Anionic Polymerizations and Copolymerizations of Methacrylates-Reactivity of Monomer and Tacticity of Polymer

Heimei Yuki[a]; Koichi Hatada[a]; Koji Ohta[a]; Yoshio Okamoto[a]

[a] Department of Chemistry Faculty of Engineering Science, Osaka University Toyonaka, Osaka, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Anionic Polymerizations and Copolymerizations of Methacrylates—Reactivity of Monomer and Tacticity of Polymer

HEIMEI YUKI, KOICHI HATADA, KOJI OHTA,
and YOSHIO OKAMOTO

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

ABSTRACT

The anionic polymerizations and copolymerizations of methacrylates were investigated. The studies were focused on the stereoregularity of the polymers and the relative reactivity of the monomers in relation to the stereospecificity of polymerization.

INTRODUCTION

Methyl methacrylate (MMA) forms an isotactic polymer in a nonpolar solvent and a syndiotactic one in THF with n–BuLi. In these polymerizations, α-methyl and ester groups play a sterically important role in controlling the tacticity of the polymer. It is, therefore, interesting to study how the bulkiness of the ester group in a methacrylate affects the stereoregularity of the polymer as well as the reactivity of the monomer. In this paper the authors

will state the outline of the anionic polymerizations and copolymeri-
zations of various methacrylates which have been investigated in
their laboratory. The studies were mainly focused on the stereo-
regularity of the polymers and the relative reactivity of the
monomers in relation to the stereospecificity of polymerization.

The monomers employed were methacrylic esters (RMA) of
benzyl (R = Bz) alcohol [1] and its derivatives, p-phenylbenzyl
(PhBz) [2], α-methylbenzyl (MB) [3], diphenylmethyl (DPM) [2],
α,α-dimethylbenzyl (DMB) [4], 1,1-diphenylethyl (DPE) [5], and
trityl (Tr) [1, 6] alcohols (Scheme 1).
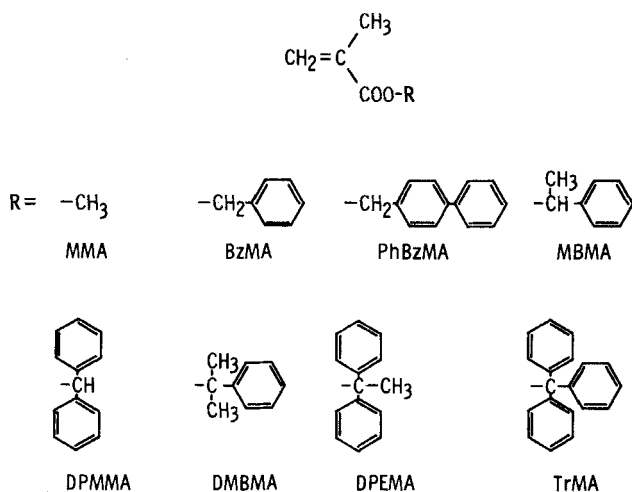
SCHEME 1.

The polymers of these methacrylates can be converted to poly-MMA
via poly(methacrylic acid) which is easily formed from the original
polymers with HBr in toluene and sometimes with HCl in methanol.
Then the tacticity of the polymethacrylates can be determined from
the NMR spectra of poly-MMA's thus obtained.

The polymerizations of methyl esters of α-ethyl, α-n-propyl,
and α-phenyl acrylic acids (MEA [7], MPA [7], and MPhA [8],
respectively) (Scheme 2) were also investigated in order to learn
the effect of the α-substituent.

$$CH_2=C \begin{smallmatrix} CH_2-CH_3 \\ \\ COO-CH_3 \end{smallmatrix} \qquad CH_2=C \begin{smallmatrix} CH_2-CH_2-CH_3 \\ \\ COO-CH_3 \end{smallmatrix} \qquad CH_2=C \begin{smallmatrix} \bigcirc \\ \\ COO-CH_3 \end{smallmatrix}$$
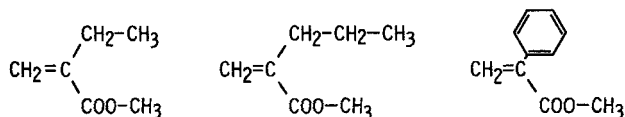
SCHEME 2.

TACTICITY OF POLYMETHACRYLATE

Table 1 shows the triad tacticity of polymethacrylates which were prepared with radical initiators. Similarly to MMA, most methacrylates formed rather syndiotactic polymers. However, atactic rather than syndiotactic polymers were obtained from DMBMA and DPEMA having tertiary ester groups. Almost complete atacticity, namely I:H:S = 1:2:1, was observed in the polymer of MPhA, which has the largest steric effect among the monomers. On the other hand, TrMA which has the largest ester group, gave a rather isotactic polymer even by a radical initiator.

The results of the polymerization by n-BuLi in toluene are listed in Table 2. Isotactic polymers were produced from most

TABLE 1. Stereoregularity of Polymethacrylates Obtained by Radical Initiator

Monomer	Initiator	Solvent	Temperature (°C)	I	H	S
MMA	AIBN	Toluene	60	6	36	58
BzMA[a]	BPO	Toluene	60	7	37	56
PhBzMA	AIBN	Toluene	80	5	38	57
DL-MBMA[a]	AIBN	Toluene	60	9	33	58
DPMMA	AIBN	Toluene	60	2	41	57
DMBMA	AIBN	Toluene	85	13	47	40
DPEMA	AIBN	Toluene	60	19	49	32
TrMA	AIBN	Toluene	60	64	22	14
MPhA	AIBN	None	60	21	50	29

[a]K. Matsuzaki et al., Makromol. Chem., 174, 215 (1973).

TABLE 2. Stereoregularity of Polymethacrylates Obtained by n-BuLi in Toluene

Monomer	Initiator	Solvent	Temperature (°C)	I	H	S
MMA	n-BuLi	Toluene	-78	72	17	11
MMA	n-BuLi	Toluene	0	81	14	5
BzMA	n-BuLi	Toluene	-78	81	15	4
BzMA	n-BuLi	Toluene	0	73	22	5
PhBzMA	n-BuLi	Toluene	-78	87	8	5
PhBzMA	n-BuLi	Toluene	0	76	20	4
D-MBMA	n-BuLi	Toluene	-78	78	17	5
DL-MBMA	n-BuLi	Toluene	-78	56	35	9
DL-MBMA	n-BuLi	Toluene	0	70	24	6
DPMMA	n-BuLi	Toluene	-78	99	1	0
DPMMA	n-BuLi	Toluene	0	93	4	3
DMBMA	n-BuLi	Toluene	-78	68	19	13

DMBMA	n-BuLi	Toluene	0	60	27	13
DMBMA	n-BuLi	$\dfrac{\text{Toluene}}{\text{THF}} = \dfrac{99}{1}$	-78	38	22	40
DPEMA	n-BuLi	Toluene	-78	23	28	49
DPEMA	n-BuLi	Toluene	0	52	37	11
TrMA	n-BuLi	Toluene	-78	96	2	1
TrMA	n-BuLi	Toluene	0	93	4	3
MEA	n-BuLi	Toluene	-78	70	11	19
MEA	n-BuLi	Toluene	0	97	2	2
MPA	n-BuLi	Toluene	-78	62	36	2
MPA	n-BuLi	Toluene	0	95	4	1
MPhA	n-BuLi	Toluene	-78	56	25	19
MPhA	n-BuLi	Toluene	-30	22	52	26
MPhA	n-BuLi	Toluene	0	-	-	-

monomers as well as MMA. Among these, poly-DPMMA and poly-TrMA showed the highest isotacticity. On the other hand, at -78°C DPEMA gave a syndiotactic polymer in this nonpolar solvent, although the polymer became isotactic at 0°C. This is surprising because DPEMA has an ester group whose bulkiness is similar to those of DPMMA and TrMA. Most of the monomers gave polymers of lower isotacticity at elevated temperatures, but some monomers, particularly MEA and MPA, formed highly isotactic polymers at 0°C. MPhA gave a rather isotactic polymer at -78°C, but an atactic one with a I:H:S = 1:2:1 ratio at -30°C. It is noticeable that the isotacticity of the polymer of optically active D-MBMA was higher than that of the racemic monomer. By the addition of a small amount of THF to the solvent, DMBMA formed a so-called stereoblock or stereocomplex-type polymer, which has been found in the polymerization of MMA. The same phenomenon may be expected for the polymerizations of other monomers.

The results of the polymerization by n-BuLi in THF are shown in Table 3. At -78°C, syndiotactic polymers were mainly obtained. DPMMA gave a polymer of especially high syndiotacticity. On the other hand, TrMA formed a highly isotactic polymer not only in toluene but also in this polar solvent. The large trityl ester group may prevent the syndiotactic placement of the incoming monomer to the growing chain end. In general, the polymers became less stereoregular at 0°C, while DPEMA and MPhA gave atactic polymers even at -78°C.

Table 4 shows the stereoregularity of the polymers obtained by phenylmagnesium bromide and by dialkylaluminum diphenylamide in toluene. These results are also very similar to those in the case of MMA. Most methacrylates formed isotactic polymers by PhMgBr and syndiotactic ones by R_2AlNPh_2. However, there is one exception, i.e., by PhMgBr only an atactic polymer was obtained from DPMMA, which produced highly isotactic and syndiotactic polymers by n-BuLi in toluene and in THF, respectively. Contrary to the behavior of DPMMA, DPEMA gave a polymer of extremely high isotacticity in spite of the very low stereoregularity of the polymer obtained by n-BuLi.

The general view of the above results, shown in Tables 1-4, indicates that most of the methacrylates behave very similarly to MMA in their stereospecific polymerizations. However, pronounced steric effects come out in the polymerizations of DPMMA, DMBMA, DPEMA, and TrMA. The steric control in their polymer formations does not seem to depend simply on the bulkiness of the ester groups, since the individual monomer exhibits quite different behavior in the

stereospecific polymerization. The stereoregulation may be deli-
cately concerned with the geometrical size of the ester group, as well
as the counterions produced from initiators. It is obvious that the
steric influence of α-substituent is more striking than that of the
ester group.

MONOMER REACTIVITY RATIOS AND RELATIVE REACTIVITY IN COPOLYMERIZATION [9, 10]

Although monomer reactivity ratios are important as fundamental
information, only a few data [11-13] have been reported on the
reactivity ratios in anionic copolymerizations, except for styrene
derivatives [14].

The monomer reactivity ratios in the copolymerizations of MMA
(M_1) with other methacrylates (M_2) by n-BuLi at -78°C were deter-
mined by analyzing the compositions of the initial copolymers.
Ethyl (Et), isopropyl (i-Pr), and tert-butyl (t-Bu) methacrylates
were also employed as the comonomer M_2.

It is known that in the anionic polymerization of MMA the greater
part of initiators are consumed in side reactions and the formation
of oligomers. Table 5 shows the results of the copolymerization of
MMA with BzMA. No difference was observed between the compo-
sitions of the oligomers and the corresponding polymers, regardless
of the monomer composition in the feed and the solvent used. Similar
results were obtained in the copolymerization of MMA and EtMA.
However, as shown in Table 6, the compositions of methanol-soluble
and -insoluble parts differed in the MMA—i-PrMA and MMA—t-BuMA
systems. The differences were slight, but they had a large effect on
the values of the monomer reactivity ratios. Since poly-t-BuMA is
slightly soluble in methanol, the copolymer rich in t-BuMA may be
soluble in methanol. However, it is not clear at present whether
the differences in compositions indicate different mechanisms in
the formations of the oligomer and the polymer or not.

All the copolymer composition data fitted well on the theoretical
curves with given r_1 and r_2 values as shown in Fig. 1.

The monomer reactivity ratios at -78°C are summarized in
Table 7. Only BzMA was more reactive than MMA both in toluene
and THF. In most cases the relative reactivity of the monomer
was not greatly affected by the solvents, but DMBMA and TrMA
showed extremely lower reactivity in toluene than in THF. t-BuMA
also showed low reactivity, not only in toluene but also in THF.

TABLE 3. Stereoregularity of Polymethacrylates Obtained by n-BuLi in THF

Monomer	Initiator	Solvent	Temperature (°C)	I	H	S
MMA	n-BuLi	THF	-78	6	38	56
MMA	n-BuLi	THF	0	31	32	37
BzMA	n-BuLi	THF	-78	6	31	63
BzMA	n-BuLi	THF	0	18	33	49
PhBzMA	n-BuLi	THF	-78	9	30	61
D-MBMA	n-BuLi	THF	-78	12	28	60
DL-MBMA	n-BuLi	THF	-78	8	31	60
DL-MBMA	n-BuLi	THF	0	16	39	45
DPMMA	n-BuLi	THF	-78	2	11	87
DPMMA	n-BuLi	THF	0	2	31	67
DMBMA	n-BuLi	THF	-78	10	29	61
DMBMA	n-BuLi	THF	0	11	37	52

DPEMA	n-BuLi	THF	-78	21	46	33
DPEMA	n-BuLi	$\dfrac{\text{Toluene}}{\text{THF}} = \dfrac{9}{1}$	-78	11	33	56
DPEMA	n-BuLi	THF	0	17	48	35
TrMA	n-BuLi	THF	-78	94	4	2
TrMA	n-BuLi	THF	0	81	13	6
MEA	n-BuLi	THF	-78	12	13	75
MPhA	n-BuLi	THF	-78	26	50	24

TABLE 4. Stereoregularity of Polymethacrylates Obtained by PhMgBr or R_2AlNPh_2 in Toluene

Monomer	Initiator	Solvent	Temperature (°C)	I	H	S
MMA	PhMgBr	Toluene	30	99	1	0
BzMA	PhMgBr	Toluene	30	85	11	4
PhBzMA	PhMgBr	Toluene	30	82	12	6
DL–MBMA[a]	PhMgBr	Toluene	20	75	21	4
DPMMA	PhMgBr	Toluene	20	28	36	36
DMBMA	PhMgBr	Toluene	30	74	16	10
DPEMA	PhMgBr	Toluene	0	97	3	0
TrMA	PhMgBr	Toluene	30	–	–	–
MMA	Et_2AlNPh_2	Toluene	–78	1	14	85
PhBzMA	Bu_2AlNPh_2	Toluene	–78	2	22	76
D–MBMA	Et_2AlNPh_2	Toluene	–78	4	17	79
DL–MBMA	Et_2AlNPh_2	Toluene	–78	4	20	76
DPMMA	Et_2AlNPh_2	Toluene	–40	8	27	65
DMBMA	Et_2AlNPh_2	Toluene	–78	1	17	82
DPEMA	Et_2AlNPh_2	Toluene	–40	12	34	54
MEA	Bu_2AlNPh_2	Toluene	–40	14	12	74
MPhA	Bu_2AlNPh_2	Toluene	–78	20	32	48

[a]K. Matsuzaki et al., Makromol. Chem., 174, 215 (1973).

TABLE 5. Anionic Copolymerization of MMA (M_1) and BzMA (M_2) by n-BuLi at -78°C[a]

Solvent	f_1	CH$_3$OH insoluble		CH$_3$OH soluble	
		Yield (wt%)	F_1	Yield (wt%)	F_1
Toluene	0.90	3.1	0.85	3.9	0.84
Toluene	0.70	3.0	0.55	2.4	0.58
Toluene	0.40	3.1	0.31	2.5	0.30
Toluene	0.30	2.9	0.25	2.1	0.22
Toluene	0.15	2.6	0.10	2.0	0.11
THF	0.90	2.5	0.86	4.5	0.86
THF	0.70	3.0	0.62	3.6	0.58
THF	0.50	4.7	0.42	3.7	0.37
THF	0.30	4.2	0.20	3.3	0.20
THF	0.15	3.9	0.10	2.9	0.12

[a]$[M_1]_0 + [M_2]_0$, 15 mmole; solvent, 15 ml; [n-BuLi], 0.30 mmole; time, 5 min in toluene; 1 to 2 min in THF; f_1 and F_1, mole fractions of M_1 in feed and polymer, respectively.

TABLE 6. Anionic Copolymerization of MMA (M_1) and Methacrylates (M_2) in THF by n-BuLi at -78°C[a]

M_2	f_1	CH$_3$OH insoluble		CH$_3$OH soluble	
		Yield (wt%)	F_1	Yield (wt%)	F_1
i-PrMA	0.35	2.0	0.57	7.5	0.53
i-PrMA	0.70	5.5	0.83	6.6	0.74
i-PrMA	0.85	6.2	0.93	5.8	0.82
t-BuMA	0.30	0.7	0.91	4.5	0.79
t-BuMA	0.50	0.7	0.94	5.6	0.87
t-BuMA	0.70	1.9	0.99	4.9	0.93

[a]$[M_1]_0 + [M_2]_0$, 15 mmole; THF, 15 ml; [n-BuLi], 0.30 mmole; time, 3 to 7 min; f_1 and F_1, mole fractions of M_1 in feed and polymer, respectively.
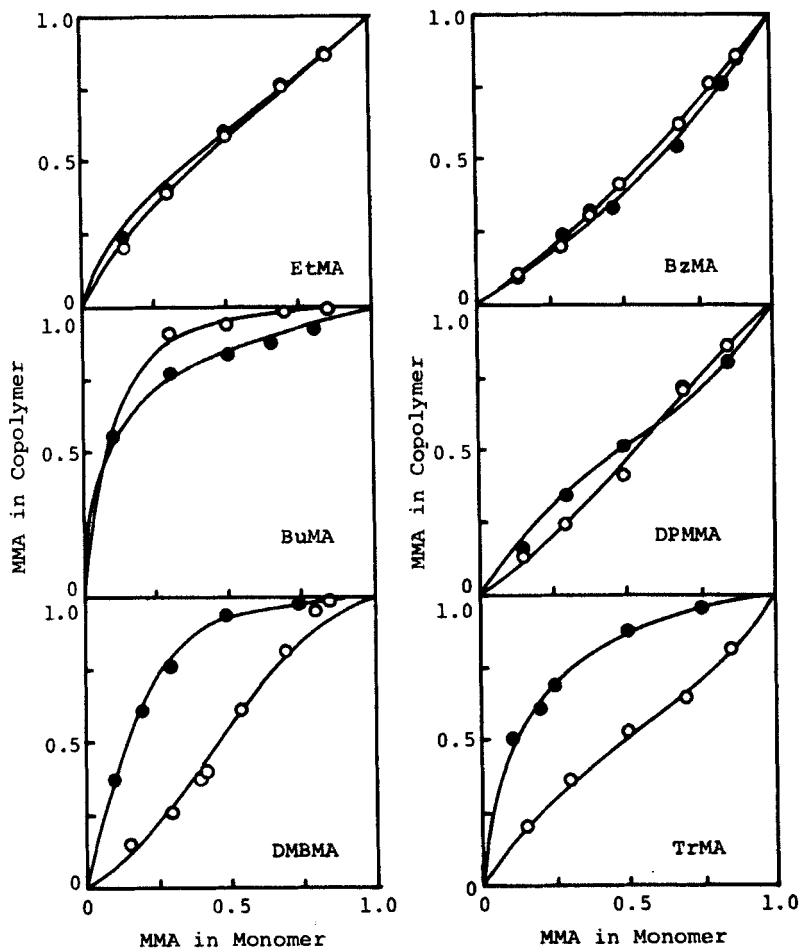
FIG. 1. Copolymer composition curves for anionic copolymeri-
zations of MMA (M_1) and methacrylates (M_2) by n-BuLi at -78°C in
toluene (●) and in THF (○).

An ideal copolymerization will be expected in the MMA-BzMA
system because the product $r_1 \times r_2 = 1$. The methoxy resonances
of MMA unit in the NMR spectra of copoly(MMA-BzMA)'s (Fig. 2)
were much broader than that of PMMA, and each peak of the spectra
shifted gradually to the downfield side with an increase of MMA

TABLE 7. Monomer Reactivity Ratios in the Copolymerizations of MMA (M_1) with Various Methacrylates by n-BuLi at -78°C[a]

M_2	In toluene		In THF	
	r_1	r_2	r_1	r_2
EtMA	1.10 ± 0.10	0.38 ± 0.22	1.13 ± 0.07	0.52 ± 0.18
EtMA			(1.23 ± 0.02)	(0.49 ± 0.05)
i-PrMA	2.75 ± 0.45	0.20 ± 0.37	2.29 ± 0.18	0.42 ± 0.20
i-PrMA	(2.22 ± 0.31)	(0.31 ± 0.26)	(0.97 ± 0.38)	(0.28 ± 0.03)
t-BuMA			36 ± 27	0.43 ± 0.75
t-BuMA	(4.41 ± 2.55)	(0.02 ± 0.05)	(5.07 ± 2.16)	(0.02 ± 0.09)
BzMA	0.59 ± 0.07	1.60 ± 0.42	0.70 ± 0.06	1.46 ± 0.36
BzMA	(0.57 ± 0.01)	(1.49 ± 0.05)	(0.69 ± 0.06)	(1.84 ± 0.36)
DL-MBMA	1.68 ± 0.17	0.78 ± 0.32	2.04 ± 0.16	1.52 ± 0.25
DPMMA	0.57 ± 0.15	0.55 ± 0.61	1.11 ± 0.22	1.57 ± 0.61
DMBMA	19.1 ± 4.0	0.56 ± 0.39	2.59 ± 1.35	2.00 ± 1.10
TrMA	6.28 ± 0.30	0.13 ± 0.07	0.62 ± 0.08	0.62 ± 0.32

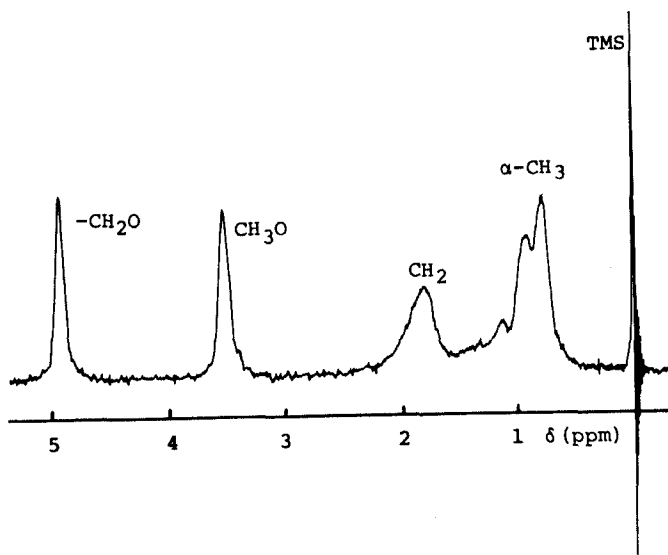[a]Parentheses denote the data from methanol soluble products.

FIG. 2. NMR spectrum of copoly(MMA-BzMA) obtained in THF (100 MHz, CCl$_4$, 60°C).

content as shown in Fig. 3. These facts indicate that the arrangement of the monomeric units in the copolymers was more or less random, as expected.

The copolymerizations of MMA with MBMA and DMBMA in THF showed both r_1 and r_2 were greater than unity, indicating block structures of the copolymers. On the other hand, the copolymerization with DPMMA in toluene and that with TrMA in THF may give rather alternating structures of the copolymers. These structures could be confirmed as follows [15]. By the treatment with methanolic hydrochloric acid the copoly(MMA-DMBMA) and copoly(MMA-TrMA) yielded quantitatively copolymers of MMA and methacrylic acid (MAA), where only the hydrolysis of DMB and Tr ester groups proceeded selectively (Scheme 3). The NMR spectra of α-methyl groups of the copoly(MMA-MAA) thus obtained are shown in Fig. 4. The complete triads assignments of the six peaks in the spectrum have been done by Klesper et al. [16]. Peak 1 contains all of the tactic triads (I, H, S) of MAA sequences, and peak 6 is assigned to the syndiotactic triad of MMA sequences. In the spectrum A of copoly(MMA-MAA) derived from copoly(MMA-DMBMA) the intensities of peaks 1 and 6 were strong relative to the other peaks. On the contrary, those in the
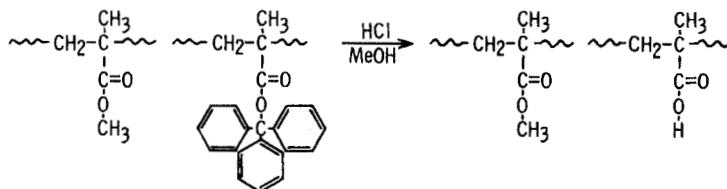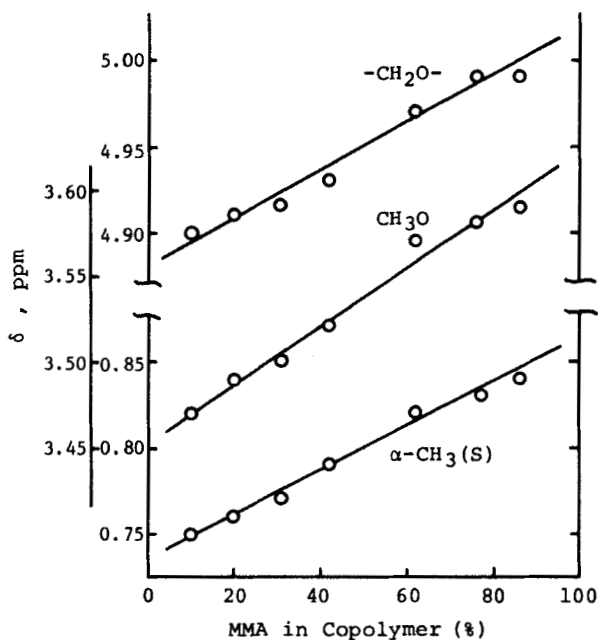
SCHEME 3.

FIG. 3. Chemical shifts of α-CH$_3$(syndio), CH$_3$O, and CH$_2$O of copoly(MMA-BzMA) obtained in THF by n-BuLi at -78°C (100 MHz, CCl$_4$, TMS, 60°C).

spectrum B of the polymer, which was originated from copoly(MMA-TrMA), were weak. These data indicate that copoly(MMA-DMBMA) contained rather long sequences of MMA and of DMBMA, while copoly(MMA-TrMA) had some alternating structure as expected from the r$_1$ and r$_2$ values.

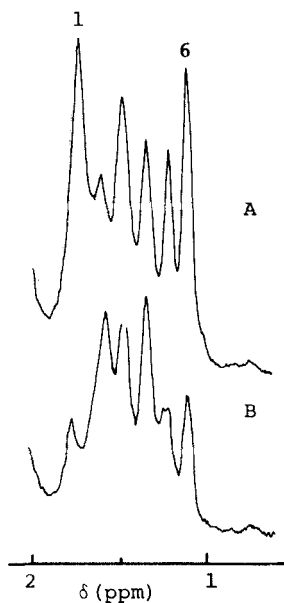The relative reactivity of a monomer toward an anion will

FIG. 4. NMR spectra of copoly(MMA-MAA)s which were derived from copoly(MMA-DMBMA) (A) and copoly(MMA-TrMA) (B) (100 MHz, pyridine-d_5, HMDS, 100°C). Polymerization conditions: $[MMA]_0 = [M_2]_0$, 2.5 mmole; THF, 10 ml; [n-BuLi], 0.25 mmole; -78°C; 24 hr. Yield: 88% (A); 100% (B); [MMA]/[DMBMA] in copolymer, 1.2; [MMA]/[TrMA] in copolymer, 1.0.

depend on the electron density on the β-carbon of the monomer. The logarithm of relative reactivity $(1/r_1)$ of the methacrylates toward MMA anion was plotted against the ^{13}C chemical shift of the β-carbon as shown in Fig. 5. Most data showed a linear relationship, though they are a little scattered. However, the points for DMBMA and TrMA in toluene deviated greatly from the line. The plots of the ^{13}C chemical shift of β-carbon against Taft's σ^* value of the ester group are shown in Fig. 6. A fine linear relationship was observed between the electron density of β-carbon and the polar effect of the ester group. A good linearity was also obtained between the chemical shift of [1]H (cis to the carbonyl group) of the monomer and the σ^* value. Consequently, the reactivity of the methacrylates toward an anion is explained as being governed by the polar effect of the ester group, not only
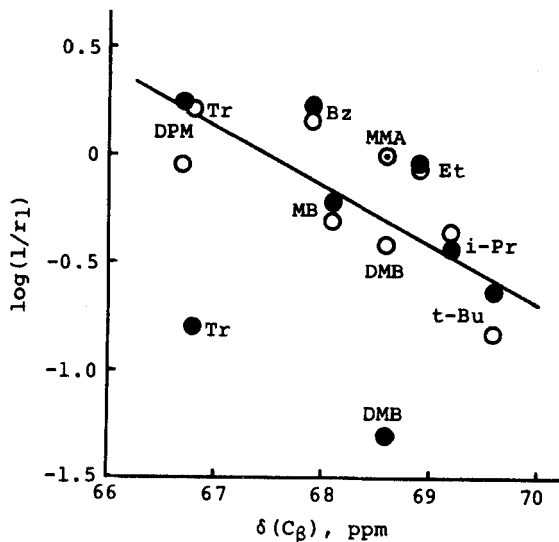
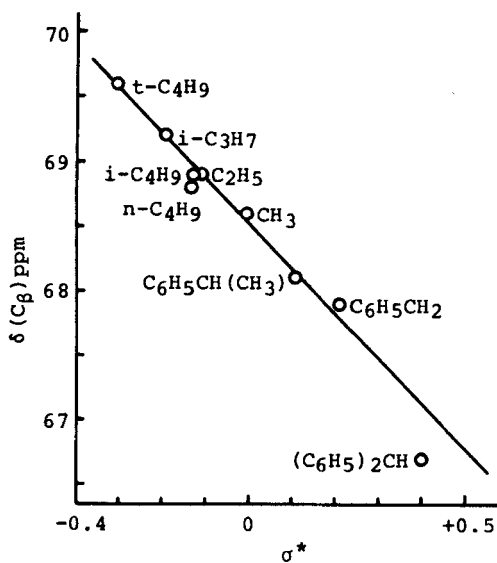FIG. 5. Plots of $\log(1/r_1)$ vs $^{13}C_\beta$ chemical shifts of methacrylates: (●) in toluene; (○) in THF.

FIG. 6. Plots of Taft σ^* vs $^{13}C_\beta$ chemical shifts of methacrylates.

in THF but also in toluene. The only exception is the extremely low reactivity of DMBMA and TrMA in toluene, suggesting that the mechanisms of the copolymerizations of MMA-DMBMA and MMA-TrMA systems in toluene are distinct from the other mechanisms.

TACTICITY OF COPOLYMER [9, 10]

Few studies have been reported on the stereoregularity of copolymers. The authors investigated the tacticity of the copolymers of the above methacrylates with each other in order to learn the effect of bulkiness of the monomer on the stereoregulation of the copolymer.

Table 8 shows the stereoregularity of the copolymers formed from equimolar amounts of feed monomers by n-BuLi in toluene at -78°C. The isotacticity of the copolymer of MMA and BzMA slightly exceeded those of poly-MMA and poly-BzMA prepared under similar reaction conditions. However, the isotacticity of most copolymers lay in between those of the corresponding homopolymers. In some cases where the copolymers contained bulky monomers, their isotacticity was lowered, for example, the copolymers of TrMA-DPMMA, TrMA-DMBMA, and TrMA-DPEMA.

The data of the copolymers obtained in THF are listed in Table 9. They are similar to the copolymers obtained in toluene, but in this case the syndiotacticity of the copolymer was in between those of the corresponding homopolymers. It must be mentioned that the isotacticity of the copolymers which contained TrMA as one of the comonomers increased with increasing bulkiness of another comonomer, suggesting the steric influence of TrMA on the stereoregulation of the copolymer in THF.

As stated previously, the methacrylates formed the polymers with a variety of tacticity even under the same reaction conditions. It has been postulated that in the course of the stereospecific polymerization of MMA, the propagation may proceed with a preferred helical conformation [17]. We can consider a similar situation in the stereospecific polymerization of other methacrylates. If the copolymerization of the methacrylates proceeds stereoregularly also with a helical conformation of the growing chain, the differences in size and shape of the ester groups may cause the following cases: 1) If once a monomer forms a helical chain in the initial stage of the copolymerization, it excludes the incorporation of the comonomer, growing to a stereoregular homopolymer; 2) if both monomers copolymerize initially, where the helical conformation is disturbed, both can continue to add to the chain end, forming a less tactic copolymer; 3) it is more probable that in the copolymerization

both the monomers have tendencies to take individual tacticity
in the same polymer chain, producing a copolymer of mean stereo-
regularity. In an extreme case, one monomer having a tendency of
forming high stereoregularity may force the comonomer to take
identical tacticity in the same helical chain, yielding a stereoregular
copolymer. These are represented schematically in Scheme 4.
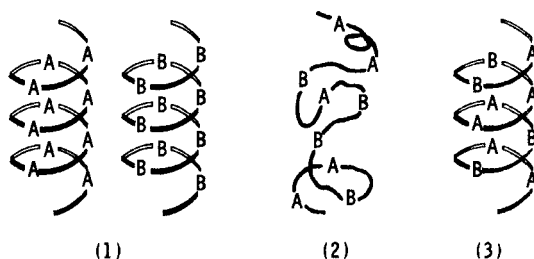
SCHEME 4.

Most of the data shown in Tables 8 and 9 seem to belong to the
third case, although higher stereoregularity than those of homo-
polymers was found only in copoly(MMA-BzMA) obtained in
toluene. The isotactic propagation of TrMA was completely
disturbed by the incorporation of a small size comonomer, and
to some extent the isotacticity was retained in the copolymeri-
zation with a comonomer having similar bulkiness. It was found
that the copolymerization of MMA and TrMA in toluene produced a
highly isotactic poly-MMA (I:H:S = 83:11:6) and a less stereoregular
copolymer simultaneously. The copoly(MMA-TrMA) obtained was
converted to copoly(MMA-MAA), which was then fractionated with
methanol. The insoluble fraction was proved to be the poly-MMA
and the soluble one the copolymer (Fig. 7). A similar result has been
observed in the copolymerization of MMA and MPhA by n-BuLi
in toluene (Table 10) [18].

The copolymerization of equimolar amounts of these monomers
gave only an isotactic homopolymer of MPhA at -78°C, while above
30°C an alternating copolymer, which was completely atactic, was
produced. On the other hand, the product at -40°C was found to
consist of a highly isotactic poly-MMA and a copolymer. These
facts indicate that in the copolymerization with MMA an extremely
bulky comonomer can incorporate only in the growing chain with
random conformation. The extremely low reactivity of TrMA in

TABLE 8. Stereoregularity of Copolymethacrylates Obtained in Toluene by n-BuLi at -78°C

	M2 homo-polymer			M1 MMA				BzMA				DL-MBMA				DPMMA				DMBMA				DPEMA			
M2	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S
MMA	70	17	13																								
BzMA	81	15	4	1.1	84	10	6																				
DL-MBMA	56	35	9	1.0	66	27	7	1.1	79	15	6																
DPMMA	99	1	0	2.0	80	16	4	0.9	79	16	5	1.1	65	28	7												
DMBMA	68	18	13	5.3	61	25	14	5.9	69	21	10	1.5	65	26	9	1.2	68	23	9								
DPEMA	23	28	49	4.3	60	27	13	-	-	-	-	-	-	-	-	4.3	66	22	12	-	-	-	-				
TrMA	96	2	2	6.4	74	17	9	8.9	81	12	7	4.1	59	28	13	-	72	20	8	0.7	41	37	22	1.0	27	37	36

TABLE 9. Stereoregularity of Copolymethacrylates Obtained in THF by n–BuLi at –78°C

M_2	M_2 homopolymer			M_1 MMA				BzMA				DL–MBMA				DPMMA				DMBMA				DPEMA			
	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S	$\frac{m_1}{m_2}$	I	H	S
MMA	6	40	54																								
BzMA	6	31	63	1.1	8	34	58																				
DL–MBMA	8	32	60	1.0	7	37	56	1.0	8	27	65																
DPMMA	2	11	87	1.2	6	30	64	0.9	6	26	68	0.8	11	23	66												
DMBMA	8	30	62	1.1	7	31	62	0.9	13	40	47	1.0	8	33	59	1.0	7	27	66								
DPEMA	21	46	33	1.0	10	36	54	–	–	–	–	–	–	–	–	1.0	8	28	64	–	–	–	–				
TrMA	94	4	2	1.0	19	40	41	1.0	16	40	44	1.1	22	39	39	–	26	35	39	1.1	38	41	21	1.0	51	34	15

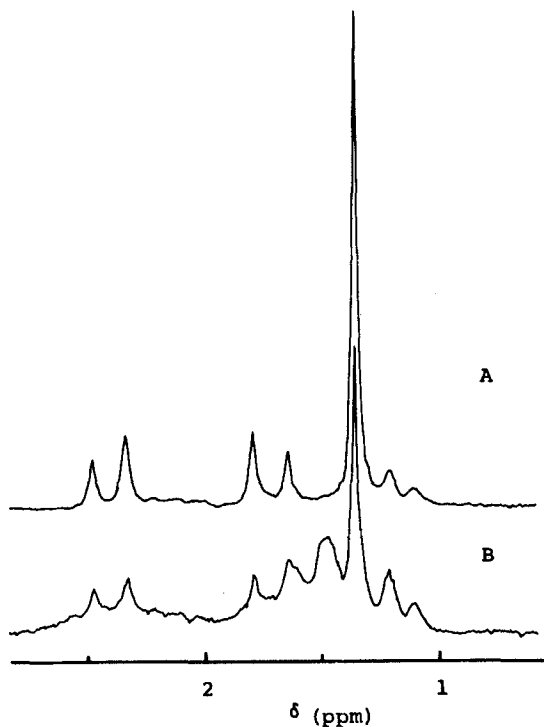FIG. 7. NMR spectra of fractions of copoly(MMA-MAA) which
was derived from copoly(MMA-TrMA) obtained in toluene by n-BuLi
at -78°C. (A) Methanol-insoluble fraction; (B) methanol-soluble
fraction (100 MHz, pyridine-d_5, 100°C, HMDS).

toluene may be explained by the difficulty of incorporation into
the isotactic polymer chain in the copolymerization.

In this paper the authors have described three topics on the
anionic polymerization of a series of methacrylates: the stereo-
regulation in the polymerization, the relative reactivity of the
monomers in the copolymerization, and the stereoregularity
of the copolymers. These are correlated with each other and
involve many unsolved problems. Further investigations are
continuing.

TABLE 10. Anionic Copolymerization of MPhA and MMA by n–BuLi in Toluene[a]

Temperature (°C)	Time (hr)	Yield (%)	MPhA unit in copolymer (mole %)	Alternate sequence (mole %)
-78	24	15	97	0
-40	72	68	44	31
0	72	80	47	93
30	96	59	47	100[b]

[a]MPhA, 6.8 mmole; MMA, 6.8 mmole; n–BuLi, 0.68 mmole.
[b]Cotacticity: I, 24.8%; H, 50.4%; S, 24.8%.

REFERENCES

[1] H. Yuki, K. Hatada, T. Niinomi, and Y. Kikuchi, Polym. J., 1, 36 (1970).
[2] H. Yuki et al., Unpublished Data.
[3] H. Yuki, K. Ohta, K. Ono, and S. Murahashi, J. Polym. Sci., A-1, 6, 829 (1968).
[4] H. Yuki, K. Ohta, K. Hatada, Y. Okamoto, K. Kamanaru, K. Obayashi, and M. Mochida, To Be Submitted to J. Polym. Sci., Polym. Chem. Ed.
[5] H. Yuki, Y. Okamoto, K. Ohta, Y. Shimada, and K. Hatada, To Be Published.
[6] H. Yuki, K. Hatada, Y. Kikuchi, and T. Niinomi, J. Polym. Sci., B, 6, 753 (1968).
[7] H. Yuki, K. Hatada, T. Niinomi, and K. Miyaji, Polym. J., 1, 130 (1970).

[8] H. Yuki, K. Hatada, T. Niinomi, M. Hashimoto, and J. Ohshima, Ibid., 2, 629 (1971).

[9] H. Yuki, Y. Okamoto, and K. Ohta, Preprints, 23rd Symposium on Macromolecular Science, Japan, Tokyo, 1974.

[10] H. Yuki, Y. Okamoto, K. Ohta, and K. Hatada, Polym. J., 6, 573 (1974); J. Polym. Sci., Polym. Chem. Ed., 13, 1161 (1975).

[11] K. Ito, T. Sugie, and Y. Yamashita, Makromol. Chem., 125, 291 (1969).

[12] J. C. Bevington, D. O. Harris, and F. S. Rankin, Eur. Polym. J., 6, 725 (1970).

[13] P. Vlcek, D. Doskocilova, and J. Trekoval, J. Polym. Sci., Polym. Symp. Ed., 42, 231 (1973).

[14] M. Szwarc, Carbanions, Living Polymers, and Electron-Transfer Processes, Wiley-Interscience, New York, 1968, p. 520.

[15] H. Yuki, Y. Okamoto, K. Ohta, and K. Hatada, Unpublished Results.

[16] E. Klesper and W. Gronski, J. Polym. Sci., B, 7, 661 (1969).

[17] D. L. Glusker, I. Lysloff, and E. Stiles, J. Polym. Sci., 49, 315 (1961).

[18] K. Hatada, J. Ohshima, T. Komatsu, S. Kokan, and H. Yuki, Polymer, 14, 565 (1973).