Behavior of Metallocene Olefin Polymerization Catalysts under High Pressure[†]

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Introduction

Since the discovery of homogeneous Ziegler−Natta catalysts, many efforts have been made in their practical application.[1] Metallocene-catalyzed olefin polymerization under high pressure has recently attracted research interest since a high-pressure polymerization process has become a probable method for the industrial utilization of these catalysts. There have been some reports on high-pressure olefin polymerization using group 4 metallocene catalysts.[2] However, the effects of pressure on various parameters, such as chain-transfer rates or the concentration of active species, have not been well described.

We recently reported that metallocene-catalyzed olefin polymerization was remarkably accelerated by high pressures up to 1500 MPa.[3] Catalytic activity was enhanced due to the high pressure in most catalysts, although maximum activity was observed at 250−500 MPa. This activity became saturated or decreased at higher pressures. The molecular weight of the obtained polyhexene increased under elevated pressures, although the enhanced ratios were often smaller compared to the acceleration of catalytic activities. These results prompted us to examine termination processes under high pressure. Herein we wish to describe the behavior of group 4 metallocene complex−methylaluminoxane (MAO) catalyst systems under high pressure in terms of their termination processes in olefin polymerization. The effects of high pressure on some chain-transfer reactions and the concentration of active species are discussed.

Results and Discussion

Analysis of Unsaturated Chain Ends of Polyhexene Obtained under High Pressure. In metallocene-catalyzed olefin polymerization reactions, three kinds of chain-transfer reactions are considered as major termination processes: (i) β-hydrogen elimination to the metal center (TM), (ii) β-hydrogen transfer to the coordinated olefin monomer (TO), and (iii) transmetalation of the polymer chain to alkylaluminum compounds (Scheme 1).[4] The former two processes give an unsaturated C−C bond at the end of the liberated polymer chain. To obtain information about these termination processes, we examined the olefinic end groups of the polyhexenes produced by metallocene catalysts under various reaction pressures by ^{1}H NMR spectroscopy. We observed three signals assignable to vinylidene groups ($CH_2{=}CRR'$, 4.7 ppm), *trans*-vinylene groups ($R{-}CH{=}CH{-}R'$, 5.4 ppm), and trisubstituted olefins ($RR'C{=}CHR''$, 5.1 ppm).[5] Figure 1 shows ^{1}H NMR spectra of polyhexene produced by $(CH_4Me)_2ZrCl_2$ (**1**) under 0.1 and 500 MPa. The ratio of these three unsaturated groups (viniyldene:*trans*-vinilyene:trisubstituted olefins) was 88:12:0 in the polymer obtained under 0.1 MPa. Note that the polymer produced under 500 MPa has predominantly *trans*-vinylenes as its polymer end, and the ratio was 22:77:1. The infrared spectroscopy of the polymers supported these results.[2a] Interestingly, this tendency was observed in various catalysts (**1**−**7**) (Table 1). The vinylidene groups form via β-hydrogen elimination or β-hydrogen transfer from propagating species **10** (Scheme 1). The possible paths for the formation of *trans*-vinylenes and trisubstituted olefins in hexene polymerization were proposed by Chien et al. with $C_2H_4(Ind\text{-}H_4)_2ZrCl_2$ as catalysts (Scheme 2).[5] It is likely that trisubstituted olefin forms via path B. For *trans*-vinylene, on the other hand, β-hydrogen elimination or transfer from “2,1-last inserted” species **11** (path A) seems more plausible. If it forms via path B, which involves migration of zirconium, vinyl groups should be formed when 1-butene is used as a monomer (R = H). In our study on the polymerization of 1-butene with **1** as a catalyst precursor under 0.1 and 500 MPa, no vinyl groups were detected in the obtained poly-1-butene regardless of the reaction pressures.[6]

One may suppose that the increase in *trans*-vinylene ends under high pressure is ascribed to more frequent 2,1-insertion. This may be facilitated under high pressure to some extent. However, the 2,1-last inserted species **11** are thought to be inert for the next monomer insertion because of steric hindrance, and so these species stay as a “dormant site” despite their cationic character.[7] Acceleration of 2,1-insertion will cause a decrease in “real” active species. Therefore, the idea of more frequent 2,1-insertion under high pressure seems inconsistent with the acceleration of polymerization due to high pressure. To get insight into the increase in *trans*-vinylene groups, we investigated the dependence of each termination process on pressure (vide infra).

β-Methyl elimination has been reported in propene polymerization with $(C_5Me_5)_2ZrCl_2$ (**3**).[8] However, β-butyl elimination was unlikely during polymerization of 1-hexene catalyzed by **3** regardless of the reaction pressures, because no terminal vinyl groups were detected in our study.

Effect of High Pressure on Termination Processes. In the present study, we chose $(C_5H_4Me)_2ZrCl_2$ (**1**) as a typical example of metallocene catalyst precursors and investigated the pressure dependency of the chain-transfer reactions in 1-hexene polymerization with **1**. We previously reported remarkable enhancement of the catalytic activity of **1**-MAO and the molecular weight of the obtained polymers under high pressure as shown in Figure 2.[3a]

First, we examined the third termination process, transmetalation to alkylaluminum. After polymerization under 0.1 and 500 MPa, the reaction mixture was quenched with MeOD/D_2O. A ^{2}H NMR observation of the obtained polymer revealed that the amount of D-ended methyl or methylene groups was not more than their natural abundance. Furthermore, the number-

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[†] Dedicated to Prof. Ei-ichi Negishi (Herbert C. Brown Distinguished Professor of Purdue University) on the occasion of his 65th birthday.

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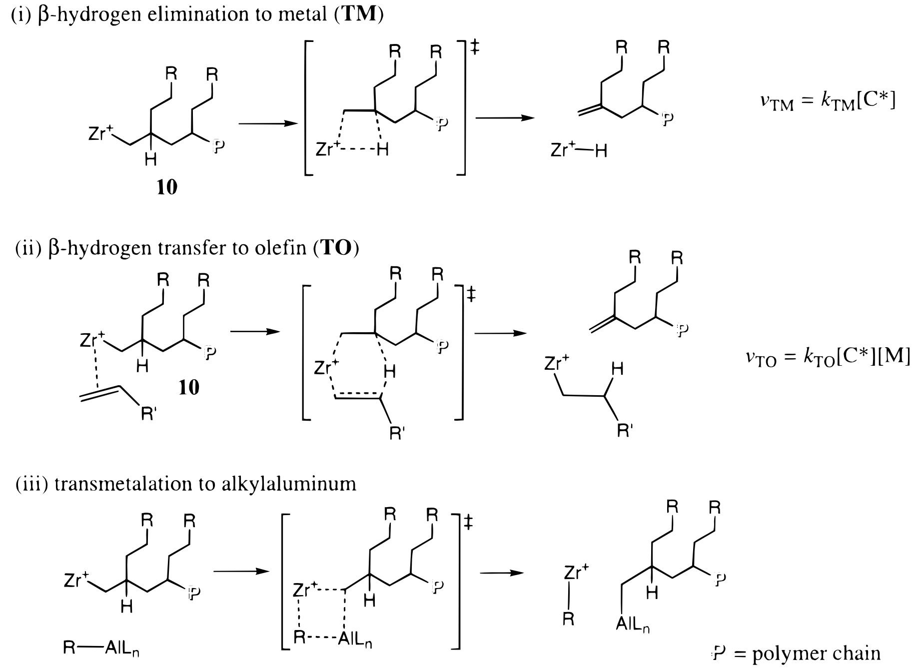
Scheme 1. Termination Processes in Olefin Polymerization



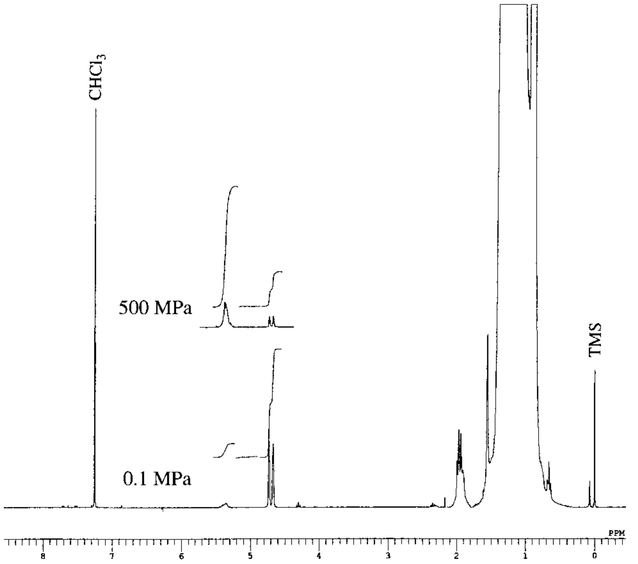


Figure 1. ^{1}H NMR spectra of polyhexene produced under 0.1 and 500 MPa.

average molecular weight calculated by using the ^{1}H NMR data of unsaturated groups was no larger than the M_n obtained by GPC, indicating that unsaturated ends are predominant in this catalyst. Therefore, the transmetalation to aluminum could be ignored in this catalyst system. The discrepancy between the M_n obtained by ^{1}H NMR and GPC is probably due to the calculation of the GPC data based on polystyrene standards.[9]

Second, we investigated the termination processes that involve abstraction of β-hydrogen according to the method reported by Brintzinger and co-workers.[10] The total rate of termination processes is described as eq 1.

$$v_T = v_{TM} + v_{TO} = k_{TM}[C^*] + k_{TO}[C^*][M] \qquad (1)$$

where v_T, v_{TM}, and v_{TO} are rates of total termination, β-hydrogen elimination to metal, and β-hydrogen transfer to olefin, respectively, k_{TM} and k_{TO} are rate constants, and [C*] and [M] are the concentration of active species and monomers, respectively. A plot of the reciprocal number-average polymerization degree ($1/P_N$) versus the reciprocal concentration of 1-hexene (1/[M]) gives k_{TM}/k_P as the slopes and k_{TO}/k_P as the y-axis intercepts (k_P = rate constant of propagation). Figure 3 shows the results at 0.1 and 500 MPa. The ratio of each termination process, TO and TM, in our standard reaction conditions (in neat hexene, [M] = 8.0 mol L^{-1}) was estimated according to these results and eq 1 as follows.

$$v_{TM} = k_P[C^*](k_{TM}/k_P) = k_P[C^*](7.46 \times 10^{-2})$$

$$v_{TO} = k_P[C^*][M](k_{TO}/k_P) = k_P[C^*](8.0) \times (1.31 \times 10^{-2}) = k_P[C^*](1.05 \times 10^{-1})$$

Thus, the ratio v_{TO}/v_{TM} at 0.1 MPa can be estimated as 1.4, indicating that the termination process TO was slightly more frequent than TM at 0.1 MPa. The value v_{TO}/v_{TM} at 500 MPa was similarly evaluated as 11.3 ($v_{TM} = k_P[C^*](2.19 \times 10^{-3})$ and $v_{TO} = k_P[C^*](2.47 \times 10^{-2})$). This suggests that β-hydrogen transfer to olefin (TO) was dominant under high pressure.

Third, we estimated the total rate of termination processes (v_T) according to the equation $P_N \approx v_P/v_T$ (v_P = the rate of polymer growth),[11] which is shown in Figure 4. Interestingly, v_T monotonically increased as pressure elevated. These results imply that β-hydrogen transfer to olefin (TO) accelerated under high pressure.[12]

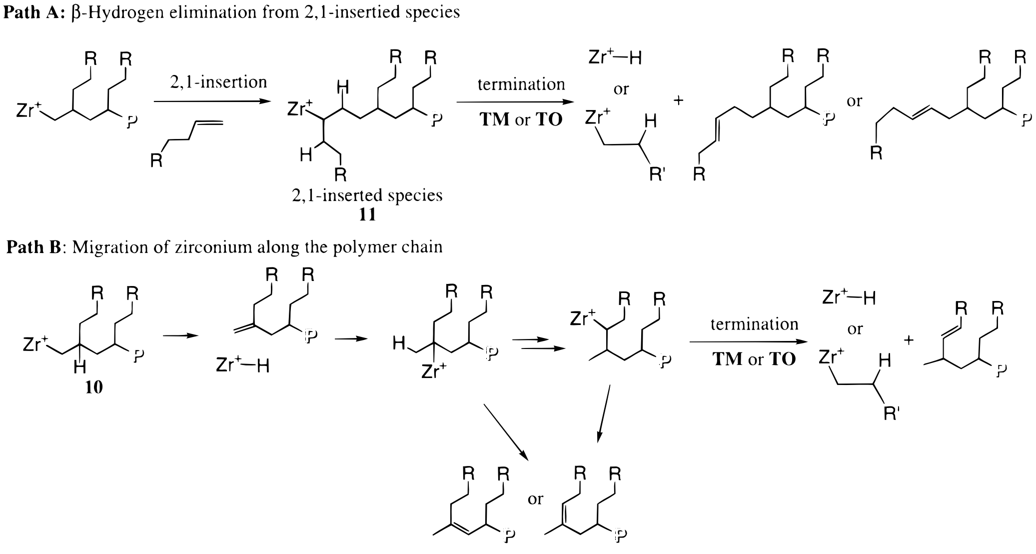
It is possible that 1,2-insertion to the cationic species with secondary alkyl groups **11** is also facilitated due to high pressure, and this should give more tail-to-tail and/or head-to-head units in polyhexene produced under high pressure. Although a full assignment of regioirregular units in ^{13}C NMR spectra of polyhexene could not be accomplished, the ^{13}C NMR observation of the polymer showed no increased signals in the polymer produced at 500 MPa in comparison with one at 0.1 MPa.[13] The apparent rates of polymer production at 0.1 and 500 MPa were approximately proportional to $[M]^{1.4}$

Table 1. Determination of Polymer Ends of Polyhexene by ^{1}H NMR

				GPC			ratio of unsaturated groups/%			NMR
run	catalysts	press., MPa	rate^a	M_w	M_n	M_w/M_n	$CH_2{=}CRR'$ (4.7 ppm)	$RCH{=}CHR'$ (5.4 ppm)	$RCH{=}CRR'$ (5.1 ppm)	M_n
1	$(C_5H_4Me)_2ZrCl_2$ (**1**)	0.1	2.33	8 100	5400	1.49	88	12	0	3 500
2		250	35.1	29 500	20 300	1.45	47	50	3	11 800
3		500	60.9	31 000	22 000	1.43	22	77	1	13 200
4		1000	50.8	11 100	7500	1.49	20	71	9	3 300
5		1500	50.9	9700	60 000	1.63	24	67	9	2 900
6	$(C_5H_2\text{-}1,2,4\text{-}Me_3)_2ZrCl_2$ (**2**)	0.1	8.11	267 000	141 000	1.89	70	11	19	61 500
7		250	102	392 000	192 000	2.04	24	48	28	82 400
8	$(C_5Me_5)_2ZrCl_2$ (**3**)	0.1	0.825	14 200	8 400	1.69	86	7	7	8 400
9		100	185	56 200	29 300	1.92	88	4	8	31 000
10		1500	357	237 300	92 000	2.58	9.1	35.3	55.6	57 200
11	$(C_5H_4\text{-t-Bu})_2ZrCl_2$ (**4**)	0.1	0.417	2 300	1 500	1.49	88	4	8	1 100
12		500	0.362	13 800	6 600	2.96	67	28	5	4 000
13	*rac*-$Me_2Si(C_5H_3\text{-3-t-Bu})_2$-$ZrCl_2$ (**5**)	0.1	4.10	38 500	27 900	1.38	29	42	29	12 000
14		500	11.6	19 600	13 200	1.48	3	97	0	7 000
15	*rac*-$Me_2Si{-}(C_5H_3\text{-3-Me})_2$-$ZrCl_2$ (**6**)	0.1	4.04	21 700	11 100	1.95	53	45	2	8 300
16		500	6.88	12 000	5 700	2.10	5	95	0	4 300
17	$Me_2Si(C_5H_4)_2ZrCl_2$ (**7**)	0.1	0.80	2 200	1 500	1.50	88	7	5	1 000
18		500	8.70	14 400	8 100	1.78	28	70	3	5 000
19	$Me_2C(Cp)(Flu)ZrCl_2$ (**8**)	0.1	16.7	83 500	42 800	1.95	7	86	7	24 000
20		500	13.0	25 800	13 500	1.91	7	93	0	8 500
21	*meso*-Me_2-$Si(C_5H\text{-}2,3,5\text{-}Me_3)_2$-$ZrCl_2$ (**9**)	0.1	6.4	165 000	95 800	1.72	75.6	17.1	7.3	59 800
22		250	45.0	352 000	192 000	1.73	71.5	14.3	14.3	152 000
23		500	104.3	111 000	27 000	4.11	69.6	21.5	8.9	21 000
24		1000	156.1	82 200	20 700	3.97	75	13.3	11.7	13 200

[a] Rate: $\times 10^6$ g of polyhexene/(mol of Zr h).

Scheme 2. Possible Mechanism for the Formation of *trans*-Vinylene End Groups Proposed by Chien et al.[5]



and $[M]^{1.5}$, respectively, which is similar to the reported results.[14]

Concentration of Propagating Species [C_P*] under High Pressure. The 2,1-last inserted species **11** is believed to be inert for the next monomer insertion, and it must accumulate in the reaction system unless it undergoes a certain chain-transfer reaction. Indeed, Busico and co-workers have reported in their study on 1-butene polymerization that more than 99% of cationic species stay as 2,1-last inserted species, the so-called "dormant site".[6] The rate of propagation is described in eq 2,[7a]

$$v_P = k_P[C^*][M] = (k_{PP} + k_{PS})[C_P^*][M] + (k_{SP} + k_{SS})[C_S^*][M] \approx k_{PP}[C_P^*][M] \quad (2)$$

where [C_P*] and [C_S*] are the concentration of 1,2-inserted (primary) and 2,1-inserted (secondary) active species, respectively, k_{PS} is a rate constant of 2,1-(*secondary*) insertion to 1,2-inserted (*primary*) species, and k_{PP}, k_{SP}, and k_{SS} are analogous. Accumulation of **11** in the polymerization system means a decrease in [C_P*] and increase in [C_S*].

Considering the present results, the pressure dependence of the ratio of unsaturated polymer ends, and the acceleration of the bimolecular termination process, we propose the high-pressure effect on the catalyst system illustrated in Figure 5. At normal pressure, a considerable amount of cationic species stay as a "dormant site", 2,1-last inserted species **11**, which is inactive for the monomer insertion. Under high pressures, a bimolecular termination process (β-hydrogen transfer) is facilitated

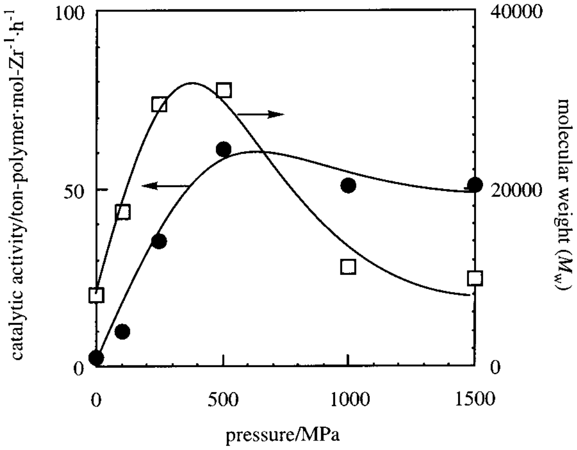
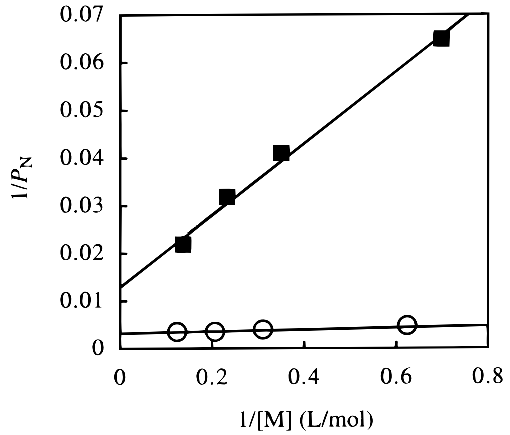


Figure 2. Catalytic activity of **1** (●) and molecular weight (M_w: □) of polyhexene under various pressures.



0.1 MPa: $$\frac{1}{P_N} = 7.46\times10^{-2}\left(\frac{1}{[M]}\right) + 1.31\times10^{-2}$$

500 MPa: $$\frac{1}{P_N} = 2.19\times10^{-3}\left(\frac{1}{[M]}\right) + 3.09\times10^{-3}$$

Figure 3. Termination processes in hexene polymerization with **1**/MAO at 0.1 MPa (■) and 500 MPa (○).

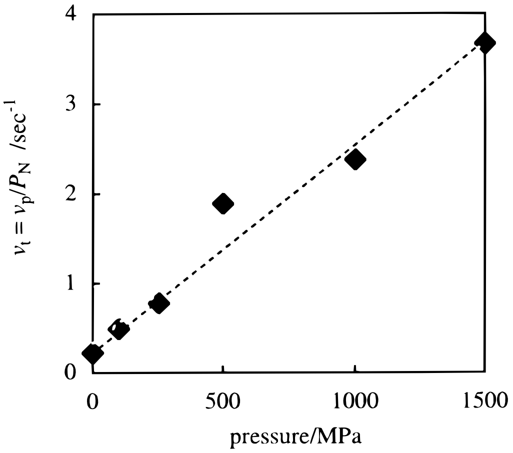


Figure 4. Rate of total termination processes in hexene polymerization with **1**.

on this cationic species **11**. This results in a polymer with a *trans*-vinylene group in its end and the cationic species with a primary alkyl group **12** that is *active* for propagation. As a result, the concentration of "real" active species, $[C_P{}^*]$, increases. The enhancement of k_{PP} under high pressure seems obvious since both the polymer yield and its molecular weight increased. It is likely, however, that an enhancement of k_{PP} as well as an increase in $[C_P{}^*]$ is responsible for the acceleration of propagation (polymerization productivity) due to high pressure.

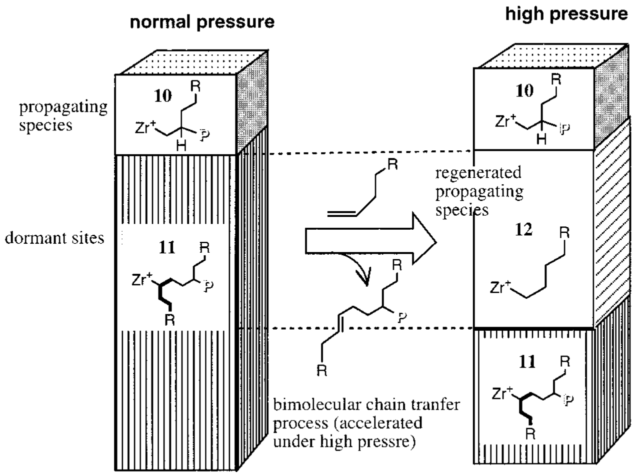


Figure 5. Regeneration of propagating species under high pressure.

There are some catalysts that do not show significant variances in polymer ends through pressures such as **8** and **9**. The polymer produced by **8** under atmospheric pressure has predominantly *trans*-vinylenes, and its ratio was only slightly enhanced due to high pressure. In the case of **9**, no significant variance in polymer ends through pressures was observed. This may be because of the difficulty of 2,1-insertion during polymerization due to the steric hindrance and the rigid structure of **9**. It seems that the catalytic behavior of metallocenes under high pressure highly depends on the structure of the complexes.

Conclusion

We investigated the termination processes of zirconocene–MAO olefin polymerization catalysts under high the pressure of 100–1500 MPa. Our results are summarized as follows: (i) the ratios of olefinic polymer ends depend on the reaction pressure, and *trans*-vinylene groups predominantly form under high pressures; (ii) β-hydrogen transfer to olefin, which is a bimolecular chain-transfer process, is accelerated under 500 MPa in hexene polymerization with $(C_5H_4Me)_2ZrCl_2$ (**1**); (iii) it is proposed that 2,1-last inserted species, a "dormant site", readily undergo bimolecular termination under high pressure to give polymers with *trans*-vinylene ends and catalytically active species and that this results in an increase in $[C_P{}^*]$; (iv) it is likely that an increase in both k_{PP} and $[C_P{}^*]$ is responsible for the enhancement of catalytic activity due to high pressure.

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Supporting Information Available: Experimental details of polymerization reactions, data on investigation of termination processes, and the NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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