

## **A new family of “ligated” anionic initiators for the “living” polymerization of (meth)acrylic esters**

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### **Summary**

A new family of ligands (dual  $\sigma$  -  $\pi$  ligand), i.e. chelating lithium alkoxides, Li-O-(CH<sub>2</sub>-CH<sub>2</sub>O)<sub>n</sub>CH<sub>3</sub>, is shown to be very effective in promoting the living anionic polymerization of methacrylic and acrylic esters, including a number of primary alkyl acrylates such as n-butyl acrylate and 2-ethylhexylacrylate.

### **Introduction**

The "living" polymerization of methacrylic and (more difficult) of acrylic esters has been the aim of frantic exploratory research in the last decade, an effort motivated (beyond the obvious mechanistic challenge) by the availability of a broad family of monomers yielding diversified materials with very desirable properties. As a result of that activity, an unexpectedly large number of new initiating systems has been reported in the literature, and will be the topic of a more systematic analysis in a forthcoming publication <sup>(1)</sup>.

Among the different strategies proposed as yet, it appears that only one, i.e. modification of classical anionic initiators by coordinating ligands, is able to answer simultaneously, the double challenge of producing high M.W. products with precisely tailored chain length and chain ends, while being at the same time perfectly compatible with many other types of monomers such as vinyl aromatics, dienes, oxirane,... That approach had been broadly explored since several decades <sup>(1)</sup>, but it is only rather recently that really efficient controls have been achieved, either by the use of  $\mu$ -binding ligands (yielding 4-center delocalized complexes <sup>(2)</sup>, such as with LiCl <sup>(3)</sup>), or of chelating and hindered  $\sigma$ -donating ones (the best one up to now being dibenzo-18-crown-6) <sup>(4)</sup>. Such optimized additives control indeed both the electron density and the steric hindrance around the ion-pair, allowing a practical elimination of secondary reactions while keeping a high polymerization rate.

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This communication describes the combination of these two different coordination modes into a unique type of dual  $\mu - \sigma$  ligand<sup>(5)</sup>, i.e. salts of chelating polyethers of formula (I),  $M-O-(CH_2-CH_2-O)_nCH_3$ . As anticipated, they provide a surprisingly good control of the anionic polymerization of (meth)acrylic esters, even allowing the quantitative "living" polymerization of a number of primary alkyl acrylates, a hitherto unmet challenge.

### **Experimental**

Lithium polyether alkoxides were prepared by reacting equimolar amounts of the corresponding polyether alcohols and n-Butyllithium in hexane at 0°C. Usual purification of monomers and solvents was described in detail elsewhere<sup>(6)</sup>.

Polymerizations were carried out under moisture and oxygen-free conditions using diphenylhexyl lithium (DPHLi) as an initiator .

Size exclusion chromatography (SEC) was performed with a Hewlett Packard 1090 apparatus equipped with 4 columns (10<sup>5</sup>, 10<sup>3</sup>, 500 and 100 Å) and a HP 1030 A refractive index detector (polystyrene standards).

### **Results and Discussion**

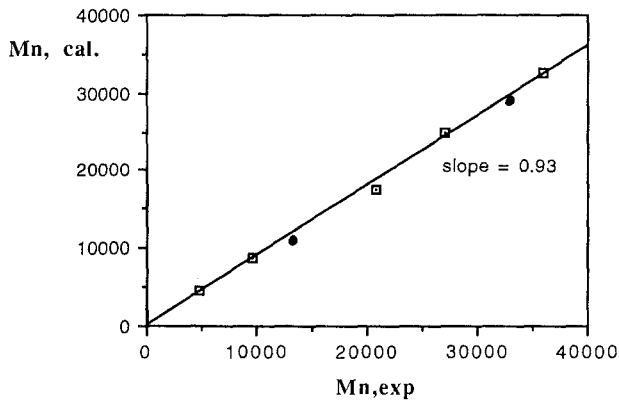
Table 1 summarizes the results obtained when anionically polymerizing different monomers in the presence of a series of Li-polyether alkoxides; only lithium was considered here, since it seemed more appropriate to use, for the sake of simplicity, the same cointercation as in the usual initiators (i.e. n-butyllithium or its monoaddition product with diphenylethylene). Several new and very encouraging features emerge at first sight from these results, and are discussed in sequence hereafter.

. For the first time, a practically quantitative polymerization of some typical primary alkyl acrylates (i.e. n-butyl and 2-ethylhexyl) becomes possible, using classical metalalkyl initiators. On the other hand, shorter alkyl esters (i.e. ethyl and methyl) still give rise to deviant secondary reactions : it is clear that we reach there the limit of the protection ensured by the added ligand, against vigorous nucleophilic attack.

. The process is essentially "living", as demonstrated by efficiency factors "f", the constancy of the  $M_{n,SEC}/M_{n,calc}$  over the whole range of investigated weight and resumption experiments (Fig. 1). Obviously enough, these characteristics open the way towards the synthesis<sup>(7)</sup> of a number of new block (and star) copolymers, as

**Table 1. Anionic Polymerization of (Meth)acrylic Esters**  
 (10 minutes, at  $-78^{\circ}\text{C}$ ,  $0.5 \text{ M}\cdot\text{L}^{-1}$ , in 9 toluene/1 THF, with  $4\cdot 10^{-4} \text{ M}\cdot\text{L}^{-1}$  DPHLi + 10 L)

Monomer	Additive L	% conv.	"f" ( $M_{n,\text{calc.}}/M_{n,\text{exp.}}$ )	Mw Mn	Microstructure		
					i	h	s
2.Et.H.Acrylate	no	45	5.0	3.20			
	I, n=1	95	0.34	2.30			
	I, n=2	100	0.94	1.07		-	
	I, n=3	92	0.94	2.60			
	II	0	-	-			
n.Bu.Acrylate	I, n=1	80	0.32	3.30			
	I, n=2	100	0.96	1.15		-	
	I, n=3	85	0.81	2.20			
MMA	no	55	0.50	2.50	17	25	58
	I, n=2	97	0.92	1.04	1	16	83



**Figure 1. Anionic Polymerization of 2-ethylhexyl acrylate**  
 (10 min, at  $-100^{\circ}\text{C}$ , in 9 toluene / 1 THF, with  $4\cdot 10^{-4} \text{ M}\cdot\text{L}^{-1}$  DPHLi +  $4\cdot 10^{-3} \text{ M}\cdot\text{L}^{-1}$  I, n=2)  
 □ one-shot reaction; • 2 steps resumption experiment.

well as of  $\alpha(\omega)$ -functionalized polyacrylates.

. Another point of interest is the stereochemistry of the polymers obtained in essentially apolar solvents. An important example is the high syndiotactic content of PMMA obtained under these conditions : ca. 83% (i.e. a  $T_{g,m}$  of 135°C), compared to 58% (and 17% isotactic placements) in the absence of I. This result stems for a permanent control of the growing centers during propagation, through coordination by (I); that hypothesis has now been confirmed by  $^7\text{Li}$  and  $^{13}\text{C}$  NMR spectroscopic measurements, indicating the formation of a single strong 2:1 complex ((I)/LiR)<sup>(8)</sup>.

. Still another fact of importance is the total inefficiency of a corresponding "diglyme" compound, i.e.  $\text{H}_3\text{C}-(\text{CH}_2-\text{CH}_2-\text{O})_2\text{CH}_3$  (II), lacking the metal-alkoxide bond able to promote the  $\mu$ -type coordination. That behaviour strongly supports the relevance of our basic idea of building up a cooperative dual  $\mu - \sigma$  coordination environment around the active ion-pair<sup>(8)</sup>.

. Finally, one should stress the amazing selectivity of that ligand-ion pair interaction, most probably due to conformational factors governing a subtle balance of steric hindrance and electronic distribution around the growing center. Not only the Li-alkoxides (I) wherein  $n = 2$  are significantly more efficient, in terms of both "f" and  $M_w/M_n$ , but substituted polyether moieties (i.e. a polypropylene oxide based alkoxide) give much poorer results.

**In conclusion**, these new achievements support and extend our previous claims on the interest of applying coordination chemistry principles for controlling otherwise ill-defined polymerization processes, particularly by tailoring "ligated" active sites<sup>(9)</sup>. Further work in progress will confirm these results and views in more detail.

### **References and notes**

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