Effect of Lithium Chloride on the "Living" Polymerization of *tert*-Butyl Methacrylate and Polymer Microstructure Using Monofunctional Initiators[†]

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ABSTRACT: The effect of LiCl on the anionic polymerization of *tert*-butyl methacrylate (*t*BuMA) initiated with monofunctional alkali metal-based carbanionic species was investigated at -78 °C in THF. The propagation rate of the polymerization process was determined by gas chromatography and by gravimetry. It was found that, in the presence of LiCl in a molar ratio of 5 with respect to the initiator, the rate constant, k_p, is 20 times lower than that in the absence of LiCl. The polymers and oligomers were analyzed by size exclusion chromatography (SEC) and ^{13}C NMR spectroscopy. The polymers obtained in the absence of LiCl had broad molecular weight distributions and contained significant amounts of oligomers, while those obtained in the presence of LiCl were monodisperse, without any noticeable oligomers. ^{13}C NMR showed that the isotactic content of the polymers increased significantly when the molar ratio of LiCl to the initiator was higher than 2. The effect of LiCl on the rate constant and on the microstructure of the polymers was attributed to complex formation between LiCl and the living polymer chains.

Introduction

Some specific inorganic salts that are able to form μ-type complexes with carbanions are known to be very effective in promoting the truly "living" polymerization of (meth)acrylic ester monomers.[1-3] For instance, various types of secondary and transfer reactions associated with the anionic polymerization of (meth)acrylic ester monomers can be prevented in the presence of these electronically balanced cationic ligands.[4-6] This strategy has been successfully used in the molecular engineering of (meth)acrylate-based products using anionic living polymerization. In fact, living polymerization is a very effective procedure when a stringent control on molecular weight, molecular weight distribution, and polymer architecture is desired.[7-9] It has been reported by Teyssie and coworkers[1] that, in the anionic polymerization of methyl methacrylate (MMA) at -78 °C in THF, the presence of lithium chloride (LiCl) improves the "living" character of the process without significantly altering the rate of propagation or the microstructure of the product. The use of LiCl provides a simple but effective pathway for the synthesis of PMMAs with predetermined molecular weights and narrow molecular weight distributions. The LiCl to initiator molar ratio has been shown to be a crucial parameter which determines the conversion and polydispersity.[4]

Both MMA and *tert*-butyl methacrylate (*t*BuMA) are important monomers in the development of a variety of commercially available methacrylate-based products.[10] The kinetics of the polymerization of MMA has been shown to be quite different from that of *t*BuMA. Polymerization of MMA in apolar solvents, such as toluene, in the presence of lithium counterion normally results in a product with a broad multimodal distribution and incomplete conversion. However, under similar conditions, the polymerization of *t*BuMA yields a polymer of narrow molecular weight distribution with over 98% conversion.[11-13] The activation energy of propagation of poly(*t*BuMA) has been found to be greater than that of poly(MMA).[14,15]

The objective of this paper is to study the effect of LiCl as a common cation ligand on the kinetics and stereochemistry of the polymerization of *t*BuMA, initiated by monofunctional alkali counterion initiators. The results will be discussed in terms of the formation of stable adducts of LiCl with the growing ion pairs of *t*BuMA.

Experimental Section

tert-Butyl methacrylate (*t*BuMA), obtained from Polysciences Inc., was first vacuum distilled from CaH_2 reflux and then stored under a nitrogen atmosphere at -20 °C. It was diluted with toluene and then treated with 10% triethylaluminum solution in hexane until a persistent greenish-yellow color was observed.[16] A few drops of dried decane was added as an internal standard to monitor the monomer conversion by gas chromatography. Finally, it was distilled under vacuum just prior to polymerization.

THF was purified by refluxing over sodium-benzophenone complex under a nitrogen atmosphere (a deep blue-violet color indicating a solvent free of oxygen and moisture). It was further distilled under dry nitrogen over oligomeric poly(styryllithium). Toluene and decane were distilled after refluxing over CaH_2 for 48 h.

LiCl (99.99% purity, Aldrich) was dried overnight at 130 °C and then dissolved in dry THF. After introduction of a desired amount of LiCl solution into a 500-mL round-bottom polymerization flask, the THF was removed under reduced pressure. The desired amount of freshly distilled dried THF was charged into the flask containing a known quantity of LiCl.

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[†] This article is dedicated to Professor Ph. Teyssié on the occasion of his retirement from academic life.

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Initiators used in this study were the reaction products of *sec*-butyllithium with a few units of α-methylstyrene (α-MS) or one unit of 1,1-diphenylethylene (DPE). A deep red color developed in THF at room temperature. Other monofunctional initiators used were (diphenylmethyl)sodium ($Ph_2CH^-Na^+$) and (diphenylmethyl)potassium ($Ph_2CH^-K^+$). They were prepared at room temperature by reacting diphenylmethane with the corresponding alkali-metal naphthalene in THF for 24 h. The solution of alkali-metal naphthalene was obtained by addition of the alkali metal to naphthalene in THF at room temperature.[17]

Anionic homopolymerization of *t*BuMA was carried out in a 500-mL glass round-bottom flask under a nitrogen atmosphere. The monomer, solvent, and initiator were transfered by syringe and capillary techniques. The initiator solution was added dropwise to the solvent until the initiator color persisted, followed by addition of a calculated volume of the initiator solution. The addition of 3–4 drops of a 0.20 M initiator solution to 250 mL of solvent was generally required to get a persistent initiator color, indicting a pure solvent and an airtight system. The purified *t*BuMA was then added to the initiator solution, previously cooled to −78 °C in a dry ice–acetone bath. Approximately 15 s was usually required to add 5 mL of monomer through the stainless steel capillary. Monomer conversion was determined both by gas chromatography using decane as the internal standard and by weighing the dried polymer after precipitation in cold methanol. The values obtained by these independent techniques agree within ±5%.

The dependence of the experimental molecular weight ($M_{n,exp}$) on the monomer to initiator molar ratio, i.e., the calculated molecular weight ($M_{n,calc}$), was investigated by determining polymer molecular weights using a Varian size exclusion chromatography (SEC) equipped with 10^3-, 500-, and 100-Å μ-Styragel columns and a refractometer as detector. THF was used as the eluent at 30 °C with the flow rate of 1 mL/min. Samples were analyzed by SEC before precipitating the polymers into a cold methanol/water mixture to reduce the loss of oligomers in the precipitation process. The molecular weight and polydispersity indices were calculated after calibration of the column with polystyrene standards. Some samples were analyzed with double detectors, i.e., a refractometer and a UV detector at 254 nm.

Chain tacticity was determined by ^{13}C NMR in $CDCl_3$ at room temperature, with $CDCl_3$ as an internal reference (77.0 ppm). ^{13}C NMR spectra were recorded on a Varian XL-300 NMR spectrometer operating at 75.5 MHz. Pulse delay times of 4–5 s were used, and longer delays were found to be unnecessary.

Results and Discussion

The effect of LiCl on the anionic polymerization of *t*BuMA in THF at −78 °C initiated by alkali metal-based monofunctional initiators will be discussed in two parts. The first part is devoted to the effect of LiCl on the molecular weight distribution of the product and on the kinetics of the anionic polymerization process. The second part focuses on the mechanism of the reaction, with discussions of the identification of oligomers, microstructure of the polymers, and the formation of stable adducts of LiCl with the growing ion pairs.

Effect of LiCl–Organolithium Monofunctional Initiator Complex on the Molecular Weight Distribution of P*t*BuMA Synthesized in THF. Table 1 lists the characteristic data for the polymerization of *t*BuMA in the presence of varying amounts of LiCl. The reactions were carried out at −78 °C in THF, using α-MS^-Li^+ as initiator.

SEC analysis of P*t*BuMA prepared in the absence of LiCl showed a rather broad molecular weight distribution (M_w/M_n = 1.35). The polymer, in fact, contained about 15% of low molecular weight oligomer (trimers and higher oligomeric species). The amount of LiCl with respect to initiator was found to be a critical parameter in the homopolymerization of *t*BuMA. When 0.5 mol of LiCl per mol of initiator was introduced, the polydispersity index of the polymer was reduced from 1.35 to 1.20 and the SEC analysis indicated the absence of any noticeable amount of oligomeric species (Table 1, entry 2). At the same time, the initiator efficiency *f*, given by the concentration of growing chains divided by the concentration of the initiator ($[P]/[I]_0$), increased. When the LiCl to initiator molar ratio reached 1, a further improvement in MWD was observed, in addition to a higher initiator efficiency. A further increase in the LiCl to initiator ratio to 2 resulted in a MWD of 1.05 and an initiator efficiency of 97%. However, above this ratio, no further improvement in MWD of the polymer was observed.

Table 1. Data for the Anionic Polymerization of *t*BuMA in THF Initiated by α-MS^-Li^+ Initiator in THF at −78 °C in the Presence of Different Amounts of LiCl[a]

sample	[LiCl]/[I] molar ratio	x_p	$M_{n,calc}$	$M_{n,SEC}$	M_w/M_n	f[b]
104A	0.0	1.00	4600	5600	1.35	0.82
103A	0.5	1.00	4600	5000	1.20	0.92
103B	1.0	1.00	4600	4700	1.15	0.97
111	2.0	0.89	4100	4300	1.05	0.95
104C	3.0	0.60	2800	3000	1.05	0.93
104B	5.0	0.55	2500	2700	1.05	0.92
103C	10.0	0.53	2500	2600	1.10	0.96
112	23.0	0.39	1800	1700	1.03	0.94
122	50.0	0.35	1600	1700	1.05	0.94

[a] $[\alpha\text{-}MS^-Li^+] = 10.4 \times 10^{-2}$ mol/L, *t*BuMA $[M]_0 = 0.338$ mol/L, reaction time = 30 min. x_p is the degree of conversion, $M_{n,calc} = 142\,[M]_0/[I]_0\,x_p$ % conversion. [b] The initiator efficiency, *f*, is given by the concentration of growing chains divided by the concentration of the initiator, i.e., $[P]/[I]_0$.

Kinetics of Polymerization of *t*BuMA Initiated by the LiCl–Poly(α-methylstyryl)lithium Initiator Complex. Both in the presence and in the absence of LiCl, the red color of the initiator disappeared instantaneously upon the addition of a few drops of monomer, which is an indication that the initiation step is very rapid. On the other hand, the LiCl/initiator molar ratio has a significant effect on the conversion of monomer to polymer. At a ratio of 2, the monomer conversion was incomplete (89% yield, Table 1, entry 4) within a reaction time of 30 min. It is interesting to note that an excess of LiCl ($[LiCl]/[I]_0$ = 23) led to only 39% monomer conversion in 30 min (Table 1, entry 8). These data demonstrate that the addition of LiCl greatly influences the rate of polymerization of *t*BuMA in THF at −78 °C.

By contrast, for the polymerization of MMA carried out under identical experimental conditions,[4] LiCl was found to have little effect on k_p. The reported k_p values in the absence of LiCl and in the presence of 5 LiCl per initiator are 15 and 17 L mol^{-1} s^{-1}, respectively. The difference between *t*BuMA and MMA in the effect of LiCl on the kinetics of polymerization is probably due to the formation of more stable μ-type complexes between LiCl and the *t*BuMA ion pairs. It is worth noting that at −78 °C, the polymerization of *t*BuMA using lithium counterion initiator in toluene or using a sodium or potassium counterion initiator in THF or toluene can yield monodisperse P*t*BuMAs with very good reproducibility (Table 2). Detailed kinetic data for these systems will be reported elsewhere.[18]

The propagation rate for the polymerization of *t*BuMA in THF at −78 °C was studied using (1,1-diphenyl-3-methylpentyl)lithium initiator (a reaction product of *sec*-butyllithium with a unit of diphenyethylene). The polymerization reactions were terminated at different time intervals, and the monomer conversions were determined by gravimentry and by gas chromatography. Tables 3 and 4 summarize the characteristic data for the polymerization of *t*BuMA with and without LiCl. The poly-

Table 2. Characteristic Data for the Anionic Polymerization of *t*BuMA in THF at -78 °C Initiated by Different Counterion Initiators[a]

sample	type of initiator	solvent	% con	$M_{n,SEC}$	M_w/M_n	f
153	DPHLi	THF	100	12 500	1.30	0.80
B	Ph_2CHNa	THF	100	12 000	1.08	0.83
149-1	Ph_2CHK	THF	100	11 000	1.05	0.90
152	DPHLi	toluene	100	11 500	1.12	0.83

[a] Initiator, 0.5 × 10^{-3} mol; solvent, 100 mL; monomer, 5.0 g; polymerization time, 20 min.

Table 3. Data for the Anionic Polymerization of *t*BuMA in THF at -78 °C Initiated by (1,1-Diphenyl-3-methylpentyl)lithium Initiator[a]

sample	reaction time (s)	x_p	$M_{n,calc}$	$M_{n,SEC}$	M_w/M_n[b]
151-1	30	0.34		bimodal	broad
151-2	60	0.50	1000	1700	1.50
151-3	120	0.81	2200	3000	1.50
151-4	300	0.94	3200	4000	1.40

[a] *t*BuMA $[M]_0 = 0.309$ mol/L, $[I]_0 = 13.0 \times 10^{-2}$ mol/L. [b] Values are calculated by not taking into account the oligomeric species.

Table 4. Data for the Anionic Polymerization of *t*BuMA in THF at -78 °C Using (1,1-Diphenyl-3-methylpentyl)lithium Initiator in the Presence of a 5-Fold Excess of LiCl with Respect to the Initiator[a]

sample	reaction time (min)	x_p	$M_{n,calc}$	$M_{n,SEC}$	M_w/M_n	f
150-1	5	0.21	1400	bimodal	1.06[b]	
A	30	0.55	2300	2700	1.05	0.82
150-2	60	0.86	3000	3200	1.05	0.93
150-3	240	0.97	3900	4300	1.05	0.90
150-4	720	1.00	4000	4500	1.10	0.88

[a] *t*BuMA $[M]_0 = 0.372$ mol/L, initiator $[I]_0 = 13.0 \times 10^{-2}$ mol/L. [b] After excluding the oligomeric species.

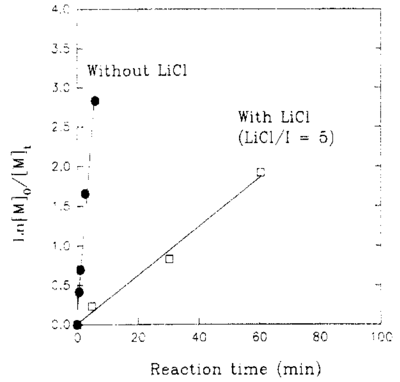

Figure 1. First-order time–conversion plots for the anionic polymerization of *tert*-butyl methacrylate initiated by (1,1-diphenyl-3-methylpentyl)lithium in THF at -78 °C.

merization of *t*BuMA is a fast reaction in the absence of LiCl (Table 3, entry 3), usually with over 80% conversion within 120 s. The initiation is very rapid, since the red color of the initiator disappeared instantaneously upon the addition of a few drops of the monomer. The polymerization is typically free of self-termination or chain-transfer reactions. This is deduced because the relationship between the degree of polymerization and the monomer conversion is linear, indicating the living nature of the system (Figure 1). SEC analysis of the product at 34% monomer conversion showed that it contained approximately 37% of oligomers (a mixture of dimers, trimers, tetramers, etc.) and 63% of polymeric species, as calculated from the area of the chromatogram. The identification of these oligomers will be described in the following section. An SEC trace of the crude product is given in Figure 2a. The percentage of oligomers in the product decreased gradually as the polymerization proceeded. At 50% monomer conversion, the resulting product still contained about 25% of oligomeric species. The elution volume for the polymeric species decreased as the monomer conversion increased, indicating an increase in the molecular weight. At approximately 81% conversion, no dimer could be detected by SEC, but trimers and higher oligomeric species (ca. 13%) were still present. The polydispersity index of the product at 94% conversion was calculated to be 1.40.

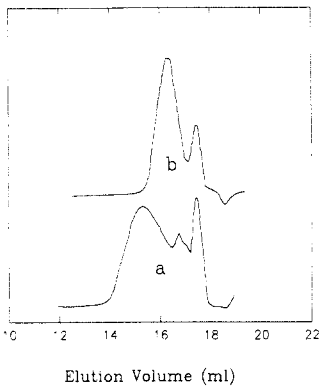

Figure 2. SEC traces of the product obtained using α-MSLi$^+$ initiatior in THF at -78 °C: (a) in the absence of LiCl at 34% monomer conversion; (b) in the presence of LiCl at 21% monomer conversion.

The monomer conversion was significantly reduced when the polymerization of *t*BuMA was carried out in the presence of 5 LiCl per initiator. In 5 min (Table 4, entry 1), only a 21% monomer conversion was obtained. SEC analysis of the product showed a bimodal distribution (Figure 2b). The MWD of the polymer calculated excluding the oligomeric species is quite narrow; i.e., $M_w/M_n = 1.06$. In 30 min of reaction time, only 55% of the monomers were polymerized, and the SEC of the product indicated a unimodal distribution without a noticeable presence of oligomeric species. The M_n of the polymer is 2700 with a M_w/M_n of 1.05. After 240 min of polymerization, only 3% of the monomers remained unreacted, as detected by gas chromatography. SEC analysis of the final product showed an increase in the molecular weight.

The polymerization in the presence of 5 LiCl per initiator is also a first-order reaction with respect to the monomer concentration, indicating the living nature of the system (Figure 1). The value of the rate constant in the absence of LiCl was found to be 0.76 L mol^{-1} s^{-1}, which is in close agreement with the literature value. However, in the presence of LiCl, the k_p for the polymerization of *t*BuMA is 0.04 L mol^{-1} s^{-1}. This significant decrease in k_p suggests the existence of tight contact ion pairs that facilitate the formation of adducts with LiCl. These results are in contrast to those of Kunkel et al.,[19] who have reported the anionic polymerization of *t*BuMA in THF at -65 °C using methyl α-lithioisobutyric initiator complexed with LiCl. In that work, the LiCl/initiator molar ratio was varied from 0 to 12 and only a 5% reduction in k_p was observed. To explain this reduction, the authors indicated that the rate constant of the LiCl-complexes species is smaller than that of the ion pairs.

Identification of the Oligomers. Different oligomeric species were identified in the early stages of polymerization of *tBuMA* in THF at -78 °C, both in the absence of LiCl and in the presence of 5 LiCl per initiator. The polymerization was initiated by (1,1-diphenyl-3-methylpentyl)-

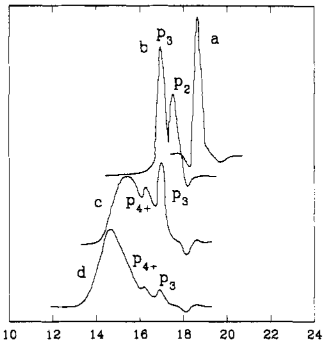

Figure 3. SEC traces of the product obtained at different initiator:monomer molar ratios in THF at −78 °C using (1,1-diphenyl-3-methylpentyl)lithium initiator: (a) 1,1-diphenyl-3-methylpentane; (b) monomer: initiator = 2.7:1 (molar ratio); (c) monomer:initiator = 8:1:1; (d) monomer:initiator = 16.25:1.

lithium. The molar ratios of monomer to initiator were kept at 2.7, 8.1, and 16.25. The reaction products were analyzed by SEC equipped with a refractometer and an ultraviolet detector. The refractometer was used to measure the total concentration of the oligomers, while the UV detector (absorbance at 254 nm) was used to measure the concentration of diphenyl groups connected to the oligomeric species. From mass balance the following equations can be derived:

$$A_{\mathrm{RI}} = kc \tag{1}$$

$$A_{\mathrm{UV}} = k' \frac{c}{M_{\mathrm{I}} + nM_0} \tag{2}$$

where A_{RI} and A_{UV} are the peak areas from the refractometer and ultraviolet detector, respectively, c is the concentration of the oligomer (g/L), M_{I} and M_0 are the molecular weights of the initiator and the monomer, respectively, n is the number of monomers in the oligomer, and k and k' are constants. In the present case, we have M_0 = 142 g/mol and M_{I} = 231 g/mol.

By dividing eq 1 by eq 2, we have

$$\frac{A_{\mathrm{RI}}}{A_{\mathrm{UV}}} = \frac{k}{k'}(M_{\mathrm{I}} + nM_0) = \frac{1}{k''}(M_{\mathrm{I}} + nM_0)$$

or

$$n = \frac{1}{M_0}\left(k''\frac{A_{\mathrm{RI}}}{A_{\mathrm{UV}}} - M_{\mathrm{I}}\right) \tag{3}$$

where $k'' = k'/k$, which was determined to be 1710 g/mol for the P*t*BuMA oligomers by analyzing the protonated initiator. Accordingly, eq 3 becomes

$$n = \frac{1}{142}\left(1710\frac{A_{\mathrm{RI}}}{A_{\mathrm{UV}}} - 238\right) \tag{4}$$

By measuring A_{RI} and A_{UV} for each oligomer peak, n was calculated to be ca. 2 for the dimer (P2) and ca. 3 for the trimer (P3). The elution volumes corresponding to P2 and P3 were found to be 18.1 and 17.5 mL, respectively. The fraction of the oligomer was determined by measuring the area under the corresponding peak. Figure 3 presents the SEC traces of products obtained in the absence of LiCl at different monomer to initiator molar ratios ([M]/[I]$_0$). At a [M]/[I]$_0$ of 2.7, the elution chromatogram displayed a narrow bimodal distribution corresponding to 37% dimers (P2) and 63% trimers (P3). It should be noted that the chromatogram did not indicate any dead species from the initiator moiety. As [M]/[I]$_0$ increased to 8.1, the dimer peak disappeared while the trimer peak was still present. In addition to trimer peaks, two other peaks corresponding to elution volumes of 15.7 and 16.7 mL were observed. The percentage of P3 decreased to 26%. A further increase in the [M]/[I]$_0$ ratio resulted in an even lower percentage of trimer and other higher oligomeric species (ca. 16%). The polydispersity index and the molecular weight of the polymeric species were found to be 1.30 and 2800, respectively. These values were calculated by excluding the oligomeric species.

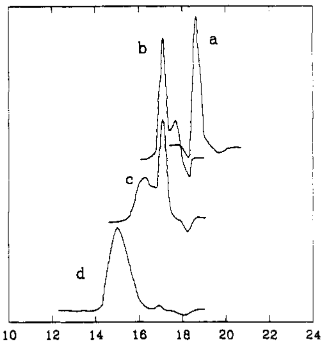

Figure 4. SEC traces of the product obtained at different initiator:monomer molar ratios in THF at −78 °C using (1,1-diphenyl-3-methylpentyl)lithium initiator in the presence of a 5-fold excess of LiCl: (a) 1,1-diphenyl-3-methylpentane; (b) monomer:initiator = 2.7:1 (molar ratio); (c) monomer:initiator = 8:1:1; (d) monomer:initiator = 16.25:1.

Table 5. Data for the Oligomerization of *t*BuMA in THF at −78 °C Using (1,1-Diphenyl-3-methylpentyl)lithium as Initiator ([I]$_0$ = 6.5 × 10^{-3} mol/L)

[M]/[I]	10^3[LiCl] (mol/L)	P2 %	P3 %	P4,P5,P6 %	polymer %
2.7	0.0	37	63		
8.1	0.0		26	20	53
16.25	0.0		8	8	84
2.7	32.5	25	75		
8.1	32.5		50	50	
16.25	32.5		2		98

The oligomerization of *t*BuMA in the presence of 5 LiCl per initiator was also investigated. The feature of the SEC traces (Figure 4) of the reaction products at a monomer to initiator ratio ([M]/[I]$_0$) of 2.7 is similar to that observed when no LiCl was used. The fractions of P2 and P3 are 25 and 75%, respectively. At a [M]/[I] ratio of 8.1, P2 disappeared while P3 was still present. It is worth mentioning here that in the presence of LiCl, only a small amount of higher molecular weight oligomers (>P3) was observed. However, when the reaction was carried out at the same [M]/[I]$_0$ ratio but in the absence of LiCl (Figure 3c), significant amounts of higher molecular weight species were present. A further increase in the monomer to initiator ratio caused a drastic reduction in the trimer concentration. The M_{n} of the resulting polymer was 1900, with a $M_{\mathrm{w}}/M_{\mathrm{n}}$ of 1.06. The initiator efficiency was calculated on the basis of oligomer to initiator ratio to be 0.98. Table 5 summarizes the results of the oligomeric species in the oligomerization of *t*BuMA.

These results clearly indicate that the carbanions modified with LiCl influence the rate of oligomerization of *t*BuMA in the initial stages of propagation. The reactivities of all the oligomeric species in the presence of LiCl appear to be modified to such an extent that the process becomes ideal without secondary transfer reactions that are normally associated with the ester moiety of the monomer. The polymerization carried out without the presence of LiCl suggests that the reactivities of the different oligomeric species are quite different, which may,

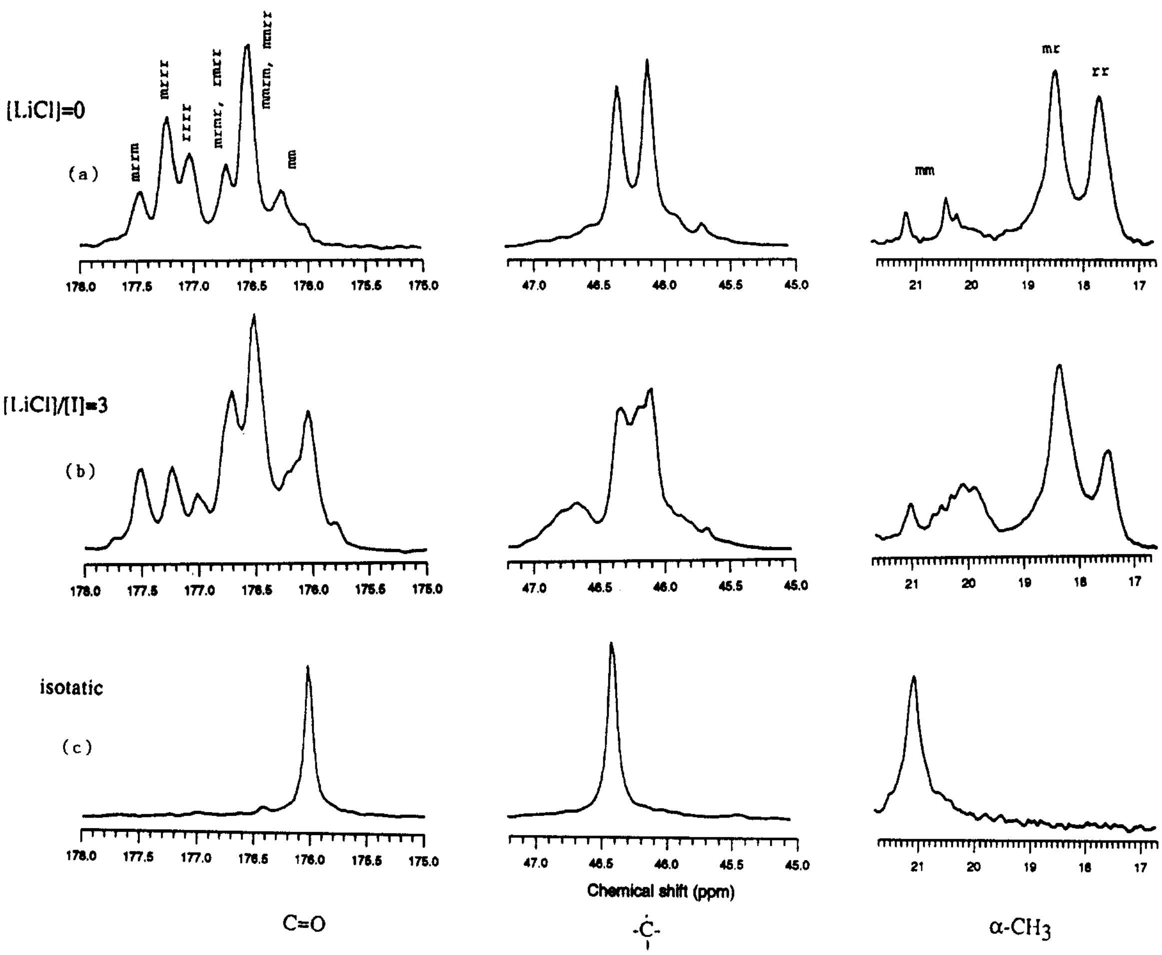

Figure 5. Carbonyl carbon, quaternary carbon, and α-methyl carbon regions of 75-MHz ^{13}C NMR spectra of P*t*BuMA prepared in THF in the absence of LiCl ([LiCl] = 0) and in the presence of LiCl ([LiCl]/[I] = 3) as well as of isotactic P*t*BuMA prepared in toluene.

Table 6. Microstructure of Poly(*tert*-butyl methacrylate) Prepared at Different LiCl Contents (−78 and 0 °C) As Determined from ^{13}C NMR

			carbonyl						α-CH$_3$		
[Li/C]/[I]	M_n	M_w/M_n	mm	mmrm mmrr	mrmr rmrr	rrrr	mrrr	mrrm	mm	mr	rr
0	5600	1.36	9.92	37.77	8.19	14.67	21.83	7.60	8.7	49.6	41.7
1.0	4700	1.20	7.76	40.47	9.09	10.43	23.51	8.74	8.4	46.4	45.2
2.0	4300	1.15	8.21	41.30	7.44	14.67	22.81	5.56	8.5	47.3	44.2
3.0	3000	1.05	25.49	30.74	22.42	3.25	8.88	9.21	26.7	53.4	19.9
5.0	2700	1.05	23.27	31.15	23.14	3.44	8.71	10.29	27.1	52.3	20.6
10.0	2600	1.10	29.34	25.25	25.66	3.22	8.03	8.49	27.4	51.9	20.7
23.0	1700	1.03	30.38	33.16	22.73	0.69	6.59	6.43	28.0	49.7	22.3
50.0	1700	1.05	28.82	31.19	24.43	1.20	5.30	8.96	30.3	50.9	18.8
0 (0 °C)	3400	1.25	13.90	9.25	10.07	1.55	19.82	5.38	14.5	40.4	45.1
23 (0 °C)	3500	1.08	36.84	22.24	26.68	1.70	8.93	3.57	34.2	50.4	15.4
50 (0 °C)	6800	1.05	33.35	18.96	30.65	2.89	8.93	5.20	34.6	48.2	17.2

in turn explain the broad distribution of the polymer. Tsvetanov and Muller et al.[20] have shown that the rate constants for the individual i-mers, k_i (for the oligomerization of MMA initiated by methyl α-lithioisobutyrate in THF at −46 °C), depend on the degree of association of the i-mer. The rate constant drops more than 1 order of magnitude as soon as another monomer unit is added (i.e., dimeric species), indicating a decrease in reactivity and a significant increase in thermodynamic stability of the growing macroanions. This has been reported for the oligomerization of MMA in THF at 25 °C, using lithium counterion initiator. This behavior in the anionic polymerization of (meth)acrylic ester monomers is due to the involvement of intramolecular solvation phenomena associated with the antepenultimate ester moiety of the growing chains.

Effect of LiCl on the Microstructure of P*t*BuMA Prepared in THF. The ^{13}C NMR signals of the carbonyl, α-quarternary, and α-methyl carbons in P*t*BuMA prepared in THF in the absence of LiCl and in the presence of 3 LiCl per initiator are illustrated in Figure 5a,b. The ^{13}C NMR signals of these carbons in isotactic P*t*BuMA prepared in toluene are also shown in Figure 5c. The assignments of the ^{13}C NMR signals were made by comparing the spectra with those of PMMA.[11,22,23] The pentads of the carbonyl carbon were clearly observed in the heterotactic acid and syndiotactic regions, while the pentads in the isotactic region were not well resolved. The complex nature of the α-quaternary carbon region precludes its use in the determination of tacticity in the present case. Here the isotactic P*t*BuMA (isotactic content over 99%) prepared in toluene at −78 °C, using lithium counterion initiator, serves as a reference. The carbonyl carbon signals of P*t*BMA prepared at various conditions were fitted to Lorentzian functions, and the results are given in Table 6. A typical example is given in Figure 6

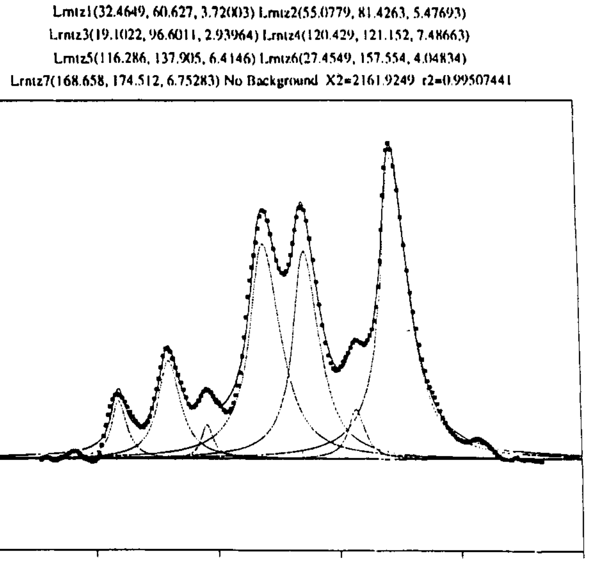

Figure 6. Curve fitting using Lorentzian functions for the carbonyl carbon region of the 75-MHz ^{13}C NMR spectrum of P*t*BuMA prepared in THF at 0 °C in the presence of LiCl ([LiCl]/[I] = 23).

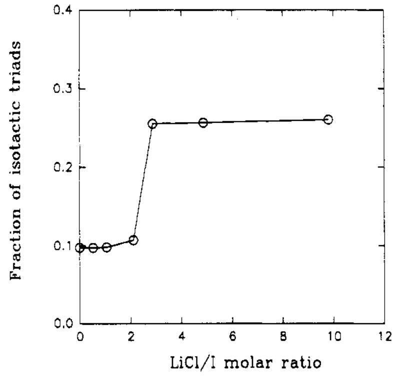

Figure 7. Effect of LiCl on the tacticity of poly(*tert*-butyl methacrylate) prepared in THF at −78 °C using α-MSLi$^+$ as initiator.

for P*t*BuMA prepared at 0 °C with LiCl to initiator molar ratio of 23. The triads of the α-methyl carbon were obtained from the integration of the carbon-13 signals. The dependence of isotactic triads on the LiCl to initiator ratio is illustrated in Figure 7. The isotactic fraction of P*t*BuMA increased sharply from 9.9% when no LiCl was added to 25.5% when the LiCl to initiator molar ratio reached 3 (Figure 7). A further increase in the ratio of LiCl to initiator did not have a significant influence on the tacticity of the polymers. The increase in the isotactic content occurred at the cost of the syndiotactic content, while the heterotactic content of the product was basically unchanged. The pentads of the carbonyl carbon of P*t*BuMA prepared in the absence and in the presence of various amounts of LiCl do not agree either with Bernoullian or with first- or second-order Markov statistics.

The microstructures of the *t*BuMA oligomers obtained at different monomer conversions have also been analyzed by ^{13}C NMR, although no effort was made to separate individual oligomeric species. Figure 8 presents the ^{13}C NMR spectra of the carbonyl carbons of *t*BuMA oligomers prepared with and without LiCl. The spectra are difficult to assign since the samples are mixtures of different oligomer species. It is of interest to note that at low conversions (<35%) a peak with a chemical shift of 176.2 ppm was observed regardless of whether the polymerization was carried out with or without LiCl (Figure 8, 1a and 2a). This peak diminished as the monomer conversion increased to 55% (Figure 8, 2b). This signal is very likely due to the dimer or the trimer. At 55% conversion, the isotactic peak at 176.0 ppm is clearly observed and its chemical shift is essentially unchanged at higher conversions and at higher LiCl to initiator ratios. The reactivities of these oligomeric species and the relationship between the reactivity and the microstructure still remain to be investigated.

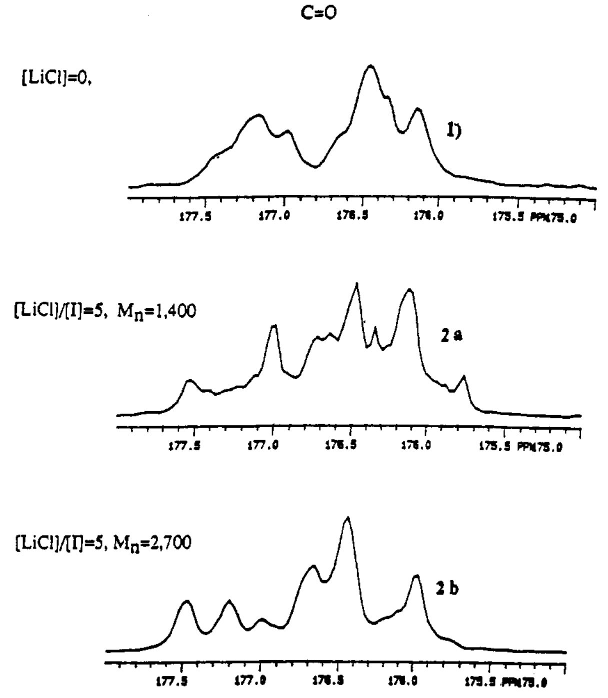

Figure 8. ^{13}C NMR spectra (carbonyl region) of oligomers of *t*BuMA prepared in THF at −78 °C using (1,1-diphenyl-3-methylpentyl)lithium initiator: (1) without LiCl, conversion at 34%. (Table 3, entry 1); (2a) with 5 LiCl per initiator, conversion at 21% (Table 4, entry 1); (2b) with 5 LiCl per initiator, conversion at 55% (Table 4, entry 2).

Apparently, at low conversions, there is no significant difference in the isotactic region (176.0 ± 0.1 ppm) between the oligomers prepared in the presence and absence of LiCl. These results can be correlated to our SEC analysis for the oligomers of *t*BuMA prepared at a monomer/initiatior molar ratio of 2.7 with or without LiCl. At this molar ratio no significant difference between the two chromatograms was detected except for the contents of dimers and trimers.

Structural and Mechanistic Aspects of the Initiator Modified by LiCl. Experimental evidence from the polymerization of *t*BuMA in THF at −78 °C, using LiCl-modified lithium cation initiator, suggests that the initiator efficiency ($M_{n,calc}/M_{n,SEC}$) is improved and the polydispersity is decreased with increasing LICl to initiating carbanion ratio. The increase in initiator efficiency and the decrease in the polydispersity index follow an asymptotic pattern, with limiting values of 0.95 and 1.05, respectively. The oligomerization studies reveal that a control of the reaction kinetic features is achieved most likely as soon as trimers are formed. The trimers can form a six-membered ring stabilized by the coordination of LiCl molecules, with the involvement of the antepenultimate ester moiety. The control of active species may depend directly on the formation of a (LiCl)$_x$- - -LiR entity. This entity might exist in the form of a four membered μ-type complex as suggested earlier.[4] The association number of LiCl molecules per growing chain is very likely to be around 2 or 3, which probably leads to the formation of an electron-deficient bond involving antepenultimate or penultimate ester. The existence of complexed living chain ends (adducts with LiCl) has been demonstrated in our kinetic studies where a decrease in the propagation rate constant, k_p, has been observed with increasing LiCl to initiator ratio. In comparison to the lithium carbanion initiators, such coordination complexes are able not only to modify the extent of the equilibrium between different types of ion pairs but also to promote the formation of new ones carrying LiCl. Whatever the nature of these new systems may be, the kinetic and structural data suggest the existence of a dominant single active carbanionic entity, formed by modifying ion pair equilibria. The reactivity of such a complexed ion pair is expected to be lower than that of the uncomplexed one. The influence of LiCl on the MWD of the polymer can be explained by the faster exchange between the free and complexed ion pairs in comparison with that between the free and the associated ion pairs. The formation of stable μ-type complexes between the growing ion pairs and the LiCl species may be enhanced by the penultimate and antepenultimate carbonyl moieties of the ester function groups.

It has been reported recently that ^{13}C and ^{7}Li NMR studies of the monomeric models of the living poly(methyl methacrylate), such as α-lithioisobutyrate, indicates the existence of two types of species. The major species are responsible for the C(α)/C(O) signals at 73.5/160.5 ppm and the minor species for the signals at 64.5/159.1 ppm. The minor species at 65.4/159.1 ppm disappear in the presence of LiCl. Furthermore, at a 1:1 LiCl:α-lithioisobutyrate molar ratio, the signals of the nonequivalent α-methyl group of the α-lithioisobutyrate were replaced by a single resonance at 18.8 ppm, indicating a strong s bond character in the C–C–(O) bond instead of the predominant enolate character without LiCl coordination. This means that the coordination between LiCl and the counterion must induce more charge delocalization. The delocalized negative charge shared by another cation from LiCl molecule(s) may enhance the s bond order.

Conclusions

The rate constant of the anionic polymerization of *t*BuMA, initiated with alkali metal carbanionic species, was found to be influenced significantly by the addition of LiCl. The isotactic content of the product, P*t*BuMA, as determined from ^{13}C NMR was also dependent on the amount of LiCl present during the polymerization. The kinetic and ^{13}C NMR studies of the P*t*BuMA and *t*BuMA oligomers strongly suggest the formation of complexes between LiCl and the growing active species of *t*BuMA macroanions, which subsequently influences the placement of incoming monomers and thereby changes the tacticity of the polymer.

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