

# Ziegler–Natta polymerization: The nature of the propagation step

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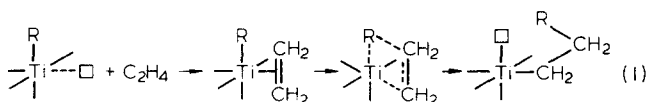
The paper discusses in detail the nature of the propagation step in Ziegler–Natta polymerization in terms of a one step or two step mechanism. A wide variety of evidence, both earlier literature results as well as current experimental data, is presented in support of a two-step mechanism comprising an initial monomer complexation at the active site followed by insertion into the growing transition metal–polymer bond. The nature of the rate determining step in the polymerization is also considered, and whereas in certain systems at low temperature insertion is clearly the main rate determinant, under other conditions both steps may together determine the overall rate.

(Keywords: Ziegler–Natta; propagation; polymerization; two-step mechanism; rate determining step)

## INTRODUCTION

Some thirty years of intensive research in Ziegler–Natta polymerization has yielded many fascinating discoveries, in terms of new types of polymers and in the development of ever higher activity catalysts and improved industrial processes. At the same time refined methods have emerged, such as g.p.c. and  $^{13}\text{C-FT}$  n.m.r., which permit detailed polymer characterization in terms of *MWD* and microstructure. Catalyst characterization has also become more sophisticated through the proliferation of methods for quantifying active site concentrations.

However, despite these advances the precise nature of the catalytic activity, in particular the mechanism of polymer growth, remains somewhat obscure. Whereas, there is fairly general agreement that chain growth occurs by monomer insertion into a transition metal–carbon bond the structure of the active centre remains speculative. The simplest and most widely accepted mechanistic scheme is that put forward by Cossee<sup>1</sup>, who proposed in accord with an earlier suggestion by Natta *et al.*<sup>2</sup> that propagation involved a two step process in which the olefin is reversibly adsorbed at the transition metal by  $\pi$ -complex formation before subsequent insertion into the transition metal–polymer bond.



Based on the Chatt and Duncanson model<sup>3</sup> the  $\pi$ -complex formation may be understood to involve a  $\sigma$ -bond formed by overlap of the olefin  $\pi$ -bonding orbitals with the relevant orbital on the transition metal, reinforced by a  $\pi$ -bond involving back-donation from the metal 'd' orbitals to the olefin  $\pi^*$  orbitals (Figure 1).

However, as acknowledged by Cossee<sup>1</sup> and confirmed in subsequent theoretical studies<sup>4</sup>, the formation of isolable metal–olefin  $\pi$ -complexes would not be expected for catalytically active metals with few or no 'd' electrons,

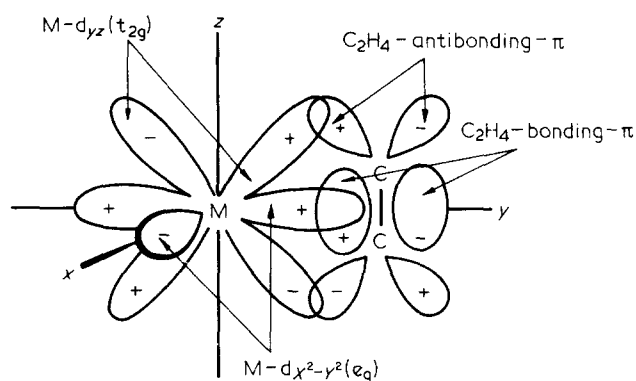


Figure 1 Bonding in the transition metal–olefin complex

because of limited  $\pi$ -back bonding. The fact that bonding in these complexes is dominated by a  $\sigma$ -donor type interaction has also been suggested independently by Ballard *et al.*<sup>5</sup> using the analogy of  $\pi$ -complex formation with aluminium alkyls where 'd' orbitals are not present.

However, 'd' orbitals are crucial for catalytic activity as apart from possible involvement in  $\pi$  complexation these orbitals provide a pathway for lowering the activation energy of olefin insertion by maintaining partial bonding of the alkyl fragment throughout the insertion process<sup>4,6</sup>. Whereas certain theoretical studies<sup>4,7</sup> have challenged some of the conclusions drawn by Cossee (notably the nature of the rate determining step), the premise of a two-step propagation mechanism has been fairly generally accepted. This provides an apt model for kinetic analysis, as demonstrated by Cossee<sup>8</sup> who showed that the mechanistic proposals were consistent with the generally observed first order dependence of polymerization rate on monomer concentration.

Thus the complex formation and rearrangement can be represented schematically as:





where C is the vacant site, C' is the new vacant site, CM the monomer complexed site and M the monomer. Under steady state conditions  $\frac{d[CM]}{dt} = 0$  and it can be readily shown<sup>8</sup> that the rate of polymerization will be given by:

$$R_p = -\frac{d[M]}{dt} = \frac{k_1 k_p C^* [M]}{k_1 [M] + k_2 + k_p} \quad (4)$$

where C\* is the total concentration of active sites both complexed and free.

First order dependence of rate on monomer arises where  $k_2 + k_p \gg k_1 [M]$ . This corresponds to one of three situations.

Case 1

$$k_2 \gg k_1 [M] + k_p$$

Here equation (4) reduces to:

$$R_p = \frac{k_1 k_p C^* [M]}{k_2} \quad (5)$$

and represents a catalysis where active sites are sparsely complexed and only a small fraction of adsorbed monomer undergoes insertion, rather than desorption.

Case 2

$$k_p \gg k_1 [M] + k_2$$

Under these conditions equation (4) transforms to:

$$R_p = k_1 C^* [M] \quad (6)$$

which depicts a reaction in which monomer complexation is rate determining. Again site coverage by monomer is low but in this case the fate of complexed olefin molecules is insertion rather than desorption.

Case 3

$$(k_p + k_2) \gg k_1 [M]$$

With this simplification equation (4) becomes:

$$R_p = \frac{k_1 k_p C^* [M]}{k_2 + k_p} \quad (7)$$

and denotes a polymerization where again complexation is the slowest step but desorption competes with insertion for the adsorbed species. This condition was not in fact delineated by Cossee<sup>8</sup> but is clearly a potential situation which should not be neglected.

All of the above three cases exemplify conditions under which the two-step proposal is fully consistent with the generally observed first order monomer dependence. Consequently the Cossee model, has been used as the basis for comprehensive kinetic schemes<sup>9,10</sup>.

However, whilst acknowledging the general acceptance of the two-step scheme, reviewers customarily emphasize that experimental support for prior monomer coordination is weak<sup>11-16</sup>. By contrast the author contends that there is in fact a wealth of evidence reported in the

literature supportive of these mechanistic proposals. This paper is concerned with drawing together that evidence and supplementing it with further kinetic results to demonstrate the experimental support for the two step reaction scheme. The relevance of these results to the nature of the rate determining step in this scheme will also be discussed.

## EXPERIMENTAL

### Materials

VCl<sub>3</sub> was the same highly pure sample of surface area 2.3 m<sup>2</sup>/g as previously described<sup>17</sup>. TiCl<sub>3</sub> Type 1.1 prepared by aluminium reduction of TiCl<sub>4</sub> and of surface area of 20.5 m<sup>2</sup>/g was kindly supplied by Stauffer Chemical Co., USA. The olefin 4-methyl-1-pentene (4MPI) of high chemical purity (>99.9%) was a gift from British Petroleum, UK. Benzene of A.R. grade and olefins (99% minimum purity) were dried over 3 Å molecular sieves<sup>18</sup>, fractionated from CaH<sub>2</sub> and stored over additional molecular sieves. Purified styrene was stored at 253 K over 3 Å molecular sieves and vacuum distilled from CaH<sub>2</sub> immediately before use.

### Procedure

Polymerization rates were measured dilatometrically as described earlier<sup>17</sup>.

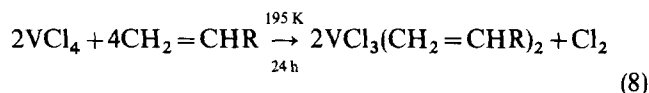
## RESULTS AND DISCUSSION

### THE EVIDENCE FOR PRELIMINARY COORDINATION

#### 1. Formation of transition metal $\pi$ -olefin complexes

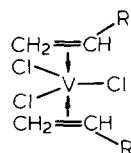
The strongest evidence for the intermediacy of olefin  $\pi$ -complexation in catalytic systems is the detection or isolation of such complexes with active transition metals. Whereas, the direct observation of  $\pi$ -complexes at catalyst sites is likely to be precluded by the low concentration and transient nature of the same it is to be anticipated that characterizable  $\pi$ -complexes might be found in related compounds of the catalytically active metals. This is indeed the case and a summary of reported  $\pi$ -complexes of vanadium, titanium and other active transition metals are given below under three heads.

(a) *Isolable  $\pi$ -complexes of titanium and vanadium.* An early patent<sup>19</sup> claimed that both 2:1 and 1:1 olefin complexes of VCl<sub>3</sub> could be obtained by treatment of vanadium tetrachloride with  $\alpha$ -olefins at low temperatures. The formation of the 2:1 complex was subsequently confirmed<sup>20</sup> for both terminal and internal alkenes, on treatment of a hexane solution of VCl<sub>4</sub> with the olefin at 195 K.



The complex precipitates as a light-brown amorphous solid in which the complexed olefin is characterized by a reduced i.r. double bond stretching frequency ( $\Delta\nu \approx 50\text{ cm}^{-1}$ ) compared to the free olefin. Whereas the complexes are insoluble in hydrocarbon solvents the olefin ligand is almost instantaneously displaced by acetonitrile at ambient temperatures with the formation of the green complex VCl<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>.

By analogy with complexes of vanadium of similar stoichiometry the olefin complexes were anticipated to exhibit a trigonal bipyramidal structure such as:



Subsequent studies<sup>21</sup> showed that these complexes, in combination with aluminium alkyls, were highly active catalysts for the polymerization of  $\alpha$ -olefins.

Analogous treatment of  $\text{TiCl}_4$ , however, only led to the formation of charge-transfer complexes (*vide infra*) and no definite olefin complexes were isolable<sup>20</sup>.

More recently<sup>22</sup> an ethylene complex of divalent titanium has been isolated and characterized. It is perhaps significant that the complex bis(pentamethylcyclopentadienyl ethylene) titanium (II) is isoelectronic ( $d^2$ ) with the vanadium complexes discussed above. Of related interest is the disclosure<sup>23</sup> of monoolefin complexes derived from phosphine derivatives of titanocene where the olefin ligand is constituted by dimethyl fumarate or maleate.

(b) *Charge transfer complexes of titanium and vanadium in solution.* Charge transfer complexes of olefins with  $\text{TiCl}_4$  in particular, as well as with  $\text{VCl}_4$ , have been widely reported. Thus coloured complexes of  $\text{TiCl}_4$  with *cis/trans* stilbene<sup>24</sup>, isobutene<sup>25</sup>, 1,1-diphenyl-ethylene<sup>26,27</sup>, hexene and cyclohexene<sup>28</sup>, 4-methyl-1-pentene<sup>20</sup> and other substituted olefins<sup>29</sup> are known. In the case of methyl-pentene<sup>20</sup>, exposure of  $\text{TiCl}_4$  to the vapour under vacuum led to a rapid distillation of the olefin into the  $\text{TiCl}_4$  reaction vessel with the concomitant exothermic formation of a yellow complex.

Elsewhere<sup>30</sup> CT-complexes of  $\text{VCl}_4$  with isobutene have been observed spectrophotometrically and implicated as reactive intermediates in radical-cation polymerization.

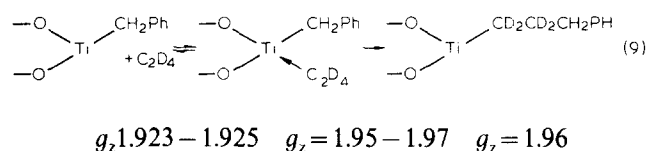
In these complexes the lack of free 'd' electrons on the transition metal restricts the nature of the bonding to relatively weak  $\pi$ -donor type and the complexes are only formed as transient species in solution.

(c)  *$\pi$ -olefin complexes on supported transition metal catalysts.* In recent years several authors have reported

the detection of olefin complexes of supported transition metals such as Hf, Zr, Ti and V (see Table 1).

Thus  $\pi$ -complexation of ethylene with hafnium and zirconium benzyls has been inferred from the increased retention times of the olefin in g.l.c. analysis<sup>31</sup>. The effects are relatively small, however, at the temperatures employed (291–298 K) indicating rather weak interactions. At much lower temperatures (120–150 K) proton n.m.r. has been utilized to demonstrate ethylene interaction with similar zirconium catalysts supported on alumina<sup>32</sup>. At these temperatures ethylene coordination of the zirconium apparently leads to a change in chemical shift of the proton resonance from 5.3 ppm (free  $\text{C}_2\text{H}_4$ ) to 1.1 ppm with respect to TMS. The adsorption process which is reversible on evacuation, precedes an insertion step.

E.s.r. studies<sup>33,34</sup> of silica supported  $\text{Ti}(\text{CH}_2\text{Ph})_4$  at 120 K again demonstrate the reversible complexation of olefin at these low temperatures through subtle changes in the Ti(III) spectrum on coordination. At higher temperatures (293 K) the complexation is followed by insertion. The whole process may be summarized as follows:



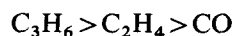
The adsorption of ethylene and propylene on  $\text{TiO}_2$  and hydrogen reduced  $\text{V}_2\text{O}_5$  has been evidenced by i.r. studies<sup>35,36</sup>. Complexation of the olefins leads to a reduction in the  $\text{C}=\text{C}$  stretching frequency.  $\Delta\nu$  values of  $15\text{ cm}^{-1}$  and  $35\text{ cm}^{-1}$  have been observed on propylene coordination with  $\text{Ti}^{4+}$  and  $\text{V}^{3+}$  ions respectively, indicating a stronger bonding interaction with the vanadium system. In both cases desorption occurs on evacuation of the sample at 293 K and adsorbed alkene or carbon monoxide are mutually exchangeable.

Micro-calorimetry<sup>37</sup> has also been used to detect the exothermic adsorption of ethylene and propylene on  $\text{Ti}^{4+}$  and other supported metal cations. Heats of adsorption of between 50–69 kJ/mol have been estimated depending on the nature of the ligand and transition metal. The heat of adsorption has been shown to be related to the shift in  $\nu_{\text{C}=\text{C}}$  as measured by i.r. High heats of adsorption correspond to large  $\Delta\nu_{\text{C}=\text{C}}$  values which in turn are indicative of

**Table 1** The observation of  $\pi$ -olefin complexes on supported transition metal catalysts

Catalyst	Species	Olefin	Method	T (K)	Observation	Ref.
Hf/Zr(Benzyl) <sub>4</sub> on diatomite		$\text{C}_2\text{H}_4$	g.l.c.	291–298	Weak complexation inferred from increased retention times	31
Ti(benzyl) <sub>4</sub> on silica		$\text{C}_2\text{D}_4$	e.s.r.	120	Reversible adsorption followed by insertion at higher T	33, 34
$\text{TiO}_2$	$\text{Ti}^{4+}$	$\text{C}_3\text{H}_6$ $\text{C}_3\text{D}_6$ $\text{C}_2\text{H}_4$ $\text{C}_3\text{H}_6$	i.r.	293	Reversible adsorption denoted by lowering of $\nu_{\text{C}=\text{C}}$ on coordination	35
$\text{H}_2$ reduced $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$	$\text{V}^{3+}$	$\text{C}_3\text{H}_6$	i.r.	300	Weak reversible adsorption with preservation of olefinic character	36
$\text{TiO}_2$	$\text{Ti}^{4+}$	$\text{C}_2\text{H}_4$ $\text{C}_3\text{H}_6$	Calorimetry	—	Heat of adsorption related to $\Delta\nu$ , decreases in order $\text{C}_3\text{H}_6 > \text{C}_2\text{H}_4 > \text{CO}$	37
Zr(benzyl) <sub>4</sub> on $\text{Al}_2\text{O}_3$		$\text{C}_2\text{H}_4$	<sup>1</sup> H-n.m.r.	120–150	Reversible adsorption	32

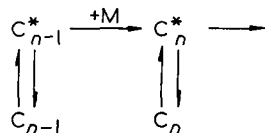
stronger bonding interactions. For  $Ti^{4+}$ , bond strengths decrease in the order:



which is consistent with the known electron donor properties of these ligands and again reinforces the relatively small contribution of back donation from the transition metal to bonding in the Ti(IV) system. (The above sequence is the reverse of the electron acceptor properties of these ligands.)

For a balanced presentation it should be pointed out that other workers have failed to detect the coordination of styrene with  $Zr(CH_2Ph)_4$ <sup>38</sup> or of <sup>13</sup>C-ethylene with  $Cp_2TiEtCl/AlEtCl_2$ <sup>39</sup> by n.m.r. methods. However, in both cases the actual catalytically active species represent only a very small fraction (0.1% or less) of the catalyst components in solution and thus probably escape detection by these methods. Consequently the suggestion made<sup>39</sup> that the failure to detect olefin coordination on the inactive 'primary complex' in the soluble titanium system implies absence of olefin coordination in the active catalyst is, in the author's opinion, misleading.

In this context it must be remembered that the ability to observe carbon resonances associated with the ethylene insertion product  $Ti-CH_2CH_2-$  does not imply the ability to directly observe the catalytic species. This follows since it has been shown<sup>40</sup> that in these systems the catalytic activity is intermittent, as may be represented by the scheme:



Under these circumstances where  $C^* \ll C$  the observed  $Ti-CH_2CH_2-$  resonance are almost certainly associated with inactive complexes.

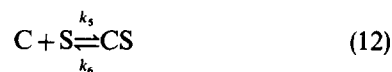
## 2. Kinetic evidence

In the event that propagation does occur with adsorbed monomer rather than by direct insertion one might anticipate a distinction by careful kinetic analysis. This has in fact proved to be the case as will be demonstrated, but first it is necessary to examine certain kinetic schemes.

In earlier comprehensive kinetic studies<sup>9,17,41-44</sup> of the polymerization of 4-methyl-1-pentene by the catalyst system  $VCl_3/AlR_3$  the rate of polymerization was most adequately described by the equation:

$$R_p = k_p \theta_M C^* \quad (10)$$

where  $k_p$  is the propagation rate constant,  $\theta_M$  the fraction of sites covered by adsorbed monomer and  $C^*$  the active site concentration. This is equivalent to the Cossee model where propagation occurs with adsorbed monomer at an alkylated transition metal site (equation (1)), but with the added refinement that equation (10) takes account of competitive adsorption of co-catalyst (A) and other species (S) at the active site. Thus in addition to monomer adsorption (equation (2)), the following processes are recognized:



Consequently on substitution for  $\theta_M$ , equation (10) becomes:

$$R_p = \frac{K_M [M] k_p C^*}{1 + K_M [M] + K_A [A] + K_S [S]} \quad (13)$$

where  $K_M, K_A$  and  $K_S$  are the equilibrium constants for the respective adsorption processes, i.e.  $K_M = k_1/k_2$  etc.

The relationship of the above kinetic model to the Cossee kinetic expression (equation (4)) may readily be seen by substitution of  $K_M = k_1/k_2$  in equation (13) and ignoring the co-adsorption of other species. Under these conditions the rate of polymerization is given by:

$$R_p = \frac{k_1 k_p [M] C^*}{k_2 + k_1 [M]} \quad (14)$$

which is equivalent to equation (4) provided that  $k_p \ll k_2 + k_1 [M]$ , i.e. the insertion step is slow compared with setting up of the adsorption equilibrium.

Zakharov *et al.*<sup>10</sup> have also used the Cossee model as the basis of their kinetic proposals but again it was found necessary to allow for co-adsorption of species such as co-catalyst. However, instead of describing this by introducing additional denominators in  $K_M$ , as in equation (13), the kinetic proposals consider different states of 'active site'. Sites complexed by co-catalyst (and presumably other species) are considered as polymerization inactive, and the number of propagating sites ( $C_p$ ) is given by the expression:

$$C_p = \frac{C^*}{1 + K_A [A]} \quad (15)$$

The overall rate of polymerization is then given by:

$$R_p = k'_p C_p [M] \quad (16)$$

where  $k'_p$  is a composite term derived from the Cossee relationship (equation (4)) and given by:

$$k'_p = \frac{k_1 k_p}{k_1 [M] + k_2 + k_p} \quad (17)$$

Whereas this is an equally valid approach, it is in the author's opinion subject to certain ambiguities in practice. Thus it is not clear whether experimental measurements of active site concentration lead to a value of  $C^*$  or  $C_p$ —the latter quantity is implied by Zakharov *et al.*<sup>10</sup> when using the <sup>14</sup>CO method but both types of site involve polymer chains bound to a transition metal and thus susceptible to assay. Furthermore, since the measured propagation rate constant ( $k'_p$ ) is a composite term its immediate significance is less apparent and comparisons under widely different conditions may be less meaningful.

Consequently, in the discussions that follow, equation (10) will be adopted bearing in mind the restrictions implied concerning the nature of the rate determining step. The validity of this equation and hence the concept of propagation with adsorbed monomer can be tested as described below.

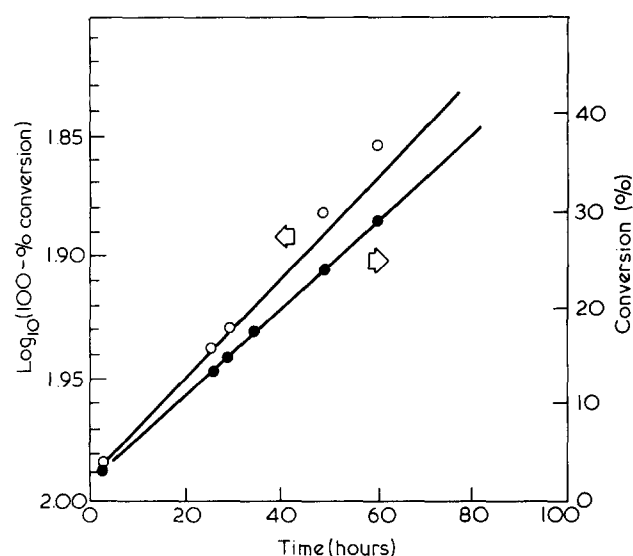
(a) *Rate dependence upon monomer concentration.* At high monomer concentration and in the absence of strong catalyst poisons it would be anticipated that the condition  $K_M[M] \gg 1 + K_A[A] + K_S[S]$  should apply and hence equation (10) should simplify to

$$R_p = k_p C^* \quad (18)$$

which infers that the polymerization rate should be independent of monomer concentration. This result has not been generally observed. However, this is not totally unexpected when one considers the values of the terms in the above simplifying condition. For example, in the polymerization of 4-methyl-1-pentene by the catalyst system  $VCl_3/Al(iBu)_3$  at 303 K,  $K_M = 0.164$  and  $K_A = 5.1$  and even polymerization in bulk monomer would not validate the above inequality. Similar considerations would be anticipated to hold for ethylene and propylene which are also only weakly adsorbed at moderate temperatures<sup>31</sup>.

The problem is not completely intractable since observation of the above phenomena is possible under two circumstances:

(i) in systems employing monomers which are strongly adsorbed at ambient temperatures;



**Figure 2** Styrene polymerization. First (○) and zero (●) order plots.  $[VCl_3] = 60 \text{ mol l}^{-1}$ ;  $[Al(iBu)_3] = 37 \text{ mol l}^{-1}$ ;  $[styrene] = 2.0 \text{ mol l}^{-1}$ ; solvent = benzene;  $T = 30^\circ\text{C}$

and (ii) at low temperatures where even simple  $\alpha$ -olefins are much more strongly adsorbed.

Styrene is an appropriate monomer to illustrate criterion (i) since it is strongly adsorbed at 303 K ( $K_M = 11$ ) by the catalyst system  $VCl_3/Al(iBu)_3$ . Thus at moderate monomer concentrations ( $[M] = 2 \text{ mol l}^{-1}$ ) the term  $K_M[M] = 22 \text{ mol l}^{-1}$  and the simplifying condition is realized. The polymerization of styrene by this catalyst is shown in *Figure 2*, which demonstrates that at 303 K the overall course of polymerization is effectively zero-order in monomer, thus confirming the validity of equation (18) and reinforcing the concept of propagation with adsorbed monomer.

The transition from first to zero order kinetics has also been observed for ethylene and propylene either by operating at low temperatures, as low as 195 K in some cases, or by utilizing very high monomer concentrations approaching  $12.5 \text{ mol l}^{-1}$ . Literature results illustrating these effects are summarized in *Table 2*. Whereas, most of the relevant systems are based on soluble catalysts at least two results supportive of propagation with adsorbed monomer were obtained in propylene polymerization based on the heterogeneous  $TiCl_3$  catalyst. That lower temperatures accentuate the effect is fully consistent with the dependence of the adsorption equilibrium on temperature, since  $K_M$  increases with decreasing temperature.

Even where strict independence of rate upon  $[M]$  is not observed these summarized results still confirm the validity of equation (13) since on inversion this becomes:

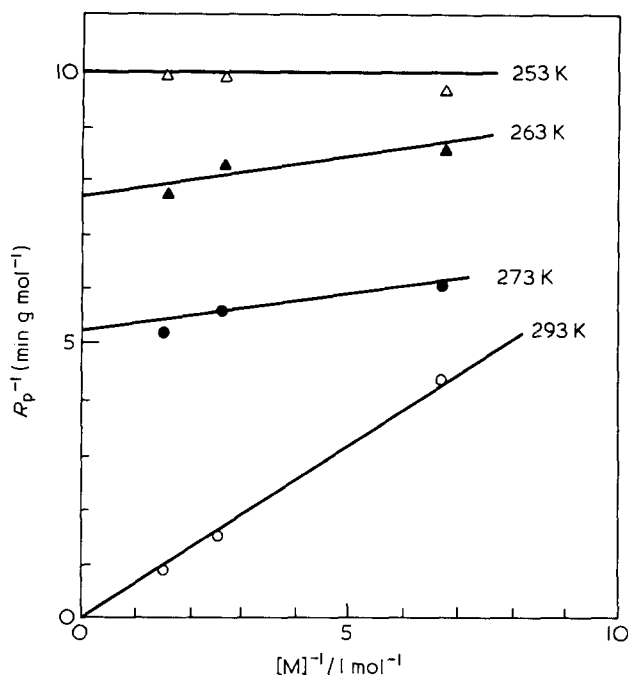
$$1/R_p = 1/k_p C^* \left( 1 + \frac{1 + K_A[A] + K_S[S]}{K_M[M]} \right) \quad (19)$$

Plots of  $1/R_p$  versus  $1/[M]$  should thus be linear but with a positive intercept as is indeed found to be the case. For example plotting of the data obtained by Zavorkhin *et al.*<sup>45</sup> for propylene polymerization (*Figure 3*) shows a series of linear plots characteristic of the polymerization temperature. Since  $K_M$  is proportional to the ratio of slope/intercept it is apparent that in this system the adsorption equilibrium constant increases rapidly at lower temperatures.

However, in a recent study<sup>46</sup> employing the soluble catalyst  $Cp_2Ti$  Propyl  $Cl/AlEtCl_2$  for the polymerization of ethylene at 203 K the authors claim that the polymerization rate was independent of  $[M]$  over the range 2.5–18.8  $\text{mol l}^{-1}$ . The interpretation of the polymerization

**Table 2** Observed dependence of polymerization rate on monomer concentration

Catalyst	Electronic configuration of TM	Monomer	$[M]$ ( $\text{mol l}^{-1}$ )	$T$ (K)	Dependence of rate upon $[M]$	Ref.
$VCl_4/AlEt_2Cl$ / Anisole	$d^1$	$C_3H_6$	—	195	$R_p \propto \frac{K_M [M]}{1 + k_M [M]}$	47
$TiCl_3/AlEt_3$	$d^1$	$C_3H_6$	0.1 – 2.3	288	Less than first order	48
$VCl_4/Al(iBu)_2Cl$	$d^1$	$C_3H_6$	0.15– 0.66	253	Zero order	45
				293	First order	
$TiCl_3/AlEt_2Cl$	$d^1$	$C_3H_6$	0.1 –12.5	293–353	Less than first order	49
$V(AcAc)_3/AlEt_2Cl$	$d^2$	$C_2H_4$	0.03– 0.28	230–253	Approaches zero order at high $[M]$	50
$VCl_4/AlEt_2Cl$ / $AlEt_2Br$ / $AlEt_3$	$d$	$C_3H_6$	1.2 –11.7	195	$R_p \propto \frac{K_M [M]}{1 + K_M [M]}$	51, 52
$Cp_2TiRCl/AlEtCl_2$	$d^0$	$C_2H_4$	2.5 –18.8	203	approaches zero order at high $[M]$ Results equivocal, but apparently first order	46



**Figure 3** Reciprocal of polymerization rate versus inverse of propylene concentration. Data from Zavorkhin *et al.* (ref. 45), for the catalyst  $\text{VCl}_4/\text{Al}i\text{Bu}_2\text{Cl}$

data is, however, equivocal as although admittedly there is no strong apparent deviation from first order dependence, the results, when replotted on a reciprocal basis (Figure 4), appear to show a positive intercept. Strict first order dependence should lead to a bisection of the origin.

Temperature and monomer concentration apart it is clear that the observed monomer dependence will be affected principally by the value of  $K_M$  which in turn will be determined by the bonding interactions of the monomer at the active site. Thus it is to be anticipated that at a given temperature  $K_M$  will be controlled by the transition metal, its valence state and the nature of the coordinating ligands. If the  $\pi$ -complexation process is dominated by a  $\sigma$ -type donor interaction then electron withdrawing coordinating ligands such as halogens may enhance the stability of the coordination and hence  $K_M$ . Conversely, if back donation from the transition metal has a reinforcing effect on the bonding then the presence or absence of 'd' electrons may be a controlling factor (Table 2).

Either explanation could rationalize the reduced effects observed with the  $\text{Cp}_2\text{TiRCl}$  catalyst system where  $K_M$  may be very much lower because of ligand effects or the absence of 'd' electrons.

(b) *Retardation by non-polymerizable olefins.* Equation (13) predicts rate retardation by donor species (S) which can competitively absorb with monomer at active centres. Such retardation effects may be obscured in the case of strong  $\sigma$ -donors such as ethers and amines since concomitant complexation of the cocatalyst normally occurs leading to more complex effects<sup>43</sup>. However, olefins, which are inactive or only sluggishly active in polymerization are ideally suited to test equation (13) since no significant interaction with co-catalysts occur, and retardation will only be apparent if  $\pi$ -complexation actually takes place.

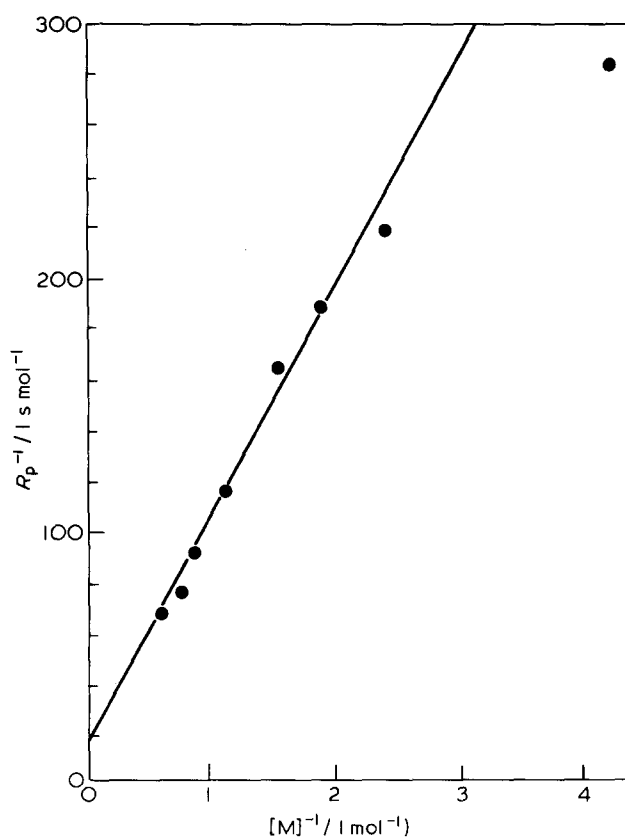
Olefins such as 2,3-dimethyl-1-butene, *cis*-4-methyl-2-pentene and styrene are indeed found to retard the polymerization of 4-methyl-1-pentene, the retardation

increasing with concentration of added olefin. The inhibition of polymerization is indicative of the blocking of coordination sites through olefin complexation which again reinforces the concept of propagation with adsorbed monomer.

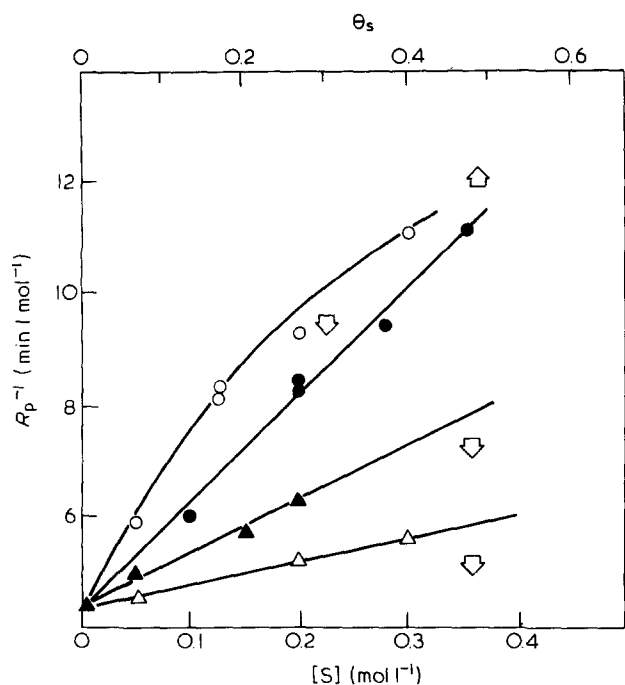
A quantitative evaluation of these effects may be obtained through the use of equation (19) which predicts that plots of  $1/R_p$  versus  $[S]$  should be linear. This is indeed the case (Figure 5) except for styrene. The deviation in the case of styrene arises since this olefin is strongly adsorbed and at even low concentration there is *self-competition* for site complexation. Thus the term  $K_S[S]$  in equation (19) is more appropriately substituted by  $\theta_S$ , whereupon, a plot of  $1/R_p$  versus  $\theta_S$  (Figure 4) is seen to be linear.

Similar observations have been made recently by D'yachkovskii *et al.*<sup>53</sup> in studies of propylene polymerization catalysed by  $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$ . Polymerization was accompanied by the formation of propylene dimers of both terminal and internal olefins. The dimers were shown to be partially responsible for rate retardation during polymerization, presumably by competitive adsorption with propylene at the active centres.

(c) *Inhibition by catalyst poisons.* The well documented inhibition of polymerization by poisons such as carbon monoxide, phosphine or pyridine has been cited<sup>38,54</sup> as evidence for a two step mechanism of propagation. However, whereas these results point to the existence of coordination vacancies at active centres at which the poisons can bond, it does not necessarily follow that monomer also coordinates at these sites. It is conceivable that even in the case of a single step mechanism, with monomer inserted directly from solution, that similar



**Figure 4** Reciprocal of polymerization rate versus inverse of ethylene concentration. Data for the system  $\text{Cp}_2\text{Ti Propyl Cl}/\text{AlEtCl}_2$  at 203 K from ref. 46

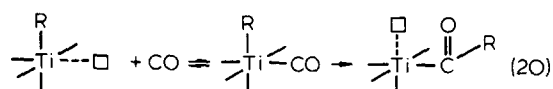


**Figure 5** Retardation by olefins in the polymerization of 4-MP-1.  $[VCl_3] = 18.5 \text{ mmol l}^{-1}$ ;  $[AlEt_3] = 37.0 \text{ mmol l}^{-1}$ ;  $[4\text{-MP-1}] = 2.0 \text{ mol l}^{-1}$ ; solvent = benzene;  $T = 30^\circ\text{C}$ ;  $\circ$ ,  $\bullet$  styrene;  $\blacktriangle$  2,3-dimethyl-1-butene;  $\triangle$  *cis*-4-methyl-1-pentene

observations would be made. In that case, poisons could inhibit sterically or by modification of the transition metal carbon bond reactivity.

The effect of catalyst poisons is of course fully consistent with the two-step proposals and could be treated kinetically by equation (13). It is of considerable interest that catalyst poisons include two classes of compounds namely strong  $\sigma$ -donors, e.g. pyridine and strong  $\pi$ -acceptors such as CO. This suggests that both types of bonding are of importance at the active site.

Inhibition by CO could be a consequence of the changed reactivity of the active titanium bond following insertion, as in the scheme below:



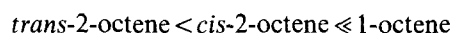
However, against this is the observed dependence of polymerization rate on adsorbed carbon monoxide<sup>55,56</sup>. Thus whereas CO does become incorporated into the polymer, through an insertion reaction<sup>57</sup> the primary source of initial rate inhibition appears to be site complexation<sup>58</sup>.

(d) *Polymerization activity of ring substituted styrenes.* Quite early on, Natta *et al.*<sup>2</sup> revealed the surprising result that the polymerization activity of *m*- and *p*-substituted styrenes in both homo- and co-polymerization clearly depended on the Hammett  $\sigma$ -parameter of the substituent attached to the ring. Electron releasing substituents led to enhanced reactivity and this was interpreted to mean that the rate determining step was electrophilic in character. Since other experimental results convincingly demonstrated that the polymerization was anionic in nature Natta *et al.*<sup>2</sup> were forced to conclude that the primary rate-controlling step was  $\pi$ -coordination of the olefin at an electron deficient titanium atom.

These results cannot be readily interpreted in terms of a single step mechanism and thus provide cogent support for monomer coordination.

### 3. Monomer involvement in catalyst reduction

Apart from direct observation of monomer complexes, and deductions from polymerization kinetics,  $\pi$ -complex formation by monomers at the polymerization active sites may also be inferred indirectly. Thus olefin coordination is evidenced by the effect of such species on catalyst reduction. The homogeneous catalyst system  $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$  readily undergoes bimolecular deactivation with concomitant reduction of  $\text{Ti(IV)} \rightarrow \text{Ti(III)}$  and the evolution of ethane and ethylene. This reduction is considerably accelerated by the presence of olefins<sup>59–61</sup>. Furthermore, Olivé and Olivé<sup>59</sup> showed that the rate of reduction was dependent on the nature of the added olefin and for octenes this increased in the following order



This is suggestive of  $\pi$ -complex formation since the order parallels the increasing tendency of the octenes to form metal-olefin  $\pi$ -bonds.

The experimental evidence cited above is consistent with the concept of  $\pi$ -complexation by olefins and with the proposal of Cossee<sup>1</sup> that such coordination lead to a weakening of the transition metal–carbon bond.

### THE NATURE OF THE RATE DETERMINING STEP

In the author's opinion the results discussed in the previous section supply compelling evidence as to the validity of the two-step propagation mechanism, with chain growth occurring by insertion of monomer complexed at an active transition metal centre. The thorny question that remains, however, is which step in the scheme is rate-determining—complexation (equation (2)) or insertion (equation (3))?

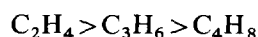
Thus Cossee<sup>8</sup> postulated that monomer insertion should be the rate determining step on the grounds that it is difficult to associate an activation energy of the order of 11–14 kcal mol<sup>-1</sup> with the process of complexing a neutral molecule in a vacant position at the active site. On the other hand Natta *et al.*<sup>2</sup>, Schindler<sup>62</sup>, Armstrong *et al.*<sup>4</sup>, Boucheron *et al.*<sup>49</sup> and Zakharov *et al.*<sup>7,63,64</sup> have proposed that complexation is rate determining largely on the basis of kinetic evidence or theoretical calculations.

(a) *Quantum-chemical considerations.* In the Cossee model<sup>8</sup> which was also adopted by Begley and Pennella<sup>65</sup> the activation energy is associated with the energy required to promote a bonding electron from the  $\sigma_R$  bonding orbital to a partially filled or vacant  $d_\pi$  orbital of the transition metal, i.e. is related to scission of the Ti–C bond. In contrast, Armstrong *et al.*<sup>4</sup> and subsequently Zakharov *et al.*<sup>7</sup> have suggested that the observed activation energy is derived from a rearrangement in the structure of the active centre from trigonal-bipyramidal to octahedral symmetry on co-ordination of the monomer. This follows since according to CNDO calculations the total energy of the active centre is a minimum in the former structure. According to this view, after coordination, the system runs downhill energy-wise with insertion occurring in a concerted fashion, with

restoration of the bipyramidal configuration. This latter mechanism is attractive in that it avoids the necessity of an additional alkyl-migration step, as required with the Cossee model, to explain the possibility of isotactic stereoregulation by an asymmetric centre.

However, quantum-chemical studies cannot be taken as the sole arbiter of this question as the results of such calculations are notoriously dependent on the precise detail on the adopted model, on the simplifying assumptions and on the values assigned to the various parameters involved.

(b) *Polymerization of ring substituted styrenes.* The central argument in the assertion that adsorption is rate determining is derived from the early observations of Natta *et al.*<sup>2,66</sup> on the homo- and co-polymerization activity of ring substituted styrenes. It was observed that monomer reactivity was enhanced by electron releasing substituents in the aromatic ring. This is of course in contrast to the order of decreasing activity in olefin polymerization of:



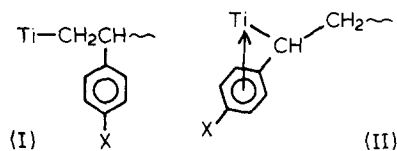
but here arguably steric factors might predominate.

The observed rate enhancement by electron releasing substituents appeared to accord with the concept that the rate determining step was electrophilic in character, and since insertion was generally associated with an 'anionic' process it followed that the  $\pi$ -complexation must be the slow step.

However, our present studies of the polymerization of styrene and 4-MP-1 by the catalyst systems  $VCl_3/Al iBu_3$  and  $TiCl_3$  Type 1.1/ $Al iBu_3$  throw fresh light on this problem. Thus it can be seen (Table 3) that, whereas styrene is much more strongly adsorbed than 4-MP-1 at the active site ( $\times 67$ ), the latter monomer is considerably more active in polymerization on both catalysts studied ( $\times 33$  and  $\times 55$ ). Since it appears that the  $C^*$  values are similar for both monomers on the same catalyst, it follows that at least in the case of styrene polymerization, adsorption is *not* the slowest step.

These findings would appear to be in direct conflict with the copolymerization results discussed about, however, it must be appreciated that the factors determining the effect of electron-modifying substituents are complex, as changes of electron density may variously affect: the ability of the olefin to complex at the active site; the stability of the resultant transition metal-polymer bond; as well as the overall energy of the intermediate transition states involved. The effect of electron-releasing substituents on styrene complexation is dependent on the nature of the bonding. Thus for styrene complexes of first

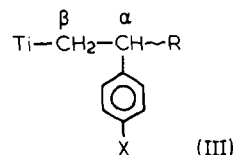
row transition metals such as Ag(I) and Cu(I) where the bonding is dominated by  $\sigma$ -donor type interactions, electron-releasing substituents enhance complexation<sup>67</sup>. On the other hand for second row transition metals such as Ni(O) and Pt(O), (II) where  $\pi$ -bonding is important the opposite effect is observed<sup>68</sup>. Furthermore, the effects will also be dependent on the nature of the insertion process, whether primary (I) or secondary(II):



In the latter case by analogy with the structure of zirconium and titanium benzyls<sup>69</sup>, there is significant donation of ring  $\pi$ -electrons to vacant d orbitals. Such an effect, which stabilizes the Ti-C bond will be enhanced by electron-releasing substituents.

The complex nature of these effects is well illustrated by the work of Ballard *et al.*<sup>69</sup> who studied the polymerization activity of Zirconium tetrabenzyl compounds. With these catalysts electron-releasing substituents in the benzyl group were found to reduce rates in ethylene polymerization but activate them in the case of styrene.

However, the results of Natta *et al.*<sup>2,66</sup> are of particular interest as the close correlation between the activities of substituted monomers in both homo- and co-polymerization studies appears to indicate that the polymerization activity is independent of the preceding monomer unit and hence of the structure of the transition metal-polymer bond:



i.e. the reactivity of the  $Ti-C_\beta$  is relatively unaffected by the nature of X. This is perhaps not too surprising considering the remoteness of the  $\beta$ -carbon from the ring and the supposed nature of the catalysis.

The variation in activity of substituted styrenes must therefore be relegated to the effects of monomer polarity on the insertion or complexation steps. Whereas, it has been tacitly assumed that electron releasing substituents will destabilize the transition state for olefin insertion this may not necessarily be the case for a concerted mechanism where preservation of  $\pi$ -bonding overlap with the transition metal d orbitals is at a premium<sup>4</sup> rather than stabilization of a free anion. (Indeed the classification of this type of catalysis as 'anionic' may in fact be misleading, based as it largely is on the supposed polarity of the transition metal-polymer bond, when one considers that at least in some vanadium systems<sup>71,72</sup> the diagnostic quenching with tritiated alcohols fails to confirm such characteristics.)

An alternative possibility that would reconcile the different experimental results is that the polymerization activity is determined by *both* complexation and insertion steps as is indeed implied in equation (10). That is not to say that complexation is the slowest step, but that both complexation and insertion may be rate determining concurrently. This is analogous to the kinetic derivations

**Table 3** Activity of styrene and 4-methyl-1-pentene in polymerization by  $VCl_3/Al iBu_3$  and  $TiCl_3$  Type 1.1/ $Al iBu_3$

Monomer	$K_M$ (1 mol)	$R_p$ (mol/1-min mol $MCl_3$ )	
		$VCl_3$	$TiCl_3$ , Type 1.1
4-methyl-1-pentene	0.164	0.229	3.13
Styrene	11	0.0041	0.0934

$[MCl_3] \approx 18.8 \text{ mmol l}^{-1}$ ;  $[Al iBu_3] = 37.0 \text{ mmol l}^{-1}$ ;  $[Monomer] = 2.0 \text{ mol l}^{-1}$ ; Solvent = benzene;  $T = 30^\circ C$



of Ballard *et al.*<sup>70</sup> who concluded that the polymerization rates of ethylene and styrene with supported zirconium tetra-benzyl catalysts could best be described by the relationship:

$$R_p = K_2 k_1 \sum_1^{\infty} |D_n| |M|$$

where  $K_2$  is the equilibrium constant for monomer adsorption and  $k_2$  the insertion rate constant. In the case of the polymerization of substituted styrenes by Ziegler–Natta catalysts, the variation in activity could thus be due to enhancement of site coverage by adsorbed monomer as would be signified by increased values of  $\theta_M$  (equation (10)).

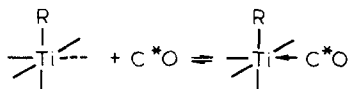
This explanation does not imply that complexation is the slowest step, as there is convincing evidence, *vide infra*, that at least at low temperatures insertion is largely rate controlling.

(c) *Temperature effect on reaction order.* As discussed earlier, the effect of reducing the reaction temperature in a number of polymerization systems is to decrease the order with respect to monomer to zero. The only reasonable explanation of this phenomenon is that at low temperatures (equation (4))  $k_1[M] \gg k_2 + k_p$ . That is, the rate of monomer adsorption is very much greater than desorption or, insertion and hence active sites are saturated with monomer and insertion is the *slow rate controlling step*.

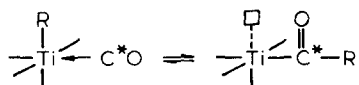
The reversion of the overall kinetic dependencies to first order with respect to monomer, as the temperature is raised, implies that the insertion step is characterized by a much higher activation energy than monomer adsorption, and hence becomes relatively more favourable at elevated temperatures.

This argument is reinforced by the observation that whereas monomer adsorption is favoured at low temperatures, at very low temperatures insertion is completely inhibited<sup>33</sup>.

(d) *Mechanism of catalyst interaction with carbon monoxide.* A further observation that sheds some light on the relative importance of adsorption *versus* insertion is the use of carbon monoxide as a catalyst poison. It is generally observed that the addition of carbon monoxide to an active polymerization system leads to an almost instantaneous deactivation of the catalyst activity<sup>73</sup>. Although there is still debate in this area, it would appear that the primary cause of rate deactivation is blocking of active sites by adsorption of carbon monoxide at coordination vacancies:



This initial coordination is followed by a somewhat slower insertion step:



which leads to incorporation of the carbon monoxide into the polymer chain.

This interpretation is supported by the lengthy period required to attain quantitative incorporation of carbon

monoxide<sup>74,75</sup> compared to the almost instantaneous quenching of the polymerization.

Although the activity of carbon monoxide will be vastly different from the olefin monomers nevertheless this example does illustrate another instance, with the same catalyst system, where insertion appears to be rate determining.

(e) *Rate control by adsorption and insertion steps.* It seems evident that the nature of the slow step in chain growth will be dependent on the reaction temperature, the nature of the catalyst (particularly transition metal and ligands) and the monomer size and polarity as all these factors will affect the relative values of the rate constants  $k_1$ ,  $k_2$  and  $k_p$ . For a given system it is evident that temperature is the main determinant, since the ratio  $k_1/k_2$  will decrease with increase in temperature with a corresponding reduction in the concentration of adsorbed monomer whereas, the insertion rate for adsorbed monomer will increase. One could thus visualize insertion control at low temperatures transformed to adsorption/desorption control at higher temperatures. Both of these eventualities are covered in the kinetic equation for propagation with adsorbed monomer (equation (10)).

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