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NEW PROSPECTS IN HOMOGENEOUS RING-OPENING POLYMERIZATION OF HETEROCYCLIC MONOMERS

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Since the early days of ring-opening polymerization of oxirane and related monomers, many initiators have been described for this type of chain reaction, belonging respectively to acid-base, ionic, and coordination catalysis. In particular, it has been shown that the highly active coordination type initiators are the only ones able to promote the ring-opening polymerization of methyloxirane (propylene oxide, PO) to high molecular weight, and eventually stereoregular, polyethers. Unfortunately, most of the catalytic systems described (see f.e. ref. 1 to 4) do not lend themselves to a straightforward analysis of their structural and kinetic behaviour, owing to the often ill-defined composition and struc-

ture of the active site precursors.
However, from the indications obtained in these investigations, two important requirements for the efficient production of a high molecular weight, stereoregular polymer (PPO) from methyloxirane became apparent:

- 1) the methods of preparation of the active catalysts generally imply the formation of M...X...M groupings (mainly M...O...M ones resulting from the hydrolysis of metal alkyls or alkoxides);
- 2) the possibility of obtaining stereoregular crystalline polymers from monomers which, like PO, do not induce any important "chain-end control" of the tacticity implies in turn, a "catalyst site control" as proposed by Vandenberg (5) and Tsuruta (6). This type of control as well as the linear three-center structure implied by the rear attack (with inversion) of the monomer unsubstituted carbon, definitely necessitates the presence of several metal atoms involved in a polynuclear site, as already suggested by Vandenberg (7).

On the basis of the preceeding conclusions, it appeared worthwhile to synthesize purposely, in an easily reproducible manner, well defined compounds linked together by oxygen bridges and to study their behaviour in ring-opening polymerization.

I. Bimetallic μ -oxoalkoxides : a new family of ring-opening polymerization catalysts.

A. Preparation.

1. After different exploratory attempts, a straightforward and reproducible method has been developed, yielding a whole family of compounds enjoying a set of interesting properties, in particular a very high solubility in organic solvents, including apolar hydrocarbons. It implies a 2 steps condensation between a metal (M) alkoxide and a metal (M) acetate, according to the following scheme:

ding to the following scheme $2\dot{0}\circ c$ $2 \times m^1$ (OR) $+ \times m^2$ (OAc) $2 \times m^1 - c - m^2$ (Y) $m - c - m^2$ $m + 2 \times m^2$ (OAc) $m - c - m^2$

where X is usually an OR group.

The reaction can be drawn to completion by continuous removal of the resulting ester by distillation.

Under careful control of the thermal condensation conditions, a large family of compounds having a composition which corresponds exactly to the expected structure (I) has been obtained, including transition metals known for their activity in heterogeneous catalysis. Their composition has been confirmed within \pm 5 % of the expected values by elemental and functional analysis (amount of ester evolved, % C,H,O, ratio M $^{\prime}$ by

complexometric analysis, ratio OR/M1 by g.l.c.)

2. These conclusions have received a further confirmation from another alternative preparative procedure, based on the use of Meerwein's mixed alkoxides (8) which are then carefully hydrolyzed in an alcoholic medium. This method summarized in the following scheme, has been applied successfully to aluminium—zipc alkoxides:

Again, analytical data fit with the expected structure; furthermore, both the general and catalytic properties of the products obtained correspond very closely to those of the compounds prepared by the thermal condensation procedure described above.

It is worthwhile to point out that this behaviour indicates clearly the greater stability of the AlOZn bridges over the AlOAl ones, favouring the expected intramolecular reaction.

3. Another important point is the ease of exchange of OR groups in metal alkoxides: this property opens a very convenient way for the preparation of compounds carrying different R'groups, starting with OR groups of which the corresponding alcohol is very volatile (i.e. isopropoxide) and displacing them in an alcoholysis reaction using R'OH as the solvent. Quantitative exchanges have been obtained by this technique even with very bulky groups.

B. Properties

1. Catalytic activity. In perfect agreement with the structural hypothesis discussed above, these compounds rank among the best catalysts known for the ring-opening polymerization of several heterocyclic monomers; a practical indication of their activity is given in Table I.

Monomer		{Zn}/mol.1 ⁻¹	{ M}/mol.1 ⁻¹	Solvent	T/°C	t' _{1/2} /m	
Methyloxirane	Al ₂ ZnO ₂ (OBu ¹¹) ₄	16.6 x 10 ⁻³	1.0	heptane	30	20	_
Methylthiirane			1.0	heptane	30	13	
$\epsilon\text{-Caprolactone}$	Al ₂ ZnO ₂ (OPr ¹) ₄	5×10^{-3}	1.0	toluene	0	5	

Table I Acitvity of bimetallic oxoalkoxides in polymerization.

2. Physical properties: Obviously, these compounds will arrange themselves to fulfil the vacant coordination positions on metals M and M by the electron pairs available on the OR groups of the same or other oxoalkoxide molecules, resulting in a reversible coordinative association (characteristic of all metal alkoxides). This mean degree of association n in {(RO) 4Al 2 0 M } - compounds has been determined by cryoscopic measurements, and ranks from 1 to about 8 in benzene or cyclohexane solutions. It depends as expected on the nature of the solvent, of the metals, and of the R groups; it is important to note that some specific ligands like alcohols lead to a complete dissociation of these aggregates. This aggregation might explain the striking solubility of these compounds in saturated hydrocarbons, as being due to a compact oxide structure surrounded by a lipophilic layer of alkoxide groups. It also accounts for the electronic delocalization, put in evidence by spectroscopic and magnetic measurements.

In conclusion, these soluble bimetallic oxoalkoxides represent in fact small fragments of mixed oxides, maintained in organic solution by alkoxide groups, and in which scrambling of ligands can occur: accordingly they represent an interesting model inbetween homogeneous and heterogeneous

catalysis.
Owing to their activity, their well-defined composition, and the possibility to modify systematically their structure, they represent certainly one of the best models on which to undertake a detailed study of the ring-opening polymerization processes, in particular the eventual topochemical influence of the aggregate on the active sites behaviour. The following sections will summarize the exploratory studies performed in this prospect.

II. Polymerization of lactones A. Activity. It has been shown in table I that oxoalkoxides are exceptionnally efficent catalysts for ε -caprolactone polymerization (relative $k.10/\min^-=141$). This efficiency decreases in the series δ -valerolactone (17.0), β -propiolactone (1.1), γ -butylolactone (\circ 0). Disubstitution of the α -carbon atom, as well as monosubstitution of the β -carbon, have also an adverse influence. The equilibrium is shifted towards the open chains to an extent of more than 99 %.

B. Living character. It has been ascertained by the proportional increase of by with conversion, the linear relationship between DP and $\{M\}/\{c\}$ ratios at 100 % conversions, and the resumption of the polymerization on addition of fresh monomer to a polymerized reaction mixture (with a proportional increase of DP). High molecular weights (up to 150.000) and narrow distributions $(Mw/_{Mn}=1,05)$ can be reached by avoiding side-reactions. C. Mechanism of chain growth. The living character of the propagation reaction and the low dispersity of the products obtained allow to perform polymerization where the growing chain is limited to 1 or 2 monomeric units ($\{M\}/\{c\}=1$ or 2). After hydrolysis, the structure of the resulting organic product (determined by elemental, functional and spectroscopic analyses) support the following reaction course:

(RO)
$$_4$$
 Al $_2$ O $_2$ M^{II} + caprolactone _____ Al $_2$ O (CH $_2$) $_3$ -CO) OR $_1$ -2

$$H
\downarrow H
\downarrow O - (CH2)5 -CO \
\downarrow O - OR
\downarrow O - (CH2)5 -CO \
\downarrow O - OR
\downarrow O - OR$$

This scheme, confirmed for different catalytic systems, implies clearly a chain propagation proceeding through insertion of the lactone units in the Al-OR bonds, with a specific cleavage of the acyl-oxygen bond, resulting in the permanent binding of the growing chain to the catalyst through an alkoxide link (rather than a carboxylate one). It corresponds very well to an anionic type coordinated insertion mechanism.

D. Number of active sites.From the living polymerization experiments, it can be calculated that every (RO) $_4^{\rm Al}{}_2^{\rm O}{}_2^{\rm Zn}$ catalytic unit generates only one polyester chain, in spite of the presence of 4 potentially active OR groups. This behaviour is due to the burrying of 3 OR groups over 4 in the coordination process giving rise to the aggregates, as supported by NMR measurements; this is confirmed by experiments in the presence of alcohol, where each of the dissociated units is now able to generate four polymeric chains. In other words, the number of available active sites will depend closely on the value of \overline{n} , i.e. on controllable structural and kinetic conditions.

E. Course of the polymerization reaction. Although rather simple under dissociative conditions (R = k (M) (C) with E_A = 11,2 Kcal.mol , the polymerization kinetics is complicated by the presence of higher aggregates ($2^{\frac{1}{2}}$ order in catalyst, initiation period).

On the other hand, Job's continuous diagrams have established that the association of the catalytic units is not perturbed by the growth of the polymeric chains, resulting in a starshaped entity as confirmed experimentally by viscometric experiments. All these data can be rationalized by a basically simple coordination—insertion mechanism, implying a determinant local dissociative step: this process takes place on specific OR groups on the aggregates, by an alternate (flip-flap) reaction scheme, involving 2 (temporarily) vicinal metal atoms.

III. Polymerization of oxiranes

A. Overall course of the reaction: As confirmed by the same type of experimental approach, these polymerizations follow a pattern very similar to the one described in the case of lactones, with the following characteristics: a simple overall kinetics ($R_j = k_j = k_j$

In addition, copolymerization experiments have indicated that the formation constants of the different competing complexes involved might be responsible for a powerful and unexpected thermodynamic control of the apparent reactivity ratios. Interesting examples include the preferential incorporation of epichlorohydrin (ECH) over PO in benzene solution, although its homopolymerization rate is about 250 times slower, and the reversal of this behaviour in polar solvents like o.dichlorobenzene. Similarly, an equimolar mixture of PO and methylthiirane (PS) yields essentially PPO in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) $_4$ Al $_2$ O $_2$ Fe and PPS in the presence of (RO) and RO $_2$ Fe and PPS in the presence of (RO) and RO $_2$ Fe a

B. Importance of the aggregates : There are however strong indications that these reactions are by no means simple ones. Indeed, by fractionating a typical polymerization product, i.e. PPO, two main fractions are isolated: a relatively monodisperse low Mw linear ologimer ($\overline{\rm DP}$ usually between 4 to 12), and a high Mw partially isotactic. product with a rather broad distribution (Mw/Mn \leq 10) The ratio of these 2 products depends very strongly on the structure of the catalyst : it can be modified from practically pure polymer (97 %) to a high content in oligomers (up to 75 %). This situation has been investigated into more detail, since it was suspected to be related to specific types of aggregates, involving different steric environments and topochemical controls.

 1°) Formation of high Mw polymers: selective poisoning experiments with LiCl have stablished that less than 4% of the catalytic units were able to yield a high polymer chain.

These very efficient active centers are highly stereoselective under strongly associative conditions, as confirmed by experiments with enriched optically active monomers. However the isotactic fraction may decrease from 75 to 5% when dissociative factors take over (ΔT , more bulky R groups, addition of alcohol, polar solvents).

 2°) Formation of specific oligomers: The oligomeric fraction has been shown to consist essentially out of linear polyesters having a $H(OC_3H_6)$ n OR composition.

It could be proved , by experiments with optically active monomers and high resolution HNMR spectroscopy, that they are formed in a non-stereospecific manner, in a parallel and independent reaction. Most interestingly, their MW distribution is not monotonous : GPC chromatograms indicate the presence of 6, 12 and 35-mers, the proportions of which depend on the association parameters in the aggregates. Complete dissociation leads to dimeric species.

In summary, the high MW chains could be produced by a few very active centers on large aggregates, in a steric environment which controls the stereospecificity of the reaction. On the other hand, other Al-OR groups could start chains moving successively to different Al atoms until termination occurs at low $\overline{\rm DP}$ values reflecting the lenght of the chain path, itself proportional to some extent to the size and shape of the aggregates, i.e. putting in evidence a new type of topochemical control.

IV. Synthesis of new block copolymers

The living character of the lactones polymerization has open new

ways of access to different block copolymers, with well-controlled sequence lengths.

A. Poly lactone - polylactone blocks :

Consecutive polymerization of 2 different lactone monomers has been performed successfully; however, high yields of block copolymers (>90%) are attained only under complete dissociation of the aggregates, ensuring the use of all potentially active OR groups ,which otherwise might start homopolymer chains of the second added monomer. As a typical example, caprolactone - propiolactone copolymers have been obtained which exhibit interesting mixed crystalline morphologies, depending on the thermal history of the samples.

B. Polylactone - polyether (or thioether) blocks:

Under the same critical conditions, these block products have been obtained in satisfactory yields (up to 80%). Since these A-B copolymers are always -OH terminated (cfr polymerization mechanism), any efficient coupling technique may lead to the corresponding (eventually thermoelastic A-B-A structures.

C. Polylactone - poly-X blocks :

The structural and kinetic behaviour of the oxoalkoxide entities allow their easy binding to any polymer chain (PX) carrying a suitable functional group: in this frame, PX - polylactone materials have been prepared as grafted, A.B block, and A-B-A block copolymers.

They display very intersting phase separations into small domains (below 1.000 o), resulting in valuable and sometimes unexpected properties of the materials as such and in blends (typical dispersion patterns, fracturation

Conclusions.

hehaviour ...)

The good control and knowledge of these oxoalkoxides structures have led to a better understanding of the key factors governing the ring-opening polymerization processes; the results emphasize dramatically the determinant influence of the association phenomena in the catalytic species. They have also promoted the discovery of new phenomena (like the topochemical controls of the chains formation), and of new synthesis methods (for the block copolymers), which could most probably be extended to more classical catalysts. There is little doubt that these species constitute a very promising tool for many problems in polymer and general chemistry.

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