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LIVING ANIONIC POLYMERIZATION OF (METH)ACRYLIC ESTERS : NEW MECHANISTIC CONCEPTS AND RESULTING MATERIALS

Philippe Teyssié*, Janusz Baran[a], Philippe Dubois, Robert Jérôme, Jin-shan Wang, Jianming Yu, Yisong Yu and Thomas Zundel

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium
[a] Institute of Fundamental Chemistry, Technical University of Szczecin, Al. Piastow, 42, 71065 Szczecin, Poland

Abstract : As an illustration of the frantic development of (meth)acrylic esters anionic polymerization during the last decade, three significant breakthroughs will be presented and analyzed :

- extension of the LAP (ligated anionic polymerization) concept to the practical synthesis of both high iso- or syndio high MW PMMA;
- the production of "perfect" hydrocarbon gels from tailored PMMA-polybutadiene-PMMA triblock copolymers;
- the use of reactivity "boosters" allowing to climb back up the nucleophilic reactivity scale, i.e. initiating styrene, dienes and (meth)acrylates polymerization with alcoholates and silanolates.

The amazing awakening of anionic (nucleophilic) polymerization, from a time-honored method into an ebullient field pushing new frontiers, has been mainly centered on the controlled polymerization of (meth)acrylic esters. There are of course strong incentives behind that choice, such as the increasing availability of those monomers (ca. 5.10^6 tons/year) at econonomically acceptable conditions, and the fact that they represent the most versatile class of building blocks in polymer synthesis. They indeed provide access to very diversified

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materials (plastics, elastomers, adhesives,...) with a broad range of glass transition temperatures (ca. -60 up to 200°C) and a wealth of useful available reactive groups (oxirane, hydroxyl, carboxyl, dialkylamino...).

In the frame of this presentation, too short to lend itself to a comprehensive review, we wish to illustrate the renewed power of that anionic approach and the sophistication of its achievements, by shortly analyzing three recent developments of both fundamental and practical significance.

1. Extension of the LAP (ligated anionic polymerization) concept for the controlled polymerization of (meth)acrylic esters

The coordination of active sites (P-Li) in living anionic process has proven to be a very powerful tool to control MW, MW distribution, nature of end-groups and to some extent stereochemistry of enchainment. μ-ligands (LiCl), σ-ligands (hindered crown-ethers), and μ-σ ones (Li-polyetheralkoxides) have been successfully used, depending on the requirements of the reaction and final products (1). More recently, this methodology has been shown to encompass all of the methacrylates, and even the acrylates with the sole exception of the lower primary ones, C_3 to C_1, in agreement with the relative scale of nucleophilic attack on the carbonyl group (2).

A more direct control of the propagation stereochemistry remained however an important challenge, particularly for PMMA. Under solvating conditions, a predominantly syndio (80 %) stereostructure is obtained, providing for an interestingly high Tg (ca. 130°C) : this is the case in THF, or in a more desirable hydrocarbon solvent (toluene) when using Li-polyetheralkoxide ligands. A practical method for tailoring high iso, high MW PMMA at high rate was however very much wanted, since that kind of product yields by interaction with essentially syndio PMMA a stereocomplex with a high semi-crystalline melting point (ca. 180°C). It can thus be used to reinforce s.PMMA-based materials, i.e. the triblock PMMA-PBD-PMMA copolymers mentioned below. We now found that a new class of μ-ligands, lithium silanolates, were very efficient in meeting that challenge. The synthesis is straightforward, starting from octamethyltetracyclosiloxane (D_4) which by a cascade reaction with s.BuLi ($k_1 < k_2, k_3, k_4$) yields s.BuMe$_2$SiOLi. Coordination of that μ-ligand to s.BuLi produces a single type of active species, i.e. {s.BuLi, 5sBuMe$_2$SiOLi}, able to initiate MMA polymerization in toluene at 0°C. Quantitative conversion is achieved in one hour, with an efficiency ($M_{n,th}/M_{n,SEC}$) of 90 % yielding a 40.000 MW polymer of narrow MWD (M_w/M_n = 1,10) and essentially iso (93 %) microstructure (3).

Moreover, that initiator being also efficient for styrenes and dienes (over 90 % 1.4 units), a number of new block copolymers are becoming available, a plentiful source of new materials, "per se" or by association through stereocomplexation.

2. High-performance applications of s.PMMA-PBD-s.PMMA triblock copolymers

During the last five years, a basic study of the reaction between bis-isopropenylbenzene and s.(t).BuLi has led to a perfectly difunctional initiator (9), very efficient for the synthesis of well-tailored, high MW-triblock copolymers of the above structure. These products more than displayed the expected beneficial physico-mechanical properties : excellent phase separation, very high stress at break (typical σ_B up to 40 MPa) and elongation at break (ε_B ca. 1000 %) (4). They constitute in fact serious potential competitors for styrene-based Kratons, also in terms of use-temperature (Tg ca. 130°C) and possibility of reinforcement by stereocomplex formation with high iso- high MW PMMA, the more if industrial-scale methods can be developed for their production (5).

The efficient physical cross-linking and phase separation of those products have also been the bases for an application as hydrocarbon gels, "shape-friendly" hydrophobic insulating materials broadly used in electrotechnical applications. Although styrene-based Kratons have mainly been used as yet, they suffer from a too-low gel-melting temperature, typically from 50 to 120°C depending on the copolymer MW.

10 % gels of these PMMA-based triblocks in paraffin oil display much higher T_m's, around 170°C, even for relatively modest MW's (15-70-15 KD), together with very satisfactory ε_B (6). From a more fundamental point of view, they present two interesting characteristics. As shown by special TEM observations, they are very homogeneous and isotropic with a very open structure (ca. 8 μ "pores"). Second, when investigated on the basis of the current scaling/percolation theory, they display a Δ exponent, in the relationship $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$

at gel point, which is exactly the predicted 0.70 one, whatever the concentrations, MW's, T°C, and gelation times. This result supports the formation of a "perfect" gel, a common situation for chemical gels (epoxys, PUR, ...), but unique for synthetic physical reversible gels, a basic requirement for a number of important applications (only natural pectin exhibits that kind of behaviour).

3. Climbing back up the nucleophilic relative reactivity scale

This last, but not least, development came as a tentative answer to an old challenge in anionic polymerization, i.e. to become independent of the relative initiator vs. monomer reactivity, in other words to be able to somehow reverse the hitherto obliged sequence dienes ≥ styrene > (meth)acrylates > oxiranes > siloxanes, a constraining feature in macromolecular engineering (particularly for triblock copolymers synthesis).

The silicon-silicon bond being much less stable than a C-C bond, and very sensitive towards nucleophilic attack, disilanes are prone to generate organosilyl anions under proper basic conditions (7). Different polymerizations, i.e. of styrene and methacrylates, were thus performed in the presence of an otherwise inactive "initiator", such as a silanolate or an alkoxide, and successfully achieved thanks to the simple addition of several $R_3Si\text{-}SiR_3$ compounds in a 1 to 5 molar ratio (8). This is undoubtedly a kinetically complex system, since involving three consecutive reactions : formation of the silylanion by nucleophilic cleavage, initiation of the monomer polymerization, and usual carbanionic propagation, notwithstanding the fact that this scheme is subject to detrimental secondary reactions in particular the homopolymerization of the cyclodisilanes which have to be used to synthesize block copolymers. Nevertheless, quantitative styrene and MMA homopolymerizations have been achieved in a few minutes at -20°C from K-silanolate initiators, yielding polymers of reasonable MWD (ca. 1,5) with an efficiency of ca. 60 % for styrene and 35 % for MMA.
Similarly, a block copolymer was obtained with a 66 % efficiency by initiating styrene polymerization from a living PEO-K added with tetramethylcyclopentadisilane, paving the way to the direct synthesis of triblock copolymers from difunctional oxyanion initiators.
Although these results obviously have to be optimized, they convincingly demonstrate that the use of a disilane "reactivity booster" permits a tailoring of the active species, allowing an

anionic polymerization to proceed irrespective of the monomers relative reactivity, i.e. of the monomer addition order, since the silyl anion formed is able to initiate the polymerization of practically all of them.

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