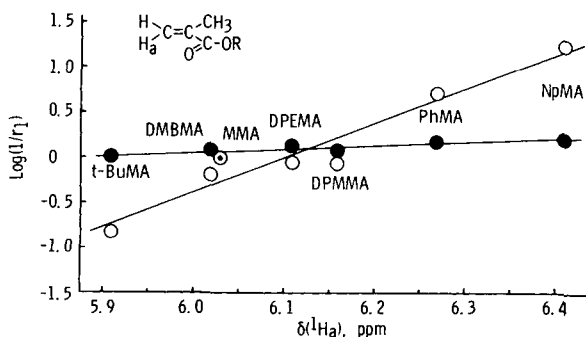


Fig. 5. Plots of  $\log(1/r_1)$  versus the chemical shifts  $\delta(^1\text{H}_a)$ , of the monomers: (○) anionic copolymerization, (●) radical copolymerization.

simple. Even in homopolymerizations by *n*-BuLi in THF it was difficult to find a clear correlation between the tacticities of the polymers and the size of the ester groups.<sup>2</sup> The existence of a lithium counterion plays an important role in controlling the stereoregularity. Among the copolymerizations shown in Table II PhMA, as well as NpMA, was copolymerized with MMA in a different way from the other  $M_2$  monomers. The  $\sigma_{12}$  and  $\sigma_{21}$  values were greater than both  $\sigma_{11}$  and  $\sigma_{22}$ . An interaction may exist between the MMA anion and  $M_2$  monomers or the  $M_2$  anions and MMA at  $-78^\circ\text{C}$  and may force them to increase in an isotactic manner. Such an interaction would be weak and would disappear in radical copolymerizations at higher temperatures. The interaction between a benzene ring and a carbonyl group which results in a higher coisotacticity has been proposed in the radical copolymerizations of styrene with acrylic esters.<sup>14</sup> It has also been reported that in the radical copolymerization of MMA ( $M_1$ ) with styrene ( $M_2$ ) the  $\sigma_{12} = \sigma_{21}$  (0.5) values are greater than  $\sigma_{11}$  (0.23) and  $\sigma_{22}$  (0.29) (ref. 15).

To confirm the validity of  $\sigma_{ij}$  values obtained in this study both radically and anionically produced copoly(MMA-DPEMA)s were converted to copoly(MMA-MAA)s by selective hydrolysis of DPEMA units. The  $^1\text{H-NMR}$  spectra of the copoly(MMA-MAA)s are shown in Figures 6 and 7. The peaks due to  $\alpha$ -methyl groups appear around  $\delta$  1–2 ppm and have been assigned to the triad sequences of MMA and MAA units by Klesper et al.<sup>4,5,16</sup> The intensities of these peaks can be calculated by using  $r_1$ ,  $r_2$ ,  $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{12}$ , and  $\sigma_{21}$ .<sup>4,5,16</sup> The observed and calculated intensities are summarized in Tables III and IV on the basis of the parameters given in Tables I and II. In these copolymerizations good

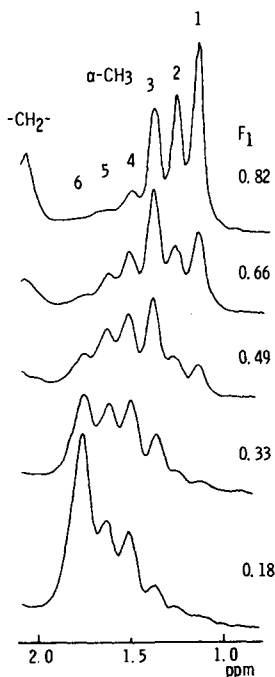


Fig. 6.  $^1\text{H-NMR}$  spectra of the copoly(MMA-MAA)s derived from copoly(MMA-DPEMA)s obtained in the copolymerizations shown in Fig. 1 (100 MHz, pyridine- $d_5$ ,  $100^\circ\text{C}$ , HMDS).



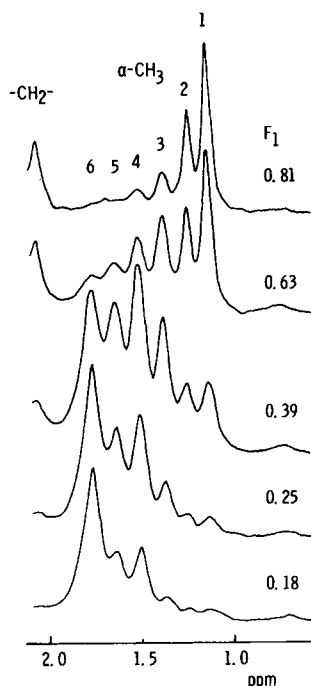


Fig. 7.  $^1\text{H}$ -NMR spectra of the copoly(MMA-MAA)s derived from copoly(MMA-DPEMA)s obtained in the copolymerizations shown in Fig. 3 (100 MHz, pyridine- $d_5$ , 100°C, HMDS).

TABLE III  
Peak Intensity of Copoly(MMA-Methacrylic Acid) Derived from Copoly(MMA-DPEMA)  
Obtained by Radical Copolymerization

$M_1$ fraction in copolymer		Peak ( $\alpha\text{-CH}_3$ )					
		6	5	4	3	2	1
0.82	Observed	1	5	10	25	24	35
	Calculated	0	4	10	29	25	32
0.66	Observed	3	12	17	34	17	17
	Calculated	2	14	18	34	18	15
0.49	Observed	10	24	25	26	10	5
	Calculated	9	25	24	26	10	5
0.33	Observed	26	29	24	15	5	1
	Calculated	27	29	25	13	5	1
0.18	Observed	51	21	18	7	2	1
	Calculated	52	23	19	4	2	0

agreement was found between the observed and calculated values, which indicated that our treatment of the copolymerizations is correct for the MMA-DPEMA combination as well as for MMA and TrMA.<sup>3</sup>

#### Application of the Parameters to the Copolymerization of Higher Conversion

In this article the parameters  $r_1$ ,  $r_2$ , and  $\sigma_{ij}$  were determined from the initial copolymer isolated at a low conversion. To determine whether these parameters

TABLE IV  
Peak Intensity of Copoly(MMA-Methacrylic Acid) Derived from Copoly(MMA-DPEMA)  
Obtained by Anionic Copolymerization

$M_1$ fraction in copolymer		Peak ( $\alpha$ -CH <sub>3</sub> )					
		6	5	4	3	2	1
0.81	Observed	1	5	11	19	28	36
	Calculated	1	4	13	24	28	31
0.63	Observed	8	12	21	23	19	17
	Calculated	8	9	22	26	19	16
0.39	Observed	26	15	26	19	8	6
	Calculated	27	16	28	17	8	5
0.25	Observed	46	19	21	10	3	1
	Calculated	46	16	24	9	4	2
0.18	Observed	57	16	18	6	2	1
	Calculated	58	14	20	6	2	1

TABLE V  
Compositions and Tacticities of the Copolymers Obtained by Radical Copolymerization<sup>a</sup>

$M_2$		Yield (wt%)	$M_1$ fraction in monomer	$M_1$ fraction in copolymer	Tacticity (%)		
					<i>I</i>	<i>H</i>	<i>S</i>
DPEMA	Observed	84.8	0.51	0.50	10	44	45
	Calculated	84.5		0.51	11	44	45
DPMMA	Observed	88.1	0.50	0.48	7	37	57
	Calculated	88.6		0.49	5	36	59
PhMA	Observed	86.2	0.50	0.45	6	39	55
	Calculated	86.8		0.47	6	38	56

<sup>a</sup> THF, 7.5 ml;  $[M_1] + [M_2]$ , 7.5 mmole; AIBN, 0.075 mmole; temperature, 60°C; time, 24 hr.

could be used for copolymerizations at higher conversion the copolymerizations were performed by starting with equimolar amounts of MMA and  $M_2$  monomers. The drifts of copolymer and monomer composition with the reaction were worked out by graphically integrating the copolymer equation according to the Skeist method.<sup>17</sup> The integration was done for each 5% yield. The triad tacticity was

TABLE VI  
Compositions and Tacticities of the Copolymers Obtained by Anionic Copolymerization<sup>a</sup>

$M_2$		Yield (wt%)	$M_1$ fraction in monomer	$M_1$ fraction in copolymer	Tacticity (%)		
					<i>I</i>	<i>H</i>	<i>S</i>
DPEMA	Observed	85.1	0.50	0.50	7	37	56
	Calculated	85.3		0.48	7	39	54
DMBMA	Observed	82.6	0.50	0.47	5	31	64
	Calculated	82.9		0.50	5	35	60
<i>t</i> -BuMA	Observed	30.3	0.50	0.72	9	39	53
	Calculated	30.5		0.85	7	38	55
DPMMA	Observed	94.6	0.53	0.52	6	33	61
	Calculated	94.7		0.52	5	33	62
PhMA	Observed	95.9	0.49	0.51	6	30	64
	Calculated	95.9		0.50	7	38	55
PhMA	Observed	56.4	0.51	0.08	7	33	60
	Calculated	56.0		0.17	7	38	55

<sup>a</sup> THF, 7.5 ml;  $[M_1] + [M_2]$ , 7.5 mmole; *n*-BuLi, 0.15 mmole.

calculated by using the  $M_1$  fractions of the copolymers and the coisotactic parameters in Table II. The results of the radical and anionic copolymerizations are shown in Tables V and VI, respectively. In the radical copolymerizations of MMA with DPEMA, DPMMA, and PhMA the observed compositions and tacticities of the copolymers were in fair agreement with the values calculated by using the parameters, which means that  $r_1$ ,  $r_2$ , and  $\sigma_{ij}$  are constant from the first stage of copolymerization until high conversion.

In the anionic copolymerizations of MMA with DPEMA, DMBMA, and DPMMA, which have reactivities similar to those of MMA, the observed compositions and tacticities agreed closely with the calculated values. Discrepancies were noted, however, between the observed and the calculated values when  $M_2$  were *t*-BuMA and particularly PhMA, whose reactivities differ greatly from those of MMA. In these copolymerizations the  $r_1$ ,  $r_2$ , and  $\sigma_{ij}$  values change as the reaction proceeds.

This work was supported in part by a grant-in-aid for scientific research from the Ministry of Education of Japan.

### References

1. H. Yuki, Y. Okamoto, K. Ohta, and K. Hatada, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1161 (1975).
2. H. Yuki, K. Hatada, K. Ohta, and Y. Okamoto, *J. Macromol. Sci. Chem.*, **9**, 983 (1975).
3. Y. Okamoto, S. Nakashima, K. Ohta, K. Hatada, and H. Yuki, *J. Polym. Sci. Polym. Lett. Ed.*, **13**, 273 (1975).
4. E. Klesper and W. Gronski, *J. Polym. Sci. B*, **7**, 661 (1969).
5. E. Klesper and W. Gronski, *J. Polym. Sci. B*, **7**, 727 (1969).
6. H. Yuki, Y. Okamoto, Y. Shimada, K. Ohta, and K. Hatada, *Polymer*, **17**, 618 (1976).
7. H. Yuki, K. Ohta, K. Hatada, and Y. Okamoto, *Polym. J.*, **9**, 511 (1977).
8. H. Yuki, K. Hatada, T. Niinomi, and Y. Kikuchi, *Polym. J.*, **1**, 36 (1970).
9. H. Yuki, K. Ohta, K. Ono, and S. Murahashi, *J. Polym. Sci. A-1*, **6**, 829 (1968).
10. H. J. Harwood, *Angew. Makromol. Chem.*, **45**, 279 (1968).
11. K. Ito and Y. Yamashita, *J. Polym. Sci. A*, **3**, 2165 (1965).
12. A. Yamada and J. Tanaka, Preprints, 23rd Symposium on Macromolecular Science, Tokyo, Japan, 1974.
13. K. Matsuzaki, T. Kanai, K. Yamawaki, and K. P. S. Rung, *Makromol. Chem.*, **174**, 215 (1973).
14. K. Ito, S. Iwase, K. Umehara, and Y. Yamashita, *Kogyo Kagaku Zasshi*, **70**, 993 (1967).
15. A. R. Katritzky, A. Smith, D. E. Weiss, *J. Chem. Soc. Perkin Trans. 2*, **1974**, 1547.
16. E. Klesper, A. Johnsen, W. Gronski, and F. W. Wehrli, *Makromol. Chem.*, **176**, 1071 (1975).
17. I. Skeist, *J. Am. Chem. Soc.*, **68**, 1781 (1946).

Received November 22, 1977

Revised February 8, 1978