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Mechanism of Anionic Polymerization of (Meth)acrylates in the Presence of Aluminum Alkyls, 6. Polymerization of Primary and Tertiary Acrylates†

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ABSTRACT: The kinetics of the polymerization of *n*-butyl acrylate initiated by lithiated ester enolates in the presence of aluminum alkyls was investigated in toluene and in toluene/Lewis base mixed solvents at −78 °C. In pure toluene, curved time−conversion plots, incomplete monomer conversion, and broad molecular weight distributions ($M_w/M_n \approx 2$) are observed—in the absence of aluminum alkyls the molecular weight distributions are significantly broader ($M_w/M_n > 14$). High monomer conversions and narrower molecular weight distributions ($M_w/M_n \approx 1.5$) are obtained when using Lewis bases (e.g., methyl pivalate) as cosolvents. The polymerization of *tert*-butyl acrylate rapidly reaches full monomer conversion with rather broad molecular weight distributions ($M_w/M_n \approx 2$); the addition of a Lewis base, however, does not have a pronounced effect on these values.

Introduction

In the past few years, several authors described the living anionic polymerization of methacrylates with lithiated initiators in the presence of aluminum alkyls.[1−3] Recently, we elucidated the mechanism of this reaction.[4−7] It was found that the polymerization deviates significantly from first-order kinetics and that the polymers have fairly broad molecular weight distributions. This results from the formation and precipitation of a coordinative polymer network, in which the lithium ions of the living chain ends are coordinated to in-chain ester carbonyl groups. Consequently, the network formation could be suppressed by the addition of Lewis bases (e.g., methyl pivalate or crown ethers), leading to linear first-order kinetics and polymers with narrow molecular weight distributions even at 0 °C.[8]

On the contrary, only a few works have been published describing the living anionic polymerization of primary acrylates. Compared to methacrylates, the acrylates lack an α-methyl group, the missing inductive effect of which is expected to increase the reactivity of the monomer but to decrease that of the corresponding living chain end. However, the decreased steric hindrance may overcompensate the latter effect, especially facilitating the "back-biting" reaction. Moreover, the abstraction of the α-proton may cause chain transfer reactions.

Busfield and Methven[9] polymerized methyl acrylate using various sodium initiators in THF at −75 °C, but they reached only low monomer conversions and the polymers had broad molecular weight distributions. The nucleophilic-catalyzed group transfer polymerization (GTP) of *n*-butyl acrylate in THF also leads to broad molecular weight distributions, as reported by Bandermann et al.[10] Using GTP catalyzed by Lewis acids (e.g., ZnI_2), Hertler et al.[11] and Reetz et al.[12] obtained polymers with narrow molecular weight distributions in toluene. However, in some cases large amounts of the catalyst were needed (10% with respect to the monomer). Similarly, Dicker et al.[13] and Müller et al.[14,15] used smaller amounts of HgI_2 or HgI_2/trimethylsilyl iodide in toluene at room temperature, but all these reactions are limited to polymers with molecular weights below 20 000. Reetz et al.[16,17] introduced the metal-free polymerization of acrylates with tetraalkylammonium counterions in THF at room temperature, but it suffers from the same limits as GTP. Vlček et al.[18,19] used lithium *tert*-butoxide as an additive for the anionic polymerization in THF and in THF/toluene

† Part 5, cf. ref 8.

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mixed solvents, but a 10-fold excess of the additive with respect to the initiator had to be used to reach narrow molecular weight distributions. Teyssié et al.[20,21] obtained high yields and narrow molecular weight distributions with lithiated alkoxyalkoxides in toluene. Due to the extremely high rates of polymerization (half-life in the range of milliseconds), this reaction can only be controlled in a flow-tube reactor.[22] Yasuda et al.[23,24] demonstrated the living coordinative polymerization initiated by lanthanocenes, giving high molecular weight polymers with narrow molecular weight distributions. However, these initiators are very expensive and difficult to synthesize. All these results indicate that the living anionic polymerization of primary acrylates still presents a challenge to the synthetic polymer chemist.

Since there is a positive effect of aluminum alkyls on the kinetics and molecular weight distributions in the polymerization of methyl methacrylate in toluene, we investigated the effect of aluminum alkyls on the polymerization of acrylates. We first present our experiments on the polymerization of *n*-butyl acrylate in toluene and in toluene/Lewis base mixed solvents. Finally, we report some orienting experiments on the polymerization of *tert*-butyl acrylate.

Experimental Section

Reagents. Ethyl α-lithioisobutyrate (EiBLi) was prepared according to the method of Lochmann and Lím.[25] *tert*-Butyllithium (tBuLi) was purchased as 1.7 M solution in pentane (Aldrich), titrated, and used without further purification. Trimethylaluminum ($AlMe_3$), triethylaluminum ($AlEt_3$), and triisobutylaluminum ($AlBui_3$) were purchased as 25 wt % solutions in toluene (Aldrich) and were used as received. *n*-Butyl acrylate (nBuA, BASF AG) was fractionated from CaH_2 over a 1-m column filled with Sulzer packing at 45 mbar, stirred over CaH_2, degassed, and distilled in high vacuum. Toluene (BASF AG) was fractionated over a 1.5-m column, stirred twice over sodium/potassium alloy, degassed, and distilled in high vacuum. Methyl pivalate (MPiv, Aldrich) was stirred over CaH_2, degassed, and distilled in high vacuum. Decane (Aldrich) was stirred over sodium/potassium alloy, degassed, and distilled in high vacuum.

Kinetics. All experiments were carried out at −78 °C (unless otherwise stated) in a stirred tank reactor under nitrogen atmosphere. First, the initiator and the aluminum alkyl were stirred for 15 min in toluene at the later polymerization temperature. After adding the Lewis base (if applicable), the solution was stirred for a further 5 min and then the monomer was added. The polymerization was quenched with methanol/acetic acid (9:1 v/v) and the monomer conversion was determined with GC using decane as the internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, filtered, and freeze-dried.

GPC. GPC was performed using THF as an eluent at a flow rate of 1 mL/min. Detectors, 2 × JASCO−UVIDEC 100 III with variable wavelength and Bischoff RI detector 8110; column set, 2 × 60 cm^2, 5 μm PSS SDV gel, 100 Å; linear, 10^2−10^5 Å. The PnBuA standards used for calibration had been synthesized in our laboratory and characterized by MALDI-TOF MS and GPC/MALLS measurements.

MALDI-TOF MS. Spectra were recorded with a Bruker Reflex mass spectrometer which is equipped with a nitrogen laser source delivering 3-ns pulses at λ = 337 nm. 1,8,9-trihydroxyanthracene was used as a matrix and potassium trifluoroacetate as cationization agent.

Results and Discussion

Effect of aluminum alkyls: First we used *tert*-butyllithium (tBuLi) as initiator for the anionic polymerization of *n*-butyl acrylate (nBuA) in the presence of aluminum alkyls ($AlMe_3$, $AlEt_3$, and $AlBui_3$) at −78 °C.

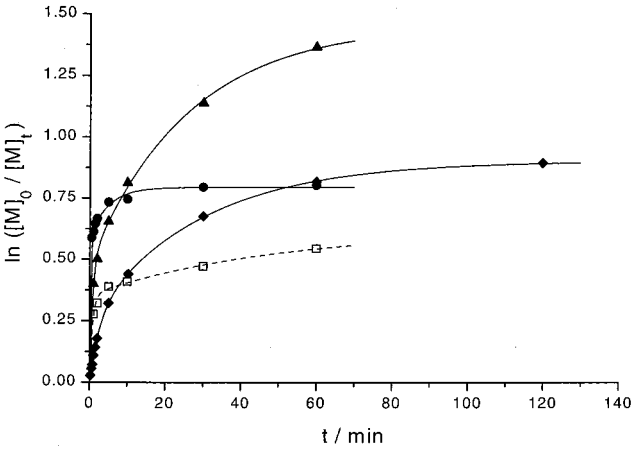


Figure 1. First-order time-conversion plots of the anionic polymerization of nBuA in toluene at −78 °C in the absence and in the presence of aluminum alkyls, AlR_3. $[EiBLi]_0 = 4.6 \times 10^{-3}$ mol/L, $[AlR_3] = 14.0 \times 10^{-3}$ mol/L, $[nBuA]_0 = 0.230$ mol/L. □ without AlR_3, ▲ $AlMe_3$, ◆ $AlEt_3$, ● $AlBui_3$.

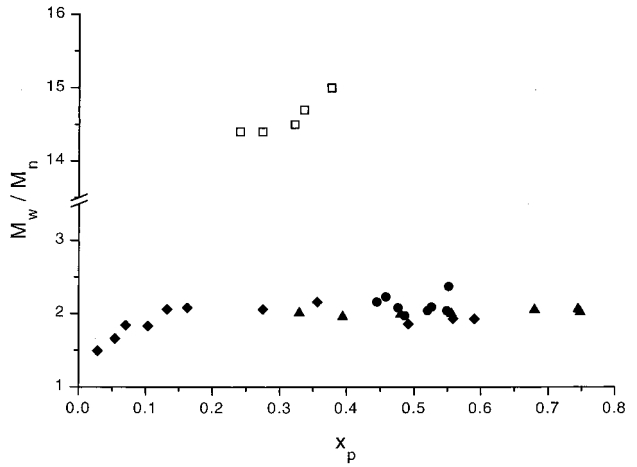


Figure 2. Plot of the polydispersity index, M_w/M_n, vs monomer conversion, x_p, for the polymerizations described in Figure 1. □ without AlR_3, ▲ $AlMe_3$, ◆ $AlEt_3$, ● $AlBui_3$.

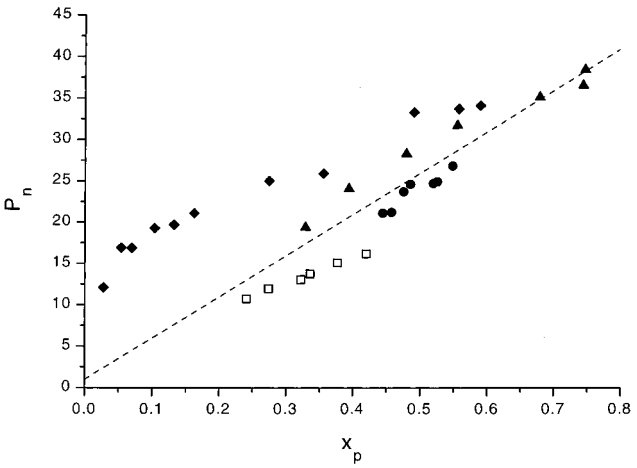


Figure 3. Plot of the number-average degree of polymerization, P_n, vs monomer conversion, x_p, for the polymerizations described in Figure 1; (- - -) calculated $P_n = x_p\,[nBuA]_0/[EiBLi]_0$.

The first-order time-conversion plots are curved and the monomer conversion is incomplete which indicates the existence of some side reactions. The MALDI-TOF mass spectra of the isolated polymers show three series of polymer chains with a repeat unit of 128 Da (=nBuA) and different residual masses. Apart from the signals

Table 1. Polymerization of *n*-Butyl Acrylate with EiBLi/AlR_3 in Toluene and in Toluene/MPiv 2.6:1 v/v at −78 °C[a]

AlR_3	solvent	k_{app}[b]/10^{-2}·s^{-1}	t_{max}[c]/min	x_p[d] at t_{max}	M_n[e]	M_w/M_n[f]	f[g]
none	toluene	0.80	60	0.42	2200	14.7	1.33
$AlMe_3$	toluene	1.12	120	0.75	4800	2.1	0.97
$AlEt_3$	toluene	0.20	60	0.56	4400	1.9	0.74
$AlBui_3$	toluene	6.49	30	0.55	3600	2.0	1.08
$AlMe_3$	toluene/MPiv	(0.06)[h]	30	0.73	15 300	1.4	0.32
$AlEt_3$	toluene/MPiv	1.64	5	1.00	17 600	1.5	0.38
$AlBui_3$	toluene/MPiv	(0.80)[h]	5	1.00	17 500	1.7	0.39

[a] For reaction conditions see Figure 5. [b] k_{app}: apparent rate constant of propagation (=slope of first-order time-conversion plot). [c] t_{max}: longest reaction time observed. [d] x_p: monomer conversion. [e] $P_n = (M_n - M_{EiBH})/M_{nBuA}$. [f] $f = P_n^{calc}/P_n^{exp}$. [g] f: initiator efficiency. [h] Only one data point in the time-conversion plot for the determination of k_{app}.

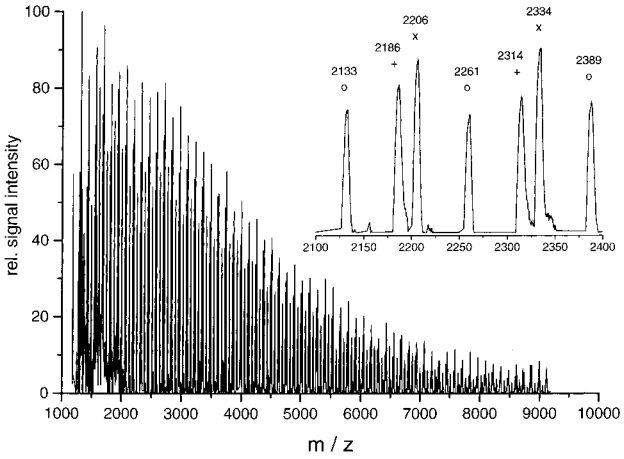


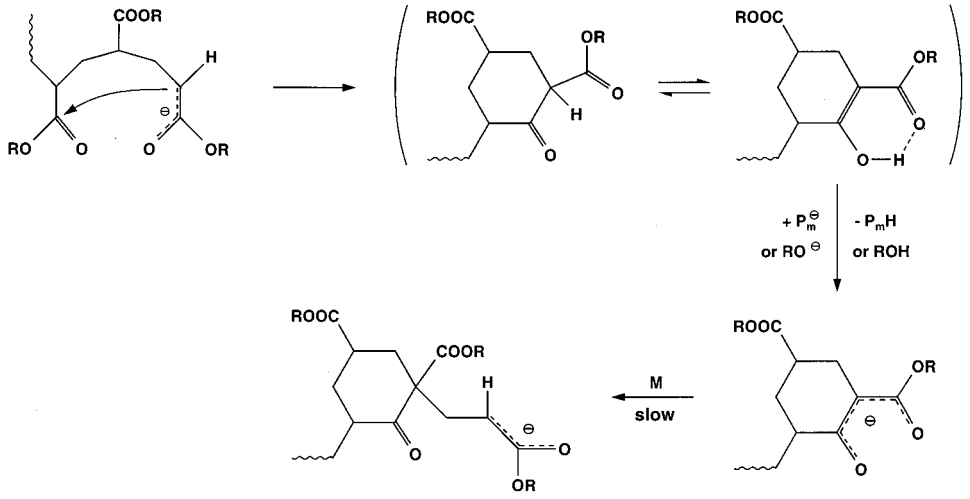
Figure 4. MALDI-TOF mass spectrum of a PnBuA obtained with EiBLi/$AlMe_3$ in toluene at −78 °C (cf. Figure 1). The masses correspond to potassium adducts [M−K^+]. Repeat unit of all series: 128.2 Da, x, linear chain (residual mass, 155 Da = m(EiB) + m(H) + m(K^+)); +, chain with two β-ketoester units (7 Da = m(EiB) − 2m(nBuO) − m(H) + m(K^+)); ○, chain with one β-ketoester unit (81 Da = m(EiB) −m(nBuO) + m(K^+)).

of the linear polymer chains (residual mass, 58 Da), those of vinyl ketone carrying (42 Da) and of cyclic β-ketoester-terminated polymer chains (112 Da) are found. The vinyl ketone units result from the addition of *tert*-butylvinyl ketone, which is formed *in situ* by the attack of *tert*-butyllithium onto the ester group of *n*-butyl acrylate,[26] and the β-ketoester units result from an intramolecular Claisen condensation (back-biting). These findings are corroborated by GPC analysis with UV detection at the absorption maxima of the ketone (λ = 285 nm)[26] and the enolized β-ketoester (λ = 260 nm).[27] The occurrence of both side reactions might explain the obtained broad molecular weight distributions (2 < M_w/M_n < 4). To suppress the formation of vinyl ketone in the initiation step, ethyl α-lithioisobutyrate (EiBLi) was used as the initiator for the further investigations.

Figure 1 shows the first-order time-conversion plots for the anionic polymerization of *n*-butyl acrylate using ethyl α-lithioisobutyrate as the initiator in the absence and in the presence of aluminum alkyls at −78 °C.

Without aluminum alkyls, the monomer conversion is incomplete (x_p < 0.45) and the molecular weight distributions are extremely broad (M_w/M_n > 14). This may be explained by a slow exchange between various aggregates of the ester enolate chain ends[28] and by termination reactions (e.g., back-biting). Upon the addition of aluminum alkyls, the maximum monomer conversion increases up to 75% and the molecular weight distributions of the polymers narrow drastically (1.8 < M_w/M_n < 2.5 (cf. Figure 2)). Similar to the polymerization of methyl methacrylate,[8] the first-order time-conversion plots are curved. This leads to the assumption that the formation of a coordinative polymer network might play a role during the polymerization of *n*-butyl acrylate, too. In fact, a gel is observed as a polymer film on the glass wall of the reaction vessel. This gelation, in addition to termination reactions (see below), could be responsible for the incomplete monomer conversions. The plots of the number-average degree of polymerization, P_n, versus monomer conversion, x_p (Figure 3) are linear except in the presence of $AlEt_3$. Thus, in general, transfer reactions are quite improbable. However, the addition of aluminum alkyls leads to a slight decrease of the initiator efficiency (see Table 1).

Scheme 1. Formation and Reinitiation of a Cyclic β-Ketoester-Terminated Polyacrylate Chain End



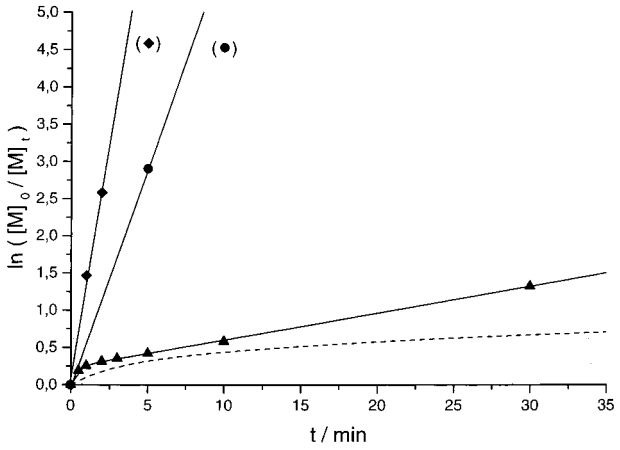


Figure 5. First-order time-conversion plots of the polymerization of nBuA with EiBLi/AlR_3 in toluene/MPiv 2.6:1 v/v at −78 °C. $[EiBLi]_0 = 4.6 \times 10^{-3}$ mol/L, $[AlR_3] = 14.0 \times 10^{-3}$ mol/L, $[nBuA]_0 = 0.234$ mol/L. ▲ $AlMe_3$, ◆ $AlEt_3$, ● $AlBui_3$. (- - -) Polymerization with EiBLi/$AlEt_3$ in toluene.

The MALDI-TOF mass spectra of the obtained polymers (Figure 4) show—apart from the linear and the cyclic terminated polymer chains—a further series of signals with a repeat unit of 128 Da (=nBuA). The β-ketoester end group formed in the back-biting reaction has a very acidic proton between two carbonyl groups which can be abstracted by the released lithium butoxide or by other living chain ends.[27] This could lead to a slow reinitiation and a further growth of the polymer chains (Scheme 1). These chains can then undergo a second back-biting reaction leading to the observed third series of signals in the mass spectra. However, polymer chains carrying three or more cyclic β-ketoester groups are not detected.

Effect of Lewis bases. To prevent the formation of a coordinative network, the addition of Lewis bases such as crown ethers or esters was shown to be effective in the polymerization of methyl methacrylate.[8] In fact, the precipitation of a gel is never observed in the presence of Lewis bases. Nevertheless, the addition of crown ethers does not support a controlled polymerization of *n*-butyl acrylate at −78 °C; the monomer conversion is still incomplete and the polymers have broad molecular weight distributions ($M_w/M_n > 3$). On the other hand, the control is much improved in the presence of methyl pivalate ([MPiv] = 2.1 mol/L, toluene/MPiv = 2.6:1 v/v) (i.e., quantitative monomer conversions and rather narrow molecular weight distributions ($M_w/M_n \approx 1.5$) are obtained). Compared to the polymerization in pure toluene, the rate of propagation increases dramatically (cf. Figure 5), and the molecular weight distributions of the polymers are narrower (cf. Table 1 and Figure 6). The first-order time-conversion plots are usually linear when using triethyl- or triisobutylaluminum as an additive, whereas it is strongly kinked with trimethylaluminum. In any case, the GPC traces a lack of any UV signal at the absorption maximum of the β-ketoester ($\lambda = 260$ nm), and the plots of the number-average degree of polymerization, P_n, versus monomer conversion, x_p, are linear. Since neither termination nor transfer reactions do occur, the polymerization has living character. However, large amounts of methyl pivalate are needed, [MPiv] > 2 mol/L, to preserve the livingness and the control of the reaction. The initiator efficiency is rather low (f < 40%, cf. Table 1) which possibly results from an attack of the initiator onto the ester group of methyl pivalate.

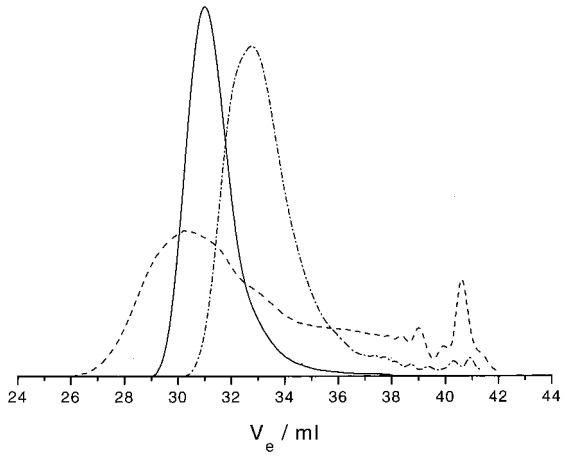


Figure 6. GPC eluograms of PnBuAs obtained with EiBLi in toluene (- - -), EiBLi/$AlEt_3$ in toluene (- · -), and EiBLi/$AlEt_3$ in toluene/MPiv 2.6:1 v/v (—); cf. Table 1.

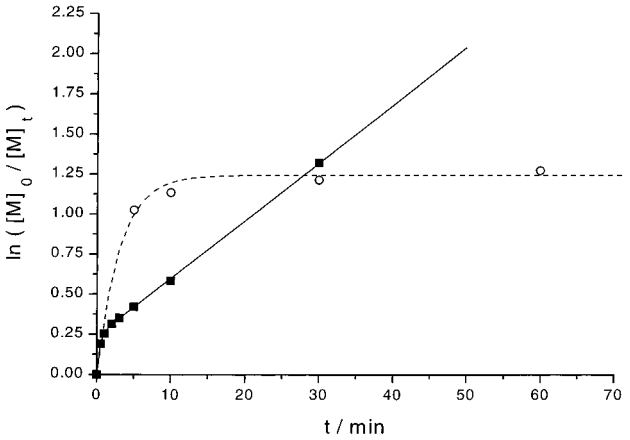


Figure 7. First-order time-conversion plots of the polymerization of nBuA with EiBLi/$AlMe_3$ in toluene/MPiv 2.6:1 v/v at −78 °C (■) and at −55 °C (○). $[EiBLi]_0 = 4.6 \times 10^{-3}$ mol/L, $[AlMe_3] = 14.0 \times 10^{-3}$ mol/L, $[nBuA]_0 = 0.240$ mol/L.

Table 2. Effect of Temperature on the Polymerization of nBuA in the Presence of $AlMe_3$ in Toluene/MPiv 2.6:1 v/v[a]

T/°C	t_{max}/min	x_p at t_{max}	M_n	M_w/M_n	f
−78	30	0.73	15 300	1.4	0.32
−55	5	0.64	9800[b]	1.6[b]	0.45[b]

[a] For reaction conditions see Figure 7. [b] Only soluble fraction (gelation observed).

Temperature Dependence. The polymerization of *n*-butyl acrylate in toluene/methyl pivalate 2.6:1 v/v mixed solvent loses its living and controlled character when the reaction temperature is increased. Already at −55 °C, the first-order time-conversion plot is strongly curved (Figure 7) and termination reactions occur, as indicated by GPC analysis with UV detection at $\lambda = 260$ nm. It appears that both termination and gelation of the living chain ends cannot be suppressed at higher temperatures, even at high methyl pivalate concentrations. As expected, the molecular weight distribution broadens with increasing temperature ($M_w/M_n > 1.5$, Table 2).

Polymerization of *tert*-Butyl Acrylate (tBuA). In the absence of aluminum alkyls, the polymerization of *tert*-butyl acrylate with ethyl α-lithioisobutyrate in pure toluene at −78 °C leads to incomplete monomer conversion ($x_p^{max} \approx 0.3$) and the polymer has an extremely broad molecular weight distribution ($M_w/M_n > 60$).

Table 3. Polymerization of tBuA with EiBLi and EiBLi/$AlMe_3$ in Toluene and in Toluene/Methyl Pivalate 2.6:1 v/v[a]

AlR_3	solvent	k_{app}/ 10^{-2}·s^{-1}	t_{max}/ min	x_p at t_{max}	M_n	M_w/ M_n	f
none	toluene	0.04	30	0.31	8200	67	0.78
$AlMe_3$	toluene	8.8	1	1	93 000	1.6	0.33
$AlMe_3$	toluene/MPiv	3.6	2	1	192 000	1.9	0.16

[a] $[EiBLi]_0 = 0.98 \times 10^{-3}$ mol/L, $[AlMe_3] = 14.0 \times 10^{-3}$ mol/L, $[tBuA]_0 = 0.234$ mol/L.

Upon the addition of trimethylaluminum, we obtain quantitative monomer conversion and—compared to the polymerization of *n*-butyl acrylate—the polymerization is considerably faster with a half-life below 1 min. The polymer has a fairly broad molecular weight distribution ($M_w/M_n \approx 1.6$). In toluene/methyl pivalate 2.6:1 v/v mixed solvent, full monomer conversion is reached within 2 min, but the molecular weight distributions are even broader ($M_w/M_n \approx 1.9$, cf. Table 3). It appears that the Lewis base has no pronounced effect on kinetics and on molecular weight distributions, possibly due to the steric hindrance of the tertiary ester groups.

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