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THE INITIATION OF POLYMERIZATION BY ORGANOMETALLIC COMPOUNDS—III

KINETICS OF THE POLYMERIZATION OF ACRYLONITRILE BY TETRA*KIS*(DIMETHYLAMIDO)TITANIUM(IV)

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Abstract—The polymerization of acrylonitrile, initiated by tetra*kis*(dimethylamido)titanium(IV), has been investigated over a wide range of experimental conditions. The results indicate that the simple kinetic scheme previously applied is only valid for a limited temperature range, significant deviations being observed at temperatures above and below 25°. Some interpretations of the deviations from simple behaviour are discussed.

Previous papers in this series(1,2) have described principally the polymerization of acrylonitrile (AN) initiated by tetra*kis*(dimethylamido)titanium(IV), (T_4), in hydrocarbon solutions. Kinetic investigations of the reaction at 20° showed that the polymerization is essentially second-order with respect to monomer, although it displays a significant induction period. This induction period was attributed to a two-stage initiation process in which T_4 reacts rapidly with the monomer to yield a product A which is able to initiate polymerization over a long period; it was concluded that the polymerization kinetics could be adequately described by an equation of the form:

$$-\frac{\mathrm{d}[M]}{\mathrm{d}t} = K\,[\mathrm{T}_4]_0[M]^2\,[1 - \exp^{(-k[M]_0t)}] \tag{1}$$

where $[\mathrm{T}_4]_0$ and $[M]_0$ are the initial concentrations of initiator and monomer respectively and K and k are constants. The experiments previously described(2) were conducted by means of a very simple technique in which initiator solutions were handled with nitrogen-flushed pipettes and polymerizations were performed in nitrogen-filled apparatus. Although the results were sufficiently reproducible to be analysed in terms of a proposed reaction mechanism, subsequent investigation has shown that significantly higher polymerization rates can be achieved if high vacuum techniques are employed to minimize the decomposition of initiator by adventitious impurities. This paper reports the results of more rigorous and extensive studies of the polymerization of acrylonitrile initiated by T_4; a great deal more about the behaviour of the system is revealed by study over a range of temperatures.

EXPERIMENTAL

Materials

Tetra*kis*(dimethylamido)titanium(IV) was prepared by the method previously described(2) and stored in ampoules sealed under high vacuum. Acrylonitrile (ex Koch Light) was fractionally distilled, the middle fraction (b.p. 77·7°/760 mm) being collected and dried over calcium hydride. The monomer was degassed and stored over calcium hydride on a vacuum line.

Methylcyclohexane and cyclohexane were freed from aromatic impurities by repeated passage through silica gel columns, until GLC analysis showed no impurities; the solvents were dried over calcium hydride, degassed, and stored on the vacuum line over calcium hydride. Methylcyclohexane and cyclohexane were adopted as solvents in the present work in preference to the petroleum ether used previously since they are more readily characterized and easier to purify. Furthermore, the low freezing point of methylcyclohexane enables kinetic measurements to be extended to lower temperatures. In practice, solutions of AN in this solvent show phase separation at temperatures below −20° so that the need to maintain a homogeneous solution requires that temperatures be no lower than this value. Polymerization rates measured by the technique described below were unaffected by the change from cyclohexane to methyl cyclohexane.

Nitrogen boil-off gas from the liquid was purified by passage successively through columns of activated copper catalyst (BASF BTS catalyst), to remove oxygen, and columns of molecular sieve to remove water. The purification train was constructed entirely from metal and glass; only the minimum amount of plastic tubing was used to connect apparatus to the gas supply.

Polymerization techniques

When a series of polymerization reactions was performed under the conditions previously described,(2) it was found that, although the general reaction features persisted, the rate constant of polymerization (measured as the slope of a second-order plot) tended to vary over a total range of about a factor of two in a manner which could not be associated with any systematic variation in the polymerization conditions. Runs performed after the initiator solutions had been allowed to stand for periods of up to 24 hr showed random variations in rate within the same range as those performed with the freshly prepared solution; ageing of the initiator, therefore, does not appear to be significant over this time scale. Similarly, runs carried out in the dark were indistinguishable from those performed on an open bench. After many attempts to refine the simple experimental technique, it was concluded that the variation in rate arises from a minor level of decomposition of the initiator solutions during their preparation and handling. The following technique was therefore adopted since it was found to give the highest rates of reaction for given concentrations of reactants and also a high degree of reproducibility, although only reasonably simple operations are involved.

Preparation of initiator solutions

Pure initiator and its solutions were handled under high vacuum conditions in ampoules of the type shown in Fig. 1a. Ampoules were constructed from B10 skirted cone joints, the lower skirt being drawn out into an offset fine capillary to form a break-seal. The contents of the ampoule could then be dispensed by fitting the cone into a socket and rotating the ampoule until the capillary was fractured by a dimple in the tubing below the socket. Break-seals of this type are simple to construct and completely reliable in operation; whilst the presence of a ground joint would prevent their use in extremely rigorous conditions, such as are required with anionic polymerization, they have proved eminently suitable for the present work. Ampoules of pure initiator were prepared by distillation under high vacuum and sealed under vacuum; weighing of the ampoule before filling, and of the two sections left after filling and sealing, allowed the weight of initiator in each ampoule to be determined.

Initiator solutions containing a known concentration of T_4 in methylcyclohexane were prepared by means of the apparatus shown in Fig. 1b. The lower bulb A carried a side-arm, which was dimpled to provide a breaking surface for ampoules, and was joined by a greaseless tap B (Quickfit Rotaflo) to the upper bulb C which carried six side-arms terminating in B10 cones. A second greaseless tap D enabled the whole apparatus to be attached to the vacuum line. In operation, the apparatus was assembled with an ampoule of pure T_4 in the side-arm of bulb A and with six empty and weighed ampoules on the arms of bulb C. The whole apparatus was evacuated and flamed out; the required quantity of solvent was distilled from its storage bulb via a graduated tube into the bulb A. After taps B and D had been closed and the apparatus removed from the vacuum line, the ampoule of pure T_4 was broken and the resulting solution thoroughly mixed. Tap B was opened and about 2·5 ml of the resulting solution passed into one of the empty ampoules; B was closed, the ampoule sealed off and the procedure repeated until all six ampoules had been filled. The ampoules and sockets were reweighed to determine the exact weight of initiator solution in each. Titrimetric estimation of the amount of dimethylamine liberated on solvolysis of initiator solutions with isopropanol showed excellent agreement with the calculated initiator concentrations and established that solutions stored in this manner are stable.

Polymerization reactions

Polymerizations were performed in a 100 ml flask fitted with a side-arm for introduction of initiator solution via a break-seal ampoule. The neck of the flask was fitted with a tap for connection to the vacuum line and a side-arm for admission of nitrogen. A glass-cased magnet was placed in the flask

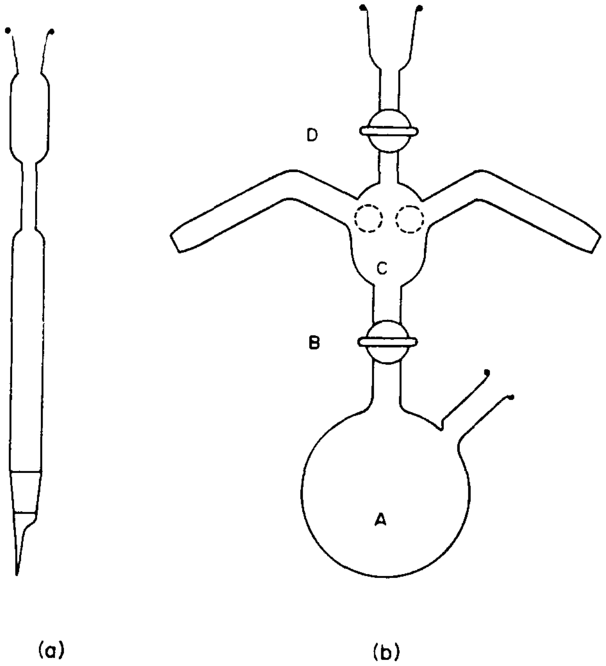


FIG. 1 (a). A break-seal ampoule. (b). Apparatus used for filling ampoules.

to enable its contents to be stirred. The required quantities of monomer and solvent were distilled into the reaction vessel which was then isolated from the vacuum line and placed above a submersible magnetic stirrer in a water or alcohol bath maintained at the required polymerization temperature, with an accuracy of ±0·1°. When thermal equilibrium was attained, the initiator solution was added by breaking its ampoule.

In order to follow the rate of polymerization, the vacuum was broken with purified nitrogen and samples removed at intervals: the residual initiator was destroyed by quenching in a large excess of iso-propanol and the polymer filtered off, dried and weighed. Several attempts were made to follow the reaction under vacuum by dilatometry but in all cases the results were highly irreproducible and in very poor agreement with gravimetric results. This effect undoubtedly results from the fact that precipitation of polymer in the stem of the dilatometer very quickly causes the meniscus to become increasingly distorted as reaction proceeds.

RESULTS AND DISCUSSION

Reproducibility

Figure 2 shows the conversion-time plots for a series of polymerizations performed under identical conditions using the high vacuum technique described above. For comparison the results presented previously(2) are also included, together with data from an experiment in which the conditions were identical except for the use of the high vacuum technique. It can be seen that not only is the measured curve highly reproducible but also the absolute value of the polymerization rate is somewhat higher than that reported previously. It should be noted that the general profile of the curve is unchanged and, in particular, that the reaction rate does not immediately assume its maximum value, in agreement with our earlier findings. This conclusion is confirmed by a second-order plot of the data, as displayed in Fig. 3, which demonstrates that the

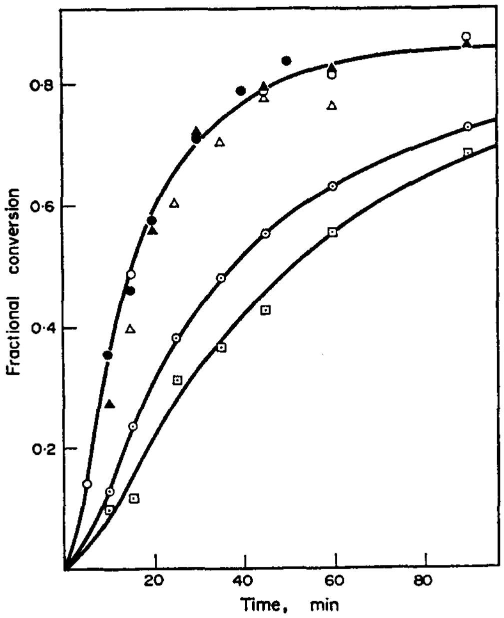


FIG. 2. Relation between fractional conversion and time at 25°. ⊡ denotes results of a run using the technique described in reference (2) while ⊙ denotes results from a run under identical conditions except for the use of high vacuum technique. $[T_4]_0 = 3{\cdot}11 \times 10^{-3}$ mol l^{-1}, $[M]_0 = 0{\cdot}684$ mol l^{-1}.

○, ●, △, ▲ represent four runs, ostensibly identical; the results indicate the degree of reproducibility. $[T_4]_0 = 4{\cdot}46 \times 10^{-3}$ mol l^{-1}, $[M]_0 = 0{\cdot}755$ mol l^{-1}.

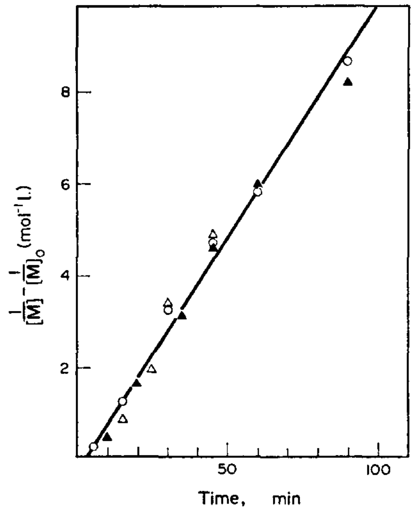


FIG. 3. Demonstration of apparent second-order dependence on monomer, based on data for the top curve as in Fig. 2.

reaction apparently follows second-order kinetics over the greater part of its course and further that it shows an induction period of about 6 min. In view of the very satisfactory reproducibility, we have proceeded to apply the high vacuum technique to investigate the effects of initiator concentrations and polymerization temperature.

Effect of initiator concentration

Several reactions were carried out in which the initial concentration of T_4 was varied between 2·08 and 7·16 × 10^{-3} mol l^{-1}. All such experiments confirmed that the kinetic behaviour corresponds to a second-order dependence on monomer after an induction period of approximately 6 min; a selection of typical plots is shown in Fig. 4. According to the simple theory put forward previously,(2) the apparent second-order rate constants (defined by the slopes of the lines in Fig. 4) should show a first-order dependence on the initial concentration of initiator. A plot of the apparent second-order rate constant against the initial concentration of initiator is shown in Fig. 5; the results are essentially in agreement with first-order kinetics provided that allowance is made for curvature at low initiator concentrations. It was possible to demonstrate that this curvature is a genuine feature of the reaction and is not caused by decomposition of a reproducible amount of initiator during the preparation of solutions since, as mentioned previously, analysis of initiator solution by determination of amine, liberated in reaction with isopropanol, showed that solutions of initiator

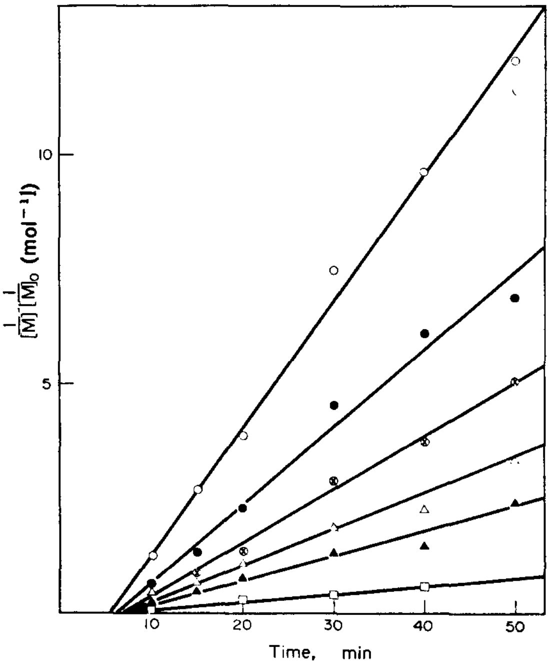


FIG. 4. Demonstration of apparent second-order dependence on monomer for runs at several initial T_4 concentrations. $T = 25°$, $[M]_0 = 0·755$ mol l^{-1}, $10^3\,[T_4]_0$ as follows: ○, 7·16; ●, 5·12; ⊗, 4·18; △, 3·82; ▲, 2·74; □, 2·08 mol l^{-1}.

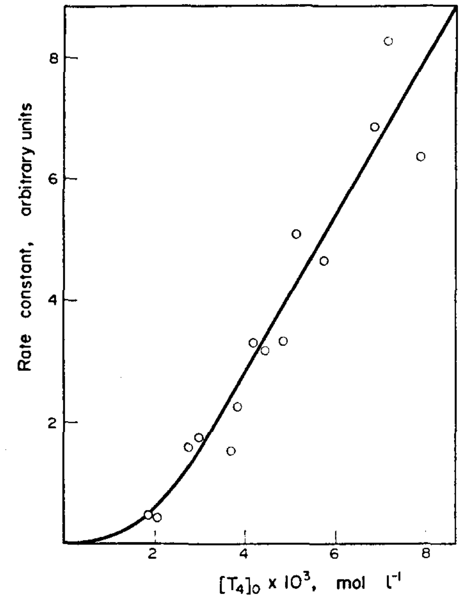


FIG. 5. Apparent second-order rate constant (as measured by the slopes of the lines in Fig. 4) as a function of initial concentration of T_4.

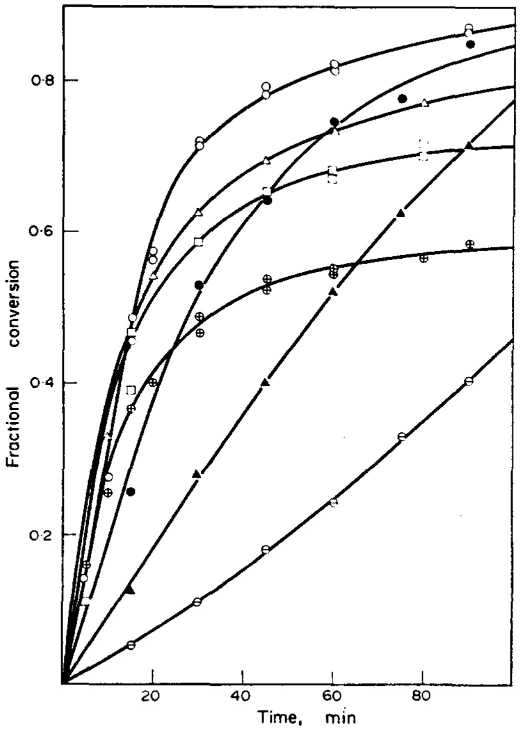


FIG. 6. Dependence of fractional conversion on time as a function of temperature. $[T_4]_0 = 4{\cdot}46 \times 10^{-3}$; $[M]_0 = 0{\cdot}755$ mol l^{-1}. Temperature as follows: ⊕, 50°; □, 45°; △, 35°; ○, 25°; ●, 10°; ▲, 0°; ⊖, −10°.

were not decomposing during the preparation for a run. Furthermore, as illustrated in Fig. 5, experiments with very low concentrations of initiator show reproducible polymerization behaviour.

It will be seen that the data presented so far are in good agreement with those reported previously, in particular as summarized in Eqn. (1).

Effect of temperature on polymerization

Since almost all of the results presented so far were obtained from polymerizations performed in the neighbourhood of ambient temperature, it was decided to explore the temperature range in both directions. Figure 6 shows the results of a series of measurements, with constant initiator and monomer concentrations, over the range from —10 to 50°. The surprising conclusion from these results is that the rate of polymerization is at its maximum near 25° and decreases both with increasing and decreasing temperatures. Furthermore, when the results are presented in the form of second-order plots, as in Fig. 7, it becomes apparent that the second-order behaviour observed at 25° is quite fortuitous since at all other temperatures the plots are

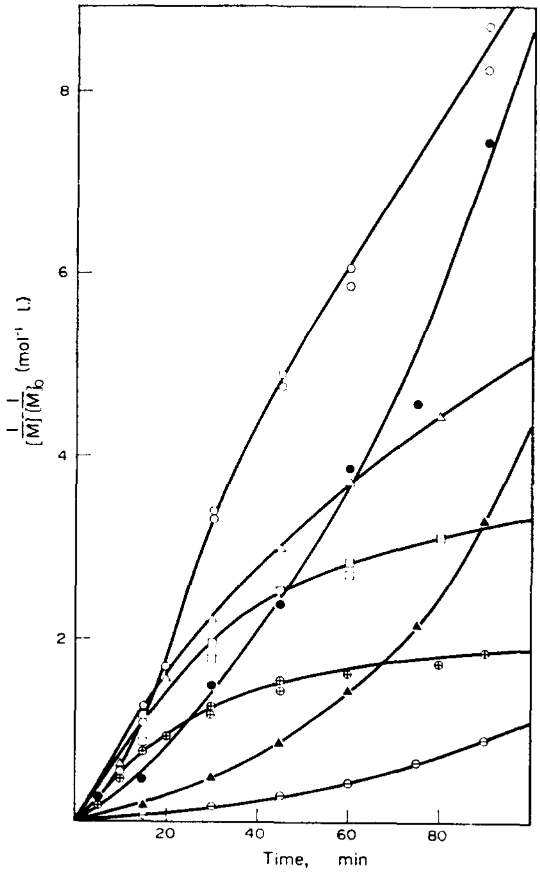
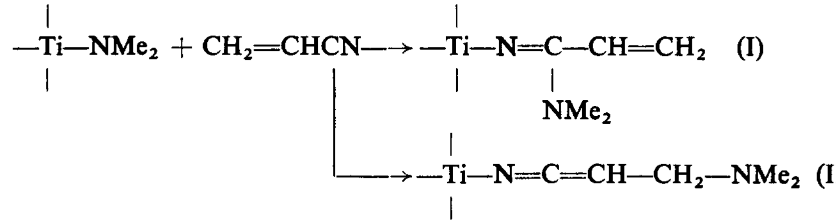


FIG. 7. Second-order plots for runs as in Fig. 6.

distinctly non-linear over the whole conversion range. Evidently the choice of temperatures near 25°, based on convenience of operation, could easily lead to misinterpretation of the results arising from the misleadingly simple appearance of the reaction profile in this intermediate range.

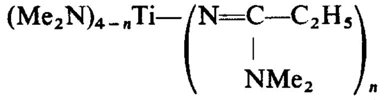
In previous discussions of this polymerization process, it was concluded that the induction period could be attributed to a two-stage initiation reaction which may be formulated as involving an initial addition of a Ti—N bond of T_4 across the nitrile group of the monomer or as a 1,4 addition across the whole monomer molecule,



$$-\overset{|}{\underset{|}{\mathrm{Ti}}}-\mathrm{NMe_2} + \mathrm{CH_2{=}CHCN} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Ti}}}-\mathrm{N}{=}\underset{\underset{\mathrm{NMe_2}}{|}}{\mathrm{C}}-\mathrm{CH{=}CH_2} \quad \mathrm{(I)}$$

$$\longrightarrow -\overset{|}{\underset{|}{\mathrm{Ti}}}-\mathrm{N{=}C{=}CH-CH_2-NMe_2} \quad \mathrm{(II)}$$

structures of types (I) or (II) being regarded as the active initiators, capable of addition to the carbon–carbon double bond of the monomer in a reaction which produces a Ti—C bond. An alternative explanation of the induction period, which cannot be excluded on the direct evidence presented previously, is the possibility of a single-stage initiation in which the Ti—N bond adds directly across the C=C bond of the monomer in a reaction significantly slower than the subsequent insertion of monomer into the resulting Ti—C bond, the process which constitutes the propagation step. The known reactivity of Ti—N bonds in the formation of adducts of type (I) with nitrile groups suggests that reactions of this type are very probable and we have obtained direct evidence that structures of this type are reactive initiators for acrylonitrile polymerization. Thus when propionitrile (1·56 g, 28·4 m mol) is reacted with T_4 (0·42 g, 2·2 m-mol) in methylcyclohexane solution at ambient temperature for 18 hr, 0·16 g (2·9 m-mol) of propionitrile is consumed and no dimethylamine liberated. Removal of volatiles yields a dark brown viscous liquid having an i.r. spectrum which shows no nitrile absorption at 2220 $\mathrm{cm^{-1}}$ but a strong absorption at 1600 $\mathrm{cm^{-1}}$, indicative of the $-\mathrm{N}{=}\mathrm{C}\!<$ grouping. It is concluded that this compound is a mixture of products of the form:



$$(\mathrm{Me_2N})_{4-n}\mathrm{Ti}-\left(\mathrm{N}{=}\underset{\underset{\mathrm{NMe_2}}{|}}{\mathrm{C}}-\mathrm{C_2H_5}\right)_n \qquad \mathrm{(III)}$$

the overall composition corresponding to approximately 33 per cent of the amidine ligand. Figure 8 shows the conversion plot for an experiment in which this adduct was used to initiate the polymerization of acrylonitrile; the results of an experiment with a similar concentration of T_4 are included for comparison. It can be seen that (III) is a very effective initiator, producing behaviour comparable with that of T_4 at high temperatures; in particular, there is no induction period. Although this result does not exclude a single-stage initiation mechanism, it provides strong indirect support for the view that adducts of type (III) may be the effective initiating species in the polymerization of AN by T_4. Further studies of the reaction of T_4 with propionitrile and the behaviour of the adducts as initiators are in progress; the results will be reported elsewhere.

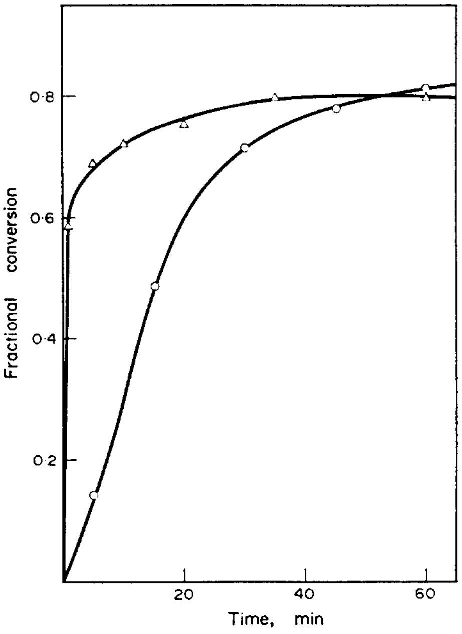


FIG. 8. Dependence of fractional conversion on time. $T = 25°$, $[M]_0 = 0{\cdot}755$ mol l^{-1}. ○, reaction initiated by $4{\cdot}46 \times 10^{-3}$ mol l^{-1} T_4. △, reaction initiated by a pre-formed adduct of T_4 with proprionitrile using the same quantity of T_4 as in the comparative experiment.

The results of experiments performed at low temperatures suggest that, under these conditions, the effective rate of initiation is increasing continuously during the reaction, implying that the activation energy for initiation is significantly higher than that for propagation. At higher temperatures, the results are at least qualitatively consistent with the view that the effective initiator concentration decreases during the reaction, leading ultimately to kinetics of the "dead-stop" variety. Unfortunately, a direct analysis of the kinetics is complicated by the fact that it is apparent that the fractional rates of change of initiator and monomer concentrations are comparable, so that the assumption of constant monomer concentration in considerations of initiator decomposition, or of constant initiator concentration in treatment of monomer consumption, can only arise as special cases in limited temperature ranges.

The nature of the initiation reaction has implications in terms of the rate of removal of T_4 from the system. A two-stage initiation process would imply that the initiator precursor T_4 is consumed in a time scale comparable with the length of the induction period, whereas a single stage process would imply that T_4 is consumed slowly, the observed second-order kinetics at 25° being due to the finite time required to establish a steady concentration of active centres at this temperature.

It is clear that detailed interpretation of the more complex kinetic situation revealed in the present study requires additional information about the nature of the initiation and termination reactions and an analysis of the changes in initiator concentration during the reaction. Accordingly, we have attempted to develop methods for the progressive analysis of initiator concentrations and have applied radiochemical methods to the study of termination mechanisms. The result of these studies and their application to an analysis of the polymerization kinetics will be presented in subsequent papers in this series.

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Résumé—On a étudié la polymérisation de l'acrylonitrile amorcée par le tetra*kis*(diméthylamido titane (IV) dans un vaste domaine de conditions expérimentales différentes. Les résultats indiquent que le schéma cinétique simple appliqué antérieurement, est valable seulement dans un domaine de température limité on observe des déviations significatives pour des températures supérieures ou inférieures à 25°. On discute les interprétations possibles des déviations du comportement normal.

Sommario—Con una larga gamma di condizioni spermentali, si è investigata la polimerizzazion dell'acrilonitrile iniziata da tetra*kis*(dimetilamido)titanio(IV). I risultati indicano che il semplice schema cinetico applicato precedentemente, è solamente valido per una limitata gamma di temperature; si sono infatti notate notevoli deviazioni a temperature superiori e inferiori a 25°. Si sono discusse alcune interpretazioni delle deviazioni dal comportamento normale.

Zusammenfassung—Die Polymerisation von Acrylnitril mit Tetra*kis*(dimethylamido)titan (IV) wurde über einen weiten Bereich experimenteller Bedingungen untersucht. Die Ergebnisse zeigen, daß das bisher angewandte einfache kinetische Schema nur für einen begrenzten Temperaturbereich gültig ist und daß bei Temperaturen über und unter 25° deutliche Abweichungen beobachtet werden. Für die von dem einfachen Verhalten abweichenden Befunde werden einige Deutungen diskutiert.