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Group transfer polymerisation of acrylonitrile

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Summary

The polymerization of acrylonitrile, initiated by titanium amides, is interpreted in terms of a group-transfer mechanism.

Introduction

Several years ago, some studies were carried out in this laboratory on the polymerisation of acrylonitrile initiated by amides of titanium, hafnium and zirconium.[1] Most of the work was based upon the use of tetra(dimethyl- amido)titanium as the initiator, and the most important features of the general reaction can be summarised as follows.

1. The reaction displays an induction period, typically of about 25 min. at 20° C, after which polymerisation proceeds steadily to consume some 50% of the monomer in 50 min. and 75% in 150 min. Beyond the induction period, the reaction is second order with respect to monomer concentration at 20° C.

2. Scavengers of free radicals have no effect on the reaction, and no copolymerisation takes place if styrene is present in the reaction mixture.

3. Amides of hafnium and zirconium are much more reactive initiators than those of titanium. With Hf or Zr derivatives, methacrylonitrile also polymerises readily.

4. The reaction system does not require highly rigorous purification of the type necessary for an anionic or cationic process.

The mechanism suggested at the time to account for the kinetics and the other mechanistic evidence was based upon a two-step initiation process with first-order termination; in its most basic form, the kinetic scheme can be written symbolically as:-

$$\begin{array}{lll} T_4 + M \rightarrow A & \text{fast} \left.\right\} & \text{initiation} \quad (1) \\ A + M \rightarrow X_1 & \text{slow} & (2) \\ X_n + M \rightarrow X_{n+1} & & \text{propagation} \quad (3) \\ X_n \rightarrow P_n & & \text{termination} \quad (4) \end{array}$$

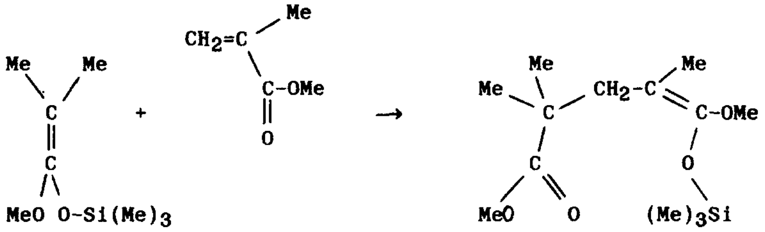
where T_4 represents $Ti(NMe_2)_4$, A is the primary reactive intermediate, X is the chain carrier, M is the monomer, and P is the polymer; n denotes the number of incorporated monomer units.

The actual process is complicated by the possibility that more than one ligand attached to a given titanium atom can undergo reaction (1). Moreover, the polymer precipitates from the reaction medium, so that it would be imprudent to place too great a reliance on interpretation of the observed kinetics, even though the apparent first-order nature of the termination process suggests that the severe complications that arise when the meeting of two polymer chains is an important feature of the polymerisation (as in radical polymerisation) are absent.

A scheme of chemical reactions was put forward to correspond to the kinetic equations. Although it proved possible to offer a chemical basis for each step, it was always recognised that a weakness of the sequence was the need to postulate the participation of an intermediate containing titanium directly bonded to carbon. In the light of the recent disclosure of the novel technique of Group Transfer Polymerisation (GTP),^{2} it now seems to be possible to find a more convincing explanation of the T_4-initiated polymerisation of acrylonitrile in terms parallel to those employed in connection with the methyl methacrylate/silyl ketene acetal system investigated by Du Pont.

New Reaction Scheme

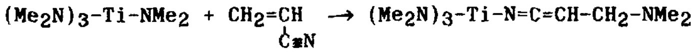
According to the mechanism for GTP advance by the Du Pont group, a trimethylsilyl (TMS) group migrates from an oxygen atom in the α position to a carbon-carbon double bond in the initiator to the keto oxygen atom in a monomer ester group, with a concomitant cyclic electron switch over the whole system. With the TMS enolate of methyl isobutyrate as the initiator and methyl methacrylate as the monomer, the process may be represented in the following manner.



(5)

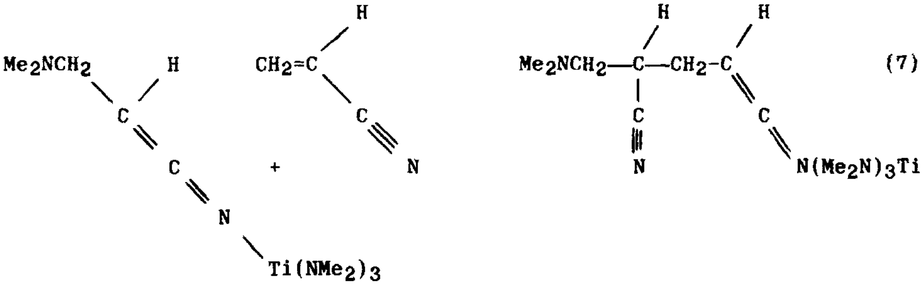
Since the product is chemically identical to the initiator with respect to its silyl ketene enolate character, the process can be repeated with an indefinite number of monomer molecules.

In the case of the polymerisation of acrylonitrile initiated by the compound T_4, no structure analogous to the silyl enolate exists until one molecule of T_4 has reacted with one molecule of acrylonitrile. As speculated previously,[1] this process is most likely to occur in the 1,4-mode, as in (6).



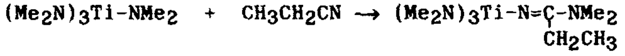
$$(Me_2N)_3\text{-Ti-NMe}_2 + \underset{C\equiv N}{CH_2{=}CH} \rightarrow (Me_2N)_3\text{-Ti-N=C=CH-CH}_2\text{-NMe}_2 \qquad (6)$$

If, for the moment, it is assumed that the three Ti-N bonds written to the left of Ti remain inert, the product (T_3) can be regarded as the analogue of a silyl enolate, so that initiation of polymerisation would be brought about by a cyclic electron switch, parallel to that shown for equation (5).



(7)

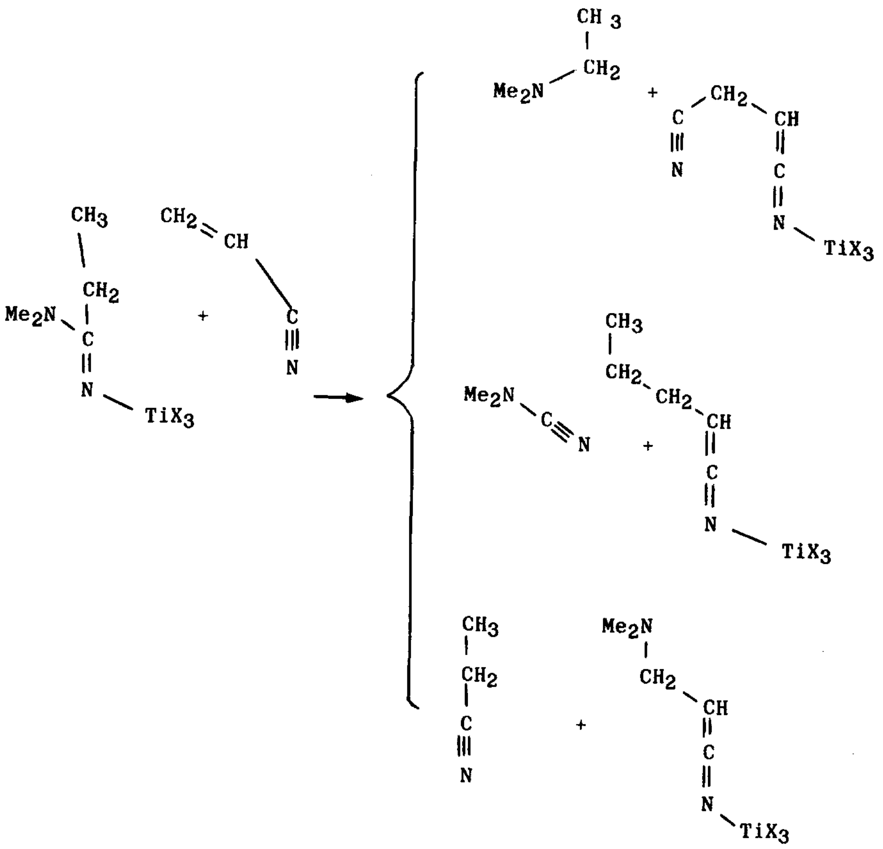
In our earlier work, we noted that the induction phase of the reaction could be eliminated by preparing an initiator by reaction between T_4 and a nitrile incapable of polymerisation, e.g. propionitrile, thus:



$$(Me_2N)_3\text{Ti-NMe}_2 + CH_3CH_2CN \rightarrow (Me_2N)_3\text{Ti-N=}\underset{CH_2CH_3}{C}\text{-NMe}_2 \qquad (8)$$

When the product of this process is added to acrylonitrile, polymerisation is almost instantaneous: obviously, it is necessary to account for this fact, in the absence of any possibility of forming a ketene-imine structure, as in (6). In this case, one can postulate a reaction similar to (7) but with the concommitant elimination of a small molecule, a process which could take any of three different routes, depending on whether the expelled substance is ethylamine, propionitrile or $Me_2N\text{-}CN$ (see equation 9 below).

It is our hope to establish, by experiments using a mass spectrometer, whether any low molecular weight by-products can be detected in this reaction, and hence to confirm or refute the hypothesis that the polymerisation of acrylonotrile initiated by tetra(dimethylamido)titanium is a process of the group-transfer type.



(9a)

(9b)

(9c)

Note. As an historical aside, it may be interesting to recall that the mechanism proposed here was advanced in a conversation with Dr Art Langer (probably by Dr Langer) at a Gordon Reseach Conference in 1976, almost ten years before Group Transfer Polymerisation had been heard of.

References

1. N.C.Billingham and A.D.Jenkins, Applied Polymer Symposia, No.26, page 13,(1975), and references therein.
2. For the most recent review see D.Y. Sogah, W.R. Hertler, D.W. Webster and G.M. Cohen in Macromolecules, 20, 1673 (1987).

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