NEW PROSPECTS FOR "LIVING" ANIONIC POLYMERIZATION OF (METH)ACRYLIC ESTERS

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<u>Abstract</u> : The living low temperature polymerization in polar solvents of most methacrylates, even functional ones, can now be performed by direct and experimentally convenient anionic methods, thanks to the use of α-methylstyrene and of complex-purified monomers. A diversified family of block copolymers has thus been generated, that are used as compatibilizing agents in the designing of interesting heterophase materials : i.e. blends of polymers and inorganic fillers, and liquid-solid dispersions.
The living polymerization of acrylates (or of methacrylates under more drastic conditions) raises additional requirements : they have been met to a large extent by the use of specific ligands of the growing ion-pair. Resulting structures such as f.i. block copolymers and end-functionalized oligomers of a low dispersity, should have a great interest in the molecular engineering of (meth)acrylate-based products.
Finally, these new initiators lend themselves to structural and mechanistic studies which should shed some light on the critical features of these living propagation processes.

INTRODUCTION

Acrylic monomers constitute the basis of increasingly important polymer products and materials, with remarkably diversified applications (Ref. 1) such as transparent plastics, general purpose resins, adhesives (pressure-sensitive or hot-melt), impact modifiers and processing aids, textile and optical fibers, products for micro-lithographic applications, and even anti-cancer agents. Although acrylonitrile still takes the lion's share in that development, the corresponding esters definitely are in on a fast-pace growth pattern (see Table 1). Importantly also, the small volume functional (meth)acrylates contribute efficiently to the diversification and versatility of the final products.

Tab. 1. Worldwide production of acrylic monomers
(1985, 10^3 Tons)

Acrylonitrile	3000
Acrylamide	150
Acrylic acid	250
Alkyl acrylates (C_1, C_2, C_4, C_8)	1100
Methyl methacrylate	1100
Alkyl and functional methacrylates	growing

All of the corresponding poly(meth)acrylates-based products are
presently prepared by radical-initiated processes. In the
context of diversified growth mentioned above, it is undoub-
tedly very important to explore other polymerization pathways
which would allow close control of the molecular characteris-
tics of the resulting macromolecules, i.e. molecular weight and
molecular weight distribution (MWD = $\overline{M}w/\overline{M}n$), as well as
molecular architecture. Anionic polymerization is obviously the
method of choice to achieve that goal with a monomer carrying
an electron-withdrawing substituent, at least in principle. If
the process is perfectly living, it may provide molecular
weight control, narrow MWD if initiation is fast enough, and
architectural control (end-functionalization, block copoly-
merization, and possibly stereoselectivity). Severe problems
however arise from the sensitivity of the carbonyl groups along
the chain and of the α-hydrogen atom of the acrylates towards
nucleophilic attack, giving rise to transfer and deactivation
processes, accompanied by MWD broadening, branching, etc. This
paper will report recent progress in the control of truly "li-
ving" anionic polymerization of these (meth)acrylic esters,
using classical and ligand-modified initiators.

LIVING POLYMERIZATION OF METHACRYLATES IN THF AT - 78°C

The use of a higher polarity solvent to control ion-pairs ag-
gregation, and of a low reaction temperature to minimize the
secondary reactions reminded above, has allowed a much better
control of these anionic propagation processes : unimodal MWD
due to single-center propagation, near quantitative conversions

not limited anymore by dormant species, etc. Documented
examples of perfectly living systems are already abund in the
literature (Ref. 2), f.i. the synthesis of interesting well-
defined block copolymers. Such achievements, typically using
s.butyllithium as initiator, have been permitted among other
factors by the use of an end-capping agent converting the end
of the first living sequence into an anion better matching the
reactivity of the methacrylic ester yielding the second block;
diphenylethylene is typical in that respect.
More recently, two important improvements have strikingly fa-
cilitated the practical performing of these living copolymeri-
zations, to a point where they become convenient laboratory and
small-scale pilot experiments, using steel capil-
lary/syringe/septum techniques. The first of these improvements
implies purification of the monomers, contaminated by protic
impurities (mainly alcohols) and other esters, simply by trea-
ting them with aluminum alkyl derivatives (Ref. 3). The second
one uses α-methylstyrene (αMSt) instead of diphenylethylene as
the intermediate end-capping agent (Ref. 4), αMSt can now be
put in the reactor at the beginning of the process, often
suppressing one potentially noxious step of introduction of an
extra additive in a block copolymerization process. For
example, such techniques have been successfully applied to the
synthesis of suitable amounts of methylmethacrylate (MMA) block
copolymers used as macromolecular emulgators in the devising of
polymer alloys (Ref. 5). It is worthwhile to stress here the
generality of the method, even when applied to monomers less
common in anionic polymerization. Suffice it to cite two
interesting recent examples. The first one concerns stearyl
methacrylate which, despites some kinetic problems linked to
reaction medium high viscosity, has been polymerized in a "li-
ving" manner under controlled conditions. Its well-defined
block copolymers with styrene have proved to represent excel-
lent interfacial agents stabilizing for months carbon black
particles (ca. 400 nm) dispersions in paraffinic solvents (Ref.
6). The other achievement is the perfectly "living"
polymerization of glycidyl methacrylate, a monomer with great
potential in macromolecular engineering, as promoted again by
s.butyllithium under carefully controlled reaction conditions
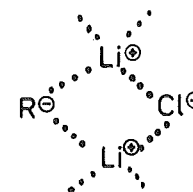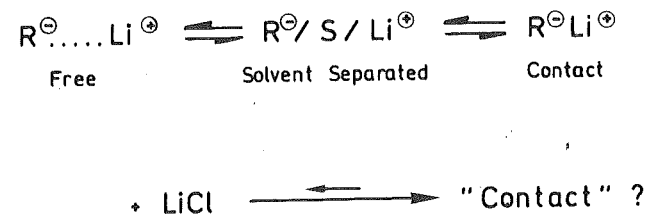(Ref. 7). The process is devoid of oxirane ring-opening

reactions and yields pure homo- or block copolymers, which can in turn be converted by treatment with sulfite into very valuable polysulfonic acids; corresponding amphiphilic diblock copolymers are remarkably efficient stabilizers for aqueous polymer latices (Ref. 5,8).

These examples clearly show that there are still very worthwhile challenges which can be met in a rather straightforward manner, simply using these improved classical methods.

ANIONIC LIVING (CO)POLYMERIZATION OF METHACRYLATES IN VARIOUS CONDITIONS

When however performed in a less polar solvent (i.e. 9V. toluene/1V. THF), MMA homopolymerization initiated at - 78°C by α-methylstyryl anions does not proceed to completion (yield ca. 80%) and produces a polymer with a broad multimodal MWD. Similarly, attempts to produce under comparable conditions a block copolymer of styrene and MMA yields a high proportion of homopolystyrene (Ref. 9).

In an attempt to modify and hopefully improve that situation a literature scan was performed to evaluate the possibilities to control the course of anionic polymerizations, and to limit if possible the extent of secondary reactions. It appeared that most of the positive (if not completely successful) attempts, were all related to the use of ligands interacting with the growing ion-pair, which could be divided into two main classes : inorganic or organo-metallic additives such as alkali and alkaline earth metal salts and alkyls on the one hand, cation-binding organic ligands such as polyethers (including crowns) and polyamines (including cryptands) on the other (Ref. 9). Hence the idea to test a number of salts able to form a 4-membered μ-type of complex with the ion-pair, and to possibly displace the classical equilibria between different types of ion-pairs (see Scheme 1).

$$R^{\ominus} \cdots Li^{\oplus} \rightleftharpoons R^{\ominus}/S/Li^{\oplus} \rightleftharpoons R^{\ominus}Li^{\oplus}$$

Free   Solvent Separated   Contact

$$+ \; LiCl \longrightarrow \text{"Contact"} \; ?$$

μ - complex ?

(dominant)

Scheme 1

The work of Lochmann et al. is worth a special mention in that respect (Ref. 17). Although a number of these salt additives improved the situation to some degree, the most efficient one found up to now is lithium chloride (LiCl). In the same lower polarity medium, it promotes the quantitative formation of a unimodal, narrow MWD, and allows the preparation of practically pure block copolymers. Under well-defined conditions, efficiency higher than 95% and $\overline{M}w/\overline{M}n$ as low as 1.02 can be obtained (Ref. 10). One intriguing aspect of its behaviour though, is its lack of influence on the microstructure of the PMMA formed, in this medium (ca. 60% syndio-, 25% hetero and 15% iso-triads) as well as in pure THF (ca. 80% syndio- and 19% hetero-triads).

ANIONIC LIVING (CO)POLYMERIZATION OF t.BUTYL ACRYLATE

It was obviously tempting to extrapolate the above-reported results to acrylates, although they are even more touchy than the methacrylates : in order to limit the difficulty, hindered

acrylates were used as models, typically the t.butyl one, since they are known to be less sensitive than n.alkyl ones. Despite that favorable feature, the classical and quantitative anionic polymerization of t.butylacrylate yields a polymer with broad multimodal MWD, even in THF at - 78°C.

Again, addition of LiCl to the s.butyllithium initiator guarantees a unimodal MWD, and a narrow $\bar{M}w/\bar{M}n$ (down to ca. 1.05). The perfectly "living" character of the propagation has been ascertained by resumption experiments, and by checking for the usual linear relationship D.P. = $[M]_o/[I]$ at 100% conversion, the validity of which was confirmed up to a M.W. of 150 000. Efficiency is also very high, i.e. 95% up (Ref. 9,11, 12). Unfortunately, these ligands do not counterbalance up to now the deleterious influence of higher reaction temperatures, and the truly "living" characteristics are lost somewhere between - 40 and - 20°C, depending on the conditions. Anyhow, such a close control of the "living" character of these polymerizations at low temperature clearly guarantees the easy synthesis of interesting block copolymers. As a typical example, characteristic data for polystyrene-poly-t.butylacrylate diblocks are given in Table 2. They confirm the excellent control achieved in that case, as well as the expected biphasic character of the materials obtained (Tg values practically equal to those of the corresponding homopolymers); that heterophase morphology has now been directly observed on transmission electron micrographs (Ref. 13).

Tab. 2. P(St-b-tBA) Diblock Copolymers (THF, - 78°C, LiCl/αMStLi = 5)

Predicted $\bar{M}n$ (x 10^{-3}) P(St-b-tBA)	Experimental $\bar{M}n$ x (10^{-3})		$\bar{M}w/\bar{M}n$	Tg (°C)
	SEC	Osmo		
105 - 80	186		1.05	41-107
60 - 50	110	106	1.05	42-107
11 - 43	54	48	1.05	46-107
25 - 25 (*)	42		1.75	41-100

(*) without LiCl

Obviously, these results open the way to an extrapolation of all the classical molecular engineering strategies used in anionic polymerization, and let us foresee the synthesis of a wealth of new products. It offers a very broad prospective indeed, the more as the t.butylacrylate unit (in homo- and copolymers) contains a very good leaving group (under acidic conditions) and thus can easily be converted into other acrylates by transalcoholysis, or into acrylic acid by hydrolysis, both practically quantitative reactions (Ref. 12,14).

Among many other possibilities of these systems, one should of course cite α- and α,ω-end-group functionalization of macromolecules, a typical and useful example of which is the synthesis (Ref. 11) of dicarboxylic telechelic poly-t.butylacrylate starting from a difunctional initiator (i.e. naphthalene-Li) and deactivating the resulting polymer with excess carbon dioxide. Here again, the use of LiCl allows the efficient synthesis (98% yield, 0.9 efficiency) of an α,ω-carboxyl-terminated polyacrylate having a functionality of 1.95 and a MWD of 1.30 for a 16 000 Mn.

STRUCTURAL AND MECHANISTIC ASPECTS OF THE INITIATOR SYSTEMS

Complex equilibrium

Both efficiency (as determined from Mn calc/Mn exper.) and MWD narrowness improve when increasing LiCl over initiating carbanion ratio from 0 to 20, and both these efficiency increase and MWD decrease follow an asymptotic behaviour, with limiting values of 0.97 and 1.02 respectively. The very fact that perfect control of the reaction kinetic features is achieved in that asymptotic manner is in itself a strong indication that the active species control may directly depend on the formation constant (equilibrium) of a (LiCl)x---LiR entity, which might exist under the form of 4-membered μ-type of complexes (x = 1 or 2) with electron-deficient bonding (see Scheme 1); however, that simple initial structure might be drastically modified by back coordination of the growing chain ester groups onto the metal atoms.

Compared to the situation existing in classical Li-R initiators, such coordination complexes are of course able to modify

the extent of the equilibria between the different types of recognized ion-pairs but also to promote the formation of new ones carrying the ligated LiCl. Whatever the nature of the actually active specie(s) in these new systems, the whole of the kinetic and structural data reviewed in the preceding sections of this paper point to the existence of a dominant single active carbanionic entity, enjoying a definite freedom of action since the reactions are both very fast (although somewhat slower than in the absence of LiCl) and not significantly stereoselective.

N.M.R._study_of the initiator

A first step to take was thus to put in evidence the interactions of the LiCl ligand with the carbanionic initiator : N.M.R. spectroscopy appeared as an informative tool for that purpose, since ^7Li and ^{35}Cl N.M.R. may give some information about the situation of both the initiator and the ligand.

It had already been shown (Ref. 9) that the ^7Li chemical shifts in these systems (versus LiCl taken as reference) were not a weighted average of those of the components, supporting the idea of a stoechiometric relatively stable complex. This is well substantiated by the fact that this shift in the LiCl/αMStLi 1:1 system remains practically constant between - 80 and 0°C, while the one of the pure αMStLi initiator undergoes a very important increase (from -1.3 to -1.8 ppm). Similarly, the T_2 relaxation time of that 1:1 system remains relatively constant over the same temperature range, while the one of the "free" anionic initiator is definitely higher and goes through a rather sharp maximum.

On the other side, ^{35}Cl NMR spectra also show important differences when LiCl is interacting with αMStLi; half-height band widths $(\Delta\nu)_{1/2}$ are considered instead of δ's because of the extreme broadness of these bands. Beside a decrease upon increasing temperature (expected increase in mobility), the spectra reveal that $(\Delta\nu)_{1/2}$ is higher for the complex, indicating a definite modification in the first solvation shell, and goes through a maximum for a 1:1 complex which is indeed the one that might have that minimum symmetry.

As rightly pointed out by Müller (Ref. 15), these results do not necessarily imply that the actual active species are these complexes, but they prove at least that the regulating in-

fluence of these ligands on the polymerization process depends on that complex formation process, even if their sole role was to displace classical ion-pairs equilibria.

Steric_and_Electronic Effects

The basic idea of the active site-control by a ligand provides for enough structural versatility to explore the key geometrical and electronic parameters at work in these systems. Electronic influences, which should be reflected in the stability and possible activity of the formed complex, are certainly some of these important features in devising these systems, as also strongly suggested by the data reported in Tab. 3.

The comparison of a series of organic acid salts with different electron withdrawing power supports the same conclusion : yields, efficiency and monodispersity in MMA polymerization in a low polarity medium at - 40°C decrease in the sequence LiCl > CH_3COOLi >> CF_3SO_3Li > CF_3COOLi.

Tab. 3. Anionic polymerization of tBu acrylate (THF, - 40°C, αMStLi) in the presence of Li salt (LiX)

X (Li)	% conversion	$\bar{M}w/\bar{M}n$	$\bar{M}c/\bar{M}n$
none	88	1.90	0.54
CH_3COO	94	3.80	0.89
I	98	1.80	0.59
Br	97	1.40	0.91
Cl	99$^+$	1.09	0.90

$\bar{M}c$ were grams of t.BA per mole of RLi, and $\bar{M}n$ experimental values were obtained from GPC (polystyrene calibration).

If electronic factors are important in controlling the formation and properties of the initiator-salt complex, it is also probable that steric hindrance around the active ion-pair will be a determinant factor in decreasing the relative importance of the noxious secondary reactions, particularly those occurring on the formed macromolecule. Since such a type of influence did not clearly appear in the preceeding results, advantage was taken of the possible use of organic ligands in order to better clarify that point (Ref. 16) . It is well known indeed that crown ethers are reagents of choice to chelate al-

kali-metal ions, surrounding them with a steric barrier blocking a given space area around the M-X ion pair (the electronic situation of which is of course simultaneously modified).
It is interesting to find out (see Table 4) that the use of specific crown ethers may indeed bring about the same benefits as other inorganic-type ligands, as clearly shown in experiment 3.

Tab. 4 : Effect of crown ethers on MMA anionic polymerization (Toluene, 15 min : at - 20°C, crown ether/initiator molar ratio = 2).

Nr.	Init.	Crown Ether	% Conv.	$\frac{\overline{M}w}{\overline{M}n}$	$\frac{\overline{M}n_{calc.}}{\overline{M}n_{exp.}}$	"Living" character
1	Ph$_2$CHNa	none	85	2.0	0.62	no
2	Ph$_2$CHNa	12,4	99	1.7	0.83	partial
3	Ph$_2$CHNa	Dibenzo-18,6	99	1.05	0.91	yes
4	Ph$_2$CHLi	none	<10	>3	–	–
5	Ph$_2$CHLi	12,4	21	2.5	–	–
6	Ph$_2$CHLi	Dibenzo-18,6	16	>3	–	–

Moreover, ligands most suitable for Na cation, such as those used here, are much more efficient for a Na-based initiator than for a Li-one, indicating a more efficient interaction with the active site sphere. Finally, the sterically more hindered dibenzo-18,6-crown is significantly the only one which simultaneously achieves high conversion and efficieny together with very low dispersity. Since these experiments were conducted in an apolar non-solvating medium, one may thus conclude to the importance of steric hindrance around the active ion-pair in minimizing undesirable side-reactions in these polymerization processes.

IN CONCLUSION, ligated anionic initiators are becoming increasingly efficient tools for controlling the "living" polymerization of methacrylic and hindered acrylic esters : already in their present state, which is still prone to optimization, they open a new era in the molecular engineering of (meth)'acrylate-based polymers. Furthermore, they also obviously represent a new key for mechanistic study of these polymerizations; in particular, the additional ligand may be considered as a probe of the ion-pairs environments and may thus provide, together with multinuclei NMR, valuable insights into the structure and fate of the most interesting initiators.

ACKNOWLEDGMENTS

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