COORDINATION CHEMISTRY : A GOLDEN TOOL FOR TAILORING POLYMERIZATION PROCESSES ?

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In our time of unexpectedly vivid renaissance of polymerization catalysis, it seemed appropriate to make out of this introductory lecture an exercise in prospective, rather than a systematic presentation of research results.

That strong and multifacet outburst of new discoveries, considered by many as improbable a decade ago, is of course of utmost importance as it opens the way to many key achievements:

-   fine control of catalyst kinetic and structural behaviour (livingness or transfer, plus chemo, regio, stereo (enantio) and chronoselectivity);

-   unraveling of new mechanisms;

-   implementation of more efficient process conditions;

-   precise tailoring of new products and materials.

The goal of this presentation is thus to convince you that coordination chemistry is a golden working tool for building up on that renaissance, a statement which will be illustrated by detailing examples taken out of our own work, while put in the perspective of current trends of ideas.

The basic concept is of course simple (on paper) and well-known : a metal-based active site , able to accomodate the monomer, can be modified by ligands (often complex ones), which will allow its fine-tuning (as demanding as the one of a speed-car) in terms of electron distribution and steric hindrance; so ensuring a much better control of the kinetics and the selectivity of the reactions involved in the building up of the chain. The main challenge here however is the extreme sensitivity of the active site performances towards minute changes in ligand structure, i.e. the narrowness of the modification "windows".

It will thus be discussed first which degree of sophistication these approaches have already reached, and thereafter, what are their actual extensions as well as the future opportunities they can still offer.
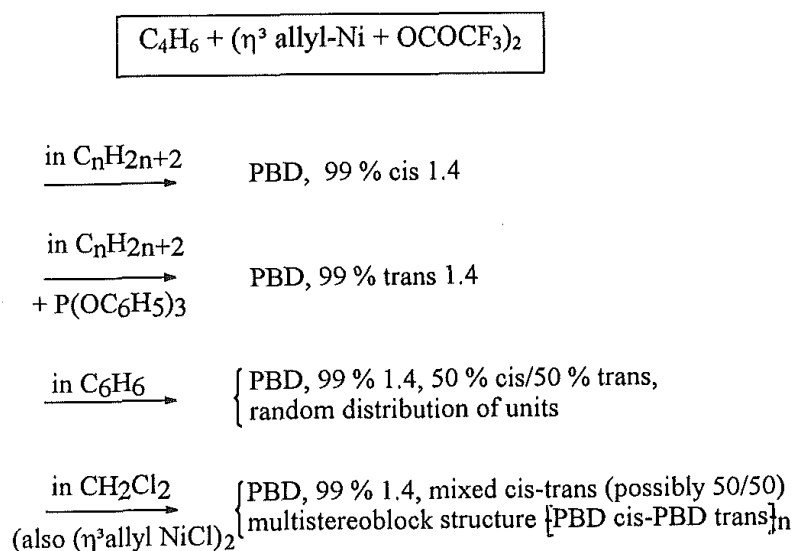
Coordination polymerization "stricto sensu"

1) <u>That kind of polymerization mechanism</u> has now been, for about four decades, the best illustration of the above statements. And after the spectacular success of the Ziegler-Natta type of catalysts (and some of their monometallic versions), <u>the last wave of discoveries again brought up a number of extremely exciting and performant new systems</u>, often structurally simple and even mononuclear, including for example :

-   different metallocene cationic complexes for the (stereo) selective polymerization of olefins (Ref. 1), but also of polar monomers such as (meth)acrylates (Ref. 2);

-    transition metal carbene complexes for the living polymerization of norbomene-type monomers (Ref. 3);

-   the totally unexpected isomerizing polymerization mechanism put in evidence by Fink using nickel-complexes, where the obtained polymer is the result of an apparent 2-ω insertion of a long-chain α-olefin (Ref. 4).

2. <u>One of the best paradigms in this field certainly remains the butadiene polymerization initiated by bis-(η^3-allyl-M_T-X) complexes</u>, a reaction where "total quality control", if not "zero-defect" could be reached by fine-tuning of the coordination sphere (Ref. 5):
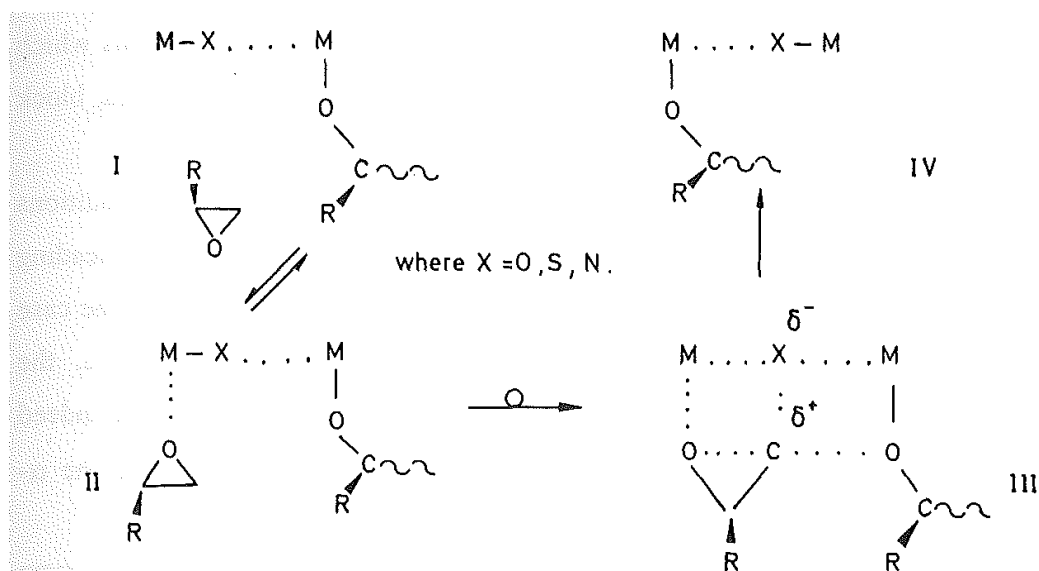
- control of the kinetics, by ligands blocking the (β-elimination sites (chloranil, small amounts of phosphites), resulting in a perfectly living polymerization; and also by election-withdrawing counteranions (e.g. CF_3-COO$^-$), bringing the overall polymerization rate to levels comparable to those of the best Ziegler Natta catalysts;

- control of the regioselectivity, essentially by the nature of the transition metal : chromium and molybdenum yielding a 1.2 structure (from γ-attack on the allyl group), while cobalt and nickel yield the 1.4 structure (α-attack), both geometries being achieved with 99 % selectivity;

- control of stereoselectivity with nickel complexes, since in paraffinic solvents a high in 1.4 content is obtained (over 98 %), while addition of an equimolar amount of trisphehylphosphite (a strong ligand blocking one coordination position for the monomer) ensures the obtention of 99 % trans 1.4 units (practically no 1.2 addition):

- and last but not least, control of the process chronoselectivity, i.e. the capability of controlling, through dynamic modifications of the coordination sphere (temperature and/or solvent contact interactions), the statistical placement of stereounits along the chain, as examplified in the following scheme :

$$\boxed{C_4H_6 + (\eta^3 \text{ allyl-Ni} + OCOCF_3)_2}$$

$\xrightarrow{\text{in } C_nH_{2n+2}}$ PBD, 99 % cis 1.4

$\xrightarrow[\text{+ P(OC}_6\text{H}_5)_3]{\text{in } C_nH_{2n+2}}$ PBD, 99 % trans 1.4

$\xrightarrow{\text{in } C_6H_6}$ $\begin{cases} \text{PBD, 99 \% 1.4, 50 \% cis/50 \% trans,} \\ \text{random distribution of units} \end{cases}$

$\xrightarrow[\text{(also } (\eta^3\text{allyl NiCl)}_2]{\text{in } CH_2Cl_2}$ $\begin{cases} \text{PBD, 99 \% 1.4, mixed cis-trans (possibly 50/50)} \\ \text{multistereoblock structure } \{\text{PBD cis-PBD trans}\}_n \end{cases}$

Scheme 1

A tentative explanation of that unexpected "chronoselectivity" has been based on a dynamic NMR study of the living system, and relies upon controlling the ratio of relative insertion and rearrangement rates of these nickel complexes, as illustrated in Scheme 2 :

Scheme 2

All of these results teach us a number of important lessons :

- mechanistic sophistication and unexpected performance tailoring are nowadays in the reach of rather simple coordination complexes (if properly adapted), as examplified by this small "3-keys informational machine" for butadiene polymerization;

- the determinant and already well-know influence of ligands (electron-donating molecules, counter-ions) is more and more confirmed and better understood;

- we begin to appreciate the importance of transient contact interactions, i.e. the key role of solvents and weak ligands as demonstrated above : something which had been vastly underestimated up to now;

- and last but not least, we may gain a growing confidence in our ability to extrapolate the underlying coordination chemistry principles to different types of substrates and mechanisms, a strong new bend that will be the topic of the following sections.

3 The typical coordination-insertion polymerization mechanism is not limited to olefinic monomers and transition metal complexes, as confirmed by a number of recent studies on the ring-opening polymerization of heteroatomic cyclic monomers by group II or III metal alkoxides.

Scheme 3

In direct support of Vandenberg's hypothesis (scheme 3), it was indeed demonstrated that (Refs. 6,7):

- monomers (including oxiranes, lactones, anhydrides, etc..) strongly coordinate to vacant positions of these metal alkoxides (simple or complex, usually of Al or Zn);

- propagation proceeds by insertion, rejecting the precursor OR group at the end of the chain, and insuring remarkable regio, stereo- and sometimes enantioselectivity.

That means of course that a proper adequation of the σ-bonded group borne by the metal and of the monomer structure, can open many new possibilities for macromolecular engineering through that kind of rather straightforward mechanism; possibilities already including selective and sometimes leaving polymerization of oxiranes, lactones, cyclic anhydrides, cyclic carbonates and even isocyanates.

Application of coordination chemistry principles to, "classical" anionic polymerization mechanisms

This other type of nucleophilic polymerization mechanism has become very important thanks to its ability to promote propagation processes devoid of any important transfer and termination reactions, so providing for "living" systems which ensure a perfect control of molecular engineering approaches (Mn, end-groups, block architecture...).

However, depending on the monomer structure and reaction medium conditions (solvent, temperature, concentration), that behaviour is sometimes perturbed, leading to ill-defined kinetic and structural characteristics. This has particularly been the case for an important class of monomers, gaining more and more interest, i.e. the (meth)acrylic esters and specially methylmethacrylate (MMA); they are prone indeed to a number of secondary nucleophilic attacks on the carbonyl groups and the α-hydrogen atoms, resulting in termination (or transfer) reactions.

Although that problem was partly solved by the use of other initiating systems (GTP (Ref. 8), transition metal complexes (Ref. 2), no-metal organic ion-pairs (Ref. 9)), none of those has simultaneously allowed the coupling of a high M.W. polymerization of (meth)acrylic esters with that of a range of classical monomers like styrenes, dienes, vinylpyridines, oxiranes, and even cyclosiloxanes, all currently used in anionic macromolecular engineering processes.

It thus seemed more promising to revisit typical anionic initiators (i.e. sec.alkylmetals, essentially Li) and to modify them using coordination chemistry approaches : hence the idea of "ligated ion-pairs" (Ref. 10). That idea was rampant in the literature since the 1960's, but never led to general, precise kinetic and structural control because of a vast underestimation of the extremely strict requirements involved in terms of the ligands structure. In fact, coordination chemistry offers us with two different families of ligands able to modify at the same time the election distribution and the steric hindrance around the ion-pah (the 2 requirements for an efficient control of the active site) : the so-called μ-(4-center delocalized) and σ-(simple dative bonds) complexes (Scheme 4), and several examples of the first type appeared during the last decade (Al-alkyls of Hatada (Ref. 11), alkali metal alkoxides of Lochmann (Ref. 12), Al-phenoxides of Ballard (Ref. 13)).

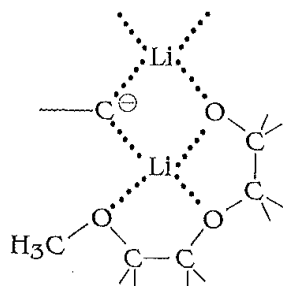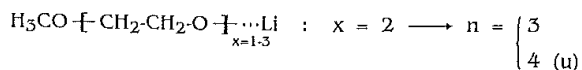### ION-PAIR COMPLEXATION
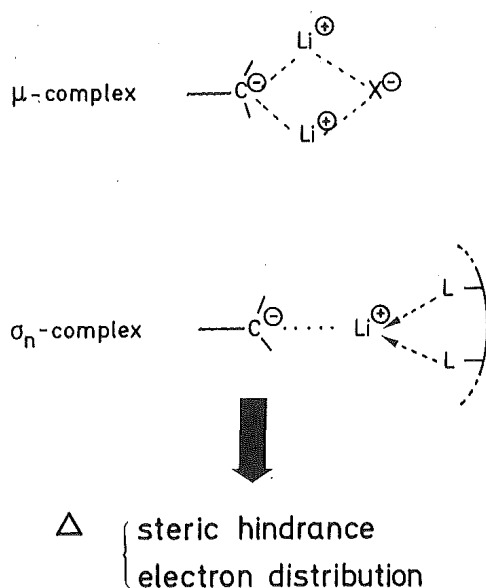
Scheme 4

We had ourselves proposed the use of LiCl for Li alkyl-initiated polymerizations (Ref. 14), a somewhat more efficient combination, but in fact none of these systems was able to meet simultaneously all of the requirements generally implied in molecular engineering : a situation which was obviously due to the selectivity of action of the ligands involved. For instance, LiCl is a very practical and efficient ligand to work with in moderately polar solvent (pure THF or its mixtures with hydrocarbons), but was unable to promote random copolymerization of MMA with ter-butylacrylate (although ensuring both homo- and block copolymerization of these two monomers in a perfectly living manner), and was as well unable to control living homopolymerization of primary acrylates.

Playing with that concept of the ligand structural characteristics, we could fust demonstrate (Ref. 15) that in non-polar (hydrocarbon) media an hindered chelating σ-ligand (i.e. dibenzo-18-crown-6-ether) was a better alternative to control a number of problems such as higher temperature (up to 20°C), random copolymerization, etc., but was less versatile for tacticity control (an important point in obtaining highly syndiotactic (ca. 80 %) PMMA, displaying a 130°C Tg).

It was hence a logical step to combine both concepts and use of a family of μ-σ dual ligands, the best example as yet (Ref. 16) being Li-(O-CH$_2$-CH$_2$)$_x$-OCH$_3$ (x = 1 to 3), giving rise to mixed complexes of the type sketched in Scheme 5, the Li-O-group yielding a (μ-complex, while the

crown ether-like moiety forms a chelating σ-one. (It is relevant at this point to stress that all complexation processes between ligands and lithium alkyls have been monitored by multinuclei NMR (Ref. 10)).

μ-σ LIGANDS : A WINNING COMBINATION

$$H_3CO\text{--}[CH_2\text{-}CH_2\text{-}O]_{x=1\text{-}3}\cdots Li \quad : \quad x = 2 \longrightarrow n = \begin{cases} 3 \\ 4 \ (u) \end{cases}$$

$$H_3CO\text{--}[CH_2\text{-}CH_2\text{-}O]_x\text{--}CH_3 \quad \cancel{\Longrightarrow}$$

NMR STUDY ⇒ LiR.[LiOEEM]₂ complex
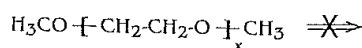
Scheme 5

These new "μ,σ-ligated anionic initiators" are remarkably efficient in controlling "living" high MW polymerizations of (meth)acrylic esters, including primary ones down to butyl, as well as their block or random copolymerization and end-group functionalization, at moderately low temperatures; all that in hydrocarbon media (a definite advantage over THF for process scaling-up), while maintaining a high (ca. 80 %) syndiotacticity.

Without going into further detail, these results clearly illustrate the power of coordination chemistry in tailoring, for the better, classical polymerization processes of which one wants to keep a number of definite advantages.

Coordination chemistry : a general tool for a hetter tailoring of all polymerization reactions ?

On the basis of these very encouraging achievements, "et l'appetit venant en mangeant" (a very french proverb), one might wonder if a general answer to the challenge of controlling chain growth (whatever its mechanism) could not simply be the implementation of reversible but strong enough interactions with well-chosen additives, able again to modify electronic density and steric hindrance around the reacting site, whichever it is, very much along the lines developed in the preceeding section. Such considerations are not purely gratuitous, since a close control of any polymer chain growth has obviously to be exerted through a dual entity consisting of the active chain end function and of a "counter-something", that we are now going to tentatively describe or at least imagine, as best as possible. In any case however, we do believe that such a "something" might belong to the vast and extremely versatile family of additives provided by coordination chemistry.

Obviously, all the considerations which follow are speculations, or at best "educated guesses"; although intuitive, they are nevertheless based on recently established and promising facts.

1. Cationic polymerization

The importance of coordinative bonding between Lewis acids and solvent, monomer, or "promoter" has long been realized in this type of process (Scheme 6).
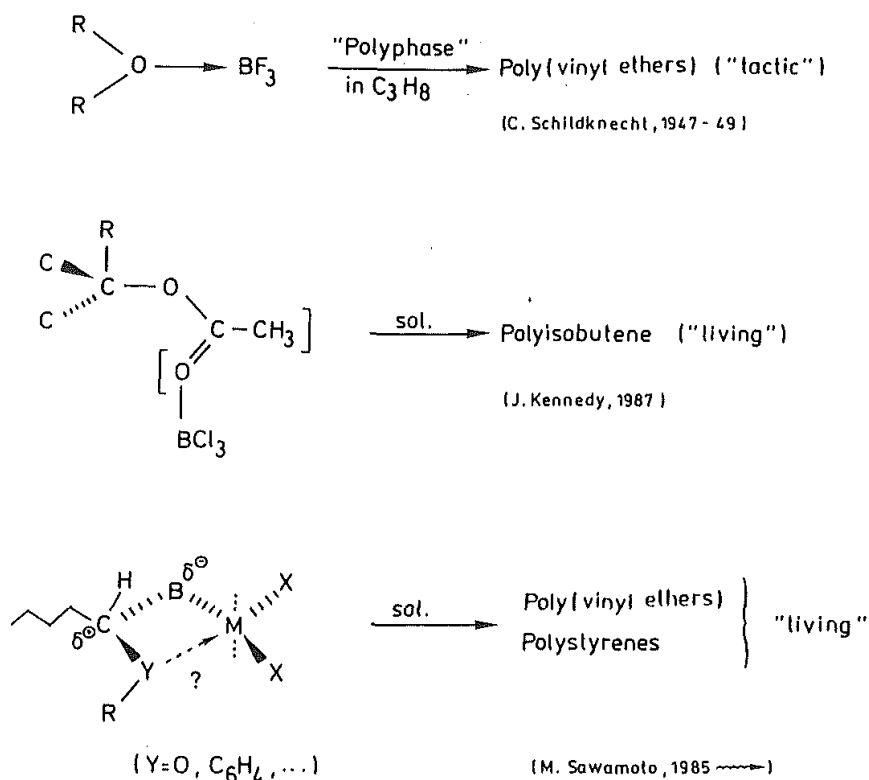
Scheme 6

Looking further, we might just reverse the approach that we took for the anionic mechanism, and play with different ligands adapted to this other kind of ion-pair. The problem here is certainly to prevent an important ion-pair separation, since that would weaken any potential strong control on the addition site : i.e. working with strong μ-ligand in non-polar solvents ?

One might even think that some of the recently proposed systems (f.i. by Sawamoto (Ref. 17)) come closer to that kind of approach (see tentative scheme 6c, where ligand Y might even be a functional group of the chain-end substituent, i.e. -OR group of a vinyl ether, or phenyl group of a styrene when M would be a transition metal such as Cu^I, Ag or Pd, and when election density and steric hindrance might be regulated by a donor X and other ligands around the metal).

2. Radical polymerization

Traditionally, radical processes have been considered as the typical example of a "free" active species, the activity and selectivity of which could essentially be regulated, and to a small extent only, by the medium composition and the temperature. In the last decades however, two fundamental breakthroughs' brought some encouragement to those looking for a control of these reactions through coordination chemistry.

The first one was the frontier orbital description of radicals as amphiphilic species, i.e. either nucleophilic or electrophilic depending on their SOMO energy relative to the LUMO or the HOMO orbital of the monomer. That readily explained the alternating copolymerization of vinyl acetate and maleic anhydride, but also the intriguing and often misinterpreted fact that monomer coordination to a Lewis acid could vastly modify their apparent relative reactivity ratios (Ref.

18).

Second but not least was the idea coming from organic chemistry that a radical could undergo a significant and durable enough overlap of its SOMO orbital with vacant orbitals of a transition metal. That has already been demonstrated in several cases, f.e. in the reorientation of some organic radical reactions as depending on the ligands of porphyrin-type Co and Rh complexes (Ref. 19), and also very elegantly in the optimization of a monoelectronic transfer reaction for methylmethacrylate polymerization (Ref. 20) (a Du Pont process for efficiently synthesizing PMMA macromonomers, scheme 7).
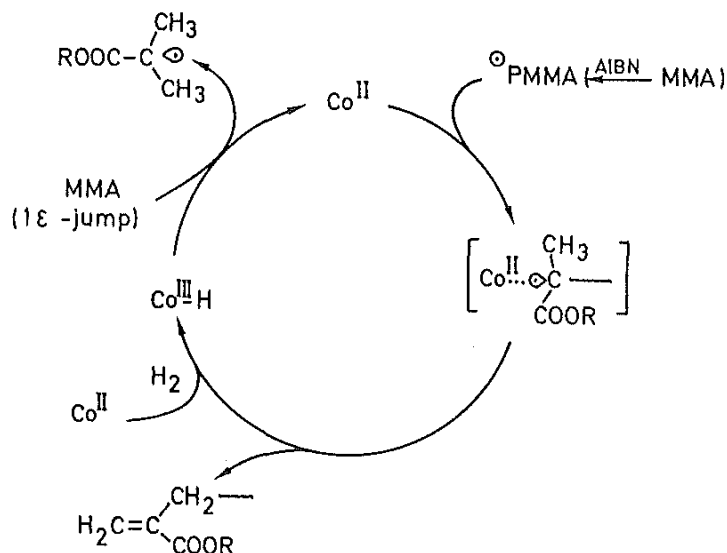
Scheme 7

In other words, we might see here the first indications (still rather faint but exciting) of the possibility of using a metal complex as a "counter-radical", very much in the same way as organic molecules (f.i. TEMPO) have been used by Rizzardo (Ref. 21) and Georges (Ref. 22) in their "living" radical polymerizations. (Although it is very tempting to also invoke along these lines the nice recent work of Matyjaszewski (Ref. 23) and Harwood (Ref. 24), it is probably premature to discuss here its mechanistic implications).

3. Step-polymerization

Although we approach there a fundamentally different type of polymerization mechanism, a short survey of the literature teaches us that metal salts and complexes have indeed been often used as "catalysts", to improve the rate and the selectivity of these reactions (stereochemistry is not as determinant here as chemoselectivity versus secondaiy reactions perturbing chain growth, and as sometimes the sensitive stoichiometric balance between reactants).

That is the case for a wealth of very diverse situations, and among them :

- the use of Sn and Ti alkoxides or salts, in e.g. polyester production;

- the role of $Cu(Li)_x$ complexes in oxidative step-polymerization (f.i. for PPO synthesis);

- the importance of Friedel Craft catalysis, e.g. in PE(E)K formation;

- the determinant catalytic action of metal-amines complexes in polyurethane formation and foaming.

It is rather obvious that again, coordination complexes can be used which have a determinant influence on the complex activated state involved at each step resulting in the bonding of an additional monomelic unit. In other words, we find here also the same overall picture as

described above. It may even be predicted, that selective catalysis might become a key to a "cleaner", hence more efficient, control of reactive processing, often a delicate 2-step procedure where optimal morphology must be achieved before freezing it in by establishment of covalent bonds between phases. One can only wish that these cases and many other ones will be the subject of much more in-depth kinetic and structural investigations, based on the principles and approaches of coordination chemistry and catalysis.

The Conclusions of the above analysis are obvious and have already been drawn for another research avenue. In the last decade indeed, we have witnessed a strong revival of polymer science due to a fresh-viewed and thorough application of organic chemistry mechanisms for the implementation of new polymerization processes (Du Pont, GTP being one of these main examples). It now becomes clear that, in a quite similar strategy, coordination (and organometallic) chemistry represent another spring of new achievements in polymerization; this is already an every day reality, but should become still more important in a near future.

At this point, it certainly is a friendly advice to encourage researchers in the field to revisit, within a few good books on the market, the coordination (and organometallic) chemistry principles, reactions and techniques, in view of adapting them for improving known polymerization processes and hopefully creating totally new reaction pathways.

Acknowledgment.

References

(1)   See f.i. J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, *J. Am. Client Soc.* 110, 6255 (188); W. Spaleck, M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, *New J. Chem.* 14, 499 (1990)

(2)   S. Collins, D.G. Ward, *J. Am. Chem. Soc.* 114, 5460 (1992); H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, ibid. 114, 4908 (1992) and *Macromolecules* 26, 7134

(3)   R.H. Grubbs, W. Tumas, *Science* 243, 907 (1989); R.R. Schrock, *Acc. Chem. Res.* 23, 158 (1990)

(4)   G. Fink, V. Möhring, *Studies in Surf. Sci. and Catal.* 25, 231 (1986)

(5)   Ph. Teyssié, P. Hadjandreou, M. Julémont and R. Warin, in *"Transition metal catalyzed polymerization",* R.P. Quirk, Ed., Cambridge University Press, New York 1988, p. 639

(6)   Ph. Teyssié, J.P. Bioul, P. Condé, J.P. Druet, J. Heuschen, R. Jérôme, T. Ouhadi, R. Warin, in *"Ring-opening polymerization : kinetics, mechanisms and synthesis",* J.E. McGrath, Ed., ACS Symposium Series 286, 97 (1985)

(7)   N. Ropson, Ph. Dubois, R. Jérôme, Ph. Teyssie, *Macromolecules* 26, 6378 (1993); ibid. in press

(8)   O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farham, F.V.R. Babu, *J. Am. Chem. Soc.* 105, 5706 (1983); D.Y. Sogah, W.R. Hertler, O.W. Webster, G.M. Cohen, *Macromolecules* 20, 1473 (1987)

(9)   M.T. Reetz, *Angew. Chem. Int. Ed.* 27, 994 (1988); S. Sivaram, P.K. Dhol, S.P. Kashikar, R.S. Khishi, B.M. Shinde, D. Baskaran, *Polym. Bull.* 25, 77 (1991)

(10)   Ph. Teyssie and J.S. Wang, "Ligated living anionic polymerization", *J. Phys. Org. Chem.*, in press

(11)   K. Hatada, K. Ute, K. Tanaka, Y. Okamoto, T. Kitayama, *Polym. Bull.* 18, 1037 (1986)

(12) L. Lochmann, M. Rodova, J.J. Trekovel, *J. Polym. Sci. (Chem. Ed.)* 12, 2091 (1974); L. Lochmann, J. Trekoval, ibid. 17, 1727 (1979) and U.S. Pat. 4.056.580 (Now. 1977) and 4,238,588 (Dec. 1980); L. Dvoranek, P. Vlcek, *Polym. Bull.* 31, 393 (1993)

(13) D.G.H. Ballard, R.J. Bowles, D.M. Haddleton, S.N. Richards, R. Sellens, D.L. Twose, *Macromolecules* 25, 5907 (1992)

(14) T. Ouhadi, R. Forte, R. Jérôme, R. Fayt and Ph. Teyssié, Lux. Pat. 85.627 (1984), U.S. Pat. 4.767.824 (1988); Ph. Teyssié, S.K. Varshney, R. Jérôme, R. Fayt, Eur. Pat. 0274.318 (1988), U.S. Pat. 4.826.941 (1989); R. Fayt, R. Forte, C. Jacobs, R. Jérôme, T. Ouhadi, Ph. Teyssié, S.K. Varshney, *Macromolecules* 20, 1442 (1987) and following papers

(15) S.K. Varshney, R. Jérôme, Ph. Bayard, C. Jacobs, R. Fayt, Ph. Teyssié, *Macromolecules* 25, 4457 (1992)

(16) Ph. Bayard, R. Jérôme, Ph. Teyssié, S.K. Varshney, J.S. Wang, *Polym. Bull.* 32, 381 (1994)

(17) M. Sawamoto, this Symposium issue

(18) I. Fleming, in *"Frontier Orbitals and Organic Chemical Reactions",* J. Wiley & Sons, London, p. 182 and 161 (1976)

(19) B.P. Branchaud, Gui-Xue Yu, *Organometallics* 12, 4262 (1994)

(20) N.S Enikolopian, B.R. Smimov, G.V. Ponomarev, I.M. Belgovskii, *J. Polym. Sci. (Chem. Ed.)* 19, 879 (1981); A.H. Janowicz, U.S. Pat. 4.746.713 (May 24, 1988), 4.886.861 (Dec. 12, 1989) and 5.028.677 (Jul. 2, 1991)

(21) G. Moad, E. Rizzardo, D.H. Solomon, *Polym. Bull.* 6, 589 (1982); *J. Macromol. Sci. Chem.* A17(l), 51 (1982)

(22) M.K. Georges, R.P. Veregin, P.M. Kazmaier, G.K. Hamer, *Macromolecules* 26, 2987 and 5316 (1993), and this Symposium issue

(23) D. Mardare, K. Matyjaszewski, *Macromolecules* 27, 645 sq. (1994)

(24) M.P. Grenel, Ph.D. Dissertation, Univ. Akron (Dec. 1992); H.J. Harwood and al., 35th IUPAC Int. Symp. on Macromolecules, Akron (July 1994), abstracts 0-1.1-2M and 0-1.1-8M; see also B.B. Wayland, G. Poszmik, S.L. Mukerjee, *J. Am. Chem. Soc.* 116, 7943 (1994)