Living and Controlled Anionic Polymerization of Methacrylates and Acrylates in the Presence of Tetraalkylammonium Halide–Alkylaluminum Complexes in Toluene**

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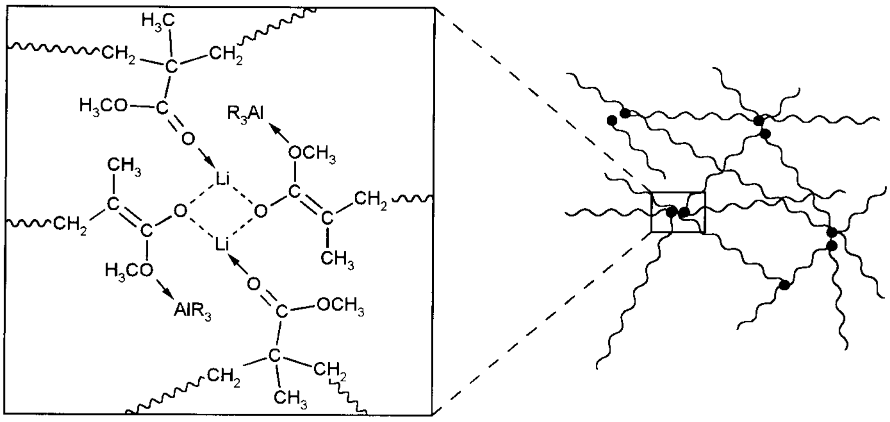

Figure 1. Structure of the coordinative network of living polymer chains.

Block copolymers of methacrylates and acrylates have the potential to combine thermoplastic–elastomeric, impact-modifying, or emulsifying properties with excellent resistance to weathering. An industrial-scale synthesis of polymers of this type with high molecular weights and narrow molecular-weight distributions would require use of a living and controlled[1] anionic, coordinative, or radical polymerization reaction, preferably carried out at ambient or elevated temperature in a hydrocarbon solvent or in bulk. Only a few anionic and coordinative polymerization processes have been reported that might fulfill these demands. Examples include anionic polymerization with lithium as the counterion in the presence of lithium alkoxyalkoxides[2] or alkylaluminum compounds,[3] polymerization with metal-free counterions,[4, 5] Lewis acid catalyzed group-transfer polymerization,[6] and coordinative polymerization with aluminum porphyrins[7] or lanthanocenes[8] as initiators. However, either the rates of polymerization are so high that the reaction can be controlled only in a flow-tube reactor,[9] or the copolymerization of methacrylates and acrylates fails to proceed satisfactorily for other reasons. Thus, molecular weights of the resulting polyacrylates are often limited to 20000 g mol^{-1}, or the initiators are very expensive, complicated to prepare, and difficult to remove from the polymer. The controlled anionic polymerization of primary acrylates continues to be a particularly great challenge for polymer scientists.

Anionic polymerization of methyl methacrylate with lithiated initiators in the presence of alkylaluminum compounds in toluene has recently been shown to possess the required living character, but it does not follow conventional first-order kinetics, and the resulting polymers display fairly broad molecular-weight distributions.[10] These circumstances have been attributed to the formation of a coordinative polymer network in which lithium ions at living-chain ends are coordinated to in-chain ester carbonyl groups (Figure 1).[11] The formation of such a polymer network can be suppressed by the use of Lewis bases such as methyl pivalate or diisooctyl phthalate as cosolvents,[12] an approach that results even at 0 °C in linear first-order time–conversion plots and syndiotactic polymers with narrow molecular-weight distributions. However, since the half-life of the polymerization is usually in the range of several hours, use of this method is restricted to the synthesis of polymethacrylates with molecular weights <20000 g mol^{-1}. Moreover, only at $-78\,^{\circ}$C can primary acrylates such as *n*-butyl acrylate be polymerized in a controlled way.[13]

We report here a different approach to the prevention of polymer-network formation in pure toluene. The underlying scheme is to substitute a less electropositive cation for lithium—for example, a tetraalkylammonium ion. Ziegler et al.[14] reported that tetraalkylammonium halides $\mathrm{NR_4X}$ form hydrocarbon-soluble complexes with alkylaluminum compounds $\mathrm{AlR'_3}$ of the type $\mathrm{NR_4^+[Al_nR'_{3n}X]^-}$ (R = Me, Et, *n*Bu; X = Cl, Br, I; R′ = Me, Et; *n* = 1, 2). We have found that these complexes support living and controlled polymerization of methyl methacrylate (MMA) initiated by ethyl α-lithioisobutyrate (EiBLi) in toluene.[15] At or below 0 °C this polymerization usually follows first-order kinetics, the number-average molecular weight M_n of the polymer increases linearly with monomer conversion, and the observed molecular-weight distributions are both unimodal and narrow (polydispersity index $M_w/M_n < 1.2$). The half-life of the reaction is reduced to a few minutes, which permits even polymers with molecular weights up to 250000 g mol^{-1} to be synthesized within a convenient amount of time. The polymethacrylate (PMMA) products are highly syndiotactic with racemic (*rr*) and mesoy (*mm*) triad fractions of about 0.75 and 0.01, respectively. In the absence of added alkylaluminum compounds, however, introduction of tetraalkylammonium halides leads predominantly to isotactic PMMAs (*mm* fraction ca. 0.65) with broad and multimodal molecular-weight distributions ($M_w/M_n > 3$).[16] Similarly, initiation with tetrabutylammonium malonates in THF leads to uncontrolled polymerization of MMA (with $M_w/M_n > 2$).[17] It is thus clear that the combination of tetraalkylammonium halides and alkylaluminum compounds is essential for obtaining a living and controlled polymerization.

Kinetic investigations show that the rate of propagation increases with the size of the tetraalkylammonium ion ($\mathrm{NMe_4^+ < NEt_4^+ < NBu_4^+}$; Figure 2), but that it remains at least two orders of magnitude lower than one might expect for an active species with a large tetraalkylammonium counterion. [18]

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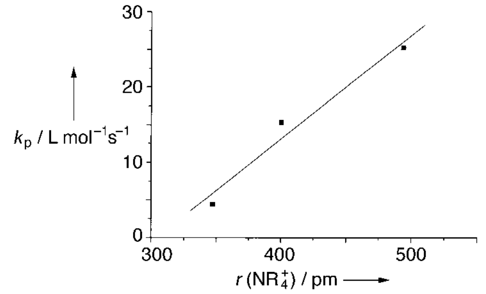


Figure 2. Dependence of the rate constant for propagation k_p on the radius r of the NR_4^+ ion during polymerization of MMA with EiBLi in the presence of $NR_4^+[Al_2Et_6Cl]^-$ in toluene at $-20\,°C$.

The rate of propagation increases also with decreasing ionic radius of the halide ($I^- < Br^- < Cl^-$; Figure 3). Ab initio calculations[19] suggest that **1** is a possible active species, in which the lithium ion is coordinated to a complex trialkylaluminum halide anion, and the tetraalkylammonium ion serves as the counterion. Structure **1** could explain the effect of tetraalkylammonium ions of different sizes upon the reactivity of the active species, but not the effect of the halide. Therefore, we assume that **1** can dissociate into the considerably more reactive ester enol aluminate **2** (with a tetraalkylammonium counterion) and a $Li^+[AlR'_3X]^-$ complex (Scheme 1). Because the heat of formation of $Li^+[AlR'_3X]^-$ increases as the radius of the halide decreases,[14] the equilibrium in Scheme 1 would be shifted toward the active species **2**, which would lead to the observed acceleration of polymerization. With regard to the low values for the rate constants of propagation, equilibrium should lie predominantly on the side of the less reactive species **1**. A detailed kinetic study will appear elsewhere.[20]

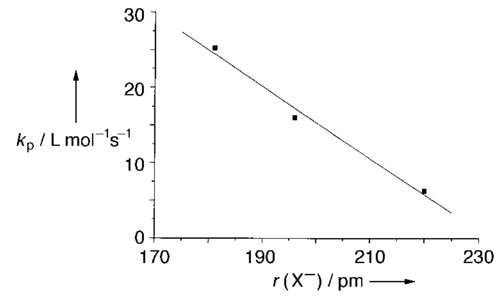
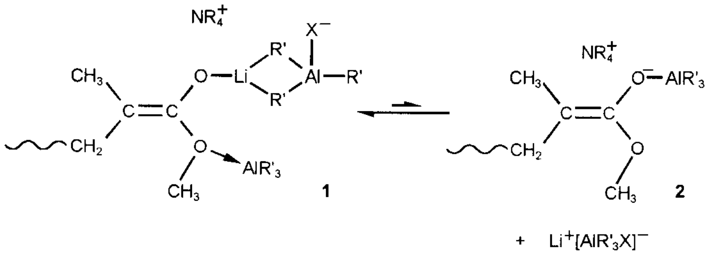


Figure 3. Dependence of k_p on the radius r of the X^- ion during polymerization of MMA with EiBLi in the presence of $NBu_4^+[Al_2Et_6X]^-$ in toluene at $-20\,°C$.

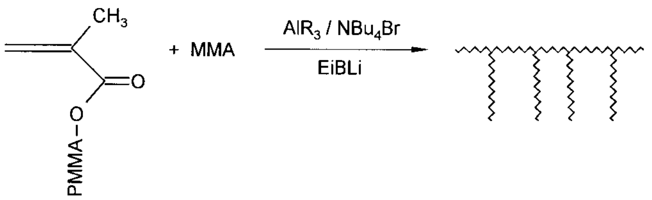


Scheme 1. Postulated equilibrium between two active species with differing reactivities in anionic polymerization with NR_4X/AlR'_3 complexes.

It is interesting to note that tetraalkylammonium salts have also been used successfully by Inoue et al. in the ring-opening polymerization of cyclic ethers, lactones, and anhydrides with aluminum porphyrins.[21] The mechanism proposed by these authors involves two polymer chains bound to the aluminum atom on opposite sides of the porphyrin ring, and the tetraalkylammonium salt enhances the reactivity of the aluminum porphyrin.

Like the polymerization of MMA, the polymerizations of *tert*-butyl methacrylate (*t*BMA) and *tert*-butyl acrylate (*t*BuA) are also living and controlled in the presence of $NR_4^+[Al_2R'_6X]^-$ at $-20\,°C$. This makes it possible to prepare block copolymers PMMA-*block*-P*t*BMA and PMMA-*block*-P*t*BuA of high molecular weight by sequential monomer addition. Hydrolysis of the *tert*-butyl ester groups results in amphiphilic block copolymers with narrow molecular-weight distributions ($M_w/M_n < 1.2$). The content of residual PMMA precursors is 1–5 wt%.

Random copolymerization of MMA with methacryloyl-functionalized PMMA macromonomers leads to comb-shaped polymers of the type PMMA-*graft*-PMMA (Scheme 2 and Figure 4). It is usually difficult to obtain such polymers by anionic polymerization, because the macromonomers cannot be sufficiently purified; the presence of the alkylaluminum compound makes the polymerization system in this case self-cleaning.



Scheme 2. Synthesis of comb-shaped PMMA through the use of a macromolecular PMMA monomer (macromonomer method).

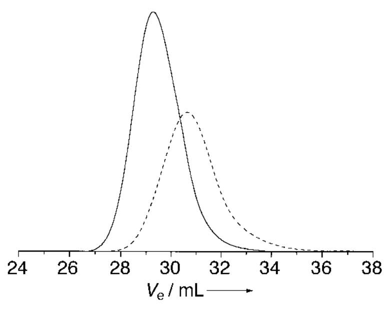


Figure 4. Elution diagram for gel permeation chromatography (GPC) of a PMMA-*graft*-PMMA comb polymer (—; $M_n = 86500$, $M_w/M_n = 1.33$) obtained in the copolymerization of MMA and a macro PMMA monomer (MM) (- - - -; $M_n = 19400$, $M_w/M_n = 1.81$) initiated by EiBLi and $NBu_4^+[Al_2Et_6Br]^-$ at $-20\,°C$. The mass ratio of MMA to MM was 1:2.3; monomer conversions: 1 (MMA) and >0.95 (MM). V_e = elution volume.

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Controlled polymerization of primary acrylates such as *n*-butyl acrylate (*n*BuA) or 2-ethylhexyl acrylate (EHA) is achieved at −78 °C. Conversion of the monomer is quantitative, and the resulting polymers have molecular weights as high as 120 000 g mol^{-} and narrow molecular-weight distributions ($M_w/M_n < 1.2$; Figure 5).

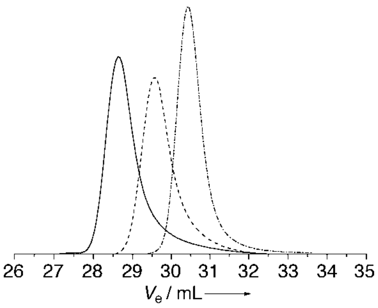

Figure 5. GPC elution diagram for PtBuA (– – – –; $M_n = 70800$, $M_w/M_n = 1.15$), PnBuA (–·–·–; $M_n = 30500$, $M_w/M_n = 1.11$), and PEHA (—; $M_n = 119000$, $M_w/M_n = 1.20$), prepared in a polymerization initiated at −78 °C with EiBLi and $NMe_4^+[Al_2Me_6Cl]^-$.

In summary, we have discovered a new initiating system that takes advantage of readily accessible and inexpensive reagents to produce polymethacrylates and polyacrylates of high molecular weight.

Experimental Section

Reagents: Ethyl α-lithioisobutyrate was prepared from ethyl isobutyrate and lithium diisopropylamide in hexane by described methods.[22] Alkylaluminum compounds were purchased from Aldrich as solutions (25 wt %) in toluene and used without further purification. Tetraalkylammonium halides (Aldrich) were suspended in benzene and freeze-dried. (Meth)-acrylic monomers obtained from BASF AG were fractionally distilled from CaH_2 at reduced pressure through a column (1 m) with Sulzer packing, stirred over CaH_2, degassed, and distilled under high vacuum. Methacryloyl-terminated PMMA macromonomers donated by Röhm GmbH were used as received. Toluene (BASF AG) was fractionally distilled through a 1.5-m column, stirred twice over Na/K alloy, degassed, and distilled under high vacuum.

Polymerizations: All polymerizations were carried out in a stirred tank reactor under a nitrogen atmosphere. The initiator ethyl α-lithioisobutyrate was added to a solution of tetraalkylammonium halide and alkylaluminum compound in toluene, and the mixture was stirred for 5 min, after which the monomer was introduced. Polymerization was quenched with methanol/acetic acid (9/1) and the monomer conversion was determined by GC with octane or decane as internal standard. After evaporation of the solvent, the polymer was dissolved in benzene, the solution was filtered, and the polymer was freeze-dried.

Polymer characterization: Gel permeation chromatography (GPC) was used for molecular-weight distribution analysis, with THF as eluent (flow rate: 1 mL min^{-1}; columns: 60 cm, 5 μm PSS-SDV gel, 100 Å and linear 10^2–10^5 Å; detectors: JASCO-UVIDEC100III and Bischoff RI8110). Appropriate methacrylate and acrylate polymer standards were used to calibrate the columns. The molecular weights of comb-shaped polymers were determined with GPC (on-line viscosity detection) by universal calibration. ^1H and ^{13}C NMR spectra (Bruker AM-400) of the polymers were recorded at room temperature in $CDCl_3$. The α-CH_3 and C=O signals were used for the determination of triad tacticities.

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Polyhomologation: Synthesis of Novel Polymethylene Architectures by a Living Polymerization of Dimethylsulfoxonium Methylide**

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We recently reported a new polymerization reaction for the synthesis of polymethylene, the simplest carbon-backbone polymer constructed one methylene group at a time.[1, 2] The ylide dimethylsulfoxonium methylide (**1**)[3] is the monomer in this reaction and serves as the source of methylene. Polymerization is initiated by trialkylboranes. All three alkyl groups

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