Mechanism of Anionic Polymerization of (Meth)acrylates in the Presence of Aluminum Alkyls. 5. Effect of Lewis Bases on Kinetics and Molecular Weight Distributions†

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ABSTRACT: The addition of esters like methyl pivalate or diisooctyl phthalate prevents the formation of the coordinative network of living polymer chains which is usually formed during the anionic polymerization of methyl methacrylate in the presence of aluminum alkyls in toluene. At a sufficiently high ester concentration, first-order time-conversion plots and polymers with narrow molecular weight distributions are obtained. The polymerization has living character in the temperature range from −78 to 0 °C. Similar results are obtained with multidentate ethers, especially crown ethers. Strong monodentate Lewis bases like tetrahydrofuran or *N*-methylpyrrolidine do also prevent the network formation, but the monomer conversion is not quantitative and the molecular weight distributions are broadened.

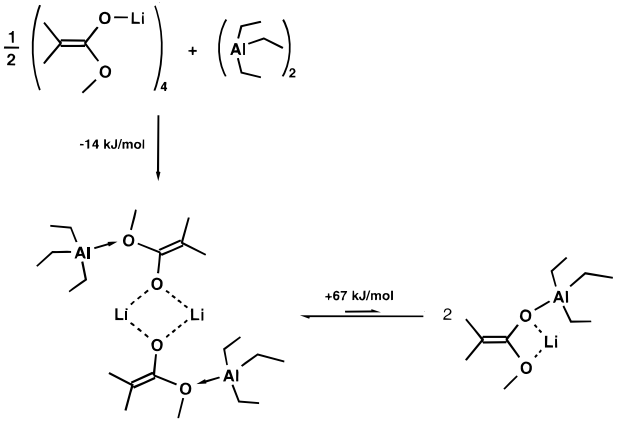
Introduction

Since 1978, several authors have described the anionic polymerization of methacrylates in the presence of aluminum alkyls in toluene.[1−3] The formation of highly syndiotactic polymers with narrow molecular weight distributions was reported and various mechanisms were proposed for the effect of the aluminum alkyl. However, we have found that the anionic polymerization of methyl methacrylate at −78 °C deviates significantly from conventional first-order kinetics. Generally, the first-order time-conversion plots show a kink at low monomer conversions; i.e., the rate of polymerization decreases strongly in the early stage of the reaction and is constant for higher monomer conversions.[4−6]

At the same time when the kink in a time-conversion plot arises, a gel is observed which preferably precipitates at temperatures above −65 °C from the reaction solution.[6] It was found that this gel is a coordinative polymer network in which the living chain ends are coordinated to in-chain ester carbonyl groups. Since in the gel the actual concentration of enolate chain ends is much higher than that in solution, the association equilibrium (see below) is shifted toward the aggregated chain ends. Consequently, the apparent rate constant of propagation, k_{app}, will decrease until the thermodynamic sol−gel equilibrium state is reached. With this model we were able to explain the kinetics of the polymerization reactions as well as the usually obtained rather broad molecular weight distributions of the polymers.[7]

Ab initio quantum chemical calculations[8,9] on the methyl α-lithioisobutyrate−triethylaluminum complex as the model compound of the propagating species provide the structures in Scheme 1 which are consistent with ^{13}C NMR studies.[10] The favored species is a dimeric associate of the lithiated esterenolate with the aluminum alkyl coordinated to the oxygen atom of the ester alcohol, but the propagating species is supposed to be a unimeric lithiated esterenolate−aluminum alkyl "ate" complex.

Scheme 1. Interaction of Ester Enolates with Aluminum Alkyls



Due to an electron deficiency at the lithium atom, the living chain end coordinates competitively to any Lewis base present in the reaction solution, i.e., to the ester carbonyl groups of both polymer and monomer.[10] Since the concentration of the monomer decreases and that of the in-chain ester carbonyl groups increases during polymerization, the sol−gel equilibrium will shift to the gel side with increasing conversion. This happens already at low monomer conversions right at the kink in the time-conversion plot which indicates that the living end group coordinates preferably to the in-chain ester carbonyl groups.

Consequently, the addition of nonpolymerizing Lewis bases should prevent the network formation up to high monomer conversions. It appears that any shift of the sol−gel equilibrium depends strongly on the concentration and the strength of the Lewis base. However, with a suitable Lewis base at a sufficiently high concentration, we should obtain linear time-conversion plots as well as narrow molecular weight distributions. This

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basic concept is corroborated by the results of Teyssié et al.[11] who used pyridine/toluene mixed solvents for the anionic polymerization of methyl methacrylate with 1,1-diphenylhexyllithium/triethylaluminum at 0 °C. Although they usually obtained polymer in quantitative yields, the polymers had only narrow molecular weight distributions at very high pyridine concentrations (pyridine/toluene > 2:1 v/v).

Methyl pivalate was supposed to be a very suitable Lewis base for kinetic investigations because it is the model compound of the polymer chain. However, its use requires initiators of lower nucleophilicity like ester enolates, e.g., ethyl α-lithioisobutyrate (EiBLi) or a living methacrylate oligomer tBu(MMA)$_n$Li, in order to prevent any attack onto the ester carbonyl group. In the present work, we describe the effect of methyl pivalate and of some other Lewis bases on the kinetics of the polymerization of methyl methacrylate in the presence of aluminum alkyls and on the molecular weight distributions and tacticities of the resulting polymers.

Experimental Section

Reagents. Ethyl α-lithioisobutyrate (EiBLi) was prepared according to the method of Lochmann.[12] *tert*-Butyllithium (tBuLi, 1.7 M in pentane, Aldrich) was double-titrated according to the method of Gilman[13] (<5% impurities) and used without further purification. Triethylaluminum ($AlEt_3$, 25 wt % in toluene, Aldrich) was used as received. Methyl methacrylate (MMA, Röhm GmbH) 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) and tetrahydrofuran (THF, BASF AG) were fractionated over a 1.5 m column, stirred twice over Na/K alloy, degassed, and distilled in high vacuum. Methyl pivalate (MPiv, Aldrich), methyl benzoate (MBz, Aldrich), 1,2-dimethoxyethane (DME, Aldrich), 2,5,8,11-tetraoxadodecane (triglyme, Aldrich), 1,4,7,10-tetraoxacyclododecane (12-crown-4, Aldrich), and *N*-methylpyrrolidine (NMP, Aldrich) were stirred over CaH_2, degassed, and distilled in high vacuum. Diisooctyl phthalate (DOP, BASF) was purified by passing over Al_2O_3. Octane (Aldrich) as internal standard for GC was stirred over Na/K alloy, degassed and distilled in high vacuum.

Kinetics. All experiments were carried out in a stirred tank reactor under nitrogen atmosphere. The esterenolate initiators were prepared by adding (1) EiBLi to $AlEt_3$ or (2) 2 equiv of MMA to tBuLi/$AlEt_3$ in toluene at the polymerization temperature. After the Lewis base was added, the solution was stirred for 15 min and then monomer was added. The polymerization was quenched with methanol, and monomer conversion was determined with gas chromatography (GC) using octane as internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, filtered and freeze-dried.

Gel Permeation Chromatography (GPC). GPC was performed using THF as the 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, 5μ PSS SDV gel, 100 Å, and linear, 10^2−10^5 Å. PMMA standards were used for calibration.

NMR. ^{1}H NMR spectra of the polymers were recorded with a Bruker AM-400 spectrometer at room temperature in $CDCl_3$. The α-CH_3 signals were used for the determination of triad tacticities.

Results and Discussion

Effect of Methyl Pivalate at −78 °C. Figure 1 shows the first-order time-conversion plots obtained for the anionic polymerizations of methyl methacrylate (MMA) with ethyl α-lithioisobutyrate/triethylaluminum (EiBLi/$AlEt_3$) and different amounts of methyl pivalate (MPiv) at −78 °C.

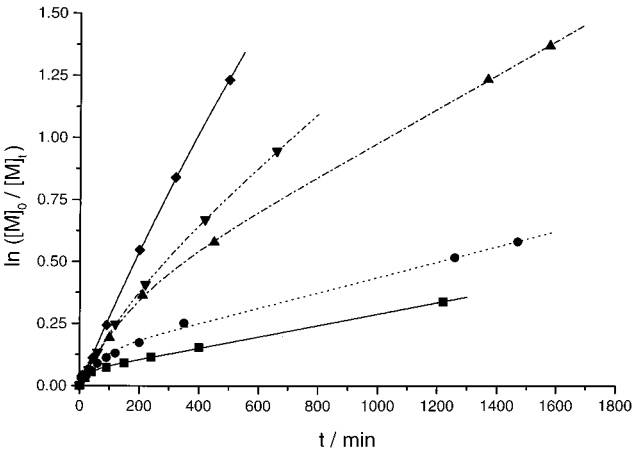


Figure 1. First-order time-conversion plots of the anionic polymerization of MMA with EiBLi/$AlEt_3$ in toluene/MPiv mixed solvents at −78 °C. $[EiBLi]_0 = 4.6 \times 10^{-3}$ mol/L, $[AlEt_3] = 1.5 \times 10^{-2}$ mol/L, $[MMA]_0 = 0.233$ mol/L. [MPiv] = 0 (■), 0.03 (●), 0.63 (▲), 1.81 (▼), 3.55 mol/L (◆).

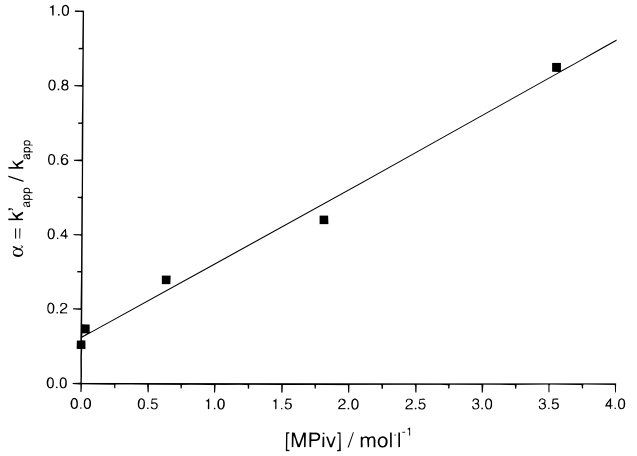


Figure 2. Dependence of the fraction of active polymer chains, α (calculated according to eq 1) on the concentration of methyl pivalate, [MPiv]. For reaction conditions see Figure 1.

With increasing concentration of methyl pivalate the plots approach linearity. Assuming that the reactivity of the chain ends in the network can be neglected, the fraction of active polymer chains in solution, α, can be calculated for each ester concentration from the initial and the final slope of any first-order time-conversion plot, k_{app} and k'_{app}.[7] After the thermodynamic sol−gel equilibrium state has been reached, the value of α is given as

$$\alpha = \frac{[P^*]_{sol}}{[P^*]_{total}} = \frac{k'_{app}}{k_{app}} \qquad (1)$$

In agreement with the above considerations, the value of α is linearly proportional to the concentration of methyl pivalate and the reaction follows external first-order kinetics in its second stage (Figure 2). Nevertheless, even at the highest ester concentration investigated, the polymer network is not quantitatively prevented (α = 0.85 at $[MPiv]/[MMA]_0 \approx 15$, cf. Table 1). This finding is supposed to result from the earlier described competitive coordination of the living chain ends to the ester carbonyl groups of the polymer and methyl pivalate. Due to a chelate effect, the polymer ester groups seem to be more efficient in binding to the end group. This is confirmed by experiments with the

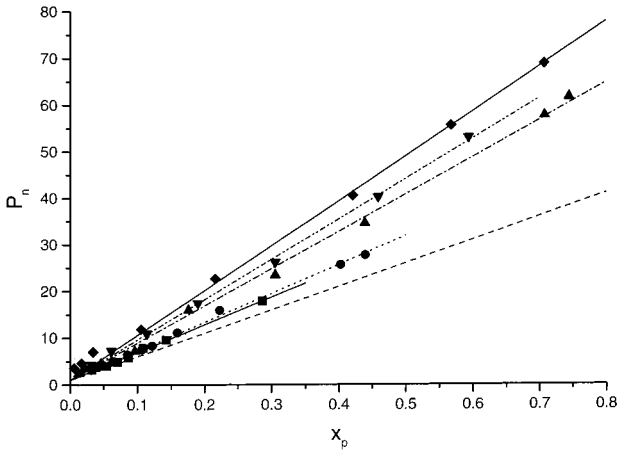


Figure 3. Plot of the number-average degree of polymerization, P_n, vs monomer conversion, x_p, for the polymerizations described in Figure 1. [MPiv] = 0 (■), 0.03 (●), 0.63 (▲), 1.81 (▼), 3.55 mol/L (◆). (- - -) Theoretical $P_n = [M]_0 x_p/[I]_0$.

Table 1. Effect of Methyl Pivalate (MPiv) on the Polymerization of MMA with EiBLi/AlEt$_3$ in Toluene at −78 °C[a]

[MPiv]/ mol·L^{-1}	$10^2 k_p$/ L·mol^{-1}·s^{-1}	$10^2 k'_p$/ L·mol^{-1}·s^{-1}	α	t_{max}/ min	x_p at t_{max}	P_n	P_w/P_n	f
0	0.94	0.10	0.10	1220	0.29	18	1.58	0.84
0.03	0.96	0.14	0.15	1470	0.44	28	1.36	0.81
0.63	1.30	0.36	0.28	1580	0.75	62	1.16	0.68
1.81	1.47	0.65	0.44	660	0.59	53	1.10	0.58
3.55	1.76	1.50	0.85	500	0.71	69	1.10	0.52

[a] For reaction conditions see Figure 1. k_p, rate constant of propagation; k'_p, rate constant of propagation for the second stage of polymerization; α, fraction of active polymer chains; x_p, monomer conversion; P_n, number-average degree of polymerization; P_w/P_n, polydispersity index; f, initiator efficiency.

diester diisooctyl phthalate where much lower concentrations of the ester are needed to reach narrow molecular weight distributions (see Table 3).

In all cases we obtain linear plots of the number-average degree of polymerization, P_n, vs monomer conversion, x_p (Figure 3). The initiator efficiencies decrease with increasing concentration of methyl pivalate (Table 1) possibly due to an attack of the initiator to the ester carbonyl group during the 15 min premixing time before monomer addition (see Experimental Section). The GPC traces lack a UV signal at $\lambda = 300$ nm which is typical of cyclic β-ketoesters resulting from an intramolecular Claisen condensation ("back-biting"). All these results suggest that the polymerization is free of any termination and transfer reaction under the given conditions; i.e., it has living character.

In the absence of methyl pivalate or at the lowest concentration investigated ([MPiv] = 0.03 mol/L) the polydispersity index, P_w/P_n, increases with monomer conversion resulting in fairly broad molecular weight distributions. At higher ester concentrations, the molecular weight distribution of the polymer narrows with increasing monomer conversion (Figure 4 and Table 1) as expected for a living process with moderately fast exchange between species of different reactivity.[14] Obviously, unimodal and narrow molecular weight distributions are obtained even when the polymerization does not follow first-order kinetics and the fraction of active chains is less than unity.

Reaction Orders. At [MPiv] = 3.55 mol/L (corresponding to a toluene/methyl pivalate 2:1 v/v mixed solvent), the effect of the polymer network on kinetics is negligible and we obtain linear first-order time-

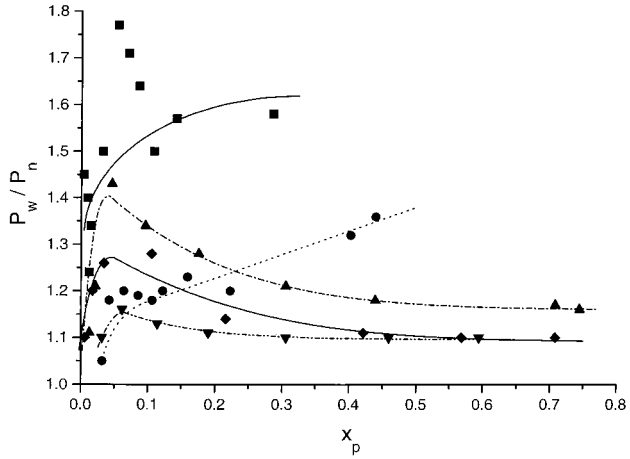


Figure 4. Plot of the polydispersity index, P_w/P_n, vs monomer conversion, x_p, for the polymerizations described in Figure 1. [MPiv] = 0 (■), 0.03 (●), 0.63 (▲), 1.81 (▼), 3.55 mol/l (◆).

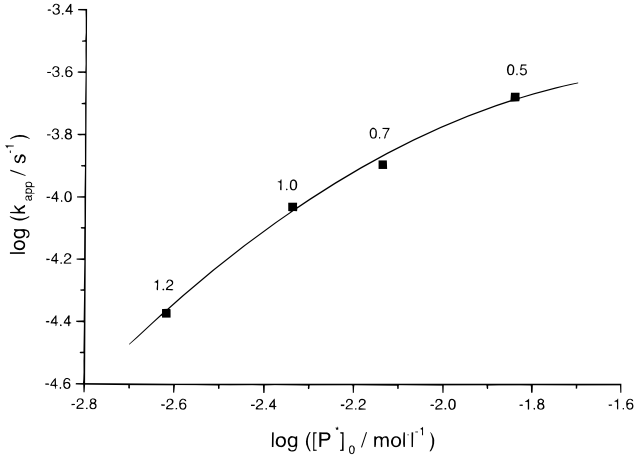


Figure 5. Determination of the reaction order with respect to the concentration of active centers, $[P^*]_0$, for the anionic polymerization of MMA with EiBLi/AlEt$_3$ in toluene/MPiv 3:1 v/v at −78 °C. $[EiBLi]_0 = (4.63-14.9) \times 10^{-3}$ mol/L, $[AlEt_3] = 15.0 \times 10^{-3}$ mol/L, $[MMA]_0 = 0.233$ mol/L, [MPiv] = 3.55 mol/L.

conversion plots at various concentrations of active centers and monomer. The reaction order with respect to the concentration of active centers, $[P^*]_0$, varies from 0.5 to unity (Figure 5)—this is consistent with the existence of an association equilibrium between unimeric and dimeric active species (see Scheme 1) where the unimeric species is the major monomer-adding species. Moreover, the polymerization follows first-order kinetics with respect to monomer concentration and zeroth-order kinetics with respect to aluminum alkyl concentration.[9]

Ab initio quantum-chemical calculations—based on density functional theory—on the methyl α-lithioisobutyrate−triethylaluminum complex in the presence of methyl pivalate corroborate an equilibrium between a unimeric species and a dimeric aggregate of enolate chain ends (Scheme 2).[8] The calculations indicate that the tendency for the dimer formation is strongly reduced upon the addition of methyl pivalate.

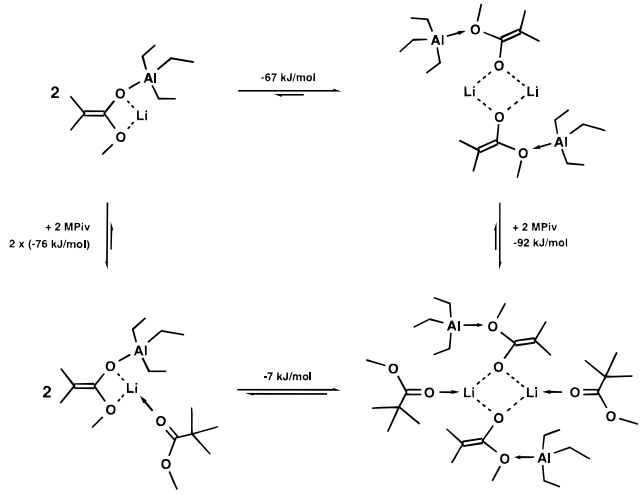
Temperature Dependence of Rate Constants. As reported recently,[6,7] the polymer network precipitates as a gel from pure toluene solution at temperatures above −65 °C. This results in curved first-order time-conversion plots and broad molecular weight distributions (Table 2). When polymerizing in a toluene/

Table 2. Effect of Temperature on the Polymerization of MMA in the Presence of $AlEt_3$ in Toluene and Toluene/MPiv Mixed Solvent[a]

solvent	initiator[b]	T/°C	$10^2 k_p$/ L·mol^{-1}·s^{-1}	t_{max}/ min	x_p at t_{max}	P_n	P_w/P_n	f	tacticity mm	tacticity rr	tacticity r	tacticity ρ
toluene	a	−78	2.8	1440	0.32	16	1.69	0.85	0.03	0.78	0.875	1.15
	a	−60[c]	(8.9)	875	0.64	49	2.1	0.70	0.04	0.70	0.830	1.09
	a	−40[c]	(16.3)	705	0.84	62	3.2	0.66	0.05	0.69	0.820	1.14
	a	−19[c]	(15.0)	520	0.77	48	3.7	0.66	0.08	0.60	0.760	1.14
	a	0[c]	(10.3)	370	0.37	24	2.3	0.78	0.12	0.52	0.700	1.17
toluene/MPiv	b	−78	(1.5)	660	0.59	53	1.10	0.58	0.02	0.81	0.895	1.11
	c	−78	(1.4)	1560	0.91	63	1.08	0.76	0.02	0.83	0.905	1.15
	c	−51	2.3	505	0.82	78	1.14	0.59	0.03	0.79	0.880	1.17
	c	−23	8.0	400	1	125	1.11	0.44	0.04	0.72	0.640	1.12
	c	0	18.9	240	1	119	1.26	0.45	0.05	0.61	0.780	1.01
	c	+22	(22.2)	1020	0.73	44	3.0	0.59	0.11	0.54	0.715	1.16

[a] For reaction conditions see Figure 6. k_p: rate constant of propagation, x_p: monomer conversion, P_n: number-average degree of polymerization, P_w/P_n: polydispersity index, f: initiator efficiency, ρ: persistence ratio. [b] a, tBuLi; b, EiBLi; c, tBu(MMA)$_n$Li. [c] Hetergeneous reaction solution (precipitation of the polymer network).

Scheme 2. Interaction of Methyl Pivalate (MPiv) with Ester Enolate−Aluminum Alkyl Complexes



methyl pivalate 3:1 v/v mixed solvent ([MPiv] ≈ 2 mol/L) instead, we do not observe any gel formation and—in the temperature range from −50 to 0 °C—the polymerization follows conventional first-order kinetics (Figure 6).

Moreover, the plots of the number-average degree of polymerization versus monomer conversion are linear and the molecular weight distributions are unimodal and narrow (Table 2). Independent of the temperature, the initiator efficiency of the *in situ* prepared living methacrylate oligomer tBu(MMA)$_n$Li/$AlEt_3$ is approximately 60% (calculated with respect to $[tBuLi]_0$). At room temperature, the polymerization does not reach full monomer conversion and the molecular weight distributions are broad indicating the occurrence of side reactions.

However, the Arrhenius plot of the propagation rate constant, k_p, for the polymerizations in toluene/methyl pivalate 3:1 v/v is curved regarding the whole temperature range between −78 °C and room temperature (Figure 7). Therefore—and due to the temperature dependence of the association equilibrium—the values for k_p and the Arrhenius parameters have to be considered as apparent values.

When calculating the activation parameters from the linear part of the Arrhenius plot between −50 and 0 °C, we obtain

$$E_a = (20.9 \pm 0.2)\ \text{kJ/mol},\ \log A = 3.3 \pm 0.1$$

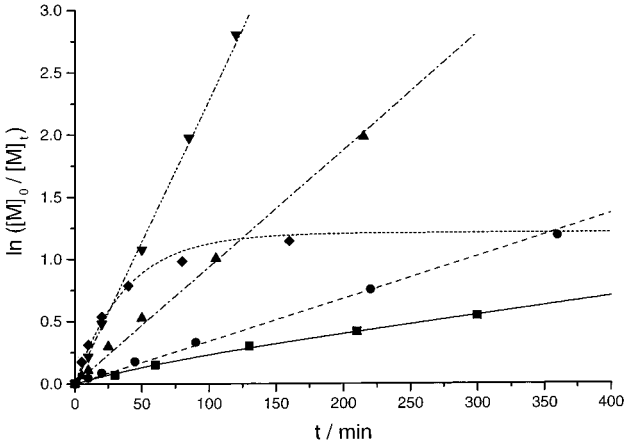


Figure 6. First-order time-conversion plots of the anionic polymerization of MMA with tBu(MMA)$_n$Li/$AlEt_3$ in toluene/MPiv 3:1 v/v at different temperatures. $[tBuLi]_0 = 4.5 \times 10^{-3}$ mol/L, $[AlEt_3] = 1.5 \times 10^{-2}$ mol/L, $[MMA]_0 = 0.233$ mol/L, [MPiv] = 2 mol/L. T = −78 °C (■), −51 °C (●), −23 °C (▲), 0 °C (▼), +22 °C (◆).

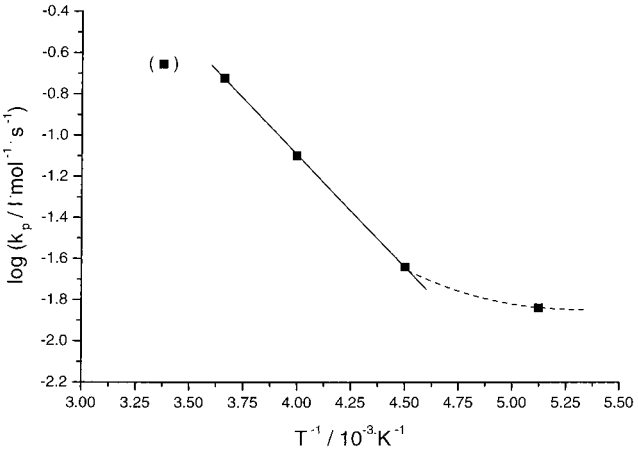


Figure 7. Arrhenius plot of the rate constant k_p for the anionic polymerization of MMA in the presence of $AlEt_3$ in toluene/MPiv 3:1 v/v mixed solvent. For reaction conditions see Figure 6.

The value for the activation energy, E_a, is comparable to that determined for anionic or group transfer polymerization of methyl methacrylate in tetrahydrofuran while that of the frequency exponent, log A, is extremely low.[6] This is another indication that the Arrhenius parameters are only apparent.

Tacticity of Polymers. The polymerization of methyl methacrylate in the presence of aluminum alkyls in toluene leads to a syndiotactic polymer (rr ≈ 0.8 at −78

Table 3. Effect of Different Lewis Bases on the Polymerization of MMA with tBu(MMA)$_n$Li/AlEt$_3$ at 0 °C[a]

Lewis base[b]	[LB]/[M]$_0$	t_{max}/min	x_p at t_{max}	P_n	P_w/P_n	MWD	f	tacticity mm	tacticity rr	tacticity r	ρ
none	0	370	0.37	24	2.3	multimodal	0.78	0.12	0.52	0.700	1.17
NMP	8.6	250	0.34	14	2.4	multimodal	1.05				
THF	2.1	280	0.50	40	2.2	multimodal	0.55				
THF	8.7	275	0.64	82	1.68	bimodal	0.39				
DME[c]	0.35	60	0.96	189	1.71	bimodal	0.30	0.03	0.66	0.815	0.99
triglyme[c]	0.35	60	1	248	1.32	bimodal	0.22	0.02	0.70	0.840	0.96
12-crown-4	0.02[e]	5	1	86	1.12	unimodal	0.60	0.03	0.63	0.800	0.94
MPiv	2.1	170	0.94	84	2.1	multimodal	0.57				
MPiv	8.6	240	1	119	1.26	unimodal	0.45	0.05	0.61	0.780	1.01
MBz	8.6	120	1	91	1.22	unimodal	0.56	0.03	0.66	0.815	0.97
DOP[d]	0.63	15	1	153	1.19	unimodal	0.35	0.04	0.75	0.855	1.15

[a] For reaction conditions see Figure 8. LB, Lewis base; x_p, monomer conversion; P_n, number-average degree of polymerization; P_w/P_n, polydispersity index; f, initiator efficiency; ρ, persistence ratio. [b] NMP, *N*-methylpyrrolidine; THF, tetrahydrofuran; DME, 1,2-dimethoxyethane; triglyme, 2,5,8,11-tetraoxadodecane; 12-crown-4, 1,4,7,10-tetraoxacyclododecane; MBz, methyl benzoate; DOP, diisooctyl phthalate. [c] [tBuLi]$_0$ = 1.1 × 10^{-2} mol/L, [AlEt$_3$] = 4.2 × 10^{-2} mol/L, [MMA]$_0$ = 0.60 mol/L, [LB] = 0.21 mol/L, ethyl benzene. [d] [tBuLi]$_0$ = 0.9 × 10^{-2} mol/L, [AlEt$_3$] = 3.2 × 10^{-2} mol/L, [MMA]$_0$ = 0.48 mol/L, [LB] = 0.30 mol/L, ethyl benzene. [e] [LB]/[I]$_0$ = 1.

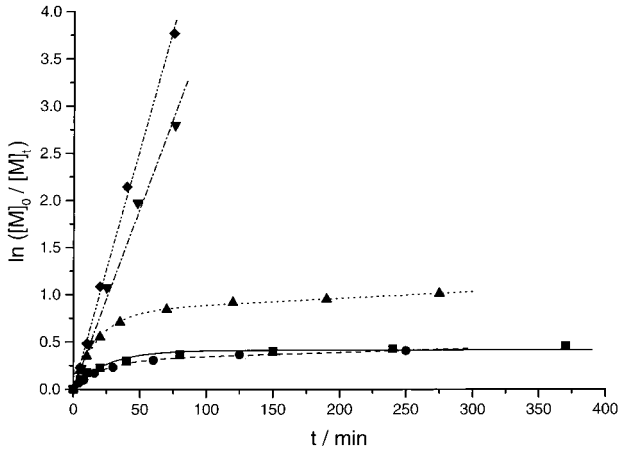


Figure 8. First-order time-conversion plots of the anionic polymerization of MMA with tBu(MMA)$_n$Li/AlEt$_3$ in different toluene/Lewis base (LB) mixed solvents at 0 °C. [tBuLi]$_0$ = 4.5 × 10^{-3} mol/L, [AlEt$_3$] = 1.5 × 10^{-2} mol/L, [MMA]$_0$ = 0.233 mol/L, [LB] = 2 mol/L. LB = none (■), *N*-methylpyrrolidine (●), tetrahydrofuran (▲), methyl pivalate (▼), methyl benzoate (◆).

°C). At temperatures above −60 °C the fraction of rr triads is approximately 10% higher when polymerizing in toluene/methyl pivalate 3:1 v/v (Table 2). A comparable tacticity was obtained with lithium in tetrahydrofuran which was attributed to the absence of monomer coordination to the lithium counterion in the transition state.[15] Thus, we can conclude that the effect of methyl pivalate on tacticity is the result of a better solvation of the lithium ion in toluene (see Scheme 2). Similar findings are obtained for other Lewis bases (see Table 3).

Effect of Other Lewis Bases. The formation of the polymer network should be prevented by any Lewis base which is strong enough to compete with the chelating polymer ester groups. Indeed, we do not observe any gel when using esters, ethers, or amines as cosolvents. However, only the polymerizations in toluene/ester mixed solvents follow first-order kinetics (Figure 8) resulting in polymers with unimodal and narrow molecular weight distributions (Table 3). With the considerably strong monodentate Lewis bases tetrahydrofuran and *N*-methylpyrrolidine, we find—under otherwise identical conditions—curved time-conversion plots and polymers having broad or even multimodal molecular weight distributions.

Since all polymers are free of cyclic β-ketoesters, we can exclude the occurrence of termination reactions via back-biting. In order to explain the experimental findings, we assume that the strong Lewis bases added in excess could remove the aluminum alkyl from the living chain end, leading to a conventional solvated lithium enolate chain end.

Orienting experiments show that multidentate ethers, especially crown ethers like 12-crown-4, at low concentrations lead to a specific complexation of the lithium ion and thus to a living polymerization as indicated by narrow molecular weight distributions (Table 3). However, broad and multimodal molecular weight distributions are obtained with 12-crown-4 in the absence of triethylaluminum.[16] Thus, both a Lewis acid and a Lewis base are necessary for a living polymerization of methyl methacrylate in toluene.

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