

Recent developments in anionic polymerization

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Abstract

The past year witnessed very significant advances in the living anionic polymerization of (meth)acrylate monomers, particularly in hydrocarbons at or below 0°C. Block polymerization of alkyl methacrylates with primary alkyl acrylates, although somewhat improved, remains a challenge. Anionic polymerization of styrene, diene and its derivatives was carried out with the aim of synthesizing functional polymers and block copolymers of various architectures. There has been a trend towards combining different living techniques in order to design polymers of unique architectures and properties.

Abbreviations

DBTMGLi	di-tert-butyl 2-lithio-2,4,4'-trimethylglutarate
EiBLi	ethyl -lithioisobutyrate
LAP	ligated anionic polymerization
LiOEM	lithium 2-(2-methoxy)ethoxy ethoxide
LiOEM	lithium 2-methoxyethoxide
MMA	methylmethacrylate
MNDO	modified neglect of differential overlap
MW	molecular weight
MWD	molecular weight distribution
PIB	poly(isobutylene)
PMMA	poly(methylmethacrylate)
PtBMA	poly(tert-butylmethacrylate)
THF	tetrahydrofuran

Introduction

The discovery of 'living' anionic polymerization by M Szwarc in the fifties was the detonator for a very broad area of action in this field [1*]. An exceptional research effort was indeed undertaken, being motivated by obvious mechanistic challenges and by the prospect of tailoring new polymeric materials, and thus of achieving what was a dream until then: the molecular engineering of polymers.

At a time when the recently discovered controlled radical polymerization [2*] is viewed as a much less demanding process, anionic polymerization still remains an important method, well-suited to kinetic studies [3*], the synthesis of polymers of predictable molecular weight (MW) with a narrow molecular weight distribution (MWD), tailoring of block copolymers [4,5*,6-9], design of nonlinear molecular architectures [10**, 11] and telechelic polymers [12-17], and stereoregular polymerization [18,19]. Major progress in mechanistic studies and macromolecular engineering reported in the past year(s) is to be found in the very challenging field of the anionic polymerization of (meth)acrylic monomers.

Anionic polymerization of (meth)acrylic esters.

These esters are one of the most attractive and versatile family among the presently available monomers. Their polymers encompass plastics, adhesives, elastomers, and their block copolymers have potential as thermoplastic elastomers, impact modifiers, or emulsifiers with excellent resistance to weathering. Imparting control or living characteristics to the anionic polymerization of (meth)acrylate implies, however, the need to minimize or to suppress a number of noxious secondary nucleophilic reactions.

Contribution of ligated anionic polymerization (LAP)

Among the possible approaches to prepare well-defined (meth)acrylate homo- or copolymers, LAP has been exploited for high efficiency. LAP is indeed the only method able to simultaneously control living homo- and copolymerization of a number of monomers to high MW, low MWD, monomer conversion close to 100%, with varying regio- and stereoselectivity. The basic concept is to use suitable ligands, that coordinatively interact with the active initiating or propagating ion-pairs and fulfill three major functions: firstly, the promotion of a new complexation equilibrium with ion-pairs and/or aggregates, hopefully leading to a single stable active species; secondly, modulation of the electron density at the metal-enolate ion-pair (i.e. stability and reactivity); and most importantly thirdly, protection of the ion-pair by an extended steric barrier, so that back-biting of the growing anion onto the antepenultimate chain unit is minimized [20]. Two groups of efficient ligated systems have been studied quite recently: firstly, μ -type ligands such as aluminum alkyls [21,22] and some inorganic lithium salts [23]; and secondly, $\mu/\text{-}$ type dual ligands, such as lithium 2-methoxyethoxide (LiOEM) [24*], lithium 2-(2-methoxy)ethoxy ethoxide (LiOEEM) [25,26], and lithium aminoalkoxide [27]. When the anionic species (Li counterion) responsible for the polymerization of methylmethacrylate (MMA) in toluene are ligated by alkylaluminum compounds, living characteristics are observed, and predominantly polymethylmethacrylate (PMMA) is formed with, however, a fairly broad MWD. This undesired feature has been accounted for by a network of coordinative interactions between lithium counterions at living chain ends and in-chain ester carbonyl groups [28]. This network is destroyed by the addition of an ester like Lewis base as the co-solvent, for example, methyl pivalate and diisooctyl phthalate [21]. Yet, even at 0°C, a syndiotactic PMMA of narrow MWD is formed. As polymerization is slow (half life of several hours), this method is restricted to the synthesis of low MW polymethacrylates, however, it is poorly efficient in the case of alkylacrylates [22]. Because of a much better solubility in hydrocarbons, LiClO₄ has been substituted for LiCl as the μ -ligand in the polymerization of (meth)acrylates.

Well-defined poly-(meth)acrylates have been accordingly synthesized in a toluene/THF (9/1, v/v) mixture at -40°C [23]. Compared to μ -type ligands, $\mu/\text{-}$ type ligands are much more efficient, particularly for the successful block polymerization of MMA and primary acrylates [24*,26]. It must be pointed out that PMMA-b poly(n-butyl acrylate) diblocks have been synthesized in toluene at -20°C by the 'flow-tube technique' [29], which allows monomer and initiator solutions to be mixed efficiently within less than 1 ms in a mixing jet, and polymerization to occur in a capillary tube (5 ms < time < 5 s) [24*]. This observation is encouraging for the scaling-up of production of engineered (meth)acrylate based materials.

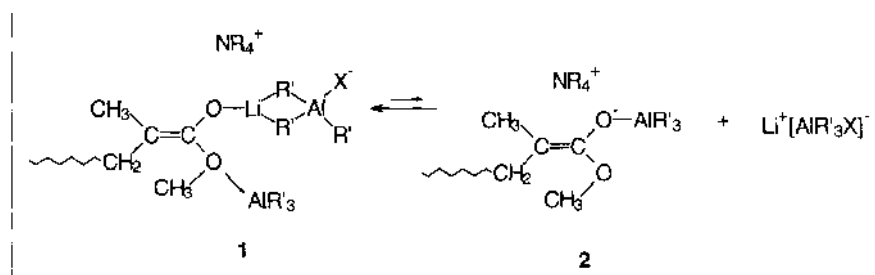


Figure 1 Postulated equilibrium between two active species with different reactivities in anionic complexation with NR₄⁺X/AIR'₃.

Analysis of the active site structure

Models for the lithiated species active in the anionic polymerization of MMA, such as μ -lithioesters, were studied, some years ago, by multinuclear NMR spectroscopy [30]. The interest of these models is, however, limited by their reactivity which does not match the reactivity of the propagating species. This reactivity changes rapidly while going from monomeric to dimeric and trimeric active species. Moreover, models for MMA species are only stable at very low temperatures, which is an experimental drawback. For these reasons, living poly(*tert*-butyl-methacrylate) (PtBMA), stable at 0°C, and its dimeric model, di-*tert*-butyl 2-lithio-2,4,4'-trimethylglutarate (DBTMGLi), have been recently studied [31,32]. The last monomer units of PtBMA have also been selectively labeled by ^{13}C atoms (^{13}C NMR analysis). A parallel NMR study ($^6,7\text{Li}$, ^1H , ^{13}C) of both the dimeric model and the growing chains has been conducted in the absence and presence of μ - and μ' -type ligands [33,34], the main conclusions of which are as follows:

1. Both DBTMGLi and living oligomers are engaged in an equilibrium between a dimeric and unimeric form in THF from -70°C to 10°C [31], the aggregation being favored at higher temperature and concentration.
2. Addition of LiCl completely perturbs the aggregation equilibrium. When the LiCl : DBTMGLi molar ratio is greater than one, a 1 : 1 complex is formed with a fast exchange rate. ^{13}C Relaxation times also indicate a dimeric aggregation for this complex, in full agreement with an MNDO (modified neglect of differential overlap) calculation. Living PtBMA oligomers also form a 1 : 1 complex with LiCl. Although no intramolecular complexation of Li^+ with the antepenultimate ester group is observed, self-termination of these oligomers still occurs at 0°C.
3. A more complex situation results from the addition of LiOEEM, which shows a strong tendency to self-aggregate into dimeric, trimeric, and tetrameric aggregates. Self-aggregation of LiOEEM competes with mixed complexation with DBTMGLi (1 : 1, 3 : 1 and probably 2 : 1 mixed aggregates) and living PtBMA oligomers. However, parts of the DBTMGLi and PtBMA oligomers remain uncomplexed even when LiOEEM is used in excess, which suggests that at least two kinds of active species may contribute to the anionic polymerization of *tert*-butyl methacrylate and account for the bimodality of the final polymer.

Last generations of ligands

In their study of the anionic polymerization of (meth)acrylates in the presence of aluminum alkyls [21,22], Müller and co-workers [33**] have studied the effect of tetraalkylammonium halides. The living anionic polymerization of MMA, initiated by ethyl μ -lithioisobutyrate (EiBLi) in toluene at or below 0°C, is very fast, because the half-reaction time is a few minutes compared to a few hours in the absence of ammonium salts. A polymer with MW up to 250,000 g/mol⁻¹ can be synthesized, which is mainly *syn*-diotactic (75%) and of narrow MWD (< 1.2). It is worth noting that the metal-free anionic polymerization of MMA initiated by tetrabutylammonium malonate in THF is poorly controlled (MWD > 2.0; [36]). The beneficial effect of tetraalkylammonium halide is thought to result from the partial dissociation of the Li enolate complexed by $\text{NR}_4\text{X}/\text{AIR}'_3$ into the considerably more reactive ester enol aluminate 2 as shown in Figure 1. Interestingly enough, the anionic polymerization of primary acrylates, such as *n*-butyl acrylate and 2-ethylhexyl acrylate, is controlled at -78°C.

A simple and economic method has been recently devised for the one-pot synthesis of an μ -lithio ester initiator together with a μ' -type ligand (T Zundel, Ph Teyssie, R Jérôme, unpublished data).

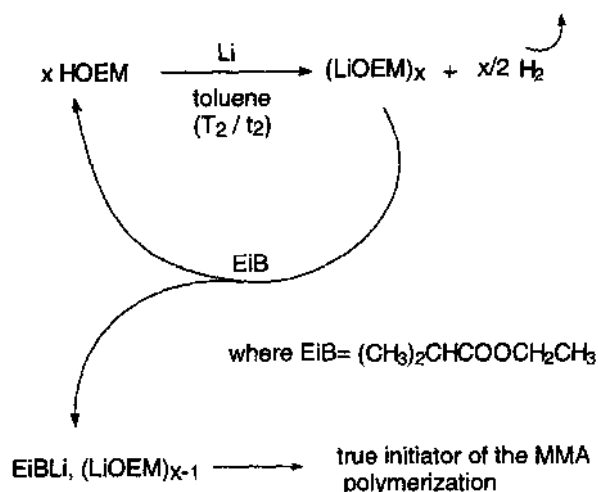


Figure 2 One pot strategy for the anionic polymerization of MMA by EiBLi in the presence of LiOEM as the ligand.

2-Methoxy-ethanol is first metallated in toluene by an excess of Li, with the formation of the expected LiOEM ligand. This Li-alkoxide is able to metallate ethylisobutyrate, thus forming the initiator (EiBLi) with the release of 2-methoxyethanol, which is reconverted into LiOEM by excess Li. This reaction pathway, which is illustrated in Figure 2, makes the ligated LiOEM/EiBLi initiator more attractive for the large scale polymerization of MMA in toluene at 0°C.

Finally, a new σ -type ligand has been discovered that allows highly isotactic PMMA to be synthesized in toluene at 0°C [37**]. According to a 'process-friendly' method, sec-butyllithium is reacted with hexa(octa)-methyl cyclotri-(tetra)siloxane (D₃ or D₄) leading to sec.C₄H₉-Si(CH₃)₂OLi, which is the actual ligand for unreacted sec.BuLi and, later on, for the propagating species of the MMA type. Figure 3 illustrates this cascade-type of reaction, which, under optimized experimental conditions (particularly the initial sec.BuLi: D₃ [or D₄] molar ratio) leads to a single mixed complex, as confirmed by multinuclear NMR spectroscopy [38]. This active mixed complex promotes the quantitative living polymerization of MMA in toluene within 1 h at 0°C, such that PMMA up to 100,000 g/mol⁻¹ can be synthesized with a narrow MWD (~ 1.1). The stereoregularity of PMMA is amazingly high, that is, 95% isotactic. The reason for this unusually high isotacticity is not yet clear. The attack of the meso-prochiral face might, however, be preferential as result of the unusual bulkiness of the ligands around the active center in the mixed complexes.

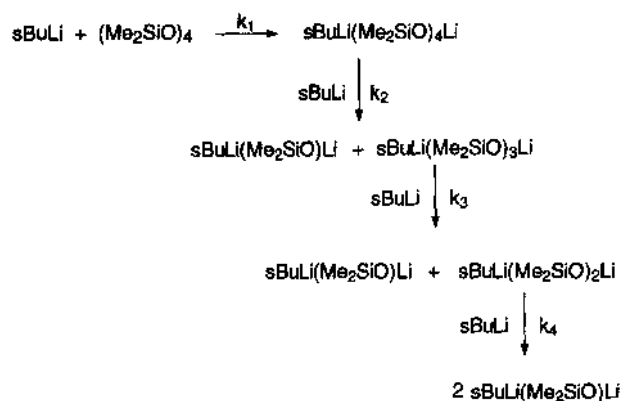


Figure 3 Reaction of secBuLi with (MeSiO)₄.

Polymerization of methacrylates in the presence of the tetraphenylphosphonium ion has also been discussed in terms of phosphorylide-mediated polymerization [39].

Climbing back up the nucleophilic reactivity scale

One of the oldest constraints in anionic polymerization is the fact that an active growing site cannot attack another type of monomer if it does not have the proper (higher) relative nucleophilicity. This requirement explains why a well-defined sequence of monomers, that is, dienes, styrenes > vinylpyridines > (meth)acrylates > oxiranes, siloxanes, has to be followed for the successful synthesis of block copolymers. However, the results described hereafter demonstrate that such a classical rule can be circumvented in some cases [40**].

The selected general strategy is illustrated in Figure 4 which basically consists of the nucleophilic attack (by an initiator or a living growing chain) of a substituted disila-cyclopentane in a polar mixed solvent, with the formation of a new silyl anion, nucleophilic enough to attack the other usual monomers. The driving force of this process comes from the energy gain by the formation of more stable bonds around the Si atom, and probably also from the release of ring strain, particularly if a disila-cyclopentane is used. Although this strategy has to be optimized, very encouraging preliminary results have been reported. Indeed, for the first time, potassium trimethylsilanolate, and living potassium poly(ethylene oxide), both of which are unable to initiate styrene and MMA polymerization, have been converted from oxyanionic active ends to silyl anionic ones by reaction with cyclic disila derivatives, thus allowing homo-olymerization and sequential (co)polymerization of styrene or MMA to proceed in a controlled way. These results pave the way to the direct synthesis of A-B-A triblock copolymers from , -difunctional living chains, in a sequence inaccessible to classical anionic initiators.

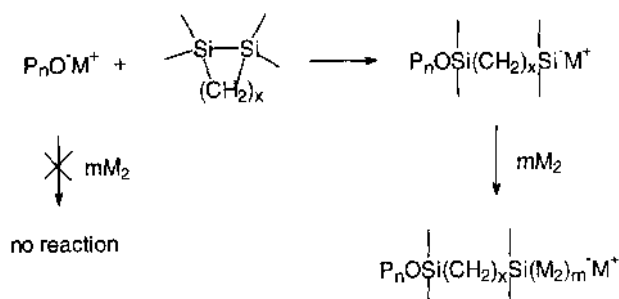


Figure 4 Use of cyclosila derivatives as reactivity amplifiers for the macromolecular engineering of new copolymers: reaction scheme. $P_nO^-M^+$ is a living polymer with an oxyanionic chain end and metal counterion; m is the number of monomer 2 (M_2).

Recent achievements in the anionic polymerization of styrene (derivatives) and dienes

Difunctional initiating system

Undoubtedly, the most successful industrial application of anionic polymerization is the production of the styrene-diene based thermoplastic elastomers (TPEs). In order to improve the upper service temperature, which is around 70°C, the synthesis of methacrylate-diene based triblocks has been considered. In contrast to styrene and butadiene, which are of quite a comparable reactivity, MMA is much more reactive than butadiene, such that it is mandatory to polymerize butadiene first, which requires the availability of a hydrocarbon soluble , -difunctional initiator. Our laboratory has recently reported on the efficiency of the diadduct of tert-butyllithium to 1,3-diisopropenyl benzene (DIB) in the presence of ether ligands, which prevent the dianionic species from aggregating while preserving a predominantly 1,4-microstructure for polybutadiene [41-45]. Substitution of MMA for styrene enabled new TPEs to be synthesized with the same ultimate tensile properties as the traditional SBS, but with an upper service temperature improved by ~50°C.

Functional polymers

The anionic polymerization of traditional monomers, such as styrene and dienes, usually fails when they are substituted by functional groups because of the sensitivity of these groups to nucleophiles.

Nakahama and coworkers [46-48,49*] have contributed remarkable progress to this field by the deliberate introduction of an appropriate electron-withdrawing group on (-methyl) styrene (para-position), such as cyano [46,47], methyl sulfide [48] and N-arylimino [49*]. Polymers of strictly controlled molecular structures have been synthesized as result of the appropriately changed reactivity of both the monomer (enhanced electrophilicity) and the carbanion produced (reduced nucleophilicity).

Conditions for the successful anionic polymerization of styrene para-substituted by a silylvinyl group have also been reported [50].

New industrial development

The anionic terpolymerization of styrene, isoprene and butadiene was reported by AF Halasa from The Goodyear Tire & Rubber Co., they achieved control of composition, microstructure and sequence distribution in a unique family of elastomeric materials [51*]. These new elastomers can be tailor-made with diverse viscoelastic responses in order to suit specific tire applications, in particular, those required for high performance tires.

Combination of anionic with other living polymerizations

Living polymerizations (i.e. anionic, cationic, radical) provide the most versatile synthetic routes for the preparation of a wide variety of well-defined polymer structures. As each living mechanism is only applicable to a limited number of monomers, it is highly desirable to combine at least two living polymerization techniques in order to prepare novel polymeric materials. Recent publications have dealt with the combination of living anionic polymerization with cationic [52**,53*.54,55,56*,57], controlled radical [58], and group transfer [59] polymerizations.

In a very inventive series of papers [52**,53*,54], Ruckenstein and Zhang reported on new methacrylate monomers, such as 2-(vinylxy)ethyl methacrylate (VEMMA) and 1-(isobutoxy)ethyl methacrylate (BOEMA), that can be anionically polymerized in a living way. These methacrylates are substituted by groups that can either polymerize cationically (vinylxy group in VEMMA) or initiate the cationic polymerization of vinyl ethers in presence of $ZnCl_2$ (1-isobutyoxyethyl ester). These difunctional monomers can be used advantageously to prepare copolymers with complex molecular architectures, for example, comb-like, block-graft, and star-shaped structures.

In another series of papers, Müller and co-workers [55,56*] proposed the combination of living anionic and cationic polymerization, in order to prepare poly(isobuty-lene) (PIB)-based linear and star-shaped block copolymers. The strategy consists of the end-capping of living PIB chains by 1,1-diphenyl ethylene, followed by quantitative metallation with a K-Na alloy. The resulting stable macrocarbanion can initiate the living anionic polymerization of tBMA and, after exchange of Li^+ for K^+ , the MMA polymerization.

Conclusions

Fundamental and practical developments in anionic polymerization have been reviewed for the past year. New concepts, initiating systems, reaction processes and materials have been discovered and put into practice. This is very encouraging for an area which is somewhat considered as 'dormant'. On the other hand, envisioning further development in efforts in anionic polymerization might sound unrealistic, at a time when so-called 'living' or controlled radical polymerization is viewed as a more easily implemented process. Nevertheless, the performances of a controlled radical polymerization are limited by a number of serious drawbacks, including the requirement for an oxygen-free system, the difficulty to reach quantitative conversion, the poor or nonreactivity of some important monomers (dienes, oxiranes, cyclosiloxanes, etc.), the too high metal residue in ATRP (atom transfer radical polymerization), and so on. In brief, living anionic polymerization is still an important method to be preferentially chosen in the years to come for precise tailoring of complex materials.

Acknowledgements

R Jerome is deeply indebted to all his co-workers mentioned in the publication listed below. He is also grateful to the 'Services des Affaires Scientifiques, Techniques et Culturelles' for general support in the frame of the 'Poles d'Attraction [interuniversitaires: PAI4/11'].

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