Mechanistic and kinetic studies of template polymerization of 4-vinyl pyridine

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The template polymerization of 4-vinyl pyridine (4VP) with poly(methyl methacrylate) (PMMA; $\bar{M}_v = 80\,120$), at 65°C for 90 min in dimethylformamide, has been studied dilatometrically in order to examine the effect of concentration and average molecular weight of template, monomer concentration and initiator concentration upon the kinetics and mechanism of template polymerization. The viscometric measurements showed that the complexation between P4VP and PMMA was at a maximum when the template:polymer ratio was 1:1 and the time required for complete complexation was ~9 min. The value of the interaction coefficient was maximum for dioxane (2.90) and minimum for DMF (1.50). The overall energy of activation was 55 and 48 kJ mol^{-1} in the absence and presence of PMMA, respectively.

(Keywords: kinetics; polymerization; 4-vinyl pyridine)

INTRODUCTION

Template polymerization belongs to the field of polymer catalysis. The aim of template polymerization is to achieve the polymerization of monomers regulated by the structure of the template. The salient features of template polymerization are:

1. Complex formation takes place between two polymers[1–3].
2. The rate of polymerization increases as the concentration of template increases. Rate enhancement is due to the decrease in the termination rate constant[4].
3. The structural and conformational features of the template are reflected in the corresponding daughter polymers.

Template polymerization[5] has been divided into two categories. In the first category (mechanism I), the initiation and propagation stages of polymerization occur after the monomer is adsorbed by or complexed to template macromolecules. It is characterized by a continuous increase in the relative rate of polymerization, V_R, with template concentration until a maximum rate ($V_{R,max}$) is reached at a template:monomer ratio of 1:1. At higher ratios, the rate drops.

In the second category (mechanism II), the active oligomers created in free solution are complexed with template macromolecules and continue to propagate along the template. It is characterized by a constant $V_{R,max}$ at and above the critical template concentration.

Although the literature references[6–8] on template polymerization of vinyl monomer are rapidly growing, data on the application of poly(methyl methacrylate) (PMMA) as template for the polymerization of 4-vinyl pyridine (4VP) is still scarce. We report here the first results of template polymerization of 4VP in the presence of PMMA template at 65 ± 0.1°C for 90 min.

EXPERIMENTAL

Materials

Reagent grade methyl methacrylate (MMA, Robert Johnson) and 4VP were purified[9,10] according to standard procedures. α,α′-Azobisisobutyronitrile (AIBN) (m.p. 102°C) was recrystallized twice from methanol. Atactic PMMA with a predominance of syndiotactic sequence[11], used as a template, was obtained by polymerizing MMA in dry benzene ([MMA] = 5.32 M) under nitrogen at 65°C using ([AIBN] = 0.01 M) as initiator. Samples of PMMA of different viscosity average molecular weights ($\bar{M}_v$) were obtained by replacing benzene by a chain-transfer promoting solvent, namely toluene.

The $\bar{M}_v$ values of template (eq. (1)) and daughter polymers[12] (eq. (2)) were determined in benzene at 30°C and in ethanol at 25°C, respectively, using the following equations[13,14]:

$$[\eta] = 8.35 \times 10^{-5} \bar{M}_v^{0.73} \tag{1}$$

$$[\eta] = 2.50 \times 10^{-4} \bar{M}_v^{0.68} \tag{2}$$

The coefficient of interaction between PMMA and poly(4-vinyl pyridine) (P4VP) was determined at 65 ± 0.1°C in solutions of a mixture of these two polymers in dioxane, dimethylformamide (DMF) and dimethylsulphoxide (DMSO) by using the method of intrinsic viscosity measurement in a 'polymer solvent'[15]. Solutions used in the viscosity measurements were prepared in the following way: the polymer, whose solution was used as the solvent, was dissolved to give a series of solutions of different concentrations. After dissolution and filtration through a sintered glass filter (G2), the second polymer was dissolved in the solutions. The basic solutions were then diluted with respect to the second polymer using the solution of first polymer as solvent.

According to this method the intrinsic viscosity of polymer A, $[\eta_A]_B$, is determined in a number of

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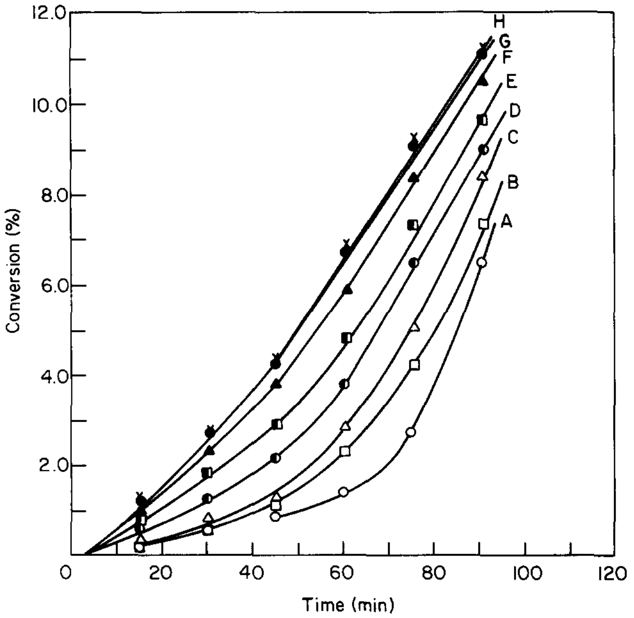

Figure 1 Relationship between per cent conversion *versus* time for the template polymerization of 4VP. Template (base M): A, 0.00; B, 0.40; C, 0.45; D, 0.50; E, 0.55; F, 0.58; G, 0.60; H, 0.65, 0.70, 0.75

concentrated solutions of polymer B which served as solvent and vice versa. For $[\eta_A]_B$ we have:

$$[\eta_A]_B = [\eta_A]/[\eta_r]_B(1 + 2K_{AB}[\eta_B]c_B + \cdots) \qquad (3)$$

where $[\eta_r]_B$ is the relative viscosity of polymer B at concentration c_B, and $[\eta_A]$ and $[\eta_B]$ are the intrinsic viscosities of polymers A and B in pure solvent. The constant K_{AB} is the coefficient of interaction between macromolecules A and B. The plot:

$$f = [\eta_A]_B[\eta_r]_B/[\eta_A] - 1/2[\eta_B] \qquad (4)$$

versus reduced concentration ($\tilde{c} = [\eta_B]c_B$) gives K_{AB} directly from the intercept on the ordinate axis. The case where polymer B is the dissolved component and solution A is the solvent is treated similarly and gives the same value ($K_{AB} = K_{BA}$).

Rate of polymerization

The rates of polymerization (R_p) were measured isothermally for 90 min under an inert atmosphere of nitrogen at 65 ± 0.1°C by employing a dilatometric apparatus. Dilatometric measurements were carried out by injecting the reaction mixture of PMMA, 4VP and AIBN in DMF into the dilatometer. The progress of reaction, monitored as volume contraction by meniscus movement (in cm) per unit volume per unit time, was measured by a cathetometer. The polymerized contents were poured into a large volume of distilled water:acidified methanol (65:35) to precipitate the polymer. The polymer was then purified by reprecipitation and dried in a vacuum oven at 50°C. The template and daughter polymers were separated by refluxing with methanol for ~1 h. The daughter polymer was completely soluble in methanol whereas the template remained insoluble and hence was removed. However the separation was not complete. The R_p was calculated from the slopes of the initial linear zone of per cent conversion *versus* time plots (*Figure 1*).

RESULTS AND DISCUSSION

Viscometric measurements

In order to investigate complexation of PMMA and P4VP, the polymers were separately dissolved in DMF and mixed just before measurement. The viscosity measurements were carried out at 65 ± 0.1°C. The change in reduced viscosity, $\eta_{red} = (\eta_{sp}/c)$, of the mixture of PMMA and P4VP in DMF as a function of composition is shown in *Figure 2*. Also the change in η_{red} of the mixture of two polymers in DMSO and dioxane, as a function of composition, is shown in *Figure 2*. It is clear that in all three cases maximum complexation took place when the polymer ratio was 1:1, and the strength of complexation was maximum in dioxane and minimum in DMF. *Figure 3* illustrates that complexation was virtually complete in 6 min in dioxane, 8 min in DMSO and 9 min in DMF. These data further support the fact that the tendency of the polymers to complex in dioxane is greater than in DMSO or DMF. The rapid drop in η_{red} within 10 min down to a level that remained constant, signifies that complexation was virtually complete within 10 min. Early reports[16,17] on complex formation in template polymerization also showed that the time required for complete complex formation is generally 10–20 min.

Determination of the interaction coefficient

The values of the interaction constant (K_{AB}) are 1.50, 2.10 and 2.90 for DMF, DMSO and dioxane,

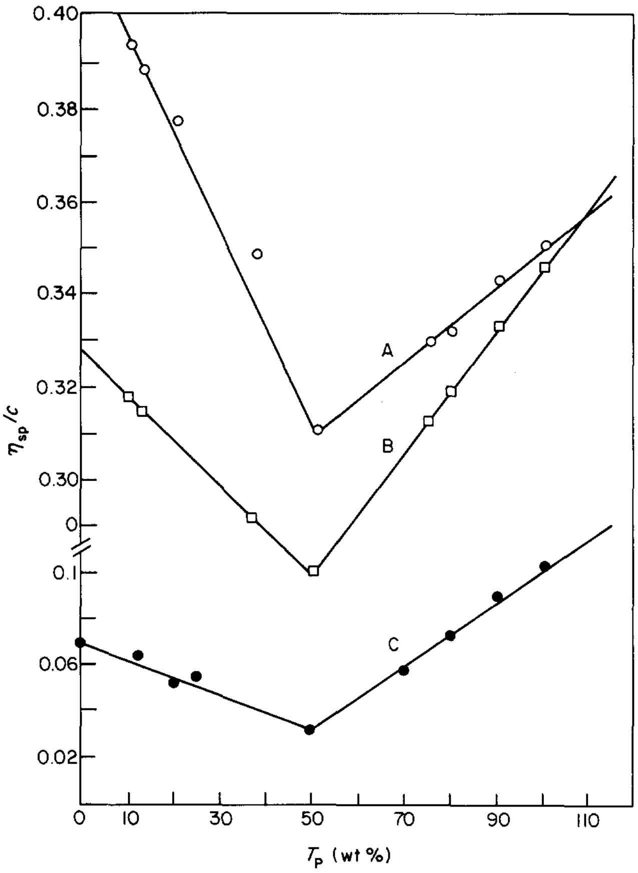

Figure 2 Reduced viscosity (η_{sp}/c) as a function of weight per cent of PMMA for a PMMA/P4VP mixture in: (A) DMF; (B) dioxane; (C) DMSO. Temperature = 65°C; concentration of polymers = 1×10^{-3} g cm^{-3}

respectively (*Figure 4*). The K_{AB} values, determined for the three solvents are high compared with the K_{AB} coefficient reported in the literature[18] (~0.2–0.3). The difference can be explained only by an exceptionally strong interaction between PMMA and P4VP. It is clear from *Table 1* that the intensity of the formation of the stereocomplex is strongest in dioxane medium and weakest in DMF. However, these data differ from those obtained by Quadrat and Belnikevitch[18], who reported a maximum value for K_{AB} for DMF medium in dioxane, with a minimum value in chlorobenzene, for stereocomplex formation between syndiotactic and isotactic PMMA.

Effect of template concentration

The influence of the [template], expressed as V_R:

$$V_R = \frac{\text{Rate of polymerization in the presence of template}}{\text{Rate of polymerization in the absence of template}}$$

is given in *Table 2*. There is a continuous increase in V_R with [template] until a maximum rate ($V_{R,\max}$) is reached at PMMA:polymer = 1:1 and then it becomes constant (*Figure 5*). This shows[19] that the system follows

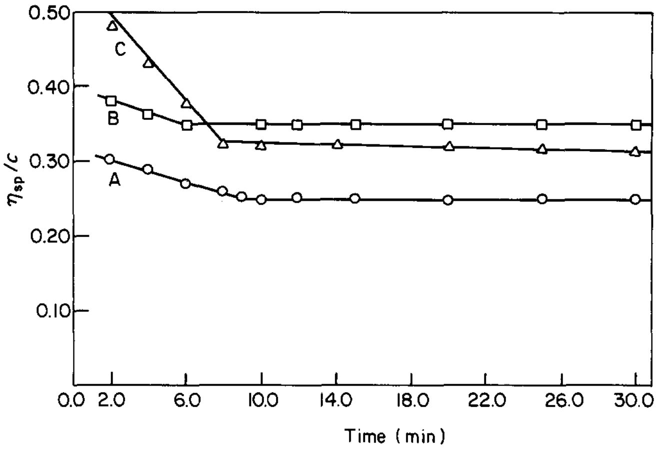

Figure 3 Reduced viscosity (η_{sp}/c) *versus* time, as a function of molar mass of PMMA for a PMMA/P4VP mixture in: (A) DMF; (B) dioxane; (C) DMSO. Temperature = 65°C; concentration of PMMA and P4VP = 4×10^{-3} g cm^{-3}

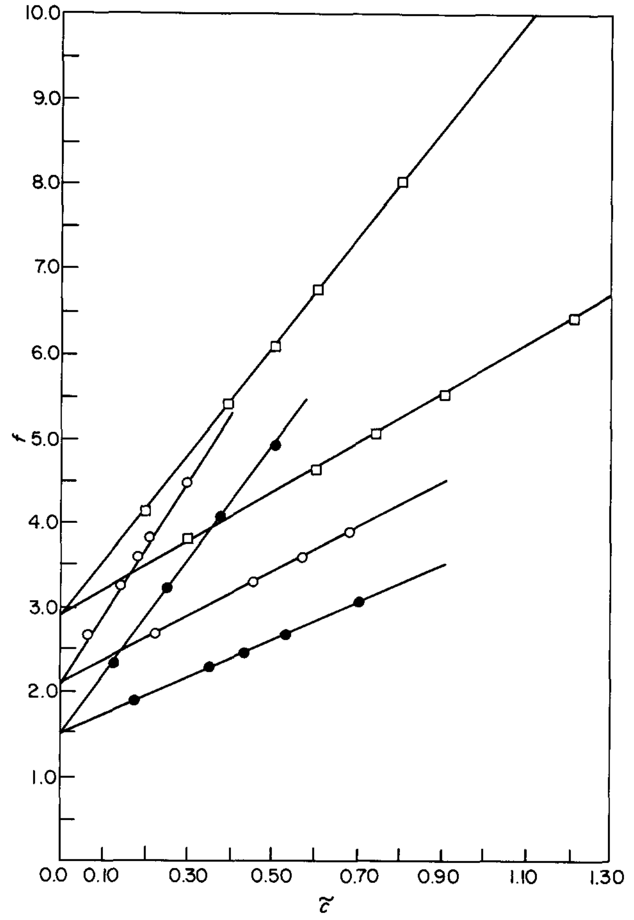

Figure 4 Dependence of parameter f (eq. (4)) on reduced polymer concentration (mol l^{-1}), $\tilde{c}$, for the determination of the value of $K_{AB} = K_{BA}$ in: (●) DMF; (○) DMSO; (□) dioxane. Temperature = 65°C

Table 1 Determination of the interaction coefficient between PMMA and P4VP

Sample no.	Solvent	c_B (g cm^{-3})	$[\tilde{\eta}_A]_B$	c_A (g cm^{-3})	$[\eta_B]_A$	$K_{AB} = K_{BA}$
1	DMF	0.000	5	0.000	7	1.50
		0.025	122	0.025	150	
		0.050	150	0.050	201	
		0.062	158	0.062	220	
		0.075	170	0.075	250	
		0.100	198	0.100	295	
2	DMSO	0.000	3	0.000	9	2.10
		0.025	132	0.025	139	
		0.050	158	0.050	163	
		0.062	170	0.062	173	
		0.075	181	0.075	180	
		0.100	223	0.100	204	
3	Dioxane	0.000	8	0.000	12	2.90
		0.025	460	0.025	502	
		0.050	550	0.050	651	
		0.062	590	0.062	710	
		0.075	635	0.075	770	
		0.100	740	0.100	870	

Table 2 Effect of [PMMA] on the template polymerization of 4VP[a]

[PMMA] (base M)	Conversion (%)	R_p ($\times 10^6$) (mol l^{-1} s^{-1})	V_R	$\bar{M}_v$ of daughter polymer
0.00	6.65	3.00	0.00	57 290
0.40	7.35	3.33	1.11	63 240
0.45	8.47	3.60	1.20	67 350
0.50	9.00	5.00	1.66	71 520
0.55	9.77	7.14	2.38	–
0.58	10.55	10.00	3.33	73 640
0.60	11.10	12.50	4.16	77 640
0.65	11.12	12.51	4.17	78 340
0.70	11.12	12.51	4.17	79 430
0.75	11.12	12.51	4.17	79 800

[a]Conditions: [4VP] = 0.6 mol l^{-1}; [AIBN] = 5.54×10^{-2} mol l^{-1}; $\bar{M}_v$ of [PMMA] = 81 100; time = 90 min; temperature = 65 ± 0.1°C

Table 3 Effect of PMMAs of different molecular weight on the template polymerization of 4VP[a]

PMMA	$\bar{M}_v$	R_p ($\times 10^6$) (mol l^{-1} s^{-1})	V_R	$\bar{M}_v$ of daughter polymer
1	60 990	8.70	2.90	59 270
2	64 220	10.00	3.33	61 250
3	74 200	11.36	3.78	69 420
4	80 100	12.50	4.16	77 640

[a]Conditions: [4VP] = 0.6 mol l^{-1}; [AIBN] = 5.54×10^{-2} mol l^{-1}; [PMMA] = 0.6 base M; time = 90 min; temperature = 65 ± 0.1°C

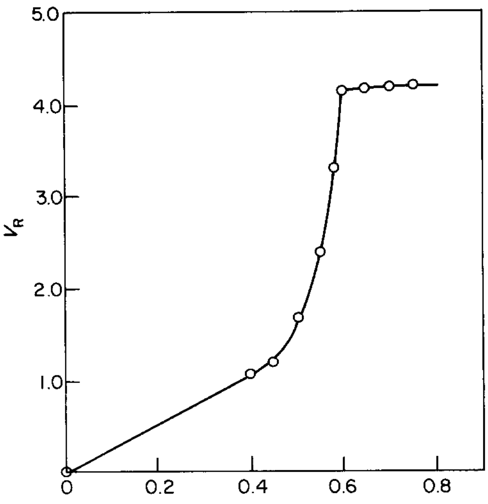

Figure 5 Relationship between relative rate of polymerization (V_R) and template concentration ([T])

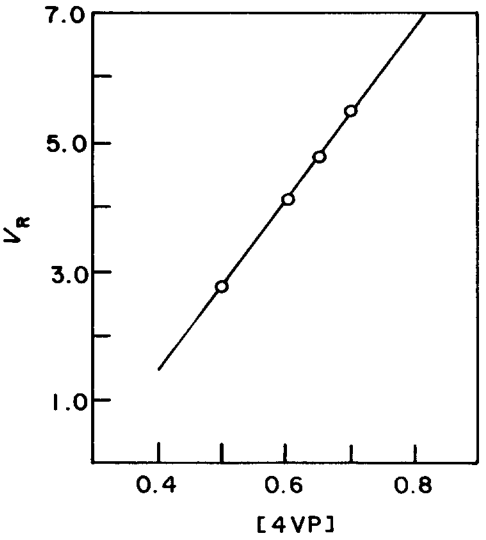

Figure 6 Relation between relative rate of polymerization (V_R) and monomer concentration ([4VP])

mechanism II described earlier. This also suggests that the growing oligomer, created in solution, can form a complex with its template. Since complexation is a co-operative process, the oligomer should attain a minimum critical chain length before it becomes attached to the template, and propagation proceeds by reaction with monomer from the surrounding solution.

Table 2 shows that as [template] increases the $\bar{M}_v$ of the daughter polymer also increases as reported in the literature[2] for other template systems. However, the maximum $\bar{M}_v$ is 79 800 which is low in comparison to that of the template. This might be due to the chain transfer reaction to the template.

Table 3 shows the influence of $\bar{M}_v$ of the template on V_R and $\bar{M}_v$ of the daughter polymers. It is clear that the V_R and $\bar{M}_v$ of the daughter polymers increase with the average molecular weight of template. The $V_{R,max}$ occurs with the template of $\bar{M}_v = 80\,120$; V_R decreases as $\bar{M}_v$ of the template decreases, as expected for template polymerization.

Effect of monomer concentration

The effect of [4VP] on polymerization rate has been investigated. The results are shown in *Figures 6* and *7*. The plot of V_R against [4VP] gives a straight line which shows[20] that there is preferential adsorption of oligomers onto the template. Mechanism II is in operation in the present system because in the case of mechanism I (i.e.

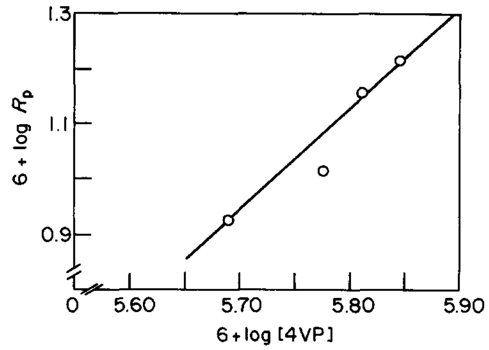

Figure 7 Relationship between log(rate of polymerization, R_p) *versus* log[4VP]: [4VP] = 0.4 mol l^{-1}; [PMMA] = 0.6 base M; [AIBN] = 5.5 × 10^{-2} mol l^{-1}; time = 90 min; temperature = 65 ± 0.1°C

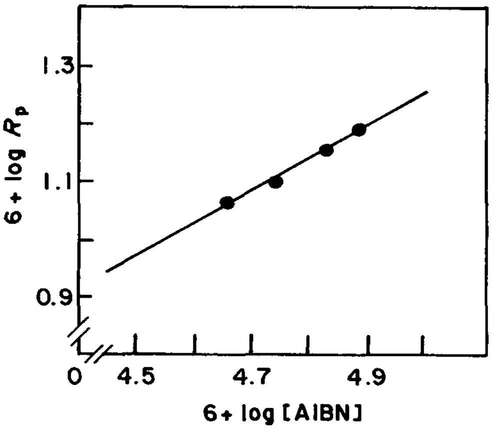

Figure 8 Relationship between log(rate of polymerization, R_p) and log[AIBN]: [PMMA] = 0.6 base M; [P4VP] = 0.6 mol l^{-1}; time = 90 min; temperature = 65 ± 0.1°C

monomer adsorption) the slope of the curve would have been concave[21,22]. According to Telvine *et al.*[23], if the reaction order is greater than unity both k_p and k_t depend on the medium, i.e. both k_p and k_t increase with increasing [4VP].

Effect of initiator concentration

The influence of [AIBN] on R_p has been studied, and the order of reaction with respect to AIBN, calculated from the plot of log R_p *versus* log[AIBN], is 0.50 (*Figure 8*).

Effect of temperature

The overall energy of activation in the presence of template is 48 kJ mol^{-1}, which is less than the blank polymerization in the absence of template (55 kJ mol^{-1}) (*Figure 9*).

Effect of an analogue of 4VP

In order to confirm that mechanism II was applicable for the present system the effect of 2-ethyl pyridine, an analogue of saturated 4VP, was examined. The results (not shown) indicate that it has no effect on R_p.

CONCLUSION

From the experimental data and its interpretation, it is concluded that the present system follows mechanism II and the value of K_{AB} is 1.50 at 65°C in DMF.

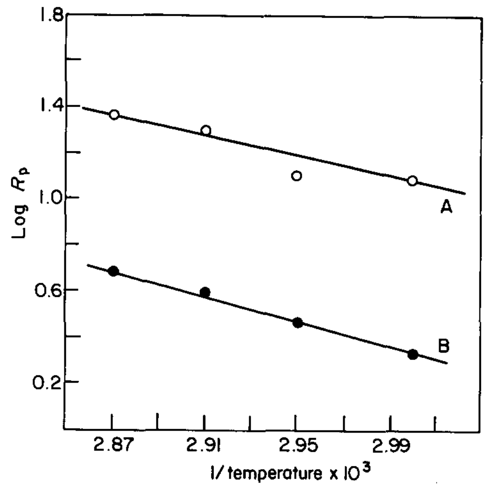

Figure 9 Relationship between log(rate of polymerization, R_p) and the inverse of polymerization temperature (°C) in (A) presence and (B) absence of the template: [4VP] = 0.6 mol l^{-1}; [PMMA] = 0.6 base M; [AIBN] = 5.54 × 10^{-2} mol l^{-1}; time = 90 min; temperature = 65 ± 0.1°C

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