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Novel Initiating Systems for the Living Polymerization of Acrylates and Methacrylates

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Abstract: The polymerization of methyl methacrylate with lithiated initiators in the presence of aluminium alkyls in toluene has living character but it deviates from conventional first-order kinetics and 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 the in-chain ester carbonyl groups. Thus, the network formation can be prevented by adding Lewis bases like methyl pivalate which coordinate to the living chain ends instead of the polymer. Alternatively, one can introduce tetraalkylammonium salts aiming at an exchange of the lithium ion by a less electropositive cation. Both approaches lead to linear first-order time conversion plots for the polymerization of methacrylates and acrylates and to narrow molecular weight distributions, i.e., to a living and controlled polymerization. With these new initiating systems, various block and graft copolymers can be synthesized.

Introduction

Since 1978, several authors have described the anionic polymerization of methacrylates with lithiated initiators in the presence of aluminium alkyls in toluene.[1-3] The formation of highly syndiotactic polymers with narrow molecular weight distributions was reported. However, we have found that the anionic polymerization of methyl methacrylate (MMA) at –78°C deviates significantly from conventional first-order kinetics, the time-conversion plots showing a kink at low monomer conversions (Figure 1). Moreover, the polymers have fairly broad molecular weight distributions ($M_w/M_n > 1.5$, Figure 2).[4] Nevertheless, the number-average degree of polymerization, P_n, is a linear function of the monomer conversion (Figure 3) and the polymers

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are free of cyclic β-ketoesters as indicated by GPC (UV detection at λ = 300 nm) and MALDI-TOF mass spectrometry (Figure 4). These results suggest that neither transfer nor termination reactions do occur, i.e., the polymerization has living character.

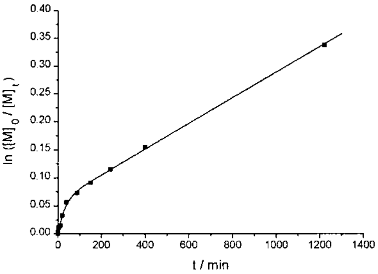


Figure 1: First-order time-conversion plot for the anionic polymerization of MMA in the presence of $AlEt_3$ at −78°C in toluene. $[EiBLi]_0 = 4.6 \cdot 10^{-3}$ mol/l, $[AlEt_3] = 15.0 \cdot 10^{-3}$ mol/l, $[MMA]_0 = 0.232$ mol/l.

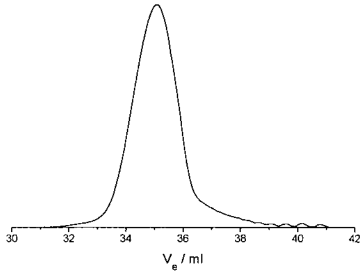


Figure 2: GPC eluogram of the PMMA obtained under the conditions described in Figure 1 after 1220 minutes (monomer conversion: 0.29), M_n = 1910, M_w/M_n = 1.58.

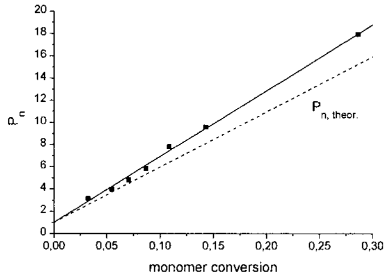


Figure 3: Plot of the number-average degree of polymerization, P_n, vs. monomer conversion for the polymerization described in Figure 1.

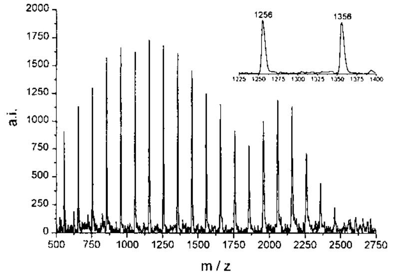


Figure 4: MALDI-TOF mass spectrum of the polymer in Figure 2. m/z = xx56: linear PMMA, signals of cyclic β-ketoesters expected at xx24.

At the same time when the kink in the time-conversion plot arises, a gel is observed which preferably precipitates from the reaction solution at temperatures above −65°C.[5] The ^{13}C CP/MAS solid state NMR spectrum of the unquenched gel (Figure 5) shows the signals of PMMA at δ = 19 (CH_3), 45 (CH_2), 53 (OCH_3), and 178 ppm (C=O). Additionally, a second signal of an ester carbonyl group arises at 184 ppm which can only result from its coordination to the living chain end. Thus, the gel must be regarded as a coordinative network of living polymer chains.[6]

Similarly, the ^{13}C NMR signal of the penultimate ester carbonyl group of di-*tert*-butyl α-lithioglutarate (lithiated dimer of *tert*-butyl methacrylate) shifts from 176 to 183 ppm when an equimolar amount of triethyl aluminium is added.[5] Since the ^{27}Al NMR signal of the complex at 160 ppm provides a four-fold coordination at the aluminium atom, the ester carbonyl group must then be coordinated to the lithium ion.[7] According to *ab initio* (DFT) quantum chemical calculations[8,9] on the methyl α-lithioisobutyrate–$AlEt_3$ complex, the preferred structure of the active species is a dimeric associate of a lithiated ester enolate carrying the aluminium alkyl at the ester alcohol (the non-associated propagating species is an 'ate'-complex in which the aluminium alkyl is bound to the ester carbonyl group[10]). All these results suggest that the coordinative polymer network has the structure given in Figure 6.

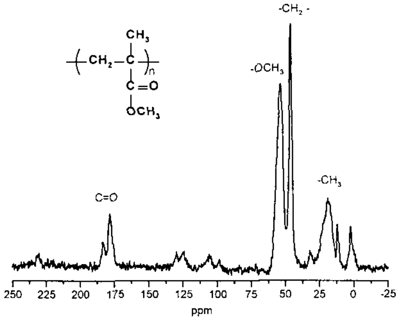


Figure 5: ^{13}C CP/MAS solid state NMR spectrum (75 MHz, room temperature) of the unquenched gel that precipitated from reaction solution.

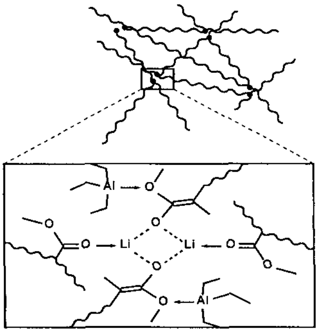


Figure 6: Structure of the coordinative network of living polymer chains.

Compared to solution, the local concentration of living polymer chains is higher in the gel, i.e., the gelated chains will be less dissociated and the rate of polymerization must decrease. It was found[7,8] that a slow equilibrium between the living polymer chains in solution and in gel will cause kinked first-order time-conversion plots and broad molecular weight distributions of the polymers.

In order to obtain a living and controlled polymerization, the formation of the coordinative network has to be suppressed by compensating the electron deficiency at the lithium ion of the living chain end. This should be achieved by (1) adding a Lewis base or by (2) replacing the lithium ion by a less electropositive ion. The results of both approaches are described in the present work.

Experimental Section

Reagents. *Initiator:* Ethyl α-lithioisobutyrate (EiBLi) was prepared according to the method of Lochmann and Lím.[11] *Aluminium alkyls:* Triethyl and triisobutyl aluminium were purchased from Aldrich as 25 wt.-% solutions in toluene and were used as received. *Lewis bases:* Methyl pivalate, methyl benzoate, diisooctyl phthalate, tetrahydrofuran, N-methyl pyrrolidine, and 1,4,7,10-tetraoxacyclododecane (12-crown-4) were purchased from Aldrich, stirred over CaH_2, degassed and distilled in high vacuum. *Salts:* Tetraalkylammonium salts (NR_4X) were purchased from Aldrich and freeze-dried from benzene. *Monomers:* Methyl methacrylate, *tert*-butyl methacrylate, *tert*-butyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate were obtained from BASF AG, fractionated at reduced pressure from CaH_2 over a 1 m column with Sulzer packing, stirred over CaH_2, degassed and distilled in high vacuum. ω-Methacryloyl functionalized PMMAs (macromonomers) were donated from Röhm GmbH and were used as received. *Solvent:* Toluene (BASF AG) was fractionated over a 1.5 m column, stirred twice over Na/K alloy, degassed and distilled in high vacuum. *Internal standards:* Octane and decane (Aldrich) were 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 initiator solution was prepared at the later polymerization temperature: (1) EiBLi was added to trialkyl aluminium in toluene and stirred for 5 minutes. After adding a Lewis base, the solution was stirred for 15 minutes. (2) EiBLi was added to a solution of tetraalkylammonium salt/trialkyl aluminium in toluene and stirred for 5 minutes. Then, the monomer was added. The polymerization was quenched with methanol or methanol/acetic acid (9:1 v/v) and the monomer conversion was determined with GC using octane or decane as internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, filtered and freeze-dried. **GPC.** GPC was performed using THF as eluent at a flow rate of 1.0 ml/min. Detectors: 2 x JASCO-UVIDEC 100 III with variable wavelength and Bischoff RI detector 8110, column set: 2 x 60cm, 5μ PSS SDV gel, 100Å and linear: 10^2-10^5Å. For the calibration of the columns PMMA and PtBMA standards were used, universal calibration was used for PtBuA ($\alpha = 0.716$, $K = 11.8 \cdot 10^{-3}$ cm^3/g)[12], PnBuA ($\alpha = 0.800$, $K = 3.30 \cdot 10^{-3}$ cm^3/g)[13], and PEHA ($\alpha = 0.815$, $K = 2.60 \cdot 10^{-3}$ cm^3/g)[14]. The molecular weights of copolymers were determined using GPC-viscosity (Viscotek H502B) on-line detection and universal calibration. **NMR.** ^1H and ^{13}C NMR spectra of the methacrylic polymers were recorded with a Bruker AM-400 spectrometer at room temperature in $CDCl_3$. The α-CH_3 (PMMA) and the C=O signals (PtBMA) were used for the determination of triad tacticities.

Results and Discussion

Polymerization in the presence of aluminium alkyls and Lewis bases. In order to suppress the formation of the coordinative polymer network during the anionic polymerization of methyl methacrylate (MMA) in the presence of aluminium alkyls in toluene at −78°C, the model compound of the PMMA chain, methyl pivalate (MPiv), was used as additive.[7,8] In fact, with increasing concentration of methyl pivalate, the deviations from first-order kinetics diminish (Figure 7) and the molecular weight distributions of the polymers narrow ($M_w/M_n < 1.2$, Figure 8). Simultaneously, the initiator efficiency decreases from 0.85 to 0.52 which might result from an attack of the initiator onto the ester carbonyl group of methyl pivalate. However, linear first-order time-conversion plots are only obtained at a very high ester concentration

([MPiv] = 3.55 mol/l, $[MPiv]/[MMA]_0 \approx 15$). In any case, the plot of the number-average degree of polymerization, P_n, vs. monomer conversion is linear, i.e., the polymerization is both living and controlled.

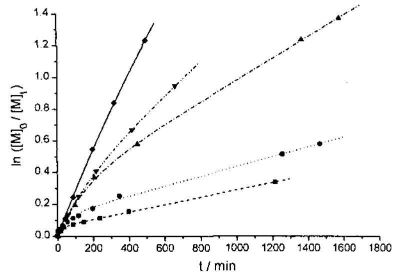


Figure 7: First-order time-conversion plots for the anionic polymerization of MMA with EiBLi/$AlEt_3$ in toluene/MPiv mixed solvents at –78°C. For reaction conditions see Figure 1/Table 1, [MPiv] = 0 (■), 0.03 (●), 0.63 (▲), 1.81 (▼), 3.55 mol/l (◆).

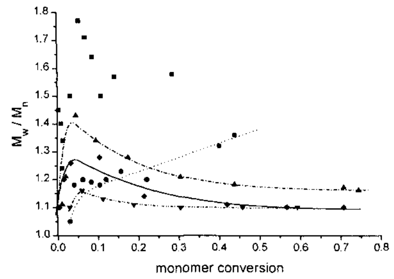


Figure 8: Plot of the polydispersity index, M_w/M_n, vs. monomer conversion for the polymerizations described in Figure 1.

For the polymerization of methyl methacrylate in a toluene/methyl pivalate 3:1 v/v mixed solvent, quantitative monomer conversion and syndiotactic polymers (rr > 0.6) with narrow molecular weight distributions ($M_w/M_n < 1.3$) are obtained up to 0°C. A precipitation of the polymer network is never observed. Similar results are found when using other esters that lack hydrogen atoms at the α-position, e.g., methyl benzoate or diisooctyl phthalate, or when using crown ethers, e.g., 12-crown-4. Usually, the initiator efficiency is in the range of 0.35 to 0.60. However, with monodentate ethers, e.g., tetrahydrofuran, or amines, e.g., N-methyl pyrrolidine, the monomer consumption is not complete and the molecular weight distributions are broad and multimodal (Table 1).[7,8]

Table 1: Effect of different Lewis bases (LB) on the polymerization of MMA with EiBLi/$AlEt_3$ in toluene at 0°C. $[EiBLi]_0 = 4.6\cdot10^{-3}$ mol/l, $[AlEt_3] = 15.0\cdot10^{-3}$ mol/l, $[MMA]_0 = 0.233$ mol/l. x_p: monomer conversion, M_n: number-average molecular weight, M_w/M_n: polydispersity index, f: initiator efficiency.

Lewis base (LB)	$[LB]/[M]_0$	t_{max} /min	x_p at t_{max}	M_n	M_w/M_n	f	Tacticity		
							mm	mr	rr
none	0	370	0.37	2500	2.3	0.78	0.12	0.36	0.52
methyl pivalate	8.6	240	1	12000	1.26	0.45	0.05	0.34	0.61
methyl benzoate	8.6	120	1	9200	1.22	0.56	0.03	0.31	0.66
diisooctyl phthalate	0.63	15	1	15400	1.19	0.35	0.04	0.21	0.75
12-crown-4	0.02	5	1	8700	1.12	0.60	0.03	0.34	0.63
tetrahydrofuran	8.7	275	0.64	8300	1.68	0.39	–	–	–
N-methyl pyrrolidine	8.6	250	0.34	1500	2.4	1.05	–	–	–

A controlled polymerization of n-butyl acrylate (nBuA) with full monomer conversions and fairly narrow molecular weight distributions (M_w/M_n = 1.4, Figure 9 and Table 2) takes place in a toluene/methyl pivalate 3:1 v/v mixed solvent at –78°C only. In contrast to the findings with methacrylates, however, 12-crown-4 does not support a controlled polymerization of acrylates (Table 2).[15]

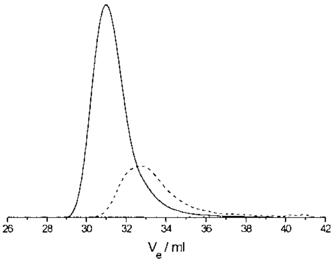


Figure 9: GPC eluograms of the PnBuAs obtained with EiBLi/AlEt$_3$ in toluene (--- M_n = 3400, M_w/M_n = 2.2) and in a toluene/methyl pivalate 3:1 v/v mixed solvent (— M_n = 17800, M_w/M_n = 1.4) at –78°C, cf. Table 2.

Table 2: Effect of different Lewis bases on the polymerization of nBuA with EiBLi/AlR$_3$ in toluene at –78°C. $[\text{EiBLi}]_0$ = $4.6 \cdot 10^{-3}$ mol/l, $[\text{AlR}_3]$ = $14.0 \cdot 10^{-3}$ mol/l, $[\text{nBuA}]_0$ = 0.235 mol/l. x_p: monomer conversion, M_n: number-average molecular weight, M_w/M_n: polydispersity index, f: initiator efficiency.

Aluminium alkyl	Lewis base (LB)	$[\text{LB}]/[\text{M}]_0$	t_{max}/min	x_p at t_{max}	M_n	M_w/M_n	f
None	None	0	30	0.38	2100	14.7	1.33
AlEt$_3$	None	0	10	0.36	3400	2.2	0.74
AlEt$_3$	Methyl pivalate	8.8	5	1	17800	1.4	0.34
AlBu$^i_3$	12-Crown-4	0.03	30	0.48	5700	3.0	0.57

Polymerization in the presence of aluminium alkyls and tetraalkylammonium salts. The second approach to prevent the network formation was to exchange the lithium ion of the living chain end by a larger and less electropositive cation, e.g., a tetraalkylammonium ion. In fact, no gelation occurs during the anionic polymerization of methyl methacrylate with EiBLi/AlEt$_3$ in the presence of tetrabutylammonium bromide ($[\text{NBu}_4\text{Br}]/[\text{EiBLi}]_0$ = 1.1) in toluene at 0°C. The resulting polymers are syndiotactic (rr = 0.66) and have narrow molecular weight distributions (M_w/M_n = 1.10). Whereas it takes hours in a toluene/methyl pivalate mixed solvent until full monomer conversion is reached (cf. Table 1), the reaction is now complete within less than five minutes. Since tetraalkylammonium halides, NR_4X, form toluene-soluble complexes with triethyl aluminium, $NR_4^+[AlEt_3X]^-$ and $NR_4^+[Al_2Et_6X]^-$,[16] the reaction solution is homogeneous.

For the polymerization of methyl methacrylate in the presence of NBu$_4$Br/AlEt$_3$ in toluene at –20°C, the first-order time-conversion plots (Figure 10) and the plots of the number-average degree of polymerization, P_n, vs. monomer conversion are linear, i.e., the reaction has living character. Due to the lower temperature, the syndiotacticity of the polymers further increases (rr = 0.73) and the molecular weight distributions narrow (M_w/M_n = 1.06, Figure 11). Similar results are obtained with other tetraalkylammonium halides, e.g., NMe_4Cl, NEt_4Cl, NEt_4Br, NBu_4Cl, and NBu_4I. Usually, the initiator efficiency is higher than 0.6.[7]

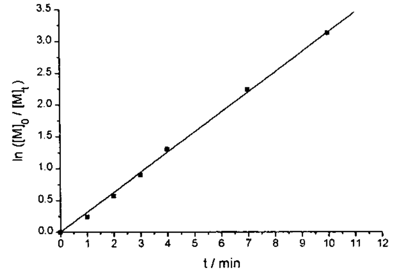


Figure 10: First-order time-conversion plot for the anionic polymerization of MMA with EiBLi in the presence of $AlEt_3$ and NBu_4Br in toluene at -20°C. $[EiBLi]_0 = 0.44 \cdot 10^{-3}$ mol/l, $[AlEt_3] = 15.0 \cdot 10^{-3}$ mol/l, $[NBu_4Br] = 6.8 \cdot 10^{-3}$ mol/l, $[MMA]_0 = 0.233$ mol/l.

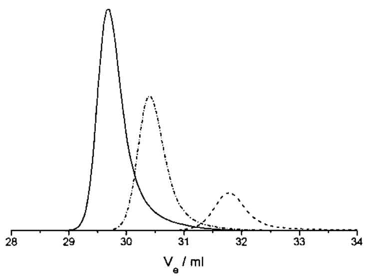
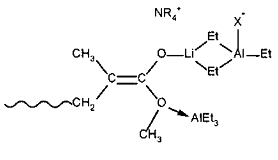


Figure 11: GPC eluograms of the PMMAs obtained under the conditions described in Figure 10 at different monomer conversions (0.21, 0.59, 1): --- M_n = 15000, M_w/M_n = 1.15; -·- M_n = 42800, M_w/M_n = 1.06; — M_n = 68600, M_w/M_n = 1.06.

Since the rates of polymerization strongly increase upon the addition of a tetraalkylammonium halide, we expect a different structure of the active species. The tetraalkylammonium halide–triethyl aluminium complex, e.g., $NR_4^+[AlEt_3X]^-$, might be coordinated to the living aluminate chain end leading to the structure given in Scheme 1. This structure, which is provided by *ab initio* quantum chemical calculations[9], shows the lithium ion coordinated to the complex anion $[AlEt_3X]^-$ and NR_4^+ as the counterion. It appears that the lithium ion is not replaced by the tetraalkylammonium ion as expected at first.



Scheme 1: Tentative structure of the living chain end in the presence of $AlEt_3$ and a tetraalkylammonium salt, NR_4X.

Nevertheless, the size of the NR_4^+ counterion should affect the reactivity of the living chain end and, in fact, the rate of propagation increases with increasing radius of the tetraalkylammonium ion (Figure 12). Due to its large distance to the carbanion, the size of the anion X^- should not change the reactivity. However it is found that the rate of propagation decreases significantly with increasing radius of the halide (Figure 13).

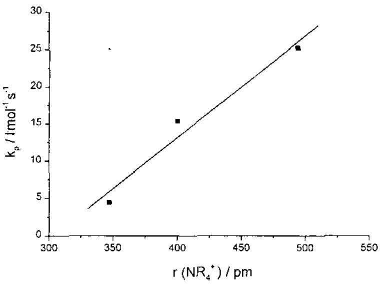


Figure 12: Polymerization of MMA in the presence of $NR_4Cl/AlEt_3$ at −20°C: Dependence of the rate of propagation on the radius of NR_4^+ (Me < Et < Bu).

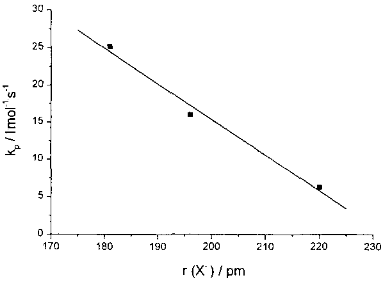
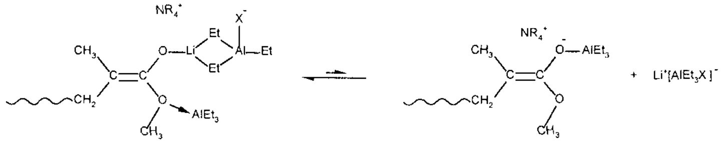


Figure 13: Polymerization of MMA in the presence of $NBu_4X/AlEt_3$ at −20°C: Dependence of the rate of propagation on the radius of X^- (Cl^- < Br^- < I^-).

Thus, we tentatively assume that the species in Scheme 1 can dissociate into a more reactive ester enolaluminate with an NR_4^+ counterion and a $Li^+[AlEt_3X]^-$ complex (Scheme 2).[7] As the heat of formation of the complex $Li^+[AlEt_3X]^-$ increases with decreasing radius of the halide,[16] the equilibrium in Scheme 2 will be shifted to the right hand side, i.e., to the more active species, leading to an increase of the rate of propagation. NMR and further kinetic investigations are necessary in order to prove the existence of both postulated species.



Scheme 2: Tentative dissociation of the active species in Scheme 1 into to a ester enolaluminate with NR_4^+ counterion and a $Li^+[AlEt_3X]^-$ complex.

Apart from the polymerization of methyl methacrylate, those of *tert*-butyl methacrylate (tBMA) and *tert*-butyl acrylate (tBuA) are also living and controlled in the presence of $NBu_4Br/AlEt_3$ in toluene at −20°C. In both cases, quantitative monomer conversions and polymers with narrow molecular weight distributions (M_w/M_n < 1.3) are obtained. The PtBMA is heterotactic (mr = 0.60), similar to that formed in tetrahydrofuran with alkali counterions, whereas it is 100% isotactic in pure toluene.[17] Block copolymers, like PMMA-*b*-PtBMA and PMMA-*b*-PtBuA, with narrow molecular weight distributions (M_w/M_n < 1.2, Figure 14) can be synthesized via sequential monomer addition.[7] The random copolymerization of methyl methacrylate with methacryloyl-terminated PMMA macromonomers leads to comb-shaped polymers, PMMA-*g*-PMMA (Figure 15). This is especially remarkable since it is very difficult to purify PMMA macromonomers – due to the presence of the aluminium alkyl, this system is self-cleaning.

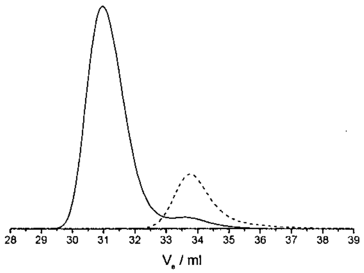


Figure 14: GPC eluogram of a PMMA-*b*-PtBuA (—) obtained with EiBLi/$NBu_4Br/AlEt_3$ at –20°C: M_n = 16600, M_w/M_n = 1.12 (without precursor); --- precursor: M_n = 3170, M_w/M_n = 1.18. Block efficiency ca. 0.8.

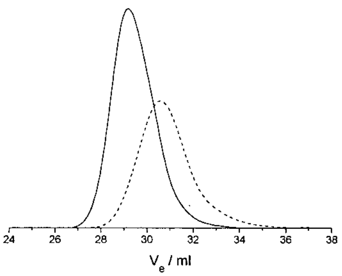


Figure 15: GPC eluogram of a PMMA-*g*-PMMA (—) obtained with EiBLi/$NBu_4Br/AlEt_3$ at –20°C: M_n = 86500, M_w/M_n = 1.33; --- macromonomer, MM: M_n = 19400, M_w/M_n = 1.81. MMA/MM = 1:2.3 w/w, conversions: MMA: 1, MM: >0.95, initiator efficiency ca. 0.6.

The controlled polymerization of primary acrylates, e.g., n-butyl acrylate (nBuA) or 2-ethylhexyl acrylate (EHA), is achieved in the presence of tetramethylammonium chloride (NMe_4Cl) and triisobutyl aluminium ($AlBu^i_3$) at –78°C. For both, quantitative monomer conversions, linear plots of the number-average degree of polymerization, P_n, vs. monomer conversion, and polymers with high molecular weights and narrow distributions ($M_w/M_n < 1.2$, Figure 16 and Table 3) are obtained.

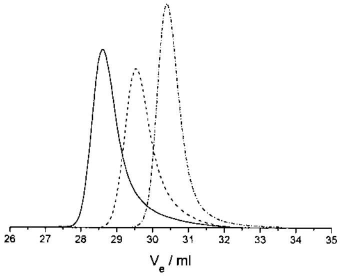


Figure 16: GPC eluograms of PtBuA (--- M_n = 70800, M_w/M_n = 1.15), PnBuA (-·- M_n = 30500, M_w/M_n = 1.11), and PEHA (— M_n = 119000, M_w/M_n = 1.20) obtained with EiBLi/$NMe_4Cl/AlBu^i_3$ in toluene at –78°C. $[EiBLi]_0$ = 0.3...5.0·10^{-3} mol/l, $[NMe_4Cl]$ = 7.0·10^{-3} mol/l, $[AlBu^i_3]$ = 14.0·10^{-3} mol/l, $[M]_0$ = 0.24...0.42 mol/l.

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