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NEW PROSPECTS IN HOMOGENEOUS RING-OPENING POLYMERIZATION OF HETEROCYCLIC MONOMERS

by

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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 structure 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 :

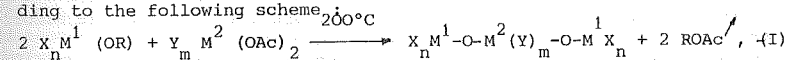
- 1) the methods of preparation of the active catalysts generally imply the formation of M...X...M groupings (mainly M...O...M ones resulting from the hydrolysis of metal alkyls or alkoxides);
- 2) the possibility of obtaining stereoregular crystalline polymers from monomers which, like PO, do not induce 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 preceding 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 (M¹) alkoxide and a metal (M²) acetate, according to the following scheme:



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 + 5 % of the expected values by elemental and functional analysis (amount of ester evolved, % C,H,O, ratio M¹/M² by

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 ($R_p = k[M][C]$), scale of relative rates (in function of the monomers structure) typical of an anionic-type process, and a coordination insertion process of the monomer into the Al-OR bonds with a stereospecific ring-opening ($Al-OR + nPO \rightarrow Al\{O - \overset{\ominus}{C}H(CH_3) - CH_2\}_n OR$). Again the aggregates seem to remain unperturbed by the growing process, and the overall behaviour fits with a flip-flap mechanism between 2 (or more) metal atoms, in agreement with the proposals of Vandenberg (7) and Tsuruta (9). However there is no indication of a truly living propagation in this case.

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 $(RO)_4Al_2O_2Fe$ and PPS in the presence of $(RO)_4Al_2O_2Zn$.

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 oligomer (DP usually between 4 to 12), and a high MW partially isotactic product with a rather broad distribution ($M_w/M_n \leq 10$). 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 established 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 $H(O_3C_3H_6)_n^-$ 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 DP values reflecting the length 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. Poly lactone - 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. Poly lactone - 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 interesting phase separations into small domains (below 1.000 Å), resulting in valuable and sometimes unexpected properties of the materials as such and in blends (typical dispersion patterns, fracturation behaviour ...)

Conclusions.

The good control and knowledge of these oxoalkoxide 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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Acknowledgements : The authors want to recognize the pioneering work of M. Osgan and the contribution of N. Kohler at the Institut Français du Pétrole, as well as communication of results by their coworkers at Liège, P. Condé, J.J. Louis, and C. Stevens. They are also grateful to the I.F.P. and the Union Carbide Co for their support.