Effect of Lithium Perchlorate on the Kinetics of the Anionic Polymerization of Methyl Methacrylate in Tetrahydrofuran

D. Baskaran† and Axel H. E. Müller*

Institut für Physikalische Chemie, Universität Mainz, D-55099 Mainz, Germany

S. Sivaram

Polymer Chemistry Division, National Chemical Laboratory, Pune 411 008, India

Received December 30, 1996; Revised Manuscript Received November 20, 1998

ABSTRACT: The kinetics of the anionic polymerization of methyl methacrylate in the presence of lithium perchlorate ($LiClO_4$) are investigated in THF using 1,1-diphenylhexyllithium as initiator in a flow-tube reactor between −30 and 0 °C. The rate constants of propagation determined in the presence of $LiClO_4$ are lower than those obtained in the absence of the salt, similar to the effect observed for LiCl. For propagation, the reaction order with respect to active center concentration is found to be 0.5 in both cases, which indicates that $LiClO_4$ does not effectively perturb the aggregation of the enolate ion pair. The formation of various mixed aggregates is proposed. The polydispersity index of the obtained PMMA is lower than that obtained in the absence of salt indicating faster aggregation−deaggregation equilibria than in the absence of salt. The rate constants of termination in absence and presence of salt are comparable. Thus, $LiClO_4$ does not affect termination reactions, again similar to LiCl.

Introduction

The anionic polymerization of alkyl (meth)acrylates proceeds in a controlled manner only under chosen reaction conditions.[1,2] The polar ester group of monomer and polymer is susceptible to various side reactions during initiation and propagation.[3,4] It was shown by Löhr and Schulz,[5] and by Mita et al.[6] that the anionic polymerization of methyl methacrylate (MMA) proceeds with insignificant or no termination using larger counterions such as Cs^+ in THF at temperatures below −60 °C. The polymerization exhibits first-order kinetics of monomer conversion, and the obtained polymers show a linear dependence of the number-average degree of polymerization on conversion as well as narrow molecular weight distribution (MWD).

Kinetic experiments suggest that externally solvated contact ion-pairs are responsible for propagation.[1,2] Tsvetanov et al.[7] and Müller et al.[8] demonstrated that the coexistence with associated ion pairs affects the rates of polymerization of MMA using Na^+ and Li^+ as counterions in THF. Kunkel et al.[9] showed that the dynamics of the equilibrium between aggregated and nonaggregated ion pairs dominates the MWD of the resulting polymers. Polymers with narrow MWD are only obtained when the rate of interconversion of these aggregated living chain ends is faster than that of monomer addition.

^7Li and ^{13}C NMR measurements of Wang et al.[10] in conjunction with VPO measurements of Lochmann et al.[11] indicate that models of the chain end, e.g. methyl α-lithioisobutyrate (MiBLi), exist as tetramers at room temperature and as a mixture of dimer and tetramer at −78 °C. This is also confirmed by recent MNDO and ab initio calculations.[12] These calculations show that an increasing degree of aggregation leads to a decreased charge density of the α-carbon atom of the enolate which is accompanied by a sharp decrease in reactivity. Due to the steric hindrance of the polymer chains, the existence of tetrameric aggregates of PMMA−Li is regarded as less probable. Thus, the propagating ion pairs in the anionic polymerization of MMA in THF are in equilibrium with less active dimeric THF-solvated ion pairs.

Recently, several strategies have been developed and widely used for the controlled anionic polymerization of (meth)acrylates. In some of these systems "uncommon" counterions were used.[13−18] In systems with lithium counterions, the addition of several μ-coordinating agents such as alkali alkoxides,[19−22] lithium halides,[23] lithium alkoxyalkoxides,[24,25] and aluminum alkyls[26−29] leads to better control of polymerization.

Teyssié and co-workers[23,30,31] showed that addition of LiCl to the polymerization of *tert*-butyl acrylate (tBuA) in THF at −78 °C yields polymers with very narrow MWD. This beneficial effect was attributed to the formation of a μ-type complex of LiCl with the PtBuA−Li ion pairs. Kunkel et al.[9] studied the effect of LiCl on the kinetics of the polymerization of MMA, *tert*-butyl methacrylate, and tBuA in THF. The kinetic data are consistent with the formation of a reactive 1:1 adduct and less reactive higher adducts of LiCl with enolate ion pairs. This was confirmed by ^7Li and ^{13}C NMR measurements of Wang et al.[32] The dramatic effect of LiCl on the MWD of the polymers formed is explained on the basis of the higher interconversion rate between free and LiCl complexed ion pair than that between free and associated ion pairs.

Other common-ion salts employed in the anionic polymerization of MMA are LiF, LiBr, $LiBPh_4$, and lithium acetate. These salts do not show an effect on the molecular weight distribution.[30] However, recently Baskaran and Sivaram[33] demonstrated the beneficial effect of lithium perchlorate ($LiClO_4$) in the anionic polymerization of alkyl (meth)acrylates. In presence of $LiClO_4$, PMMA and PtBuA with extremely narrow MWD were obtained in THF as well as in toluene/THF

† Present address: National Chemical Laboratory, Division of Polymer Chemistry, Pune 411008, India.

10.1021/ma961920y CCC: $18.00
Published on Web 02/12/1999

Table 1. Kinetic Results of the Anionic Polymerization of MMA with Li^+ Counterion in the Presence of $LiClO_4$ in THF, $[MMA]_0 = 0.2$ mol/L, Variation of Initiator, $LiClO_4$, and Temperature

run	$[DPHLi]_0 \times 10^3$, mol/L	$[LiClO_4]/[DPHLi]_0$	T_{eff}, °C	t_{max},[a] s	$x_{p,max}$[b]	$\bar{P}_{n,th}$[c] at $x_{p,max}$	$\bar{P}_{n,GPC}$[d] at $x_{p,max}$	$\bar{M}_w/\bar{M}_n$ at $x_{p,max}$	f[e]
1	9.0	10	−18.8	2.94	0.78	17.3	16.4	1.11	0.94
2	6.0	10	−17.6	2.94	0.72	24.0	23.6	1.10	1.00
3	4.0	10	−19.1	2.39	0.55	27.5	28.0	1.08	1.00
4	4.0	5	−19.5	1.74	0.38	19.0	21.7	1.14	1.00
5	4.0	3	−19.4	2.39	0.60	30.0	46.9	1.20	0.78
6	4.0	1	−19.9	2.39	0.61	30.5	51.0	1.29	0.60
7	4.0	0.6	−19.8	2.39	0.63	31.5	48.7	1.30	0.61
8	4.0	0.3	−19.3	2.39	0.64	32.0	55.4	1.30	0.57
9	4.0	0	−19.2	2.39	0.74	37.0	47.4	1.25	0.80
10	1.4	0	−20.5	2.39	0.54	77.1	74.1	1.35	0.88
11	1.4	0	−0.1	2.39	0.59	84.3	100.3	1.69	0.81
12	1.4	0	+19.2	2.39	0.55	78.6	93.5	1.95[f])	0.89
13	1.4	10	−26.8	2.94	0.33	47.1	82.5	1.13	0.66
14	1.4	10	−19.6	2.94	0.39	55.7	73.8	1.12	0.72
15	1.4	10	−9.3	3.5	0.49	70.0	103.0	1.34	0.70
16	1.4	10	0.7	2.94	0.46	65.7	99.0	1.40	0.67

[a] Longest reaction time. [b] Conversion obtained at t_{max}. [c] $\bar{P}_{n,th} = [M]_0 \times x_{p,max}/[I]_0$. [d] $\bar{P}_{n,GPC} = (\bar{M}_{n,GPC} - M_{initiator})/M_{monomer}$. [e] Initiator efficiency, $f = \bar{P}_{n,th}/\bar{P}_{n,GPC}$ averaged at the highest conversions. [f] Bimodal distribution.

(9:1 v/v) mixed solvent at −40 °C. We report now the effect of $LiClO_4$ on the kinetics of propagation and termination in the anionic polymerization of MMA in THF between −30 and 0 °C.

Experimental Section

Reagents. Methyl methacrylate (MMA, Röhm GmbH) was fractionated from CaH_2 over a 1 m column filled with Sulzer packing at 45 mbar. After degassing, the distillate was stirred over CaH_2 and distilled under high vacuum. Tetrahydrofuran (THF, BASF AG) was fractionated over a 1.5 m column, stirred twice over sodium/potassium alloy, degassed and distilled under high vacuum. Octane (internal standard, Aldrich) was stirred over sodium/potassium alloy, degassed and distilled under high vacuum. *n*-Butyllithium (nBuLi, 1.6 M in hexane, Aldrich) was used after determining its actual concentration by double titration. Diphenylethylene (DPE, Aldrich) was titrated with a small amount of nBuLi and distilled under high vacuum. 1,1-Diphenylhexyllithium (DPHLi) was prepared by reacting a known amount of nBuLi with a slight excess of DPE in THF at −40 °C. The reaction mixture was stirred at this temperature for 5 min and then allowed to warm to room temperature. The concentration of DPHLi was determined by double titration. Lithium perchlorate ($LiClO_4$, Aldrich) was dried under dynamic high vacuum at 100 °C.

Kinetics. All experiments were carried out in a specially designed flow-tube reactor.[25,33] Monomer and premixed initiator/$LiClO_4$ solution were precooled and mixed efficiently within less than 1 ms in a mixing jet and allowed to pass through a capillary tube (1 mm inner diameter). The reaction was terminated in a quenching jet at the end of the capillary tube with methanol containing a small amount of acetic acid. The temperatures of the mixing jet, T_m, and quenching jet, T_q, were determined by using fast thermocouples. The particular residence time (5 ms $\leq \tau \leq$ 3 s) of the polymerization solution was achieved by changing the flow rate ($\leq$ 6 mL/s) and tube length (4 cm $\leq l \leq$ 5 m). In all runs the flow rate was carefully chosen in order to maintain turbulent flow during the polymerization with a characteristic Reynolds number, $Re > 3000$.

Experiments were carried out at mixing jet temperatures, −30 °C $\leq T_m \leq$ 0 °C. Since the polymerization is very fast, heat transfer through the walls of the tube is negligible, leading to a nearly adiabatic behavior. Thus, the effective temperature, T_{eff}, of the each run is higher than T_m. The effective temperature of the each experiment was determined using the equation[34]

$$T_{eff} = T_m + 0.55\Delta T$$

with $\Delta T = T_q - T_m$. Hence, an appropriate T_m was selected for each conversion in order to compensate the exotherm of the polymerization and to obtain a constant T_{eff} for all experiments.

Monomer conversion was determined with GC using octane as an internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, filtered, and freeze-dried. Molecular weights and MWD were determined using GPC equipped with two UV detectors with variable wavelength, RI detector, and two 60 cm 5 μm PSS SDV−gel columns: 1 × 100 Å, 1 × linear: 10^2−10^5 Å with THF as eluent at room temperature. The calibration was performed using PMMA standards.

Results and Discussion

The polymerization of MMA using 1,1-diphenylhexyllithium (DPHLi) as an initiator in the absence and in the presence of $LiClO_4$ was performed in a flow-tube reactor. The results of the kinetic experiments performed at different temperatures, T_{eff}, different initial initiator concentrations, $[I]_0$, and different $LiClO_4$ concentrations, are summarized in Tables 1 and 2.

Reaction Orders. The polymerization of MMA in the absence and also in the presence of $LiClO_4$ follows first-order kinetics with respect to monomer concentration at −20 °C. In the first series of experiments performed at −20 °C, $[I]_0$ was varied from 1.4×10^{-3} to 9×10^{-3} mol/L in order to determine the reaction order; a 10-fold excess of $LiClO_4$ with respect to initial concentration was always maintained. As seen from Figure 1, the linearity of the semilogarithmic time−conversion plot indicates the absence of termination reactions during polymerization at −20 °C. However, a deviation from first-order linearity is observed at low initiator concentration ($[I]_0 = 1.4 \times 10^{-3}$ mol/L) indicating termination. This decreases the slope of the time−conversion plot during the polymerization.

The expression for the dependence of monomer concentration on time for a polymerization in the presence of unimolecular termination is easily derived by integrating the rate expressions for propagation and termination. It is given by eq 1, where $k_{app} = k_p[P^*]$ is the

$$\ln\frac{[M]_0}{[M]_t} = \frac{k_{app}}{k_t}(1 - e^{-k_t t}) = \frac{k_p[P^*]}{k_t}(1 - e^{-k_t t}) \quad (1)$$

apparent rate constant (i.e. the initial slope of first-order time−conversion plot), k_p and k_t are the rate constants

Table 2. Rate Constants of Propagation, k_p, and Termination, k_t, for the Anionic Polymerization of MMA in THF Using Li^+ as the Counterion in the Presence of $LiClO_4$

run	$10^3 \times$ [P*][a], mol/L	T_{eff}, °C	$[LiClO_4]/[P^*]$	k_{app}, s^{-1}	$\bar{k}_p = k_{app}/[P^*]$, L mol^{-1} s^{-1}	$k_{app}/[P^*]^{1/2} = k_{\pm}/\sqrt{2K_a}$	k_t, s^{-1}
1	8.73	−18.8	10.3	0.499	57.2	5.34	
2	6.00	−17.6	10.0	0.412	68.7	5.32	
3	4.00	−19.1	10.0	0.337	84.3	5.33	
4	4.00	−19.5	5.0	0.298	74.5	4.71	
5	3.12	−19.4	3.5	0.369	118.3	6.61	
6	2.40	−19.9	1.5	0.370	154.2	7.55	
7	2.44	−19.8	0.94	0.383	156.9	7.75	
8	2.28	−19.3	0.51	0.408	178.9	8.54	
9	3.20	−19.2	0	0.560	175.0	9.90	
10	1.23	−20.5	0	0.350	284	9.96	0.224
11	1.13	−0.1	0	0.690	608	20.44	0.590
12	1.25	+19.2	0	1.8	1440	50.9	2.2
13[b]	1.01	−26.8	15.2	0.140	151.0	4.58	
14	0.98	−19.6	14.5	0.209	216.0	6.69	0.165
15	0.94	−9.3	15.2	0.276	285.0	8.71	0.241
16	0.89	0.7	15.6	0.392	437	13.04	0.49

[a] $[P^*] = f[I]_0$. [b] Induction period (0.24 s) was noticed.

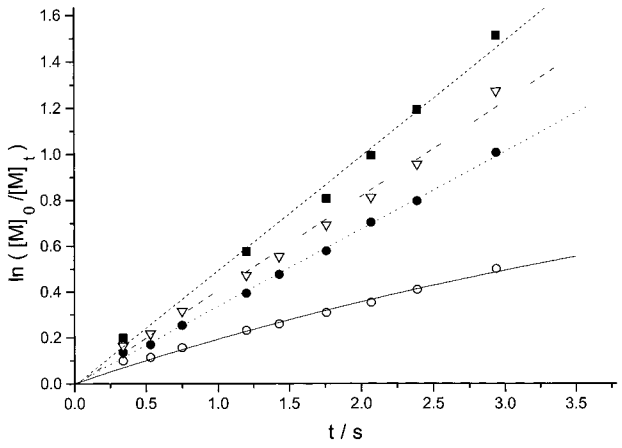

Figure 1. First-order time conversion plots of the MMA polymerization in THF in the presence of $LiClO_4$ at −20 °C. $[M]_0 = 0.2$ mol/L. $[I]_0$/(mol/L): (■) 9×10^{-3}; (▽) 6×10^{-3}; (●) 4×10^{-3}; (○) 1.4×10^{-3}.

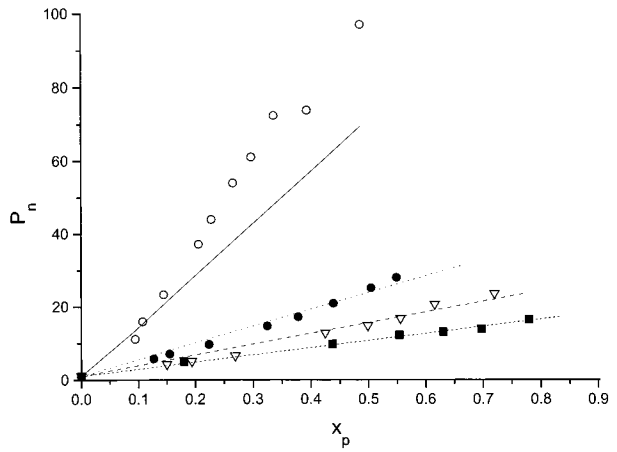

Figure 2. Number-average degree of polymerization, $\bar{P}_n$, vs conversion, x_p, at −20 °C at various initial concentrations of DPHLi. $[M]_0 = 0.2$ mol/L. For symbols, see Figure 1. All lines describe $\bar{P}_{n,theor}$.

of propagation and termination, respectively, $[P^*] = f[I]_0$ is the initial active center concentration, and f is the initiator efficiency. The maximum value of $\ln([M]_0/[M]_t)$—which is related to the maximum conversion obtained at $t \rightarrow \infty$—is given by $[P^*]k_p/k_t$. Thus, the effect of termination is more pronounced at lower chain-end concentrations. The values of k_{app} and k_t (Table 2) were determined by a nonlinear fitting procedure using eq 1.

The linear dependence of the number-average degree of polymerization, $\bar{P}_n$, on conversion, x_p (Figure 2), shows the absence of transfer reactions and high initiator efficiencies. However, at low concentration of initiator, $[I]_0 = 1.4 \times 10^{-3}$ mol/L, the obtained $\bar{P}_n$ deviates from the theoretical line, indicating that the initiator efficiency decreases. The active center concentrations, [P*], in Table 2 were determined using the initiator efficiencies calculated from the ratio of the theoretical and the experimental number-average degrees of polymerization, $\bar{P}_n$, averaged at the highest conversions.

Figure 3 shows a bilogarithmic plot of k_{app} vs [P*] resulting in linearity with a slope of 0.5, similar to the plot in the absence of $LiClO_4$; however, the rates are lower. The fractional order of the reaction indicates that the propagating ion pairs exist in equilibrium with associated species and this equilibrium is shifted toward the less active aggregates. Fractional reaction orders

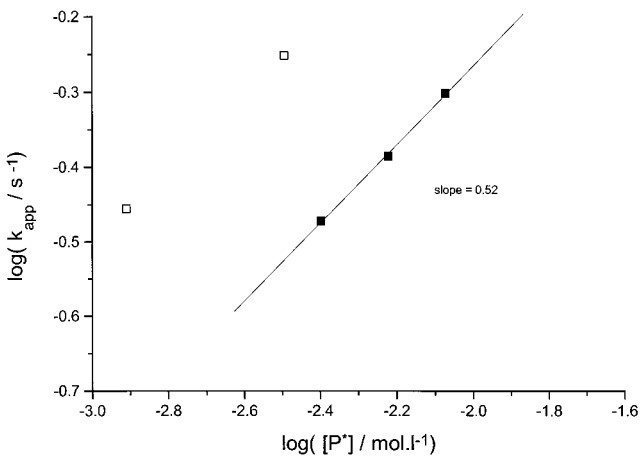

Figure 3. Reaction order with respect to initiator concentration for the MMA polymerization in THF at −20 °C: (■) with $LiClO_4$; (□) without $LiClO_4$. The data point obtained at $[I]_0 = 1.4 \times 10^{-3}$ was not used due to low accuracy caused by termination and lower initiator efficiency.

were also obtained by Kunkel et al.[9] in the absence of any additive at lower temperatures (−65 °C); however, the concentrations of the nonaggregated and aggregated species were comparable at that temperature. Thus we can conclude that aggregation is an endothermic proc-

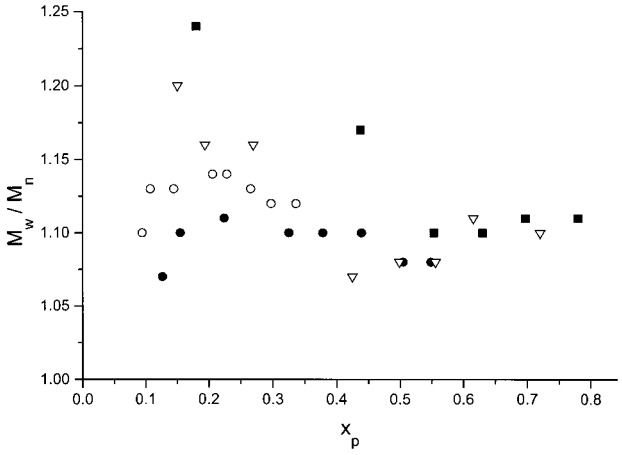

Figure 4. Polydispersity index vs conversion of PMMA obtained in the presence of $LiClO_4$ at −20 °C at different initiator concentrations. Symbols, see Figure 1.

ess, similar to the association of MiBLi dimers to tetramers.[10] It was shown that, in the presence of LiCl, aggregation of enolate ion pairs was decreased due to the formation of mixed aggregates.[9,10]

The obtained fractional order with respect to initiator concentration indicates that $LiClO_4$ does not effectively perturb the aggregation of enolate ion pairs at −20 °C. The observed lower rate constants, $\bar{k}_p = k_{app}/[P^*]$, in the presence of $LiClO_4$ (Figure 3) indicate the formation of less reactive species. The concentration dependence of the $\bar{k}_p$ values (Table 2) shows that it must be regarded as an apparent constant. For an equilibrium between unimers and dimers, it is given by eq 2, assuming that

$$\frac{k_{app}}{[P^*]} \equiv \bar{k}_p = \alpha k_{\pm} + \frac{1-\alpha}{2} k_{ass} \approx \alpha k_{\pm} \qquad (2)$$

the rate constant of propagation of aggregates is much smaller than that of the nonaggregated centers, $k_{ass} \ll \alpha k_{\pm}$,[7,9] where $\alpha = [P_{\pm}]/[P^*]$ is the fraction of nonassociated ion-pairs (unimers) which depends on the initiator concentration and on the equilibrium constant of aggregation, K_a. For strong aggregation,

$$\alpha \approx (2K_A[P^*])^{-1/2} \ll 1$$

which leads to eq 3. From this equation, the ratio $k_{\pm}/$

$$\frac{k_{app}}{[P^*]^{1/2}} = \bar{k}_p[P^*]^{1/2} = \frac{k_{\pm}}{\sqrt{2K_A}} \qquad (3)$$

$(2K_A)^{1/2}$ can be determined. At a given temperature this value should be a constant. Table 2 shows that this is the case whereas $\bar{k}_p$ depends on [P*].

The molecular weight distributions (MWD) of the polymers obtained at −20 °C are narrow (polydispersity index, $\bar{M}_w/\bar{M}_n \leq 1.12$), they are better than those obtained in the absence of ligand ($\bar{M}_w/\bar{M}_n = 1.25$). The same is observed at the other temperatures (Table 1, runs 11 and 16). Figure 4 shows the dependence of the polydispersity index on monomer conversion of the polymers obtained in the presence of $LiClO_4$ at −20 °C. For the higher conversions, the MWD decreases with conversion indicating the existence of a moderately fast equilibrium between aggregated and nonaggregated ion pairs during polymerization.[9,37] For lower conversions, this effect might be canceled due to termination.

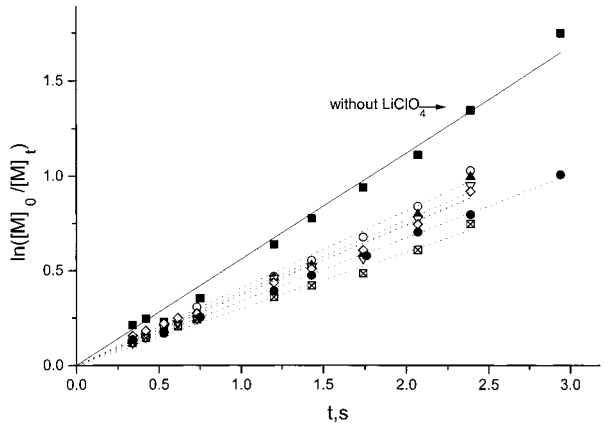

Figure 5. First-order time−conversion plots of MMA polymerization in THF in the presence of $LiClO_4$ at −20 °C. $r = [LiClO_4]_0/[DPHLi]_0$. Key: (■) $r = 0$; (○) $r = 0.3$; (▲) $r = 0.6$; (Δ) $r = 1$; (◇) $r = 3$, (⊞) $r = 5$; (●) $r = 10$.

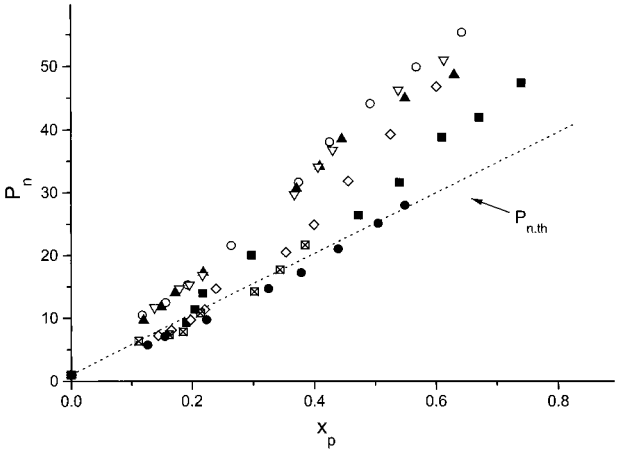

Figure 6. Dependence of number average degree of polymerization, $\bar{P}_n$, on conversion at various ratios $r = [LiClO_4]_0/[DPHLi]_0$, see Figure 5.

To determine the effect of $LiClO_4$ concentration on kinetics, experiments were performed at −20 °C at ratios, $r = [LiClO_4]/[I]_0$, from 0 to 10. The linearity of the first-order time−conversion plots at different concentrations of $LiClO_4$ shows the absence of termination reactions at the higher initiator concentration, $[I]_0 = 4 \times 10^{-3}$ mol/L (Figure 5). A linear dependence of $\bar{P}_n$ on conversion is again observed at different concentrations of $LiClO_4$ (Figure 6). However, the initiator efficiency first decreases from 80% to 60% when $r \leq 3$ and improves to 100% for $r \geq 5$. This may indicate the presence of unreactive species (mixed aggregates?) at low concentrations of $LiClO_4$ ($r \leq 3$). To compensate the decrease in active center concentration, the determined apparent rate constants, k_{app}, were divided by $[P^*]^{1/2}$, according to eq 3. Within the limits of error, this ratio monotonically decreases with increasing r (Table 2, Figure 7). The overall rate constant, $\bar{k}_p$, also decreases with increasing ratio r and gradually reaches ca. 50% of the initial value at $r = 10$ (Table 2).

Kunkel et al.[9,35] observed similar effects for the polymerization of MMA and tBuA in the presence of LiCl in THF at −65 °C. In the presence of LiCl, a maximum in the plot of $\bar{k}_p$ vs ratio r was observed in the polymerization of MMA at $r \approx 1$. This was attributed to the formation of a reactive 1:1 adduct between LiCl and the enolate ion pair decreasing the fraction of dimeric aggregates and leading to an overall increase

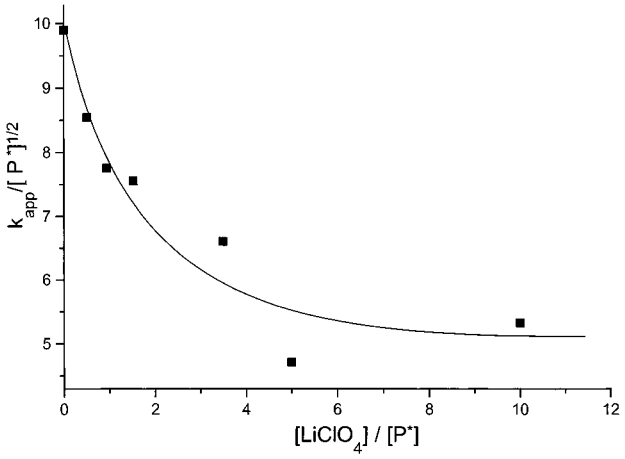

Figure 7. Effect of $LiClO_4$ concentration on the reduced rate constant of MMA polymerization in THF at −20 °C.

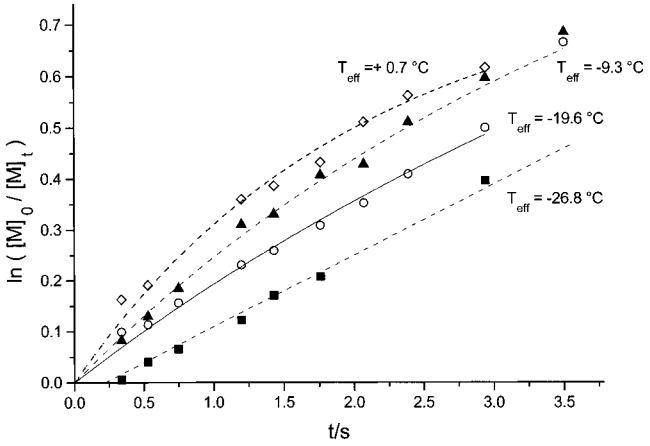

Figure 8. First-order time−conversion plots at different temperatures. $[MMA]_0 = 0.2$ mol/L; $[I]_0 = 1.4 \times 10^{-3}$ mol/L; $r = 10$.

of reaction rate. The decrease in rate at higher r values was attributed to the formation of 1:2 and higher adducts. A similar maximum is not seen in the presence of $LiClO_4$ at −20 °C (Figure 7). It was shown by Kunkel et al.[9] that the slow rate of exchange between associated and nonassociated species compared to the rate of monomer addition is the reason for broad MWD's in tBuA polymerization. In contrast to the de-aggregation of PMMA−Li observed with LiCl at −65 °C, the reaction order of 0.5 indicates that aggregates are still the predominant species at $T = -20$ °C. These could be mixed 2:2 aggregates with $LiClO_4$, $(P_\pm^*)_2(LiClO_4)_2$, which can dissociate into 1:2 and 1:1 mixed complexes. To explain the narrower MWD's in the presence of $LiClO_4$, we have to assume that the exchange rate between the 2:2 mixed aggregate and 1:2 and 1:1 aggregates is higher than that of normal dimeric aggregates, $(P_\pm^*)_2$, and unimers.

Effect of Temperature. The effect of temperature on the rate constants of polymerization and termination in the presence of $LiClO_4$ was studied in the temperature range from −30 to 0 °C at lower $[I]_0 = 1.4 \times 10^{-3}$ mol/L. The first-order time conversion plots show a downward curvature for $T \geq -20$ °C (Figure 8). This indicates the presence of termination at lower $[I]_0$. An induction period was observed in the presence of $LiClO_4$ at −30 °C. The Arrhenius plot obtained using the overall propagation rate constant, $\bar{k}_p$, shows linearity with an activation energy, $E_{a,app} = 20 \pm 1.6$ kJ/mol and frequency exponent, log $A_{app} = 6.5 \pm 0.2$ (Figure 9). The activation energy is slightly lower than that observed for Li^+ and for Li^+/LiCl, respectively, in THF at $T < -40$ °C ($E_{a,app} = 24$ and 25.3 kJ/mol, respectively; log $A_{app} = 7.4$).[35,36] This difference can still be due to experimental errors.

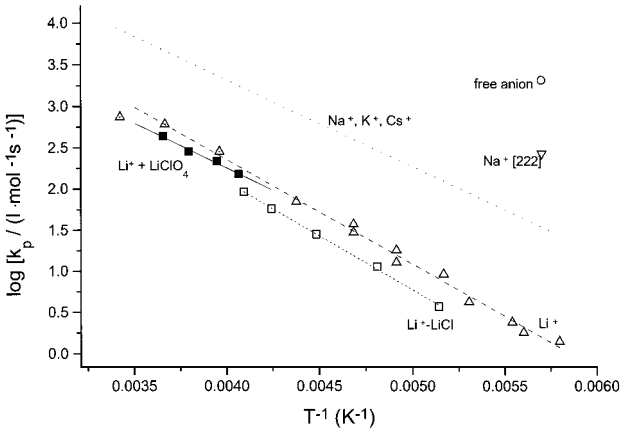

Figure 9. Arrhenius plot of the propagation rate constants, k_p, in the anionic polymerization of MMA in THF with Li counterion and $LiClO_4$ ligand and the reported rate constants for other counterions and ligands. (Aggregation was not taken into account.)

It must be stressed that the activation parameters are only apparent ones since $\bar{k}_p$ depends on the fraction of nonassociated ion-pairs, α, which is expected to depend on temperature and concentration. For an equilibrium between unimers and dimers which is shifted toward the dimers (cf. eqs 2 and 3), the overall rate constant is given as

$$\log \bar{k}_p = \log k_\pm - {}^1/_2 \log K_A - {}^1/_2 \log(2[P^*])$$

Inserting the corresponding Arrhenius and van't Hoff expressions for rate and equilibrium constants

$$\log A_{app} e^{-E_{a,app}/RT} = \log A_\pm e^{-E_{a,\pm}/RT} + {}^1/_2(\Delta H_A/2.3RT - \Delta S_A/2.3R) - {}^1/_2 \log(2[P^*])$$

and sorting temperature-dependent and independent terms, we see that the apparent activation energy also contains the enthalpy of association

$$E_{a,app} = E_{a,\pm} - {}^1/_2 \Delta H_A$$

and the apparent frequency exponent contains the entropy of association and the concentration of chain ends

$$\log A_{app} = \log A_\pm - \Delta S_A/4.6R - {}^1/_2 \log(2[P^*])$$

Since aggregation is endothermic ($\Delta H_A > 0$), $E_{a,app} > E_{a,\pm}$; i.e., the observed activation energies can only be regarded as upper limits. For the various equilibria involving mixed aggregates, the corresponding enthalpies and entropies have to be taken into account. Thus, it is difficult to compare the apparent activation parameters obtained in various systems—even more if the concentrations are not the same.

Within experimental error, the rate constants of termination, k_t, in the presence of $LiClO_4$ are close to those obtained in the absence of any additive (Figure

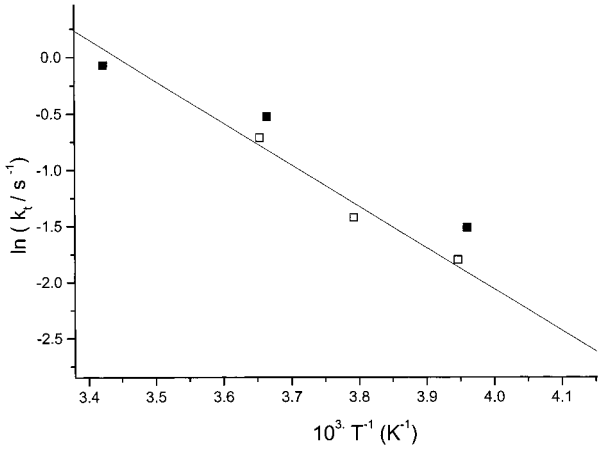

Figure 10. Arrhenius plot of termination rate constant, k_t, of the anionic polymerization of MMA (□) in the presence and (■) the absence of $LiClO_4$.

10), indicating that $LiClO_4$ is ineffective in suppressing the termination reaction, similar to LiCl.

Conclusions

The kinetic reaction orders show that PMMA−Li is strongly aggregated near room temperature ($T = -20$ °C) whereas aggregation is only partial at lower temperatures ($T = -65$ °C). Thus, aggregation of PMMA−Li ion pairs is an endothermic process. Addition of $LiClO_4$ does not significantly decrease aggregation at −20 °C. The observed rate constants and reaction orders indicate the existence of various mixed aggregates (2:2, 1:2, 1:1). $LiClO_4$ also leads to narrower MWD's, presumably due to faster exchange rates between the various active species. It has no significant effect on termination reactions, thus acting similar to LiCl.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 262. D.B. acknowledges a grant by the German Academic Exchange Service (DAAD). The authors are indebted to Prof. A. A. Arest-Yakubovich, Moscow, for helpful comments.

References and Notes

(1) Müller, A. H. E. In *Anionic Polymerization. Kinetics, Mechanisms and Synthesis*; McGrath, J. E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington 1981; p 441.
(2) Müller, A. H. E. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, England, 1988; Vol. 3, p 387.
(3) Hatada, K.; Kitayama, T.; Fujikawa, K.; Ohta, K.; Yuki, H. *Polymer Bull. (Berlin)* **1978**, *1*, 103.
(4) Löhr, G.; Schulz, G. V. *Eur. Polym. J.* **1974**, *10*, 121.
(5) Löhr, G.; Schulz, G. V. *Makromol. Chem.* **1973**, *172*, 137.
(6) Mita, I.; Watanabe, Y.; Akatsu, T.; Kambe, H. *Polym. J.* **1973**, *4*, 271.
(7) Tsvetanov, C. B.; Müller, A. H. E.; Schulz, G. V. *Macromolecules* **1985**, *18*, 863.
(8) Müller, A. H. E.; Lochmann, L.; Trekoval, J. *Makromol. Chem.* **1986**, *187*, 1473.
(9) Kunkel, D.; Müller, A. H. E.; Lochmann, L.; Janata, M. *Makromol. Chem., Macromol. Symp.* **1992**, *60*, 315.
(10) Wang, J. S.; Jérôme, R.; Warin, R.; Teyssié, P. *Macromolecules* **1993**, *26*, 6, 1402.
(11) Halaska, V.; Lochmann, L. *Collect. Czech. Chem. Commun.* **1973**, *38*, 1780.
(12) Weiss, H.; Yakimansky, A. V.; Müller, A. H. E. *J. Am. Chem. Soc.* **1996**, *118*, 8897.
(13) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.
(14) Gia, H.-B.; McGrath, J. E. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T., Smid, J., Eds.; Elsevier: New York 1987; p 173.
(15) Reetz, M. T.; Knauf, T.; Minet, U.; Bingel, C. *Angew. Chem.* **1988**, *100*, 1422.
(16) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.
(17) Adachi, T.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 1238.
(18) Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1996**, *29*, 3038.
(19) Lochmann, L.; Kolarik, J.; Doskocilova, D.; Vozka, S.; Trekoval, J. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1727.
(20) Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1990**, *191*, 1657.
(21) Janata, M.; Lochmann, L.; Vlcek, P.; Dybal, J.; Müller, A. H. E. *Makromol. Chem.* **1992**, *193*, 101.
(22) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1993**, *194*, 625.
(23) Jérôme, R.; Forte, R.; Varshney, S. K.; Fayt, R.; Teyssié, P. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Fontanille, M., Guyot, A., Eds.; D. Reidel: Dordrecht, The Netherlands, 1987; p 101.
(24) Wang, J.-S.; Jérôme, R.; Bayard, P.; Patin, M.; Teyssié, P. *Macromolecules* **1994**, *27*, 4635.
(25) Maurer, A.; Marcarian, X.; Müller, A. H. E.; Navarro, C.; Vuillemin, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 467.
(26) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem., Suppl.* **1989**, *15*, 167.
(27) Ballard, D. G. H.; Bowles, R. J.; Haddleton, D. M.; Richards, S. N.; Sellens, R.; Twose, D. L. *Macromolecules* **1992**, *25*, 5907.
(28) Haddleton, D. M.; Muir, A. V. G.; O'Donnell, J. P.; Richards, S. N.; Twose, D. L. *Macromol. Symp.* **1995**, *91*, 91.
(29) Schlaad, H.; Schmitt, B.; Müller, A. H. E.; Jüngling, S.; Weiss, H. *Macromolecules* **1998,** *31***,** 573; Schlaad, H.; Schmitt, B.; Müller, A. H. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1389.
(30) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jérôme, R.; Teyssié; P. *Macromolecules* **1990**, *23*, 2618.
(31) Teyssié, P.; Fayt, R.; Hautekeer, J. P.; Jacobs, C.; Jérôme, R.; Leemans, L.; Varshney, S. K. *Makromol. Chem., Macromol. Symp.* 1990, *32*, 61.
(32) Wang, J. S.; Jérôme, R.; Teyssié, P.; *Macromolecules* **1994**, *27*, 3376.
(33) Baskaran, D.; Sivaram, S. *Macromolecules* **1997**, *30*, 1869.
(34) Löhr, G.; Schmitt, B. J.; Schulz, G. V. *Z. Phys. Chem. (Frankfurt am Main)* **1972**, *78*, 177.
(35) Jeuck, H.; Müller, A. H. E. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 121.
(36) Kunkel, D. Dissertation, Mainz, Germany, 1992.
(37) Litvinenko, G. L.; Müller, A. H. E. *Macromolecules* **1997**, *30*, 1253.

MA961920Y