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# A Model for the Termination Stage of Some Radical Copolymerizations

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# A Model for the Termination Stage of Some Radical Copolymerizations

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## SUMMARY

The kinetic scheme proposed by us on the basis of the so-called "penultimate effect" in the termination stage of several copolymerizations is compared to the current opinions in the literature on the termination mechanism for radical polymerizations and copolymerizations. Our treatment agrees both with the chemical and physical models for termination, as it is comprehensive of all physicochemical parameters which can condition the termination-stage kinetics.

## INTRODUCTION

The termination-stage kinetics of radical copolymerizations has been, until now, under question. The first idea, suggested by Melville et al. [1] and Walling [2], that there exists a cross-termination rate constant preferred to the K values for like chains (with the introduction of the so-called $\phi$ factor) was recently rejected by several authors [3-8], who pointed out the importance of diffusion on the termination reaction in most radical polymerizations and copolymerizations. Diffusion control is usually related to the segmental rearrangement of active chain ends up to a distance of about 4 Å (required for the mutual radical termination to take place) [9-11].

Nevertheless, at present it is questionable and unclear what is the length of the chain-end segment which has to be considered. We hope to suggest a possible way to determine this length to a first approximation.

## DISCUSSION

The problem here is to correlate the mobility of the chain end bearing the reactive group with the flexibility of the whole chain. This flexibility will in turn depend on the chemical composition and conformational characteristics of the units composing the polymer chain.

Chain flexibility has a kinetic character and is a measure of the capability of a chain to change its shape (or conformations) in a given time and under an external influence; it must, therefore, depend on the height of the barriers ($E_1, E_2, \ldots$) between two successive minima in the rotational potential profile. It seems, however, that bond rotations near the end of a chain are more probable than rotations in the middle position of the chain; this follows from the varying degrees of interdependence among bond rotations, the cooperation being of increasing importance on going from one end to the central portion of a chain. From this it follows that rotations of the last four or five bonds are essentially uncorrelated and depend on the values $E_i$ of the various energy barriers, whereas bond rotations in the internal part of a chain will depend not only on $E_i$ but also on the probability of simultaneous rotation of several bonds in the appropriate conformational succession.

A quantitative evaluation of this effect [12] has revealed that, assuming typical values for the rotational energy barrier, bond flexibility near the ends of a molecule is about $10^2$ times greater than that on the rest of the chain.

This is suggesting that when one is dealing with the kinetics of a reaction where the reactive site is on one end of a chain, the diffusion rate of this end will depend on the conformational characteristics of the very last portion of the chain and not so much on the composition of the main portion of the macromolecule.

Therefore we may assume, in first approximation, that the length of the rearranging segment is given by the last four carbon atoms (penultimate effect). The termination stage may be described by 10 equations:

Termination stage:

| Reactions | Rate constants | |
|---|---|---|
| $-AA\cdot + -AA\cdot \rightarrow P$ | $K_t^{aaaa}$ | (1) |
| $-AA\cdot + -BA\cdot \rightarrow P$ | $K_t^{aaab}$ | (2) |
| $-AA\cdot + -AB\cdot \rightarrow P$ | $K_t^{aaba}$ | (3) |
| $-AA\cdot + -BB\cdot \rightarrow P$ | $K_t^{aabb}$ | (4) |
| $-BA\cdot + -BA\cdot \rightarrow P$ | $K_t^{baab}$ | (5) |
| $-BA\cdot + -AB\cdot \rightarrow P$ | $K_t^{baba}$ | (6) |

| Reactions | Rate constants | |
|---|---|---|
| $-BA\cdot + -BB\cdot \rightarrow P$ | $K_t^{babb}$ | (7) |
| $-AB\cdot + -AB\cdot \rightarrow P$ | $K_t^{abba}$ | (8) |
| $-AB\cdot + -BB\cdot \rightarrow P$ | $K_t^{abbb}$ | (9) |
| $-BB\cdot + -BB\cdot \rightarrow P$ | $K_t^{bbbb}$ | (10) |

Let us assume, now, that the cross-termination constants are equal to the geometric mean of the two self-terminations:

$$K_t^{aaab} = 2(K_t^{aaaa}\cdot K_t^{baab})^{0.5} \qquad K_t^{aaba} = 2(K_t^{aaaa}\cdot K_t^{abba})^{0.5}$$

$$K_t^{aabb} = 2(K_t^{aaaa}\cdot K_t^{bbbb})^{0.5} \qquad K_t^{baba} = 2(K_t^{baab}\cdot K_t^{abba})^{0.5}$$

$$K_t^{babb} = 2(K_t^{baab}\cdot K_t^{bbbb})^{0.5} \qquad K_t^{abbb} = 2(K_t^{abba}\cdot K_t^{bbbb})^{0.5}$$

from which, simply applying the usual steady-state conditions, it is possible to obtain the following expression for the rate of copolymerization:

$$R_p = \frac{[C]R_i^{0.5}}{x+1}\left[\frac{r_1^2x^3 + 3r_1x^2 + 2x + r_1r_2x + r_2}{r_1^2x^2\delta_A + r_1x\delta_{BA} + \dfrac{r_2x(r_1x+1)}{r_2+x}\delta_{AB} + \dfrac{r_2^2(r_1x+1)}{r_2+x}\delta_B}\right]$$

where

$r_1 = K^{aa}/K^{ab}$ $\qquad r_2 = K^{bb}/K^{ba}$

$x = [A]/[B]$ $\qquad [C] = [A] + [B]$

$\delta_A = (K_t^{aaaa})^{0.5}/K^{aa}$ $\qquad \delta_B = (K_t^{bbbb})^{0.5}/K^{bb}$

$\delta_{BA} = (K_t^{baab})^{0.5}/K^{aa}$ $\qquad \delta_{AB} = (K_t^{abba})^{0.5}/K^{bb}$

As [C], x, and $R_p$ are known, r's are determined by the copolymer composition values, and $\delta_A$ and $\delta_B$ may be derived from the polymerization rate data of the individual monomers; the only terms unknown, if the rate of initiation $R_i$ is known, are $\delta_{BA}$ and $\delta_{AB}$.

For the experimental confirmation of Eq. (1) a check on the constancy of $\delta_{BA}$ and $\delta_{AB}$ can be done, in all the range of feed compositions, by solving all the possible combinations of two-by-two equations of the system.

Some experimental data are available for verifying Eq. (1). These data are obtained from systems that show $\phi$ values different from unity and generally unsteady with monomer feed compositions, as for these pairs a terminal effect in the propagation process and a penultimate effect in the termination reactions were postulated [13, 14]. Consequently, we have applied Eq. (1) for the systems for which all the data necessary to the calculation were available.

Let us remember that Eq. (1) can be applied only when the trend of the initiation rate as a function of the monomer feed composition is known. In this case, the values of $\delta_A$ and $\delta_B$ can be easily calculated, using the well-known expression

$$\delta_M = R_i^{0.5}[M]/R_p$$

Thus, from Eq. (1), $\delta_{BA}$ and $\delta_{AB}$ are obtained.

In other cases, calculation is possible only if we assume that the initiation rate remains constant when varying the feed composition. The following ratios can be so derived:

$$R_i^{0.5}/\delta_A = R_{p(A)}/[A] \quad \text{and} \quad \delta_B/\delta_A = [B]R_{p(A)}/[A]R_{p(B)}$$

from which only the values of the ratios $\delta_{BA}/\delta_A$ and $\delta_{AB}/\delta_B$ can be calculated.

Let us examine the results obtained for the available systems.

### Styrene-Methyl Methacrylate

We tested the correctness of Eq. (1) using the data of Melville and Valentine [15], at 30°C, and those of Walling [2] and Bevington et al. [16], at 60°C.

Table 1 and Fig. 1 show the results referred to in the first paper [15]. The error limits in the evaluation of $r_1$ and $r_2$ and, especially, of initiation rates (obtained from osmotic measurements of molecular weights) easily account for the slight dispersion of experimental data from the calculated curve.

Table 2 and Fig. 2 show the data from the second paper [2]. It can be seen that there is a remarkable concordance between the experimental points and the calculated curve.

The third paper [16], whose data are quoted in Table 3 and Fig. 3, reports work carried out under the same experimental conditions as the previous one. Also, in this case there are very slight deviations.

The results quoted in Tables 2 and 3, besides demonstrating the validity of our equation, confirm that such a system presents an initiation rate practically constant for the whole range of composition, as reported in the literature [2, 17, 18].

**Table 1.** Copolymerization of Styrene and Methyl Methacrylate at 30°C, in Bulk[a] [7]

| Molar % of methyl methacrylate | x | [C], moles/liter | $R_i \times 10^8$, moles/liter-sec | $R_p \times 10^5$ moles/liter-sec | |
|---|---|---|---|---|---|
| | | | | Exptl. | Calc. |
| 0 | ∞ | 8.618 | 4.75 | 3.02 | 3.02 |
| 11.2 | 7.929 | 8.695 | 3.98 | 2.24 | 2.24 |
| 37.8 | 1.646 | 8.877 | 3.58 | 2.42 | 2.15 |
| 66.2 | 0.511 | 9.071 | 3.31 | 2.60 | 2.59 |
| 86.9 | 0.151 | 9.213 | 5.13 | 4.67 | 4.65 |
| 96.9 | 0.032 | 9.282 | 4.97 | 7.11 | 7.07 |
| 100 | 0 | 9.303 | 11.09 | | |

[a] Initiator: benzoyl peroxide (photochemically decomposed). $r_1 = 0.485$, $r_2 = 0.422$, $\delta_A = 62.5$, $\delta_B = 22.5$, $\phi^7 = 14$, $\delta_{BA} = 252.53$, $\delta_{AB} = 37.13$.

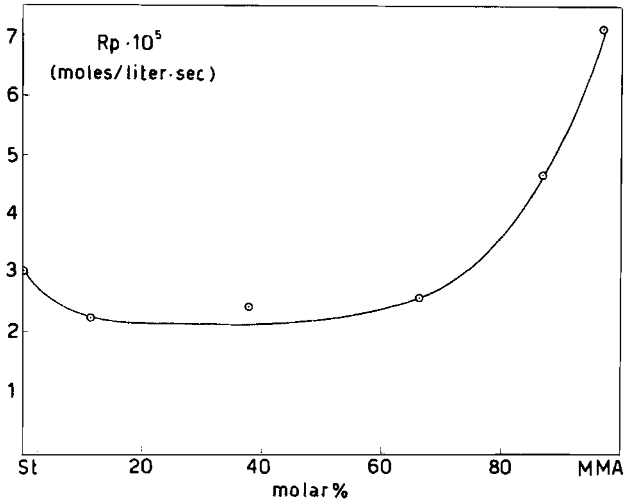

**Fig. 1.** Comparison of experimental values and calculated curve for the copolymerization of St-MMA at 30°C [7].

**Table 2.** Copolymerization of Styrene and Methyl Methacrylate at 60°C, in Bulk[a] [2]

| Molar % of methyl methacrylate | x | [C], moles/liter | $R_p \times 10^5$ moles/liter-sec Exptl. | Calc. |
|---|---|---|---|---|
| 0 | ∞ | 8.366 | 5.92-4.64-5.45 | 5.34 |
| 24.20 | 3.132 | 8.507 | 4.61-4.43 | 4.39 |
| 42.10 | 1.375 | 8.612 | 4.82-4.75 | 4.76 |
| 62.20 | 0.608 | 8.730 | 5.67-5.38 | 5.72 |
| 80.94 | 0.235 | 8.840 | 7.78-7.95 | 7.78 |
| 90.87 | 0.100 | 8.898 | 11.60-10.20 | 10.57 |
| 100 | 0 | 8.951 | 19.80-19.40 | 19.60 |

[a] Initiator: AIBN (1 g/liter). $r_1 = 0.52$, $r_2 = 0.46$, $\delta_B/\delta_A = 0.293$, $R_i^{0.5}/\delta_A = 6.379 \times 10^{-6}$ sec$^{-1}$, $\phi^2 = 13$, $\delta_{BA}/\delta_A = 3.90$, $\delta_{AB}/\delta_B = 0.78$.

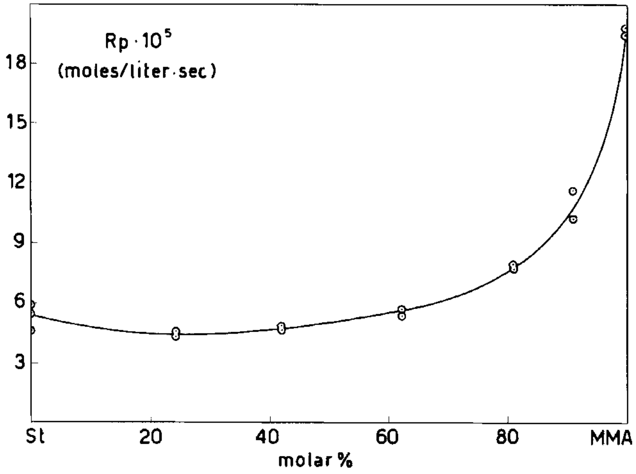

**Fig. 2.** Comparison of experimental values and calculated curve for the copolymerization of St-MMA at 60°C [2].

**Table 3.** Copolymerization of Styrene and Methyl Methacrylate at 60°C, in Bulk[a] [13]

| Molar % of methyl methacrylate | x | [C], moles/liter | $R_p \times 10^5$ moles/liter-sec | |
|---|---|---|---|---|
| | | | Exptl. | Calc. |
| 0 | ∞ | 8.366 | 2.990 | 2.99 |
| 30.1 | 2.322 | 8.542 | 2.719 | 2.68 |
| 52.2 | 0.916 | 8.671 | 3.422 | 3.06 |
| 76.6 | 0.306 | 8.814 | 3.957 | 4.14 |
| 88.9 | 0.125 | 8.886 | 5.616 | 5.78 |
| 95.2 | 0.050 | 8.923 | 8.218 | 8.16 |
| 100 | 0 | 8.951 | 13.800 | 13.80 |

[a] Initiator: $^{14}$C-AIBN (0.3 g/liter). $r_1 = 0.52$, $r_2 = 0.46$, $\delta_B/\delta_A = 0.232$, $R_i^{0.5}/\delta_A = 3.574 \times 10^{-6}$ sec$^{-1}$, $\phi^{13} = 10\text{-}31$, $\delta_{BA}/\delta_A = 3.26$, $\delta_{AB}/\delta_B = 2.80$.

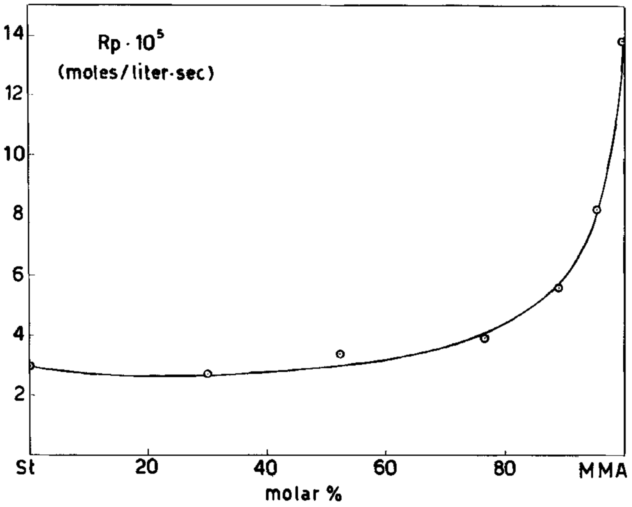

Fig. 3. Comparison of experimental values and calculated curve for the copolymerization of St-MMA at 60°C [13].

### Styrene-Butyl Acrylate

We have taken into account the works of Arlman and Melville [19] at 25°C, and that of Bradbury and Melville [20] at 60°C. Table 4 and Fig. 4 show the results obtained from applying Eq. (1) to the experimental data of the former one.

The rate of initiation was determined in [19] on the basis of the yields and molecular weights (calculated by osmometry), and assuming a mutual termination by disproportionation. The slight dispersion of values is mainly due to uncertainty in the determination of initiation rates, as can be seen from Table 4. A more precise calculation of the values corresponding to the several mixtures would lead undoubtedly to a sharp reduction of the dispersion range.

Table 5 and Fig. 5 report the data of Bradbury and Melville [20]. They calculated the initiation rate from measurements of radioactivity of the initiator and copolymer, applying the technique used by Bevington et al. [21] for the evaluation of the average kinetic chain length. The maximum error in this case is reduced to about 8%, thus allowing a remarkable narrowing of the uncertainty range. Figure 5 shows fairly good agreement with the experimental data.

## CONCLUSIONS

One of the two pairs studied by us (styrene-methyl methacrylate) can be considered as a system for which both monomers present a diffusion-controlled termination [22-24]. For the second one (styrene-butyl acrylate) the BA comonomer undoubtedly presents a chemically controlled termination reaction [24]. Notwithstanding, our kinetic treatment was applied successfully to both systems.

It means that, on the basis of the above arguments, the so-called "penultimate effect" in termination assumes a wider meaning than that attributed by Barb [13] and Arlman [14]. If it is present only in the termination of some copolymerizations, it is due in part to a closer approach of the polar groups in respect to the propagation, but above all to the enhanced mobility of the last four-atom segment in comparison with the main chain motions [12]. Therefore, subdividing our kinetic scheme for termination on the basis of the nature of the terminal and penultimate chain units, we have taken cumulatively into account all the physical and "chemical" factors (polarity, flexibility, steric effects, etc.) which can influence the reactivity of a macroradical during termination. We therefore believe that our treatment, verified up to now for only two systems with the same comonomer (styrene), can perhaps assume general validity. Bianchi's recent results [12] seem to confirm our feeling.

**Table 4.** Copolymerization of Styrene and Butyl Acrylate at 25°C, in Bulk[a] [9]

| Molar % of butyl acrylate | x | [C], moles/liter | $R_i \times 10^{10}$, moles/liter-sec | $R_p \times 10^5$, moles/liter-sec |  |
|---|---|---|---|---|---|
|  |  |  |  | Exptl. | Calc. |
| 0 | ∞ | 8.660 | 15.5 | 0.48 | 0.48 |
| 8.28 | 11.077 | 8.521 | 7.8-6.6 | 0.31 | 0.32 |
| 18.64 | 4.364 | 8.346 | 5.5-4.3 | 0.24 | 0.26 |
| 26.74 | 2.739 | 8.210 | 7.0-6.2 | 0.31 | 0.31 |
| 40.90 | 1.445 | 7.971 | 9.0-7.6 | 0.35 | 0.37 |
| 44.83 | 1.231 | 7.905 | 5.2-4.6 | 0.32 | 0.29 |
| 76.47 | 0.308 | 7.372 | 4.7-(3.2) | 0.41 | 0.36 |
| 87.97 | 0.137 | 7.178 | 7.8-6.7 | 0.59 | 0.55 |
| 100 | 0 | 6.975 | 580 | 26.90 | 26.90 |

[a] Initiator: benzoyl peroxide (photochemically decomposed). $r_1 = 0.48$, $r_2 = 0.15$, $\delta_A = 71$, $\delta_B = 6.25$, $\phi^9 = 11\text{-}151$, $\delta_{BA} = 198.1$, $\delta_{AB} \approx \delta_B$.

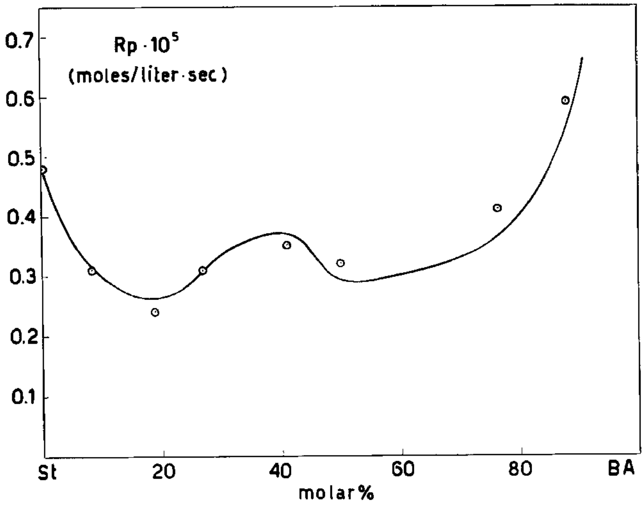

**Fig. 4.** Comparison of experimental values and calculated curve for the copolymerization of St-BA at 25°C [9].

**Table 5.** Copolymerization of Styrene and Butyl Acrylate at 60°, in Bulk[a] [12]

| Molar % of butyl acrylate | x | [C], moles/liter | $R_i \times 10^8$, moles/liter-sec | $R_p \times 10^5$, moles/liter-sec | |
|---|---|---|---|---|---|
| | | | | Exptl. | Calc. |
| 0 | | 8.366 | 9.20 | 5.85 | 5.85 |
| 30 | 2.333 | 7.869 | 8.44 | 6.86 | 6.93 |
| 50 | 1 | 7.538 | 7.14 | 7.14 | 7.09 |
| 70 | 0.429 | 7.207 | 6.74 | 7.80 | 7.73 |
| 90 | 0.111 | 6.876 | 7[b] | 10.70 | 10.77 |
| 100 | 0 | 6.710 | 6.72 | 230 | 230 |

[a] Initiator: $C^{14}$-AIBN (1 g/liter). $r_1 = 0.76$, $r_2 = 0.15$, $\delta_A = 43.5$, $\delta_B = 0.76$, $\phi^{12} = 26\text{-}113$, $\delta_{BA} = 58.28$, $\delta_{AB} = 14.33$.

[b] Extrapolated value.

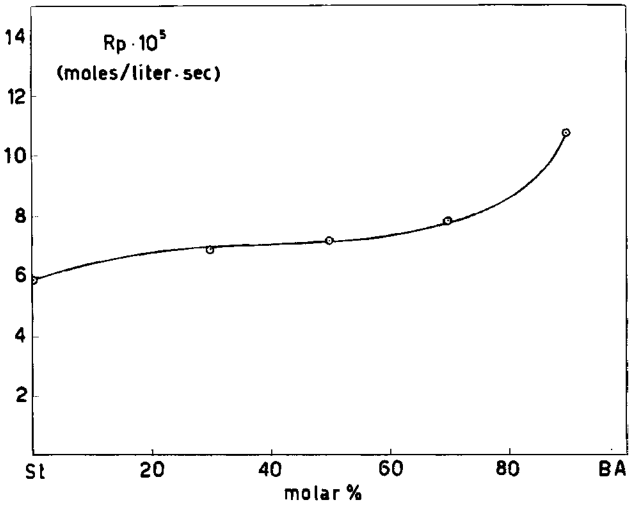

**Fig. 5.** Comparison of experimental values and calculated curve for the copolymerization of St-BA at 60°C [12].

Now we should like to clarify another important point in our kinetic treatment, in relation to the calculation of the mean of the termination rate constants used. In our scheme we assumed that the cross-termination rate constants were the 0.5 geometric mean of the self-terminations, whereas this assumption would appear to be valid [3] only for chemical reactions. For diffusion-controlled radical terminations it was suggested [3] that an arithmetic mean be used. Recently, however, it has been suggested [25, 26] that a general geometric mean be used for diffusion-controlled reactions:

$$K_t^{ab} = (K_t^{aa})^{x_1} (K_t^{bb})^{x_2} \qquad \text{with } x_1 + x_2 = 1$$

where $x_1$ and $x_2$ are the mole fractions of chains ending in A· and B·.

Indeed, there is probably only a very small difference between the arithmetic and the 0.5 geometric mean over a wide range of feed composition. The easier solution of the equations based on the geometric mean suggests that we use this assumption.

Finally, it can be observed that the ratios $\delta_{BA}/\delta_A$ and $\delta_{AB}/\delta_B$ represent the square root of the ratios between the termination constants $K_t^{baab}/K_t^{aaaa}$ and $K_t^{abba}/K_t^{bbbb}$.

We have found that the ratio $\delta_{BA}/\delta_A$, at least for the systems examined, is always higher than unity; in other words, the termination constant between the growing chains ending with —BA· is higher than that between —AA· radicals, with a ratio ranging from 1.8 to 17. In agreement with some recent hypotheses of O'Driscoll and co-workers [27] about the copolymerization of styrene and methyl methacrylate, it is probable that a chain ending with two styrene units would present a termination rate constant $K_t^{aaaa}$ lower than $K_t^{baab}$, owing to interaction between the two phenyl groups on adjacent styrene units, which can slacken the segmental motion for the hindered rotation about the main chain axis.

For the ratio $\delta_{AB}/\delta_A$, which is now under investigation, in spite of the high uncertainty range about the mean value, we hope to present some interesting interpretations as soon as possible.

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