Effect of LiClO$_4$ on Radical Polymerization of Methyl Methacrylate

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ABSTRACT: The effect of LiClO$_4$ on the polymerization of methyl methacrylate (MMA) with dimethyl 2,2′-azobisisobutyrate (MAIB) was investigated at 50°C in methyl ethyl ketone. The polymerization proceeded homogeneously even at [LiClO$_4$] as high as 3.00 mol/L. The polymerization rate (R_p) and the molecular weight of the resulting polymer profoundly increased with increasing [LiClO$_4$]. R_p at 3.00 mol/L [LiClO$_4$] was 12 times that in the absence of LiClO$_4$. The rate equation depended on the presence or absence of LiClO$_4$: $R_p = k[\text{MAIB}]^{0.5}[\text{MMA}]^{1.5}$ in the presence of 3.00 mol/L [LiClO$_4$] and $R_p = k'[\text{MAIB}]^{0.5}[\text{MMA}]^{1.0}$ in the absence of LiClO$_4$. The overall activation energies of polymerization were 38.5 kJ/mol in the presence of 3.00 mol/L [LiClO$_4$] and 77.4 kJ/mol in the absence of LiClO$_4$, respectively. The tacticities of resulting poly(MMA) were insensitive to the presence of LiClO$_4$. In the copolymerization of MMA and styrene, Q and e values of MMA increased with increasing [LiClO$_4$], leading to enhanced alternating copolymerizability. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1361–1368, 1997

Key words: radical polymerization; copolymerization; methyl methacrylate; Lewis acid effect; LiClO$_4$

INTRODUCTION

The radical polymerizations of acryl monomers such as methyl methacrylate (MMA), methyl acrylate, and acrylonitrile (AN) are reported to be accelerated in the presence of Lewis acids like ZnCl$_2$, SnCl$_4$, and AlR$_n$Cl$_{3-n}$.[1–4] Such Lewis acids are also well known to highly affect the reactivities of the acryl monomers in copolymerizations with donor monomers such as styrene (St) and butadiene where alternating copolymers are often formed.[1,4,5–9]

Bamford et al. found that the presence of LiCl causes acceleration of radical polymerization of AN and an increase in the molecular weight of the resulting polymer.[10] They explained the observed results in terms of enhanced propagation, the rate constant (k_p) of which was determined by the rotating sector method. In the preceding paper[11] we observed a high acceleration effect of LiClO$_4$ on the radical polymerization of an itaconate ester carrying two oligoethylene oxide chains {di-2-[2-(2-methoxyethoxy)ethoxy]ethyl itaconate (DMEI)} where the propagating polymer radical was ESR observable under the practical polymerization conditions. ESR-determineted k_p value increased and the termination rate constant (k_t) decreased with increasing LiClO$_4$ concentration. It was suggested that LiClO$_4$ interacts not only with the ether linkages of DMEI but also with the ester carbonyl groups. Mani and colleagues confirmed the interaction of LiCF$_3$SO$_3$ with the ester groups of poly(MMA) by means of IR spectroscopy.[12] Casaschi et al. found that Diels−Alder reactions of some α,β-unsaturated carbonyl compounds used

as a dienophile in acetone are strongly accelerated in the presence of LiClO$_4$.[13]

These observations led us to examine the effect of LiClO$_4$ as a Lewis acid on the radical homo- and copolymerizations of MMA.

The present article describes the results obtained in the polymerization of MMA and copolymerization of MMA with St at high LiClO$_4$ concentrations in methyl ethyl ketone (MEK). Dimethyl 2,2′-azobisisobutyrate (MAIB) was used as the initiator.

EXPERIMENTAL

Commercial MMA and St were washed with a 5 wt % aqueous NaOH solution and a 20 wt % aqueous NaCl solution, dried over Na$_2$SO$_4$, and distilled under a reduced pressure before use. MAIB (Wako Pure Chemicals) was recrystallized from methanol. LiClO$_4$ (guaranteed reagent, Wako Pure Chemicals) was used without further purification. MEK was used after distillation.

Polymerization and copolymerization were carried out with shaking in a degassed and sealed glass tube at a given temperature. The resulting polymers were isolated by pouring the polymerization mixture into a large excess of methanol.

^{1}H-NMR spectra were obtained with Hitachi R-24B (60 MHz) and JEOL-GX-400 (400 MHz) spectrometers with tetramethylsilane used as an internal standard. Gel permeation chromatograms (GPC) were recorded on a Toso HLC-802A apparatus at 38°C using tetrahydrofuran as eluent. From the GPC results the number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the polymers were determined with calibration by poly(St) standards.

RESULTS AND DISCUSSION

Effect of LiClO$_4$ on Polymerization of MMA with MAIB in MEK

Figure 1 shows time-conversion curves observed in the polymerization of MMA with MAIB at 50°C in MEK at various concentrations of LiClO$_4$, where the concentrations of MMA and MAIB were 1.00 mol/L and 5.00 × 10^{-3} mol/L. The polymerization proceeded homogeneously at all the LiClO$_4$ concentrations used. The polymer yield increased linearly with time without any induction
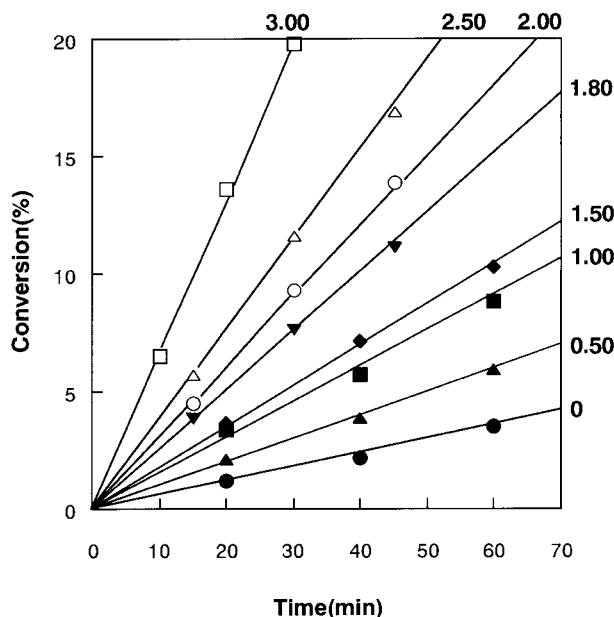

Figure 1 Time-conversion curves in the polymerization of MMA with MAIB at various LiClO$_4$ concentrations in MEK at 50°C; the numbers in the figure are [LiClO$_4$] in mol/L; [MMA] = 1.00 mol/L, [MAIB] = 5.00 × 10^{-3} mol/L.

period. Thus, the radical polymerization of MMA was found to be highly accelerated in the presence of LiClO$_4$. The initial polymerization rate (R_p) was estimated from the time-conversion curves and was plotted against the LiClO$_4$ concentration in Figure 2. R_p increased with increasing [LiClO$_4$]. The R_p enhancement with LiClO$_4$ became greater at higher salt concentrations. The R_p value at 3.00 mol/L [LiClO$_4$] was 12 times that observed in the absence of LiClO$_4$.

The LiClO$_4$ acceleration effect can be explained by the following reasons: enhanced propagation due to interaction of the salt with MMA monomer and/or propagating polymer radical, retarded termination due to increased viscosity of the polymerization system containing LiClO$_4$, and accelerated decomposition of MAIB with LiClO$_4$.

Figure 3 presents the relationship between the molecular weight of resulting poly(MMA) and the LiClO$_4$ concentration. $\bar{M}_n$ increased with increasing LiClO$_4$ concentration. The molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.6–2.3) slightly increased with LiClO$_4$ concentration. Thus, the observed relationship is similar to that between R_p and the LiClO$_4$ concentration in Figure 2, indicating that the acceleration by LiClO$_4$ is caused by
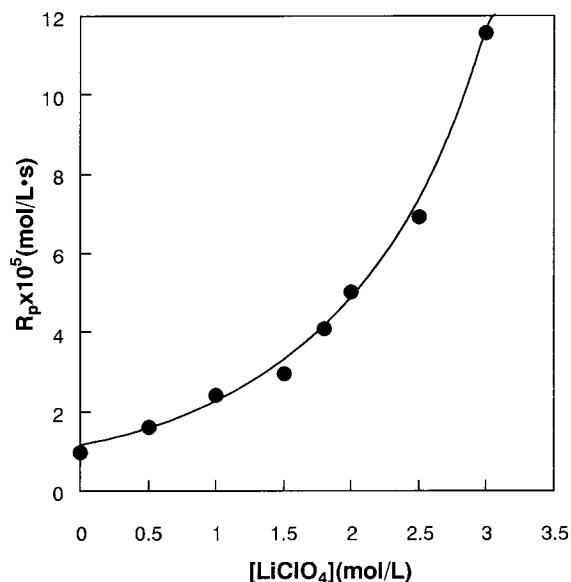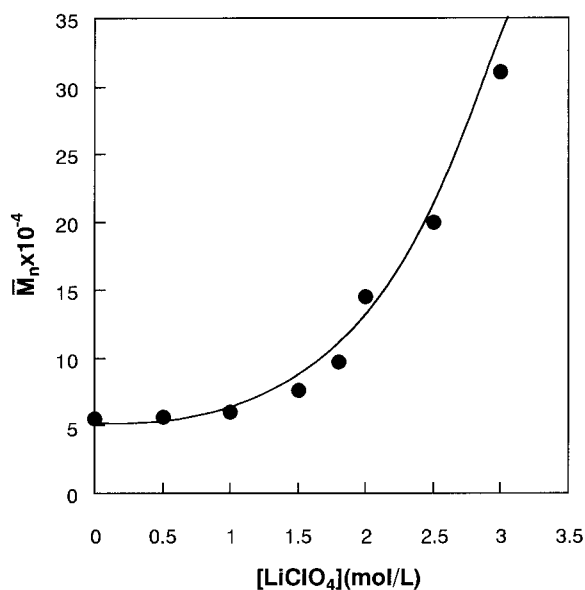
Figure 2   Effect of LiClO$_4$ concentration on the polymerization rate (R_p) at 50°C in MEK; [MMA] = 1.00 mol/L, [MAIB] = 5.00 × 10^{-3} mol/L.
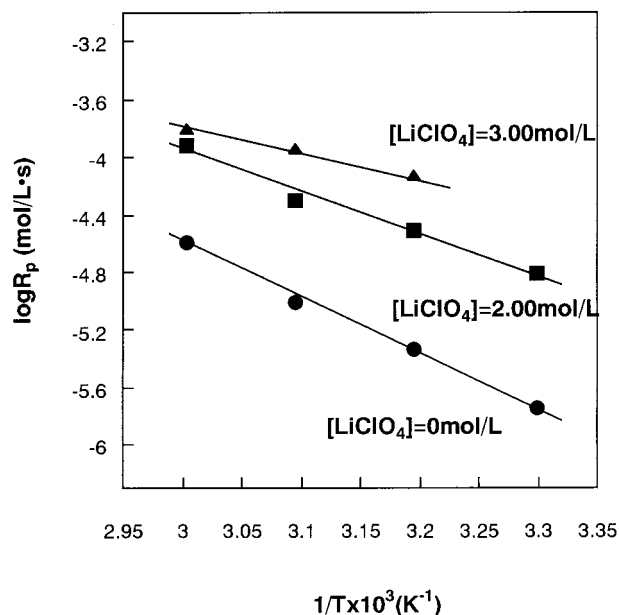
enhanced propagation and/or retarded termination due to the viscosity effect.

Kinetic Study on Polymerization of MMA with MAIB in MEK in Presence of LiClO$_4$

Temperature effect on the polymerization of MMA with MAIB in MEK was examined at different

Figure 3   Effect of LiClO$_4$ concentration on the molecular weight ($\bar{M}_n$) of poly(MMA).

Figure 4   Arrehenius plots of the polymerization rate (R_p) in MEK at different LiClO$_4$ concentrations; [MMA] = 1.00 mol/L, [MAIB] = 5.00 × 10^{-3} mol/L.
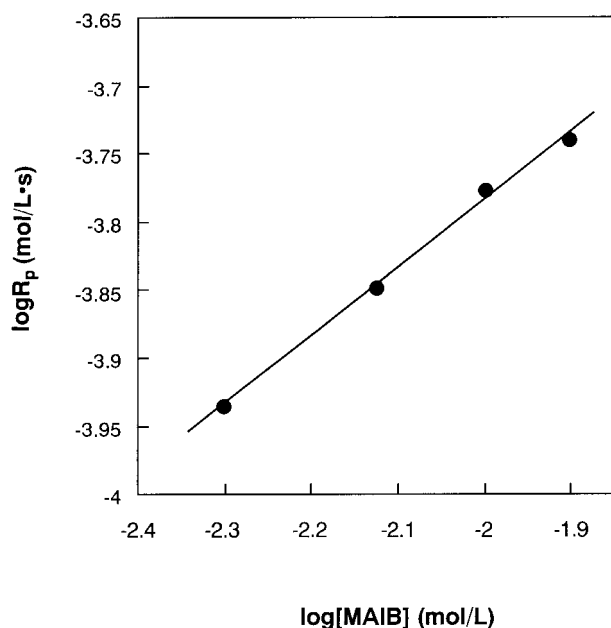
LiClO$_4$ concentrations. The concentrations of MMA and MAIB were 1.00 mol/L and 5.00 × 10^{-3} mol/L, respectively. Figure 4 shows the Arrhenious plots of R_p estimated from the time-conversion curves. The slopes of the plots gave the overall activation energies (E_a) of polymerization as shown in Table I. Thus, the lower E_a value was observed at higher LiClO$_4$ concentration. A similar decrease in the E_a value with the presence of the Lewis acid was also reported for the MMA/ZnCl$_2$,[3] the cyclohexyl acrylate/ZnCl$_2$,[4] and the diethyl itaconate/SnCl$_4$ systems.[14]

Effects of the concentrations of monomer and initiator on R_p were studied in the polymerization at 50°C in MEK at 3.00 mol/L [LiClO$_4$]. Figure 5 shows the relationship between the MAIB concentration and R_p when the MMA concentration

Table I   Effect of LiClO$_4$ on overall Activation Energy of Polymerization (E_a) in Polymerization of MMA with MAIB in MEK

[LiClO$_4$] (mol/L)	E_a (kJ/mol)
0	77.4
2.00	55.6
3.00	38.5

[MMA] = 1.00 mol/L, [MAIB] = 5.00 × 10^{-3} mol/L.

Figure 5   Dependence of the polymerization rate (R_p) on the MAIB concentration in MEK at 50°C; [MMA] = 1.00 mol/L, [LiClO$_4$] = 3.00 mol/L.

was kept constant at 1.00 mol/L. R_p was found to be proportional to the square root of the initiator concentration, indicating the occurrence of usual bimolecular termination in the presence of LiClO$_4$.

Figure 6 illustrates the dependence of R_p on the MMA concentration when the MAIB concentration was constant at 5.00×10^{-3} mol/L and the MMA concentration was varied from 0.50–1.25 mol/L. Thus, R_p increased in proportion to the 1.5 power of monomer concentration. Such higher dependence of R_p on the monomer concentration is probably ascribable to increasing viscosity with increasing monomer concentration in the presence of LiClO$_4$. It is also possible that the propagation is accelerated by enhanced aggregation at the higher MMA concentrations in the presence of LiClO$_4$.[11,15]

From the above results, R_p at 3.00 mol/L [LiClO$_4$] is given by eq. (1),

$$R_p = k[\text{MAIB}]^{0.5} [\text{MMA}]^{1.5}, \qquad (1)$$

in the presence of LiClO$_4$.

The rate equation of polymerization was similarly determined at 50°C in MEK in the absence

of LiClO$_4$. R_p was expressed as an ideal rate equation [eq. (2)].

$$R_p = k'[\text{MAIB}]^{0.5} [\text{MMA}]^{1.0} \qquad (2)$$

in the absence of LiClO$_4$.

Characterization of Poly(MMA) Formed in Presence of LiClO$_4$

Table II summarizes the molecular weights of poly(MMA)s formed under various polymerization conditions. As described above, the presence of LiClO$_4$ caused an increase in $\bar{M}_n$ of the resulting poly(MMA). The $\bar{M}_n$ of the polymer increased with increasing monomer concentration and decreased with increasing initiator concentration and with rising temperature. The $\bar{M}_w/\bar{M}_n$ was in the range of 1.4–2.5. These results are similar to those observed in the usual radical polymerization.

Table III compares the tacticities of poly(MMA)s formed in the absence and presence of LiClO$_4$, which were determined by a ^{1}H-NMR spectrum of the α-methyl group of poly(MMA). Almost identical results were observed for all the polymers. Thus, even the use of LiClO$_4$ concentration as high as 3.00 mol/L did not significantly
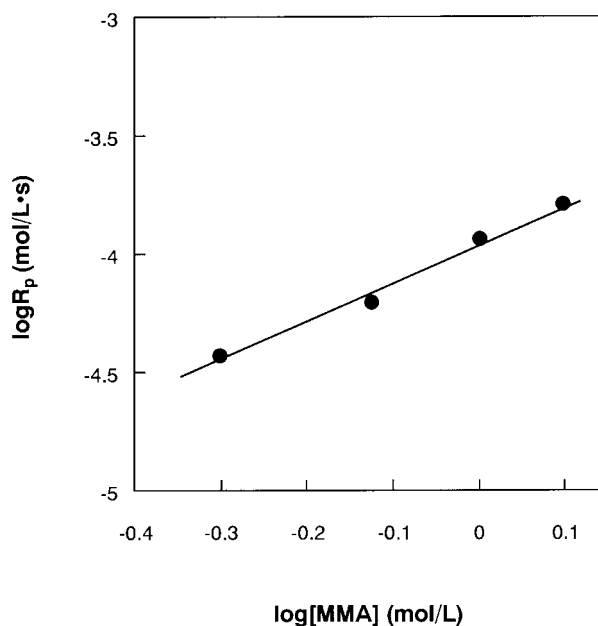
Figure 6   Dependence of the polymerization rate (R_p) on the MMA concentration in MEK at 50°C; [MAIB] = 5.00×10^{-3} mol/L; [LiClO$_4$] = 3.00 mol/L.

Table II Molecular Weight and Molecular Weight Distribution of Poly(MMA) Formed under Different Polymerization Conditions

Temp. (°C)	[MMA] (mol/L)	[MAIB] $\times 10^3$ (mol/L)	[LiClO$_4$] (mol/L)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
50	1.00	5.00	0	5.56	1.6
50	1.00	7.50	0	5.03	2.0
50	1.00	10.0	0	4.78	2.1
50	1.00	12.5	0	4.32	2.3
30	1.00	5.00	0	9.61	1.8
40	1.00	5.00	0	8.16	1.8
60	1.00	5.00	0	5.41	1.4
50	0.50	5.00	3.00	13.8	2.0
50	0.75	5.00	3.00	18.1	2.3
50	1.00	5.00	3.00	31.1	2.3
50	1.25	5.00	3.00	45.1	2.0
50	1.00	7.50	3.00	28.5	2.2
50	1.00	10.0	3.00	25.1	2.2
50	1.00	12.5	3.00	23.7	2.3
30	1.00	5.00	2.00	19.2	2.2
40	1.00	5.00	2.00	16.2	2.1
50	1.00	5.00	2.00	14.6	2.1
60	1.00	5.00	2.00	8.91	2.0
40	1.00	5.00	3.00	43.6	2.5
60	1.00	5.00	3.00	21.3	2.2

affect the microstructure of the resultant poly(MMA).

Acceleration Effect of LiClO$_4$ Discussed on Basis of Degree of Polymerization of Resulting Poly(MMA)

To clarify the reason for the enhanced polymerization in the presence of LiClO$_4$, we attempted to determine the initiation rate (R_i) and k_t/k_p^2 by using the number-average degree of polymerization ($\overline{P}_n$) of the resulting poly(MMA).

The reciprocal of $\overline{P}_n$ is related to R_p and [MMA] by eq. (3).

Table III Tacticities of Poly(MMA)s Formed in Polymerization of MMA with MAIB in MEK at 50°C at Different LiClO$_4$ Concentrations

[LiClO$_4$]/[MMA]	mm	mr	rr
0	0.042	0.307	0.651
2	0.033	0.334	0.633
3	0.038	0.322	0.640

[MMA] = 1.00 mol/L, [MAIB] = 5.00 $\times 10^{-3}$ mol/L.
mm: isotactic; mr: heterotactic; rr: syndiotactic.

$$1/\overline{P}_n = C_m + C_s[\text{MEK}]/[\text{MMA}]$$
$$+ C_1[\text{LiClO}_4]/[\text{MMA}]$$
$$+ C_i[\text{MAIB}]/[\text{MMA}]$$
$$+ k_t R_p/(k_p^2[\text{MMA}]^2), \quad (3)$$

where C_m, C_s, C_1, and C_i are chain transfer constants of monomer, MEK, LiClO$_4$, and MAIB, respectively. When the polymerization is performed varying only the MAIB concentration and keeping the concentrations of other components constant, eq. (3) is adequately approximated by eq. (4) because the value of (C_i[MAIB])/[MMA] is negligibly small.

$$1/\overline{P}_n = C + k_t R_p/(k_p^2[\text{MMA}]^2), \quad (4)$$
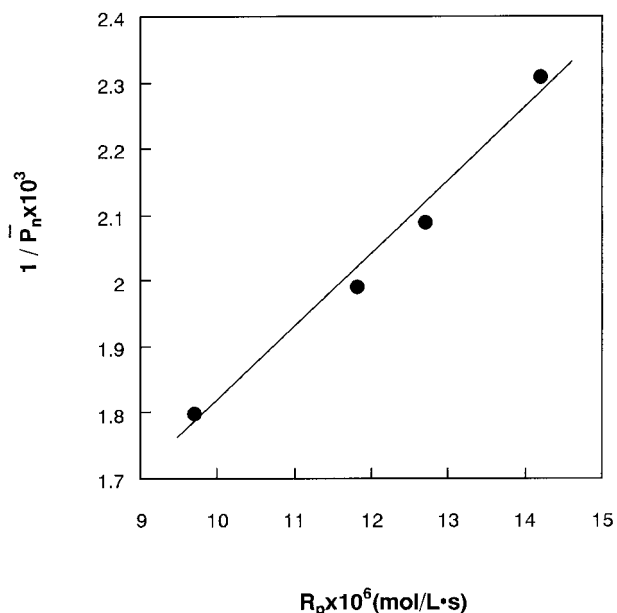
where C is a constant.

Figures 7 and 8 show the plots of $1/\overline{P}_n$ against R_p for the polymerizations at 50°C in the absence and presence of LiClO$_4$ (3.00 mol/L), where [MMA] was 1.00 mol/L. From the slopes of the plots, the k_t/k_p^2 values were estimated and are shown in Table IV. The k_t/k_p^2 value in the absence of LiClO$_4$ is 80 times larger than that in its presence (3.00 mol/L).

Figure 7   Plot of $1/\overline{P}_n$ against the polymerization rate (R_p) in the absence of LiClO$_4$ in MEK at 50°C; [MMA] = 1.00 mol/L.

R_i is estimated by eq. (5),

$$k_p^2/k_t = R_p^2/(R_i \times [\text{MMA}]^2). \qquad (5)$$

The R_i values were calculated for the polymer-
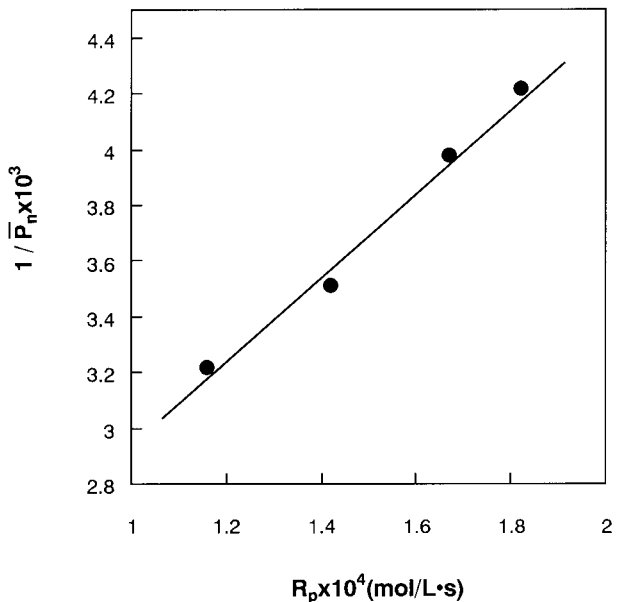
Figure 8   Plot of $1/\overline{P}_n$ against the polymerization rate (R_p) in the presence of LiClO$_4$ in MEK at 50°C; [MMA] = 1.00 mol/L, [LiClO$_4$] = 3.00 mol/L.

Table IV   Polymerization Rate (R_p) and Initiation Rate (R_i) in Polymerization of MMA Initiated by MAIB in Presence and Absence of LiClO$_4$ at 50°C in MEK

[LiClO$_4$] (mol/L)	$R_p \times 10^6$ (mol/L s)	$R_i \times 10^8$ (mol/L s)	k_t/k_p^2 (mol s/L)
0	9.72	1.13	120
3.00	116	2.02	1.5

[MMA] = 1.00 mol/L, [MAIB] = 5.00 $\times$ 10^{-3} mol/L.

izations of MMA (1.00 mol/L) with MAIB (5.00 $\times$ 10^{-3} mol/L) at 50°C in the absence and presence of LiClO$_4$ (3.00 mol/L) and are also presented in Table IV. The decomposition of MAIB is reported to be accelerated in polar solvents.[16] Using the reported rate constants (k_d) of decomposition at 50°C and an initiator efficiency of 0.5, R_i was estimated to be 1.34 $\times$ 10^{-8} mol/L s in acetonitrile[16] (k_d = 2.68 $\times$ 10^{-6} s^{-1}) and 1.11 $\times$ 10^{-8} mol/L s in benzene[16] (k_d = 2.22 $\times$ 10^{-6} s^{-1}), which is comparable to the value (1.13 $\times$ 10^{-8} mol/L s) in the absence of LiClO$_4$. This indicates that the R_i values thus obtained from $1/\overline{P}_n$ are reasonable. R_i in the presence of LiClO$_4$ (3.00 mol/L) was about 2 times that in its absence. Some Lewis acids are reported to accelerate the decomposition of MAIB.[16,17] Although the initiator efficiency (f) of MAIB is expected to be decreased by increased viscosity in the presence of LiClO$_4$, the enhanced decomposition rate of MAIB may overcome the decrease in f value.

As can be seen from Table IV, the observed acceleration effect of LiClO$_4$ stems predominantly from the marked decrease in the k_t/k_p^2 value.

^{1}H-NMR Study on Interaction of MMA with LiClO$_4$

The above results and the reported observations indicate that lithium salts including LiClO$_4$ interact with carbonyl compounds to affect their reactivities.[11–13] We examined the interaction of MMA with LiClO$_4$ in MEK at room temperature by means of ^{1}H-NMR. Signals of C$\underline{\text{H}}_2$=C and C$\underline{\text{H}}_3$O of MMA, and also of CH$_3$—C$\underline{\text{H}}_2$ and C$\underline{\text{H}}_3$CO of MEK were observed to be shifted downfield. Figure 9 shows the effect of [LiClO$_4$] on the chemical shifts of these protons. Thus, the downfield shifts increased with increasing [LiClO$_4$], although a somewhat abrupt change was observed for the
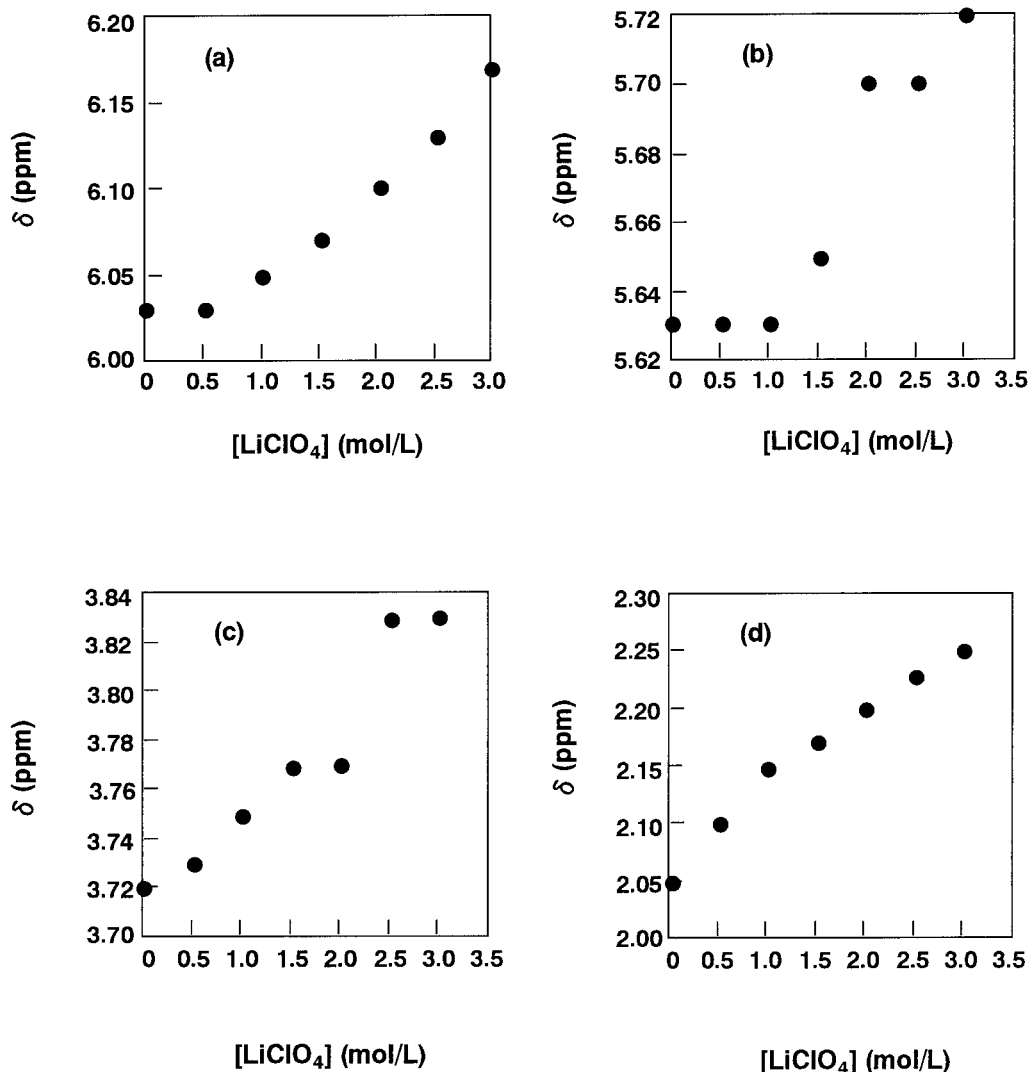
Figure 9   Effect of the LiClO$_4$ concentration on the chemical shift of (a) *cis*-vinyl proton, (b) *trans*-vinyl proton, (c) methoxy protons of MMA, and (d) acetyl protons of MEK at room temperature; [MMA] = 1.00 mol/L.

methoxy and *trans*-vinyl protons near 2.0 mol/L [LiClO$_4$]. The reason for the abrupt changes is obscure at present. The findings indicate that LiClO$_4$ can interact with the carbonyl groups of MMA and MEK in the solution of MMA in MEK, although the interactions are not so strong. Such an interaction of MMA with LiClO$_4$ is partially responsible for the enhanced reactivity of MMA observed above.

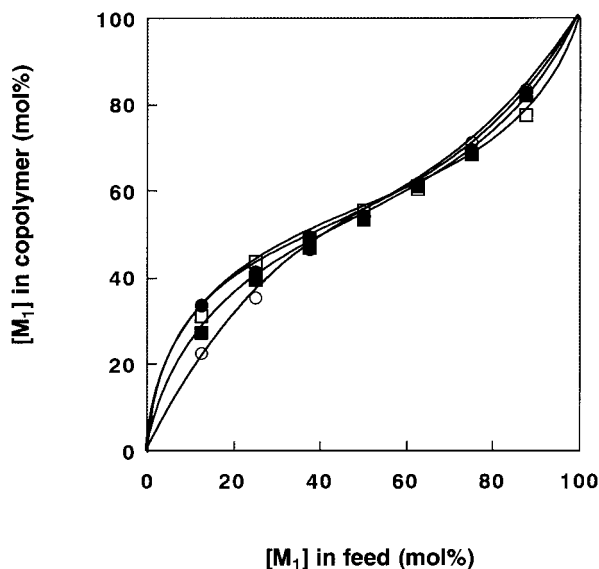### Effect of LiClO$_4$ on Copolymerization of MMA and St with MAIB in MEK

As described earlier LiClO$_4$ was confirmed to interact with MMA. The acceleration effect of

LiClO$_4$ on the polymerization of MMA seemed to be caused not only by retarded termination but also by enhanced propagation. Diels–Alder reactions of some α,β-unsaturated carbonyl compounds are reported to be much accelerated by the presence of LiClO$_4$.[13] These results led us to the examination of the LiClO$_4$ effect on the copolymerization of MMA with St.

The copolymerization of MMA (M_1) and St (M_2) with MAIB in MEK at 50°C was carried out at different LiClO$_4$ concentrations. The copolymer yields were less than 10%. The copolymerization rate and the molecular weight of the copolymer increased with increasing LiClO$_4$ concentration.

Figure 10 shows the copolymer-composition curves observed at different $LiClO_4$ concentrations. The composition of copolymers was estimated from the carbon content by elemental analysis. The monomer reactivity ratios were determined by the curve-fitting method based on a nonlinear least squares analysis and are presented in Table V.[18] Table V also shows Q and e values of MMA calculated from the monomer reactivity ratios, where $Q = 1.0$ and $e = -0.8$ were used for St. Thus, both of Q and e values of MMA increased with increasing $LiClO_4$. As a result, the alternating copolymerizability of MMA and St increased with $LiClO_4$ concentration. Such a tendency was also reported for some copolymerizations in the presence of $ZnCl_2$.[4,19]

These observations are explicable on the basis of the interaction of the lithium ion with the ester carbonyl group of MMA.

Table V   Parameters Obtained in Copolymerization of MMA (M_1) and St (M_2) at Different $LiClO_4$ Concentrations at 50°C in MEK

[$LiClO_4$] (mol/L)	r_1	r_2	Q_1	e_1
0	0.613	0.379	1.003	0.408
2.00	0.471	0.263	1.196	0.645
2.50	0.467	0.188	1.528	0.760
3.50	0.416	0.172	1.586	0.820

[MMA] + [St] = 1.00 mol/L, [MAIB] = 5.00×10^{-3} mol/L.

REFERENCES

1. J. Barton and E. Borsig, *Complexes in Free-Radical Polymerization,* Elsevier, Amsterdam, 1988.
2. V. A. Kavanov, *Makromol. Chem., Macromol. Symp.,* **10/11,** 193 (1987).
3. M. A. Diab, A. Z. El-Sonbati, H. M. Killa, and M. M. Ghoneim, *Eur. Polym. J.,* **26,** 1 (1990).
4. D.-J. Liaw and K.-C. Chung, *Makromol. Chem.,* **184,** 29 (1983).
5. Y. Gotoh, T. Iihara, N. Kanai, N. Toshima, and H. Hirai, *Chem. Lett.,* 2157 (1990).
6. J. Krstina, G. Moad, and D. H. Solomon, *Polym. Bull.,* **27,** 425 (1992).
7. H. Nakamura, M. Seno, H. Tanaka, and T. Sato, *Makromol. Chem.,* **194,** 1773 (1993).
8. H.-Y. Lee, M. S. Herman, A. B. Padias, H. K. Hall, Jr., and R. D. Tack, *Acta Polym.,* **43,** 413 (1994).
9. Y. Yuan, H. Song, and G. Xu, *Polym. Int.,* **31,** 397 (1993).
10. C. H. Bamford, A. D. Jenkins, and R. Johnston, *Proc. R. Soc.,* **A241,** 364 (1957).
11. H. Nakamura, M. Seno, and T. Sato, *J. Polym. Sci. Part A: Polym. Chem.,* to appear.
12. R. Mani, T. Mani, and J. K. Stevens, *J. Polym. Sci. Part A: Polym. Chem.,* **30,** 2025 (1992).
13. A. Casaschi, G. Desimoni, G. Faita, A. G. Invernizzi, S. Lanati, and P. P. Righetti, *J. Am. Chem. Soc.,* **115,** 8002 (1993).
14. T. Sato, H. Nakamura, H. Tanaka, and T. Ota, *Makromol. Chem.,* **192,** 2659 (1991).
15. P. Pascal, D. H. Napper, R. G. Gilbert, M. C. Piton, and M. A. Winnik, *Macromolecules,* **23,** 5161 (1990).
16. T. Otsu and B. Yamada, *J. Macromol. Sci.-Chem.,* **A3,** 187 (1969).
17. B. Yamada, H. Kamei, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.,* **18,** 1917 (1980).
18. B. Yamada, M. Itahashi, and T. Otsu, *J. Polym. Sci., Polym. Chem. Ed.,* **16,** 1719 (1978).
19. S. Masuda, T. Omochi, and T. Ota, *J. Polym. Sci., Polym. Chem. Ed.,* **23,** 2081 (1985).

Figure 10   Copolymer composition curves for the copolymerization of MMA (M_1) and St (M_2) with MAIB in MEK at 50°C at different $LiClO_4$ concentrations; [MMA] + [St] = 1.00 mol/L, [MAIB] = 5.00×10^{-3} mol/L, (○) [$LiClO_4$] = 0 mol/L, (■) [$LiClO_4$] = 2.00 mol/L, (●) [$LiClO_4$] = 2.50 mol/L, and (□) [$LiClO_4$] = 3.50 mol/L.