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Specific Salt Effect of Lithium Perchlorate in Living Anionic Polymerization of Methyl Methacrylate and *tert*-Butyl Acrylate

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ABSTRACT: Living anionic polymerization of methyl methacrylate can be achieved at −40 °C in tetrahydrofuran (THF) and at −78 °C in toluene/THF (9/1 v/v) using (1,1-diphenylhexyl)lithium as the initiator in the presence of lithium perchlorate ($LiClO_4$) as the additive. Polymerization of *tert*-butyl acrylate also proceeds in a living manner at −78 °C in THF. Polymers with narrow molecular weight distributions and high initiator efficiencies can be obtained. The use of lithium perchlorate retards the rate of polymerization. The ratio of $LiClO_4$ to initiator has a greater influence in determining the control of polymerization. The beneficial effect of lithium perchlorate is attributed to its efficient interaction with growing ester−enolate ion pairs.

Introduction

Recent years have witnessed considerable efforts toward achieving "living" polymerization of alkyl (meth)acrylate monomers.[1−9] The secondary side reactions in anionic polymerization of alkyl (meth)acrylates which involve the ester group of the monomer have prevented identification of optimum conditions for living polymerization.[10,11] Innumerable kinetic and mechanistic studies have contributed significantly to our understanding of this reaction, resulting in many strategies for enhancing the living character of methyl methacrylate (MMA) polymerization.[12]

It is now well established that the initiator should be sterically hindered to avoid carbonyl attack of the initiator on the carbonyl group of MMA.[11]. The termination reactions complicate the kinetics and broaden the molecular weight distribution (MWD) of poly(methyl methacrylate) (PMMA) in nonpolar solvents. However, in polar solvents these side reactions are less pronounced. It was shown by Löhr and Schulz[13,14] and Mita et al.[15] that anionic polymerization of MMA proceeds with insignificant or with no termination in THF at −78 °C using cesium as a counterion, leading to narrow MWD PMMA. At higher temperatures the termination reaction predominates, as evidenced by the deviation from the first-order kinetics, broadening of the MWD, and the generation of alkali metal methoxide.[16] Recent kinetic studies indicate that polymerization of MMA proceeds from more than one kind of species.[17,18] The nature of solvent and the size of cation influences the course of MMA polymerization.[17]

Generally, use of monofunctional initiators, polar solvents, and low temperatures is desirable for controlled anionic polymerization of MMA. Many ways to improve the living character of MMA polymerization are documented with respect to the synthesis of high molecular weight copolymers consisting of monomers in which carbonyl conjugation is absent.[1,3,7,19] Attempts to minimize the secondary reactions have been made by stabilizing the propagating enolate using additives such as metal alkoxide[20] and aluminum alkyls.[22] The controlled anionic polymerization of MMA in toluene at 20 °C was reported by Lochmann and Trekoval using a complex initiator system consisting of a metalated ester enolate as a nucleophile and an alkali metal *tert*-butoxide as a ligand.[1] Anderson et al.[3] and McGrath et al.[2] reported pyridine-mediated anionic polymerization of MMA at −40 °C. Teyssie and co-workers[21] demonstrated the use of metal alkoxyalkoxide as an efficient ligand in controlling the anionic polymerization of alkyl (meth)acrylates at moderately low temperatures. The group-transfer polymerization (GTP) discovered by DuPont elegantly demonstrated the use of silyl ketene acetals with a suitable nucleophile for controlled polymerization of alkyl (meth)acrylates.[4,23]

Anionic polymerization of alkyl acrylates poses a higher degree of complexity compared to that of alkyl methacrylates because of their higher reactivity and the presence of acidic hydrogen which is susceptible to side reactions with both the initiator and the living chain ends.[24] Living anionic polymerization of alkyl acrylates has been recently achieved by several methods. Lewis acid catalyzed GTP provides fairly good control of acrylate polymerization at ambient temperature.[4] Metal-free carbon or nitrogen nucleophiles have been used as initiators by Reetz et al.[8] for controlled anionic polymerization (MFP) of *n*-butyl acrylate. They used resonance-stabilized malonate derivatives as nucleophiles with tetra-*n*-butylammonium as a countercation for the synthesis of poly(*n*-butyl acrylate)s of relatively narrow molecular weight distribution at room temperature. Using this strategy, several functionalized initiators consisting of tetra-*n*-butylammonium salts of oxazoline, malonates, and fluorene were prepared by us and used for the polymerization of alkyl acrylates.[25−27]

It was found that the polymerization of alkyl acrylates using tetra-*n*-butylammonium salts proceeds with a characteristic induction period. Further, in many cases, unreacted residual initiators are found even at complete monomer conversion, thus rendering control of the polymerization difficult.[25−27] An additional problem with such a system is that, very often, synthesis of initiator in high purity is difficult. Synthesis of well-defined high molecular weight polymers of acrylate monomers with nonpolar monomers such as styrene and dienes is difficult or, in some cases, not possible by both GTP and MFP.

The excellent work of Teyssie and co-workers demonstrated a variety of new strategies for obtaining perfect control of alkyl (meth)acrylate polymerization and their copolymerization with other comonomers.[7,28,29] The use of LiCl as an additive results in its interaction with living chain ends through formation of a μ-type

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Table 1. Anionic Polymerization of MMA, tBuA in THF at −78 °C Using (1,1-Diphenylhexyl)lithium Initiator in the Presence of $LiClO_4$

run	monomer	10^3[DPHLi], mol/L	$[M]_0$,[a] mol/L	mol ratio of $[LiClO_4]/[DPHLi]$	yield,[b] %	$10^{-3}\bar{M}_{n,cal}$[c]	$10^{-3}\bar{M}_{n,SEC}$	$\bar{M}_w/\bar{M}_n$	f[d]
1	MMA	1.10	0.28	0	>97	25.45	29.56	1.18	0.86
2	MMA	1.15	0.28	0.5	100	24.35	26.56	1.14	0.92
3	MMA	1.15	0.28	1	>98	24.35	25.90	1.11	0.94
4	MMA	1.15	0.28	5	100	24.35	26.89	1.07	0.90
5	MMA	1.15	0.28	10	100	24.35	27.80	1.08	0.88
6	MMA	1.27	0.20	10	>97	16.26	18.33	1.07	0.89
7	tBuA	0.92	0.256	0	95	35.65	63.17	2.10	0.56
8	tBuA	1.20	0.065	10	100	6.90	8.62	1.18	0.80
9	tBuA	0.67	0.138	20	100	26.50	30.50	1.11	0.87
10	tBuA	0.50	0.267	20	>95	68.40	71.53	1.08	0.96
11	tBuA	0.40	0.178	20	>95	57.00	78.98	1.06	0.72

[a] Neat MMA, diluted tBuA in THF (40% v/v) was added within 5 s, and the polymerization was terminated after 10−15 min. [b] PMMA was precipitated in *n*-hexane and PtBuA was recovered by removing solvent, dissolving in benzene, and freeze drying. [c] $\bar{M}_{n,cal}$ = (moles of monomer/moles of initiator) (mol wt of monomer). [d] Initiator efficiency, $f = \bar{M}_{n,cal}/\bar{M}_{n,SEC}$.

complex and shifts a relatively slow ionic association equilibrium toward a single active species.[30] It was shown that only LiCl had the most desirable effect in changing the course of anionic alkyl (meth)acrylate polymerization to yield extremely well-defined polymers with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.05$).[7] However, even LiCl requires a polar solvent (e.g. THF) and low temperatures (−78 °C) for producing PMMA's with narrow molecular weight distribution and high initiator efficiency. Recently, Dvonanek and Vlcek demonstrated the use of LiO*t*Bu in enhancing the livingness of *n*-butyl acrylate polymerization at −60 °C.[31] Other common-ion salts have been employed in anionic polymerization of MMA. These include LiF, LiBr, $Li(Ph_4B)$, and lithium acetate. These salts decrease the rate of propagation of MMA and do not provide narrow molecular weight distribution PMMA.

The ion-pair association is known to be strongly influenced by the nature of cations.[32,33] The presence of organic and inorganic salts capable of interacting with the growing ion pair has a great influence on the course of anionic polymerization of alkyl (meth)acrylates.[34] This type of salt effect influencing the position of ionic dissociation equilibria of the anionic polymerization of alkyl (meth)acrylates mainly depends on the Lewis acidity and steric factor of the added salt.[35] Hence a better Lewis acid salt should have a greater interaction with the propagating ion pairs. To verify this hypothesis, we examined the effect of $LiClO_4$ in various alkyl (meth)acrylate polymerizations. We now present our results on the specific salt effect of $LiClO_4$ in anionic polymerization of *tert*-butyl acrylate (tBA) and MMA in pure THF and also in a mixed toluene/THF (9/1 v/v) solvent, at various temperatures.

Experimental Section

$LiClO_4$ (Aldrich) was dried under dynamic high vacuum overnight at 120 °C and then dissolved in a known amount of dry THF. THF was purified by refluxing over the deep purple sodium−benzophenone complex. Toluene was purified by refluxing over CaH_2. These solvents were further distilled under vacuum over styryllithium prior to polymerization. N_2 gas (IOC, Bombay) was purified by passing through a heated Cu column (200 °C) (1 × 1 m) and an A4 molecular sieves column (2 × 1 m) and finally was bubbled through a toluene solution of living styryllithium anion.

MMA and tBA (Aldrich) were first vacuum distilled from CaH_2 after stirring 12 h at room temperature and then stored under a nitrogen atmosphere at −15 °C. The required amount of the distilled MMA or tBA was taken into a flask to which was added drop by drop triisobutylaluminum or 10 wt % $AlEt_3$ solution in hexane until a persistent yellow green color was observed.[36] MMA and tBA were redistilled under reduced pressure, just prior to polymerization experiments.

(1,1-Diphenylhexyl)lithium (DPHLi) initiator was synthesized by reacting nBuLi with an equimolar amount of 1,1-diphenylethylene (DPE) in THF at −40 °C. Polymerization was carried out in a flamed glass reactor under a pure nitrogen atmosphere. The solvent, initiator, $LiClO_4$ solution in THF and the monomer were transferred by capillary technique or syringe. The required amount of solution of $LiClO_4$ in THF was added into the reactor containing 100 mL of THF. DPHLi solution was added drop by drop until a persistent red color was observed. It usually required 0.2−0.4 mL of the 0.08 M initiator solution for 100 mL of THF to completely quench all the impurities. Subsequently, the required amount of initiator was added and the temperature of the reactor was brought to −78 or −40 °C. The purified neat MMA or tBA (60% v/v) diluted with THF was added to the initiator solution. About 5−10 s was usually required to add 5−10 mL of diluted monomer solution through the stainless steel cannula. The reaction was terminated after 15 min with degassed methanol. The tBA conversion was determined gravimetrically after removing the solvent by vacuum. The residue, poly(*tert*-butyl acrylate) (PtBA) was dissolved in benzene and freeze dried. In kinetic experiments, unconverted monomer was determined by GC. Poly(methyl methacrylate) (PMMA) was recovered by precipitation in *n*-hexane and dried under vacuum between 60 and 80 °C for 4 h.

Characterization of PMMA and PtBA was carried out by using a Waters GPC 150C equipped with two μ-Ultrastyragel linear columns and THF as the eluent at a flow rate of 1 mL min^{-1} at 30 °C. Standard monodisperse poly(methyl methacrylate)s (Polymer Laboratory) were used for calibration.

The glass transition temperature (T_g) of the polymers was determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 instrument, calibrated with indium and zinc. The tacticity of the polymers was determined by ^1H NMR using a Bruker SE-200 MHz spectrometer.

Results and Discussion

Polymerization of MMA and *tert*-Butyl Acrylate in THF in the Presence of $LiClO_4$. It is known that $LiClO_4$ coordinates with both THF as well as the carbonyl group of the esters.[37,38] The coordination behavior of $LiClO_4$ in the presence of the propagating enolate ion pair and their aggregates in THF is expected to be different. Table 1 shows the results of polymerization of MMA and tBuA in the presence of various amounts of $LiClO_4$ with respect to the DPHLi concentration at −78 °C in THF. The anionic polymerization of MMA in THF at −78 °C using DPHLi as an initiator in the absence of any additive proceeds very rapidly, leading to 100% conversion with good control of molecular weight and relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n \leq 1.18$). It was shown by Teyssie

Table 2. Anionic Polymerization of MMA in THF at −40 °C using (1,1-Diphenylhexyl)lithium Initiator in the Presence of $LiClO_4$

run	10^3[DPHLi], mol/L	[MMA],[a] mol/L	mol ratio [$LiClO_4$]/[DPHLi]$_0$	yield,[b] %	$10^{-3}\bar{M}_{n,cal}$	$10^{-3}\bar{M}_{n,SEC}$	$\bar{M}_w/\bar{M}_n$	init eff f[c]	T_g[d]
1B	0.80	0.28	0	85	35.00	32.00	1.34	1.10	119.5
16	1.20	0.28	0.5	>96	23.33	26.98	1.13	0.86	109.0
17	1.20	0.374	1	100	31.16	32.07	1.10	0.97	122.3
18	1.20	0.374	2	>97	31.16	33.89	1.13	0.92	124.8
19	1.20	0.374	5	100	31.16	35.76	1.12	0.87	121.3
20	1.20	0.374	10	100	31.16	35.09	1.08	0.89	121.3

[a] Monomer was added within 4−6 s and polymerization was terminated after 10−15 min. [b] Polymers were precipitated in *n*-hexane. [c] Initiator efficiency, $f = \bar{M}_{n,calc}/\bar{M}_{n,SEC}$. [d] All the polymers have 70−74% syndiotacticity as determined by ^{1}H NMR and T_g's were recorded at 10 °C/min.

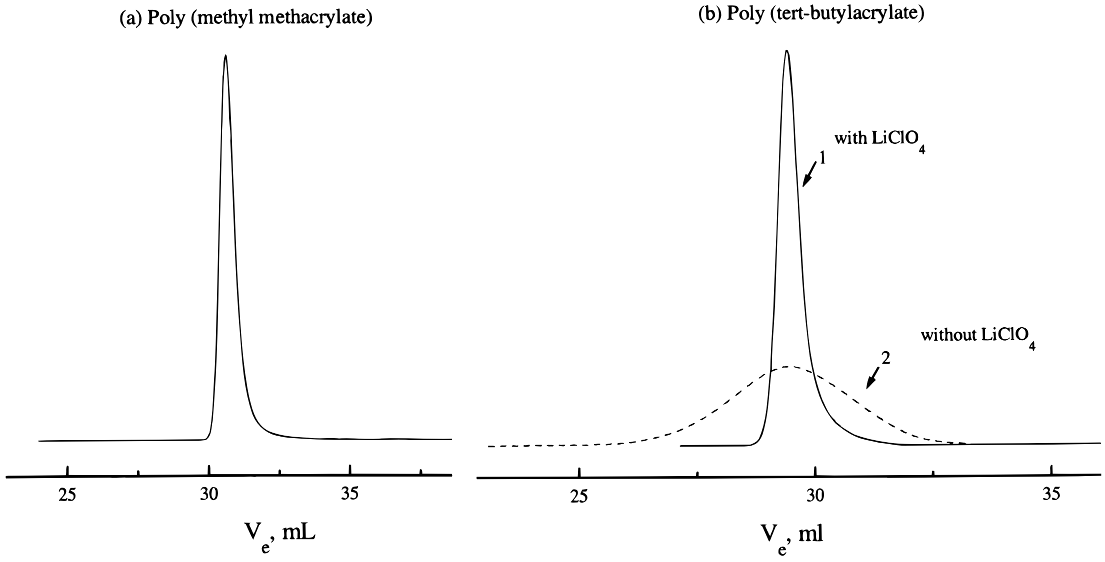

Figure 1. SEC traces showing the effect of $LiClO_4$ addition on anionic polymerization of tBuA and MMA in THF: (a) PMMA synthesized at −40 °C, $LiClO_4$/DPHLi = 10, $\bar{M}_{n,SEC}$ = 35 090, $\bar{M}_w/\bar{M}_n$ = 1.08 (run no. 20 in Table 2); (b) PtBA synthesized at −78 °C (1) in the presence of $LiClO_4$, $\bar{M}_{n,SEC}$ = 78 980, $\bar{M}_w/\bar{M}_n$ = 1.06 (run no. 11 in Table 1), and (2) in the absence of $LiClO_4$, $\bar{M}_{n,SEC}$ = 63 170, $\bar{M}_w/\bar{M}_n$ = 2.10 (run no. 7 in Table 1).

and co-workers[7,30] that the presence of lithium chloride in the anionic polymerization of alkyl (meth)acrylates leads to a μ-type complex with the growing ion pair and shifts a relatively slow classical ion-pair association equilibrium involving different types of reactive species toward a salt-complexed single active species, thus improving the molecular weight distribution (MWD) of the resulting polymers.

Experiments done in the presence of varying quantities of $LiClO_4$ with respect to DPHLi initiator at −78 °C in THF show a specific salt effect of $LiClO_4$ in further narrowing the molecular weight distribution of PMMA. It can be seen from Table 1 that a presence of only 0.5 mol of $LiClO_4$ per mol of DPHLi improved the molecular weight distribution of PMMA from 1.18 to 1.14. Increasing the ratio to 5 causes further significant narrowing of the MWD with $\bar{M}_w/\bar{M}_n$ as low as 1.07. This indicates that $LiClO_4$ can perturb the dynamics of a classical ion-pair equilibrium similar to LiCl.[7,30]

The initiator efficiency, *f*, represented by the ratio of concentration of growing chains to the initial initiator concentration is determined by the ratio of the calculated number average molecular weight ($\bar{M}_{n,cal}$) and the obtained $\bar{M}_n$ ($\bar{M}_{n,SEC}$) using SEC. In the absence of $LiClO_4$, the initiator efficiency is found to be low, 0.86. This indicates a loss of initiators due to the side reaction associated with the ester group of the monomer at the beginning of the reaction. The presence of $LiClO_4$ in the THF solvent improves the initiator efficiency to a small extent.

However, when the temperature is increased to −40 °C in the presence of the LiCl ligand, it is reported that the control of both the molecular weight and molecular weight distribution is lost.[19] In contrast, the beneficial effect of $LiClO_4$ as an additive can be seen even at −40 °C in THF using DPHLi as an initiator. The results are shown in Table 2. In the absence of $LiClO_4$, the PMMA obtained has a broad molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.34) and also a lower $\bar{M}_{n,SEC}$ than $\bar{M}_{n,cal}$. This indicates the absence of any control of the polymerization of MMA at −40 °C. This situation is dramatically improved by the addition of an equimolar amount of $LiClO_4$ with respect to DPHLi. The resulting PMMA in THF at −40 °C exhibits a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.1). The T_g's of the polymers synthesized in the presence and in the absence of $LiClO_4$ are in accordance with their microstructures (120 °C < T_g < 124 °C) (Table 2).

When the $LiClO_4$:DPHLi ratio is increased to a value of 10, better control of the polymerization is obtained resulting in an extremely narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.08) (Figure 1a). The $\bar{M}_{n,SEC}$ of the resulting PMMA is close to the value of $\bar{M}_{n,cal}$. It is evident that the presence of $LiClO_4$ provides living MMA polymerization at −40 °C in THF with complete conversion, predictable $\bar{M}_n$, and high initiator efficiency (>0.90) .

The dramatic influence of $LiClO_4$ is also seen in the polymerization of *tert*-butyl acrylate in THF at −78 °C (Table 1). The obtained poly(*tert*-butyl acrylate) (PtBA) in the absence of $LiClO_4$ salt had a broad MWD ($\bar{M}_w/\bar{M}_n$

Table 3. Polymerization of MMA in Toluene/THF (9/1 v/v) at −78 °C Using (1,1-Diphenylhexyl) lithium Initiator[a]

run	10^3[DPHLi], mol/L	[MMA], mol/L	mol ratio $[LiClO_4]_0/[DPHLi]_0$	yield,[b] %	$10^{-3}\bar{M}_{n,cal}$[c]	$10^{-3}\bar{M}_{n,SEC}$	$\bar{M}_w/\bar{M}_n$	init eff f[d]
12	0.345	0.28	0	85	68.98	43.24	2.86	1.60
13	0.345	0.28	1	65	52.75	71.94	1.10	0.73
14	0.345	0.28	2	64	51.94	63.67	1.07	0.82
15	0.345	0.28	5	66	53.56	60.00	1.08	0.89
4	1.75	0.20	10	80	9.14	10.11	1.05	0.90
7[e]	1.15	0.28	10	64	15.52	19.62	1.06	0.80
8	0.67	0.094	10	61	8.52	8.66	1.05	0.98
9[f]	0.67	0.28	10	61	25.49	27.07	1.09	0.94

[a] Monomer was added neat within 4−6 s. Polymerization was terminated at 90−150 min, before complete conversion. [b] Polymers were precipitated in *n*-hexane. [c] $\bar{M}_{n,cal}$ was determined by (grams of MMA/moles of initiator) × conversion. [d] Initiator efficiency, $f = \bar{M}_{n,cal}/\bar{M}_{n,SEC}$. [e] 68% syndiotacticity as determined by ^{1}H NMR and T_g is 110.6 °C. [f] Experiment done at −40 °C.

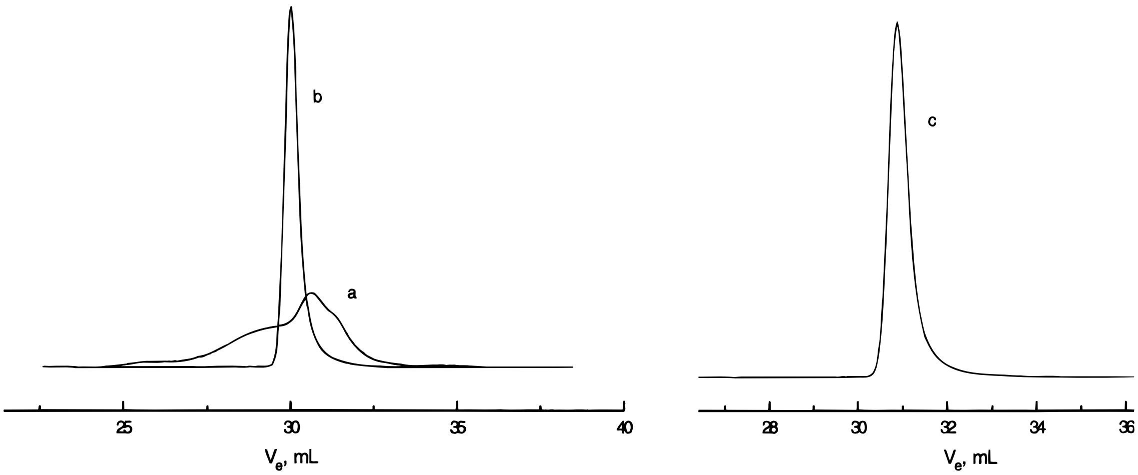

Figure 2. SEC traces of PMMA synthesized in the presence and absence of $LiClO_4$ in toluene/THF (9/1 v/v) mixed solvent at different temperatures: (a) in the absence of $LiClO_4$ at −78 °C, $\bar{M}_{n,cal}$ = 68 980, $\bar{M}_{n,SEC}$ = 43 240, and $\bar{M}_w/\bar{M}_n$ = 2.86; (b) in the presence of $LiClO_4$ at −78 °C, $LiClO_4$/DPHLi = 5, $\bar{M}_{n,cal}$ = 53 560, $\bar{M}_{n,SEC}$ = 60 000, and $\bar{M}_w/\bar{M}_n$ = 1.08; and (c) in the presence of $LiClO_4$ at −40 °C, $LiClO_4$/DPHLi = 10, $\bar{M}_{n,cal}$ = 25 490, $\bar{M}_{n,SEC}$ = 27 070 and $\bar{M}_w/\bar{M}_n$ = 1.09 (runs 12, 15, and 9, respectively, in Table 3).

= 2.1) with a low initiator efficiency (0.56) compared to the one obtained in the presence of $LiClO_4$ ($\bar{M}_w/\bar{M}_n \le$ 1.18, Table 1). This indicates that the majority of growing ester enolate ion pairs get terminated in the absence of $LiClO_4$, possibly via a back-biting intramolecular reaction. This is consistent with the earlier results obtained by Teyssie and co-workers.[34] The molecular weight of PtBA was determined by SEC referenced to PMMA calibration standards. Hence, correlation of the initiator efficiency calculated from $\bar{M}_{n,cal}/\bar{M}_{n,SEC}$ should be considered approximate. SEC traces of the PtBA synthesized in the presence and absence of $LiClO_4$ are shown in Figure 1b.

Polymerization of MMA in Toluene/THF (9/1 v/v) Mixed Solvent. The nature of the solvent plays an important role in solvation of the Li cation, thereby influencing the ion-pair association equilibrium of the anionic polymerization of MMA. It is also known that solvent polarity largely affects the reactivity and identity of the propagating species.[39] It was shown that increasing the solvent polarity causes a decrease in isotacticity and a narrowing of molecular weight distribution of PMMA.[40]

The polymerization of MMA in toluene/THF (9/1 v/v) mixed solvent was carried out in both the presence and absence of $LiClO_4$ using DPHLi as an initiator at different temperatures. The results are given in Table 3 and Figure 2. In the absence of $LiClO_4$, the polymerization process is complex, as evidenced by the formation of a gel phase. The soluble portion of PMMA shows that $\bar{M}_{n,SEC}$ is less than $\bar{M}_{n,cal}$ with a broad molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 2.8).

The usefulness of $LiClO_4$ in improving the reaction, even in solvents of such low polarity, is clearly evident. The gel phase is totally absent during polymerization in the presence of $LiClO_4$ in 9/1 v/v toluene/THF. It can be seen from Table 3 that addition of an equimolar amount of $LiClO_4$ to DPHLi provides perfect control of the polymerization, resulting in a narrow MWD PMMA ($\bar{M}_w/\bar{M}_n$ = 1.1). Increasing the mole ratio of $LiClO_4$: DPHLi to a value higher than 5 does not appear to cause further improvement. In all cases the polymerization was terminated within 90−150 min. It was found that the conversion was not quantitative. Therefore, theoretical molecular weights were recalculated on the basis of the conversion in each experiment, assuming that the polymerization is a living process. The perfect control of MMA polymerization in the presence of $LiClO_4$ in a low-polarity solvent can be seen even at −40 °C (Table 3, run 9).

To further confirm the termination and transfer free nature of this process, a kinetic experiment was performed in a toluene (90 mL) and THF (10 mL) mixture containing 0.0523×10^{-3} mol of DPHLi and 1×10^{-3} mol of $LiClO_4$ at −78 °C. Neat MMA (3 mL) was added within 3 s using N_2 pressure. Samples were taken from the reaction mixture at definite intervals and terminated with degassed methanol. The monomer conversion was determined by GC. By following the disappearance of monomer concentration with respect to time, the rate of polymerization can be determined using the equation $\ln([M]_0/[M]_t) = k_{app}t$, assuming that the reaction follows first-order kinetics. The first-order time−conversion plot is shown in Figure 3. The linear-

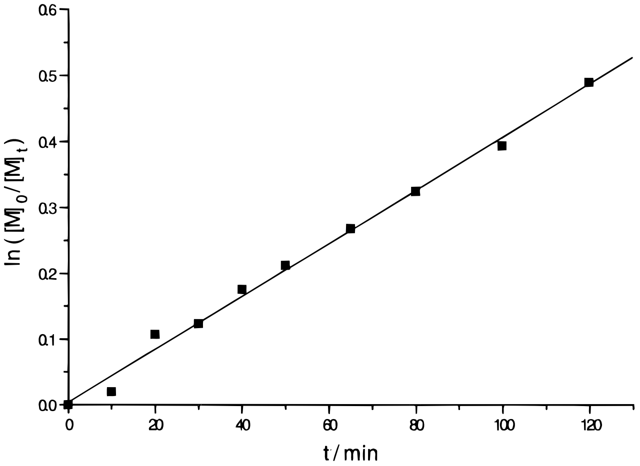

Figure 3. First-order time–conversion plot of the MMA polymerization carried out in the presence of excess of $LiClO_4$ in toluene/THF (9/1 v/v) mixed solvent.

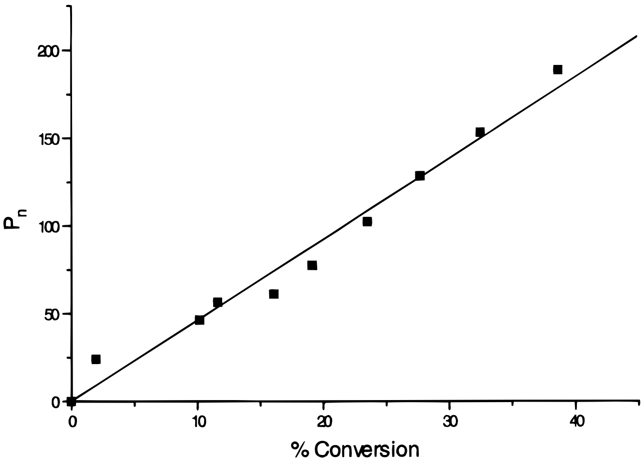

Figure 4. Linear dependency of the degree of polymerization, P_n, vs conversion for the MMA polymerization carried out in the presence of excess of $LiClO_4$ in toluene/THF (9/1 v/v) mixed solvent.

ity of the semilogarithmic conversion plot shows that the polymerization proceeds without any significant amount of termination reaction in the presence of excess $LiClO_4$ salt. The number average degree of polymerization, P_n, determined by SEC is plotted against conversion in Figure 4. Any transfer reaction would lead to the decrease of P_n during the course of polymerization. The linear dependence of P_n with respect to conversion indicates the absence of transfer reaction in this process.

It was reported[7] that under similar conditions, addition of LiCl does not provide adequate control of MMA polymerization. The solubility of LiCl is limited in a toluene/THF (9/1 v/v) mixed solvent. However, the PMMA produced using a homogeneous solution of LiCl–DPHLi (2.5×10^{-3} mol/L) had a bimodal distribution up to 50% conversion ($\bar{M}_w/\bar{M}_n = 2.35$).[7] The presence of $LiClO_4$ led to a unimodal symmetrical molecular weight distribution with a $\bar{M}_w/\bar{M}_n = 1.22$ right from the beginning of the polymerization. The relative solubilities of LiCl versus $LiClO_4$ in 9/1 v/v toluene/THF is not of major significance. The SEC traces of PMMA obtained in the presence of $LiClO_4$ at various intervals of time are given in Figure 5. It can be seen from Figure 5 that the molecular weight distribution remains narrow during the course of the polymerization and attains at 38% conversion a value $\bar{M}_w/\bar{M}_n = 1.11$. These results demonstrate the remarkable ability and efficiency of $LiClO_4$ for the synthesis of well-defined PMMA in solvents of low polarity.

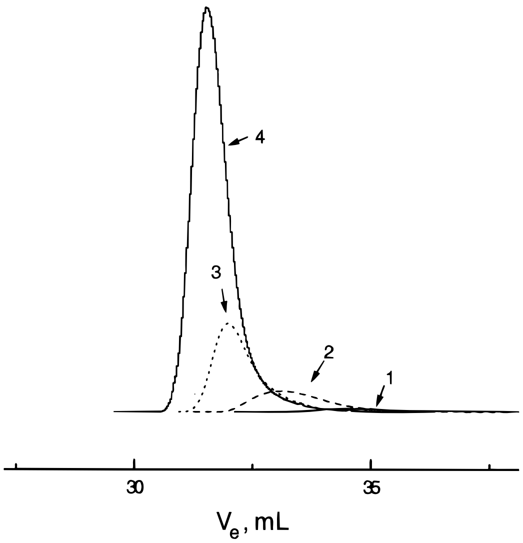

Figure 5. SEC traces of PMMA samples at various times during the polymerization in the presence of $LiClO_4$ in toluene/THF (9/1 v/v) at −78 °C: (1) after 10 min, $\bar{M}_{n,SEC} = 2638$ ($\bar{M}_w/\bar{M}_n = 1.22$, 1.96%); (2) after 40 min, $\bar{M}_{n,SEC} = 6354$ ($\bar{M}_w/\bar{M}_n$= 1.2, 16.12%); (3) after 80 min, $\bar{M}_{n,SEC} = 13\ 080$ ($\bar{M}_w/\bar{M}_n = 1.14$, 27.7%); (4) after 120 min, $\bar{M}_{n,SEC} = 19\ 100$ ($\bar{M}_w/\bar{M}_n = 1.11$, 38.7%).

It is interesting to recall a few observations on the LiCl system as reported by Teyssie and co-workers.[24] They found that different cations (Li, Na, K) associated with initiator/propagating species do not perturb the regulating influence of an excess LiCl in obtaining narrow molecular weight distribution polymers. It was also demonstrated that the addition of other common-ion salts such as LiF, LiBr, and $Li(Ph_4B)$ do not provide a perfect control compared to LiCl in MMA polymerization.[7] The present investigation clearly shows the remarkable abilitiy of $LiClO_4$ in promoting living anionic polymerization of MMA in THF and in toluene/THF (9/1 v/v) solvent. The slow rates of polymerization observed can be attributed to the steric hindrance of the growing ion pair associated with the $LiClO_4$ ligand. Thus, it seems that such a specific salt effect influencing the position of ion-pair association equilibrium in alkyl (meth)acrylate polymerization mainly depends on the electronic and steric influence of the added salt. It is not surprising that a better Lewis acid salt such as $LiClO_4$ interacts more efficiently with the living chain ends and provides a better control of polymerization in THF as well as in solvents of low polarity such as toluene/THF (9/1 v/v).

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