

## Kinetic Features of the Cobalt Dihalide/Methylaluminoxane Catalytic System in 1,3-Butadiene Polymerization

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**Abstract:** The kinetic features of polymerization with an active site comprising cobalt dihalides (CoX<sub>2</sub>, where X = Cl, Br, I) activated by methylaluminoxane (MAO) were investigated in 1,3-butadiene polymerization. The catalytic system exhibited the characteristic features of living polymerization. The initiation (*k<sub>i</sub>*) and propagation (*k<sub>p</sub>*) rate coefficients were estimated using the kinetic model for slow initiation previously reported by Shiono *et al.*<sup>1</sup> The energy of activation for the propagation reaction was calculated to be 27-30 kJmol<sup>-1</sup>. The marked changes in reaction rate observed with different halides could be adequately described in terms of variations in the initiation process, with the same Arrhenius curve fitting propagation rate coefficients estimated from all three halides, suggesting that the halide does not participate in the growing chain end.

**Keywords:** 1,3-butadiene, cobalt dihalide, methylaluminoxane, initiation rate coefficient, propagation rate coefficient.

### Introduction

A number of previous reports have been made on the Ziegler-Natta polymerization of 1,3-butadiene with transition metal complexes in combination with methylaluminoxane or trialkylaluminum compounds.<sup>1-13</sup> Kinetic studies of these systems have been limited to studies of the overall behaviour of the composite reaction, with no activation energies or frequency factors reported for the individual kinetic events in the polymerization. The activation energies for 1,3-butadiene polymerization by Ziegler-Natta catalysts reported so far are overall activation energy of initiation, propagation and in some case deactivation reactions. This overall activation energy is strongly dependent on the type of metal used, ligand, and cocatalyst, varying from 20 to 80 kJmol<sup>-1</sup>.<sup>14-18</sup> A few reports of even lower activation energies for 1,3-butadiene polymerization has been made. For instance, Marechal *et al.* reported the use of bis( $\pi$ -allyl) nickel trifluoroacetate for the polymerization of 1,3-butadiene at 30 °C in benzene, which they found to be first-order reaction on monomer and catalyst with an overall activation energy of 13 ± 0.5 kJmol<sup>-1</sup>.<sup>15</sup> Endo *et al.* estimated the activation energy for the polymerization of 1,3-butadiene with Ni(acac)<sub>2</sub>-methylaluminoxane (MAO) to be 18.0 kJ mol<sup>-1</sup>.<sup>18</sup>

This work considers the kinetics of the Ziegler-Natta polymerization of 1,3-butadiene with a CoX<sub>2</sub>-MAO catalytic system, one that has been demonstrated to be subject to a relatively slow initiation process and shows a first-order dependence on monomer concentration.<sup>1</sup> The overall kinetic scheme for this process has been suggested to be as follows:<sup>1</sup>

$$-dM/dt = k_p [M][C^*] \quad (1)$$

$$[C^*] = [I]_\alpha (1 - e^{-k_i t}) \quad (2)$$

where [C\*] is the concentration of active complexes, [I]<sub>α</sub> is the ultimate potential concentration of active species in the absence of any termination reactions, *k<sub>i</sub>* is an empirical initiation constant, and [M] is the molar concentration of monomer.<sup>1</sup> [I]<sub>α</sub> and *k<sub>i</sub>* may be estimated from the number of polymer chains present as a function of time, assuming there is no active reaction leading to the destruction of catalytic centres.

Substitution of (2) in (1) leads to the following integrated rate expression for [M]<sub>*t*</sub>:

$$[M]_t = [M]_0 e^{-k_p \alpha} \quad (3)$$

$$\text{where } \alpha = [I]_\alpha \left( t + \frac{1}{k_i} (e^{-k_i t} - 1) \right) \quad (4)$$

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The number-average molecular weight of living polymer,  $M_n$ , at time  $t$  can be estimated by dividing the concentration of monomer reacted by the average concentration of active chain ends,  $\langle [C^*] \rangle$ ,

$$M_n/M = \frac{[M]_0 - [M]_t}{\langle [C^*] \rangle} \quad (5)$$

where  $M$  is the molecular weight of the monomer. The variables  $k_p$ ,  $[I]_\alpha$  and  $k_i$  can thus be determined by fitting to eqs. (2)–(5) for  $M_n$  as a function of time. We have previously reported that the CoCl<sub>2</sub>-MAO catalytic system leads to living polymerization of 1,3-butadiene at low temperatures, and determined the number of active centers and the rate constants of initiation and propagation.<sup>1</sup> Since  $[C^*]$  is a function of time in slowly-initiated polymerizations, it is not appropriate to use the  $[C^*]$  given by eq. (2) in an analytical expression for estimating  $M_n$ .

$\langle [C^*] \rangle$  may be expressed in terms of  $[I]_\alpha$  and  $k_i$  by taking the integral of  $[C^*]$  from  $t=0$  to  $\tau$  and dividing by the integral of time from  $t=0$  to  $\tau$ .

$$\langle [C^*] \rangle = \frac{\int_0^\tau [I]_\alpha (1 - e^{-k_i t}) dt}{\tau} \quad (6)$$

$$\langle [C^*] \rangle = \frac{[I]_\alpha - [I]_\alpha \int_0^\tau e^{-k_i t} dt}{\tau} \quad (6a)$$

$$\langle [C^*] \rangle \tau = [I]_\alpha - [I]_\alpha \left[ \frac{1}{-k_i} e^{-k_i t} + A \right] \quad (6b)$$

$$\langle [C^*] \rangle \tau = [I]_\alpha \left( 1 + \frac{1}{k_i} (1 - e^{-k_i \tau}) \right) \quad (6c)$$

$$\ln(\langle [C^*] \rangle \tau) \approx \ln([I]_\alpha) - \ln\left(\frac{k_i}{k_i + 1}\right) - e^{-k_i \tau} \quad (6d)$$

If termination of growing chains by chain transfer is dominant, then the expected molecular weight will be given by

$$M_n = \frac{k_p M}{k_t} \quad (7)$$

where  $k_t$  is the rate coefficient for chain transfer and  $M$  is the molecular weight of the monomer. In an arbitrary system the experimental  $M_n$  value will be a combination of contributions from the processes described by eqs. (5) and (7).

## Experimental

Anhydrous CoX<sub>2</sub> (X=Cl, Br, I, Wako Pure Chemical Industries Ltd.), 4,4-methylenebis(2,6-di-*tert*-butylphenol) (Tokyo Kasei Kogyo Co. Ltd.), and methylaluminoxane (Tosoh Finechem) were used as received. 1,3-Butadiene supplied from JSR Co. Ltd. was purified before use by passing through columns of sodium hydroxide, potassium pentaoxide

and 4 Å molecular sieves in succession.

The required volume of toluene was saturated with an atmospheric pressure of 1,3-butadiene for preparing a stock solution, which was used for a series of experiments (Table I). After purging of a 100 mL glass reactor with nitrogen, 30 mL of monomer stock solution was introduced. Toluene solution of MAO was added, and polymerization was initiated by adding the toluene slurry of CoX<sub>2</sub> to the reactor. After a certain polymerization time, the reaction was terminated by adding a small portion of acidic solution of methanol containing about 0.001% of 4,4-methylene-bis-(2,6-di-*tert*-butylphenol) as an antioxidant. The reaction product was then precipitated in a large excess of methanol. The polymer was washed with several aliquots of pure methanol and dried in vacuum at 60 °C for 6 h.

The molecular weight distributions, number-average and weight-average molecular weights ( $M_n$  and  $M_w$ ) of polymer were determined at 40 °C by gel permeation chromatography (GPC), using a JASCO PU-980 instrument with refractive index detector using chloroform as an eluent and calibrated with standard polybutadiene samples (Japan Rubber Co.). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 25 °C on a JEOL EX-300 spectrometer in deuterated chloroform.

## Results and Discussion

GPC traces of polybutadiene prepared at 0 °C for various reaction times are shown in Figure 1, and the  $M_n$  and  $M_w$  values obtained for all polymers are summarised in Table I. NMR spectroscopy confirmed that the product was overwhelmingly 1,4-*cis*-polybutadiene.

Rather than carry out a global fit to find  $k_i$ ,  $[I]_\alpha$ , and  $k_p$  for each temperature, for which only a small number of data points were available,  $k_i$  and  $[I]_\alpha$  were estimated from the slope ( $= -k_i$ ) and the intercept ( $e^{\text{Intercept}} = \ln(k_i/k_i + 1) - \ln([I]_\alpha)$ ) of a plot of  $\ln(-\ln\langle [C^*] \rangle \tau^2)$  vs.  $\tau$  (eq. (6)). All of these plots were noticeably curved (Figure 2), making it difficult to obtain meaningful  $[I]_\alpha$  values from the intercepts. This is not surprising, as each reaction was carried out independently and variations in  $[I]_\alpha$  are expected due to catalyst aging. Thus there is no reason to expect  $[I]_\alpha$  values to remain invariant for all reactions carried out at a given temperature. An additional reason for the curvature arises from apparent inhibition periods of several minutes observed for most reactions. This implies that the effective reaction times will be less, by an unrecorded and variable amount, than the times given in Table I. Attempts were made to combine CoCl<sub>2</sub> and MAO and age the catalyst before addition of butadiene in order to minimize this inhibition period, but a rapid degradation of the catalyst with aging was observed. Table II presents yields obtained for CoCl<sub>2</sub>-MAO catalyzed polymerizations carried out at 18 °C for 30 min with various periods of catalyst aging.

Individual  $[I]_\alpha$  values were therefore calculated from  $[C^*]$

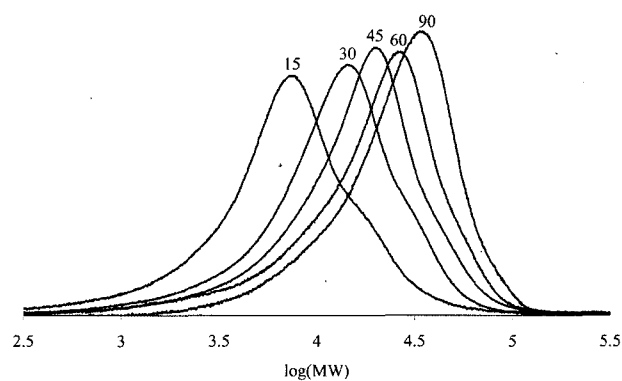
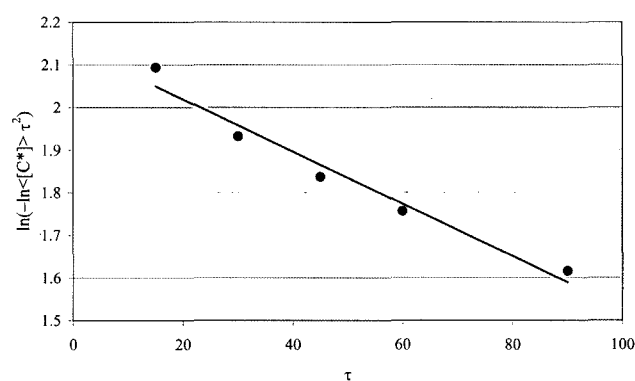
**Table I. 1,3-Butadiene Polymerization with CoCl<sub>2</sub>-MAO<sup>a</sup> Reproduced with Permission from Ref. [1] and [3]**

| Run                     | <i>t</i> (min) | [M] (mol dm <sup>-3</sup> ) | T (°C)          | Yield (%) | <i>M<sub>n</sub></i> (×10 <sup>-5</sup> ) | <i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> | <i>N<sup>b</sup></i> (μmol) |
|-------------------------|----------------|-----------------------------|-----------------|-----------|---|---|-----------------------------|
| <b>CoCl<sub>2</sub></b> |                |                             |                 |           |   |   |                             |
| 1                       | 15             | 3.00                        | 0               | 0.9       | 0.77                                      | 1.5   | 0.65                        |
| 2                       | 30             |                             |                 | 2.8       | 1.38                                      | 1.4   | 1.09                        |
| 3                       | 45             |                             |                 | 4.9       | 1.92                                      | 1.4   | 1.35                        |
| 4                       | 60             |                             |                 | 8.0       | 2.54                                      | 1.3   | 1.65                        |
| 5                       | 90             |                             |                 | 16.1      | 3.61                                      | 1.3   | 2.35                        |
| 6                       | 15             | 2.25                        | 10              | 1.8       | 0.90                                      | 1.5   | 0.80                        |
| 7                       | 30             |                             |                 | 6.3       | 1.50                                      | 1.4   | 1.66                        |
| 8                       | 45             |                             |                 | 15.2      | 2.21                                      | 1.3   | 2.65                        |
| 9                       | 60             |                             |                 | 22.8      | 2.70                                      | 1.3   | 3.30                        |
| 10                      | 15             | 1.73                        | 18              | 5.9       | 0.84                                      | 1.5   | 2.14                        |
| 11                      | 30             |                             |                 | 14.8      | 1.46                                      | 1.4   | 3.08                        |
| 12                      | 45             |                             |                 | 21.1      | 1.92                                      | 1.4   | 3.33                        |
| 13                      | 60             |                             |                 | 28.6      | 2.54                                      | 1.3   | 3.43                        |
| 14                      | 10             | 1.9                         | 40 <sup>c</sup> | 18        | 2.7                                       | 1.3   | 2.05                        |
| 15                      | 20             |                             |                 | 38        | 3.8                                       | 1.5   | 3.08                        |
| 16                      | 30             |                             |                 | 57        | 4.1                                       | 1.5   | 4.28                        |
| 17                      | 40             |                             |                 | 76        | 4.5                                       | 1.6   | 4.79                        |
| <b>CoBr<sub>2</sub></b> |                |                             |                 |           |   |   |                             |
| 18                      | 15             | 2.50                        | 0               | 0.3       | 0.51                                      | 1.5   | 0.40                        |
| 19                      | 30             |                             |                 | 1.1       | 0.92                                      | 1.5   | 0.60                        |
| 20                      | 45             |                             |                 | 2.7       | 1.28                                      | 1.4   | 1.00                        |
| 21                      | 60             |                             |                 | 5.3       | 1.72                                      | 1.4   | 1.33                        |
| 22                      | 90             |                             |                 | 13        | 2.67                                      | 1.3   | 2.13                        |
| 23                      | 15             | 2.20                        | 18              | 3.3       | 1.1                                       | 1.5   | 1.20                        |
| 24                      | 30             |                             |                 | 12        | 1.9                                       | 1.4   | 2.60                        |
| 25                      | 45             |                             |                 | 20        | 2.6                                       | 1.4   | 3.00                        |
| 26                      | 60             |                             |                 | 29        | 3.3                                       | 1.3   | 3.40                        |
| <b>CoI<sub>2</sub></b>  |                |                             |                 |           |   |   |                             |
| 27                      | 30             |                             |                 | 0.18      | 1.3                                       | 1.5   | 0.04                        |
| 28                      | 45             |                             |                 | 0.3       | 1.8                                       | 1.4   | 0.05                        |
| 29                      | 60             | 1.7                         | 18              | 0.44      | 2.3                                       | 1.4   | 0.06                        |
| 30                      | 90             |                             |                 | 0.77      | 3.3                                       | 1.3   | 0.07                        |

<sup>a</sup>Polymerization conditions: 100 mL glass reactor; Al/Co=100(mol/mol); CoX<sub>2</sub>, 6 μmol; toluene+monomer=30 mL.

<sup>b</sup>Number of polymer chains calculated from polymer yield and *M<sub>n</sub>*.

<sup>c</sup>*M<sub>n</sub>* values obtained at 40°C increase linearly with conversion, not with time, and the polydispersity broadens as the reaction progresses because of the large variation in monomer concentration over the course of the reaction.

**Figure 1.** GPC traces of polybutadiene prepared with CoCl<sub>2</sub>-MAO at 0°C for reaction times between 15 and 90 min.**Figure 2.** Determination of *k<sub>i</sub>* for polybutadiene prepared with CoCl<sub>2</sub>-MAO at 0°C for reaction times between 15 and 90 min.**Table II. Result of 1,3-Butadiene Polymerization with Aged CoCl<sub>2</sub>-MAO Catalytic System at 18°C, 30 min Polymerization Time<sup>a</sup>**

| Run | Aging <i>t</i> (min) | [M] (mol dm <sup>-3</sup> ) | Yield (%) |
|-----|----------------------|-----------------------------|-----------|
| 11  | 0                    | 1.73                        | 14.8      |
| 31  | 15                   | 2.85                        | 19.7      |
| 32  | 30                   | 2.85                        | 12.6      |
| 33  | 45                   | 2.85                        | 5.0       |
| 34  | 60                   | 2.85                        | 2.2       |

<sup>a</sup>Polymerization conditions: 100 mL glass reactor, CoCl<sub>2</sub>, 6 μmol; Al/Co=100 (mol/mol) toluene + monomer = 30 mL.

for each data point (2) and used to fit the *M<sub>n</sub>* data to obtain *k<sub>p</sub>* values for each *T* investigated (3). The *k<sub>i</sub>*, [*I*]<sub>∞</sub> and *k<sub>p</sub>* values estimated are tabulated below (Table III), for plots using all data points and for plots using only *t* ≥ 30 min in an attempt to minimize the effect of the inhibition period. There is no consistent trend in the *k<sub>i</sub>* data, but it is possible to estimate Arrhenius parameters for *k<sub>p</sub>*.

These experiments suggest an activation energy *E<sub>p</sub>* of 38

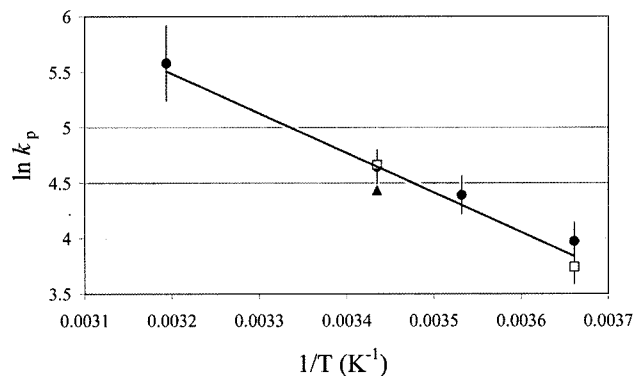
**Table III. Kinetic Parameters from  $M_n$  Analysis**

| $T$<br>(°C)             | $k_p$<br>(dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup> ) | $k_i$<br>(min <sup>-1</sup> × 10 <sup>-3</sup> ) | $[I]_0$<br>(mol dm <sup>-3</sup> × 10 <sup>4</sup> ) | Data<br>Points |
|-------------------------|---|--|--|----------------|
| <b>CoCl<sub>2</sub></b> |   |  |  |                |
| 0                       | 54.2 ± 8.5  | 6.1  | 1.65 – 2.27  | 5              |
|                         | 53.2 ± 2.9  | 5.5  | 1.81 – 2.20  | 4              |
| 10                      | 84 ± 13   | 9.9  | 1.74 – 2.33  | 4              |
|                         | 80.8 ± 3.0  | 8.0  | 2.39 – 2.75  | 3              |
| 18                      | 107 ± 15  | 6.8  | 3.14 – 6.78  | 4              |
|                         | 107 ± 6   | 4.9  | 4.15 – 6.96  | 3              |
| 40                      | 440 ± 130   | 12.7   | 4.34 – 5.72  | 4              |
|                         | 265 ± 32  | 9.1  | 4.11 – 4.29  | 3              |
| <b>CoBr<sub>2</sub></b> |   |  |  |                |
| 18                      | 109 ± 14  | 8.6  | 2.59 – 3.30  | 5              |
|                         | 106 ± 4   | 6.1  | 3.39 – 4.47  | 4              |
| 0                       | 43 ± 6  | 7.4  | 0.75 – 1.35  | 4              |
|                         | 42 ± 2  | 6.5  | 0.91 – 1.49  | 3              |
| <b>CoI<sub>2</sub></b>  |   |  |  |                |
| 18                      | 84 ± 9  | 2.8  | 0.10 – 0.16  | 4              |

kJmol<sup>-1</sup> for the propagation reaction based on the CoCl<sub>2</sub> data alone. The experiments with CoBr<sub>2</sub> and CoI<sub>2</sub> were not carried out over a wide enough range of temperatures in order to independently determine Arrhenius parameters for each of these. However, comparison of the  $k_p$  values estimated at 18°C for the three cobalt halides suggests that there is little influence of the halide on the propagation step of this polymerization, and that the variations in rate found with different cobalt halides may be attributed to the effect of the halide on the initial formation of the active site. This is supported by the observation that the microtacticity of the polybutadiene produced was independent of variations in the halide (97.3–97.5% *cis*-1,4 at 18°C; 98.2% *cis*-1,4 at 0°C).<sup>1,3</sup> The microtacticity of the polybutadiene prepared at 40°C was estimated to be 95.9% *cis*-1,4.

With the relatively limited data set available, it is not possible to rule out that the difference in apparent  $k_p$  values between the three halides (up to 20% at some temperatures) may be significant, but the data can be fit adequately by a model in which  $k_p$  is independent of the halide. The Arrhenius plot for  $k_p$  using data obtained for all three halides for reactions carried out for 30 min and longer is given below (Figure 3). The activation energy,  $E_p$ , lies between 27 and 30 kJmol<sup>-1</sup> and the frequency factor  $A_p$  lies between  $6 \times 10^6$  and  $2 \times 10^7$  dm<sup>3</sup>mol<sup>-1</sup>min<sup>-1</sup>.

This activation energy is about half of the calculated activation energy for insertion of alkenes into a Zr-C bond estimated from experiment by Karl *et al.* (72–84 kJmol<sup>-1</sup>)<sup>19</sup> and



**Figure 3.** Arrhenius plot for  $k_p$  for polybutadiene prepared with CoX<sub>2</sub>-MAO based on results of reactions carried out for 30 min or longer. X = Cl (●), Br (□), I (▲).

on the high side of the range of activation energies for insertion of ethylene into a Ti-C  $\pi$ -bond calculated by Seth and Ziegler (13–39 kJmol<sup>-1</sup>).<sup>20</sup>

For very similar catalytic systems investigated by Cass *et al.*, using *t*-butyl chloride as a halogen source, cobalt(II) octanoate and modified MAO and postulating replacement of methyl on aluminium by chloride to give the active site, X:Al ratios similar to those employed in this work gave very low rates of polymerization and a much reduced degree of 1,4-*cis*-specificity. Rates comparable to those found in this work could only be obtained with X:Al ratios approaching 1:1.<sup>7</sup> This implies that despite the similarities in these systems, the nature of the active site is different in this work.

No polymerization could be obtained using CoF<sub>2</sub> as the cobalt source,<sup>3</sup> and as the bond strength of Co-X single bonds is likely to go in the order F > O > Cl > Br > I, it is likely that the desiderata for formation of the active site in this system are:

- (1) Displacement of the ligand from cobalt by aluminium, followed by
- (2) Alkylation of Co by complexation with methyl from the methylaluminoxane, which will not be possible if this methyl has been
- (3) displaced by a soft base such as I, Br, or Cl.

The rate of reaction is first-order dependent on the monomer concentration, so it is unlikely that more than one monomer molecule is involved in the active site. In the similar system investigated by Cass *et al.*, it was suggested that the stoichiometry of cobalt and aluminium at the active site was CoAl<sub>2</sub>, and that is highly plausible in this case.<sup>21</sup>

## Conclusions

The rate coefficients for initiation and propagation in 1,3-butadiene polymerization using CoX<sub>2</sub> activated by MAO were investigated over a range of temperatures, and the

characteristic features of living polymerization observed until high conversions. The rate coefficients for initiation and propagation,  $k_i$  and  $k_p$ , were determined using a kinetic model for slowly-initiated Ziegler-Natta polymerization. Values of the activation energy and frequency factor for propagation could be calculated, with data for three cobalt halides ( $X = \text{Cl}, \text{Br}, \text{I}$ ) fitting the one Arrhenius equation and giving  $E_p = 27\text{--}30 \text{ kJmol}^{-1}$ ,  $A_p \sim 2 \times 10^5 \text{ dm}^3\text{mol}^{-1}\text{s}^{-1}$ . The degree of *cis*-1,4-specificity was also consistent and high (>97%) for all three halides. No consistent trend could be determined in initiation rate constants, while the ultimate concentration of active sites declined in the order  $\text{Cl} > \text{Br} > \text{I}$ . These results suggest that the primary effect of varying the halide in  $\text{CoX}_2$  is on the initiation step of the  $\text{CoX}_2$ -MAO catalyzed polymerization and that it plays little or no role in the active site for propagation.

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