Modeling of Transfer Phenomena on Heterogeneous Ziegler Catalysts. II. Experimental Investigation of Intraparticle Mass Transfer Resistance During the Polymerization of Ethylene in Slurry

T. F. McKENNA,* F. BARBOTIN, and R. SPITZ

CNRS.-LCPP./CPE., Bât. F308,43 Bd du 11 Nov. 1918, B.P. 2077, 69616 Villeurbanne, France

SYNOPSIS

An experimental investigation of mass transfer limitations on a single batch of high activity, heterogeneous catalysts used in the slurry polymerization of ethylene is presented. The viscosity of the continuous phase was varied, using trace amounts of inert copolymer in order to reduce the monomer diffusivity, and the activity levels were varied using hexene as an activator. These changes were intended to clearly identify situations in which the polymerization becomes mass-transfer-limited due to diffusion resistance in the pores of the catalyst. Increasing the observed activity of the catalyst from approximately 9000 to 40,000 grams of polymer per gram of catalyst per hour (g/g/h) revealed no evidence of mass transfer resistance, even when the diffusivity of the monomer in solution was reduced by a factor of six. Analysis of the molecular weight as a function of particle size supported this conclusion but did suggest that there might be slight chemical differences between large and small particles. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The economic importance of polyolefin production on heterogeneous catalysts is at the origin of an extensive body of experimental and theoretical work, aimed at explaining reaction kinetics, molecular weight and polymer microstructural development, and fundamental chemical engineering aspects such as heat and mass transfer. One of the major incentives of investigating catalyst behavior is process optimization, i.e., trying to maximize catalyst yield in a given time. In order to be able to do so, it is important to understand whether the polymerization is limited by mass or heat transfer resistance or by the chemical nature of the catalyst itself. In other words, is the reaction controlled by diffusion or by kinetics? One of the commercially important polyolefin processes is the slurry process. In this case, the heterogeneous catalyst and growing polymer particles form a suspension in an inert hydrocarbon diluent such as hexane or heptane. In such a process, it is the diffusion of the monomer in the pores of the particles that is usually considered to be the potential rate-limiting step. This is the issue that will be addressed in the current work.

The morphology of Ziegler-type catalysts is described rather well by the Multigrain Model (MGM).[1] According to this representation, which is supported by results of electron microscopy studies, the catalyst particle is an agglomeration of smaller primary crystals, referred to as microparticles. Diffusion phenomena occur at three different levels in a growing polymer particle: (1) through the external boundary layer into the pores of the particle, (2) through the pores of the particle to the active sites located on the surface of the microparticles, and, finally, (3) through the layer of polymer formed around the microparticles. It has been demonstrated[2,10] that mass transfer resistance will almost always be negligible at the level of the microparticles and through the external boundary layer. However, for large particles of highly active

catalysts ("highly active"[2-10] refers to peak activities less than 5000 g/g/h), these same studies have predicted that mass transfer resistance can exist in the pores of the growing polymer particle and, in particular, during the early stages of the reaction.

Despite the time and energy invested in kinetic and transport modelling and model verification, little experimental work has dealt with the identification of transport limitations of highly active catalyst systems. Different modelling and/or experimental works[11,12] have dealt with catalyst activities that rarely surpassed peak values of 6000–10,000 grams of polymer per gram of catalyst per hour (g/g/h), but as pointed out,[13] activities of 40,000 g/g/h and higher are common with newer generation catalysts. Furthermore, classic reaction diffusion models predict massive mass transfer resistances in polymerizations of this level activity (between 10,000–40,000 g/g/h), mass transfer resistances that are not necessarily seen in laboratory or industrial scale reactors. This and similar discrepancies prompted us to undertake an investigation of the limits of mass transfer in highly active heterogeneous catalysts during the slurry phase polymerization of ethylene. In this fashion, it is hoped that more light can be shed on the potential importance of mass transfer during this type of polymerization and/or to identify areas in which process models could be improved in order to better describe the underlying physics of transport phenomena in and around highly active heterogeneous catalysts.

As pointed out in earlier works,[1-13] significant mass transfer resistance would lead to the formation of concentration gradients inside the particles, with the concentration decreasing from the outside to the center of the particles. As shown schematically in Figure 1, the observable consequences of such gradients would include a decrease in the initial rate of reaction and a lower overall average molecular weight, since both quantities depend on the local concentration of monomer. Here, the dotted lines represent the intrinsic activity of the catalyst, i.e., the rate that one would observe in the absence of any gradients (curves 1). In this event, the concentration everywhere inside the particle is more or less equal to the bulk concentration. However, as the mass transfer resistance or diffusion control of the reaction increases (curves 2 and 3), the peak rate is shifted to the right of the intrinsic rate (2), or even suppressed altogether (curve 3). The observed rates at time t are a result of concentration gradients. In certain instances, with significant mass transfer resistance (e.g., very high intrinsic activities and slow diffusion), the concentration at the centre of the
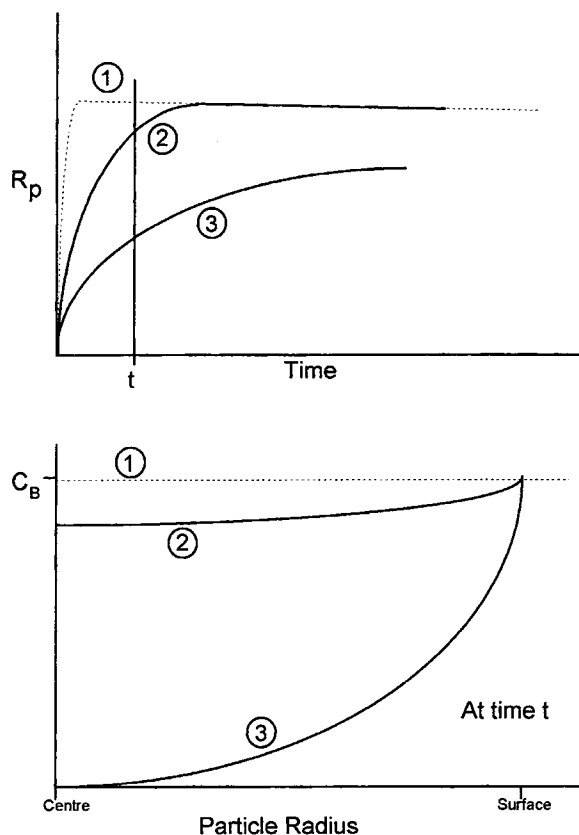

Figure 1 Schema of the effects of mass transfer resistance on the rate of reaction and establishment of concentration gradients inside the particles.

particle could even reach zero. Also, one would expect to find a higher polydispersity in the molecular weight distributions (MWD) of the resulting polymers as mass transfer resistance became more and more significant.

The investigation presented in this article centered on the independent adjustment of two important process variables: the activity of the catalyst through the addition of trace amounts of hexene (not enough to produce a copolymer, but just enough to increase catalyst activity), and the diffusivity of the monomer in suspension through changes in the viscosity of the suspension medium. This last adjustment was accomplished by adding trace amounts of a highly soluble ethylene-hexene copolymer. These variations were made in the attempt to provoke diffusion resistance (i.e., identify shifted maxima, higher polydispersity) in order to be able to affirm under what conditions it can actually be observed and, thus, to test the predictions of currently available transport models.

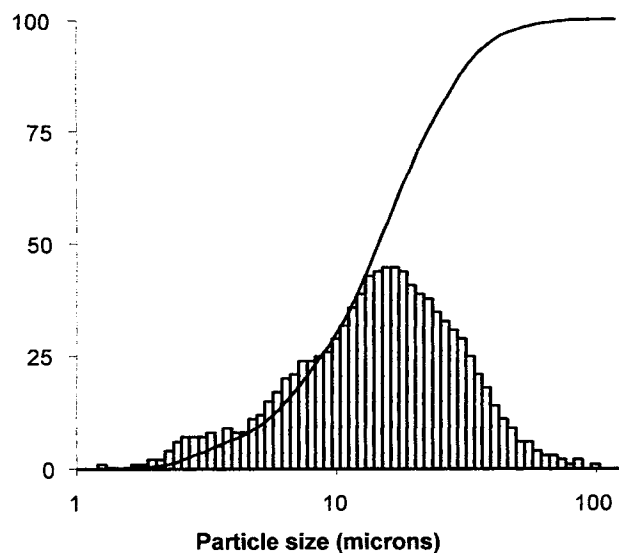While no attempt was made to directly evaluate the diffusivity of ethylene in the solutions of differ-

Figure 2   Particle size distribution of the virgin catalyst particles used in the kinetic study. Note that the distribution is relatively large.

ent viscosity, it is probably safe to assume that a variant of the Stokes-Einstein equation

$$D_{AB} \propto \frac{1}{\eta_B} \tag{1}$$

describes the relationship between solution viscosity (η_B) and the diffusivity of a diluent concentration of a diffusing species (D_{AB}). In the current study, A would represent ethylene, and, B, the mixture heptane/copolymer.

In this manner, it was hoped that by reducing the diffusivity of ethylene, the existence of a diffusion limitation on the rate of polymerization would be observed at some point during the experiments under conditions for which mass transfer resistance occurred could be clearly identified. Mass transfer resistance in this type of situation would be reflected by "flattened" rate curves, where both peak activities drop, and the time it takes to reach the maximum observed activity would increase as mass transfer resistance increases. Furthermore, concentration gradients would become established in the larger particles in cases where mass transfer resistance was important, leading to average molecular weights lower than would normally be obtained in the absence of such gradients (e.g., in the smallest particles).

EXPERIMENTAL

Catalyst System and Particle Size

A heterogeneous, in-house, $TiCl_4/MgCl_2$-supported catalyst was used for all of the experiments reported in this work and prepared according to the method outlined in a patent to ATOCHEM.[14] A large particle size distribution, evaluated using a Malvern particle counter and shown in Figure 2, was sought purposely in order to exaggerate any mass transfer limitations that might occur. The median particle diameter is on the order of 15 μm, but 10% of the batch of catalyst was composed of particles greater than 30 μm in diameter, and 30% were greater than 20 μm.

Sieving was used to compare initial and final particle size distributions in order to test for the rupture of growing particles.

Polymerizations

Nine polymerizations were carried out in a heptane diluent. Three millimoles per liter of triethyl aluminium cocatalyst and ten milligrams of catalyst were added to 300 mL of heptane diluent. The mixture was then transferred to a well-stirred reactor at 80°C. The reactor was pressurized with two bars of hydrogen and six bars of ethylene, and the rate of reaction was evaluated by recording the pressure drop in the monomer feed tank. The different quantities of hex-1-ene and an ethylene-hexene copolymer introduced are outlined in Table I. Note that the amount of hexene added during experiments 5–9 is not enough to produce a true copolymer. The hexene was premixed with the catalyst, cocatalyst, and heptane. This mixture was then fed into the reactor containing the copolymer at the temperature of reaction.

Table I   Additions of Hexene and Copolymer to Different Experiments

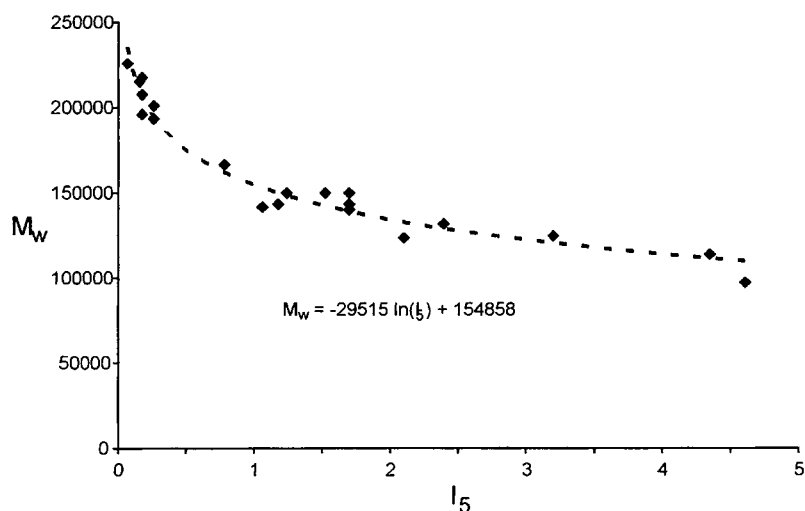| Experiment	Mass Copolymer	Vol. Hexene (mL)
1	0	0
2	2	0
3	4	0
4	6	0
5	0	1
6	2	1
7	6	1
8	0	3
9	6	3

Figure 3   Weight average molecular weight of high density polyethylene samples as a function of the melt index I_5.[15]

The weight average molecular weight of the ethylene-hexene copolymer was estimated to be on the order of 60,000, with a polydispersity of 2.2. At temperatures of near 80°C, the copolymer is readily soluble in the organic phase and totally dissolves in well under one minute. The densities of the polymers produced in experiments 5–9 were on the order of 0.95 g/cm^3 versus 0.96 g/cm^3 in the first four experiments. The mass of the heptane/copolymer solutions was verified after each experiment in order to be sure that no waxes were absorbed by the polymer produced during the polymer. In all cases, all of the copolymer was almost completely recovered.

The ethylene-hexene copolymer used to increase the viscosity was prepared on an homogeneous metallocene catalyst in a heptane diluent. 30 cm^3 of hexene was added to 300 mL of heptane and was copolymerized with 4 bars of ethylene at 65°C for 1 h.

Viscosity and Melt Flow Measurements

The viscosity of the heptane-copolymer solutions was evaluated using a Hubblelhode viscometer. The solution viscosity varied linearly with the quantity of copolymer added to the mixture, with the addition of 6 g of copolymer per 300 mL of heptane leading to a viscosity six times that of heptane.

The melt flow indices I_2 and I_5 were measured at 190°C using a 10 mm piston loaded with weights of 2.16 and 5 kg, respectively. Values of I_5 were used to estimate the weight average molecular weight of the polyethylene samples using the data shown in Figure 3.[15]

RESULTS AND DISCUSSION

The activity curves obtained for the slurry polymerization experiments are shown in Figures 4–6, grouped according to the amount of hexene added to increase the intrinsic activity of the catalyst sites. In these figures, only the points represent experimental data; the curves are included for the sake of clarity.

It can be seen in Figure 4 that for activities on the order of 8500–10,000 g/g/h, the addition of 2, 4, and 6 g of copolymer (experiments 2–4) had no effect at all on the kinetic rate curves. In these experiments, the viscosity of the slurry was increased by factors of two, four, and six times. It can be supposed that the diffusivity of ethylene was reduced by the same factor each time. In the event that mass
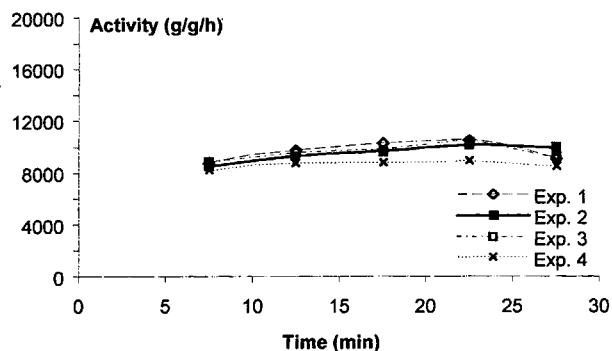

Figure 4   Activity of experiments 1 through 4; no hexene added; increasing quantities of copolymer added to slurry solution. For corresponding concentrations, see Table I.
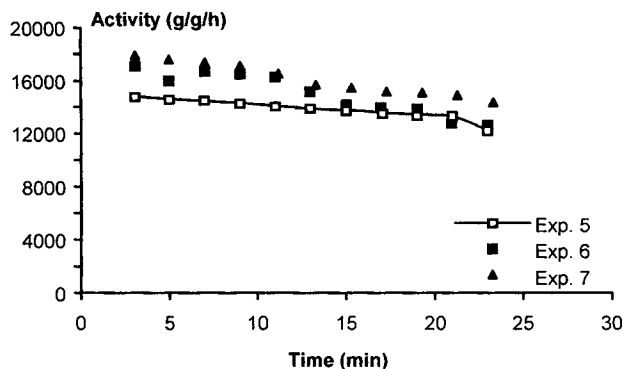
Figure 5 Activity of experiments 5 through 7. 1 mL of hexene added to reaction mixture and increasing quantities of copolymer added to slurry solution. For corresponding concentrations, see Table I.

transfer resistance were important, one would expect experiment 4 to exhibit a lower activity than experiment 1 and to take longer time to attain its maximal activity. Such is obviously not the case, and it can therefore be concluded that, at this level of activity, mass transfer resistance is not encountered in the pores of the growing polymer particles in any of the experiments, even when the diffusivity of the monomer is reduced by an order of magnitude. It should be pointed out here that the relatively low molecular weight of the copolymer ($\sim$ 60,000) and the fact that it dissolves in the heptane diluent in well under one minute both suggest that it is reasonable to assume that the solution viscosity in the pores of the growing particles is actually increased by the copolymer and that the copolymer is not present in only the bulk phase of the reactor.

A similar conclusion can be drawn for the series of experiments in Figure 5. In these experiments, trace amounts of hexene (1 ml) were added at the beginning of the batch in order to increase the activity of the catalyst system. A comparison of Figures 4 and 6 shows that the addition of this small amount of hexene increased the initial activity of the polymerization by a factor of almost two. The rate curves demonstrate classic kinetic behaviour, with high initial activities that decrease as the hexene is consumed. As in the previous series of experiments, there is no evidence of mass transfer resistance in this set of more active polymerizations. It appears that the activity curves are essentially independent of the diffusivity of the ethylene monomer, in fact, the lowest activity curve is for the experiment with no copolymer added at all. The rapid increase in the measured rates after only three minutes shows that increasing the viscosity did not impose a mass transfer limitation on the reaction.

The evidence obtained from experiments where the intrinsic rate of reaction was increased even further through the addition of 3 ml of hexene to the initial mixture is slightly more difficult to interpret with confidence. The curves in Figure 6 differ slightly during the initial instants of these highly active polymerizations. Experiment 8, with no copolymer, is somewhat more active during the first few minutes of the reaction than is the polymerization in the more viscous slurry. At first glance, this might appear to be evidence of a diffusion-limited reaction; however, it should be noted that the time it takes to attain the maximum activity is relatively short in experiment 9, shorter than would be expected if diffusion resistance were a major factor in determining the level of observed activity and not measurably different from the rapid time-to-maximum observed in experiment 8. Also, it should be pointed out here that experiment 9 was performed with a different batch of ethylene-hexene copolymer than were experiments 1-8. It is possible that trace amounts of impurities in this product might have had a detrimental effect on the rate of reaction. Finally, the difference between the two experiments is not too large to be explained by simple experimental error or batch-to-batch variations.

In order to corroborate the evidence presented in Figures 4-6 against the existence of any mass transfer resistance, an analysis of the molecular weight of the polymer formed as a function of particle size was also performed. Sieving revealed no particle rupture or breakage during the reaction, even with the highly active polymerizations of experiments 8 and 9. The results are shown in Figure 7 and Table II (melt flow indices). The ratio of the melt flow indices I_5/I_2 can be taken as an indication of the
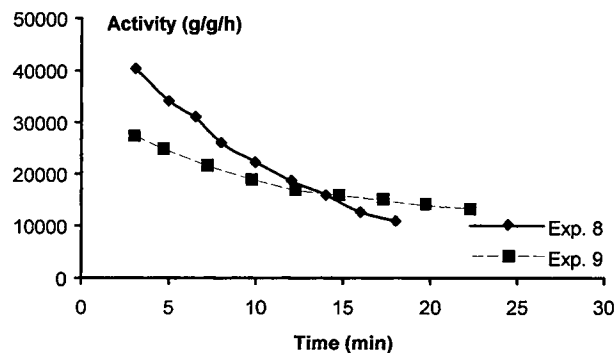

Figure 6 Activity of experiments 8 and 9. 3 mL of hexene added to reaction mixture, and increasing quantities of copolymer added to slurry solution. For corresponding concentrations, see Table I.
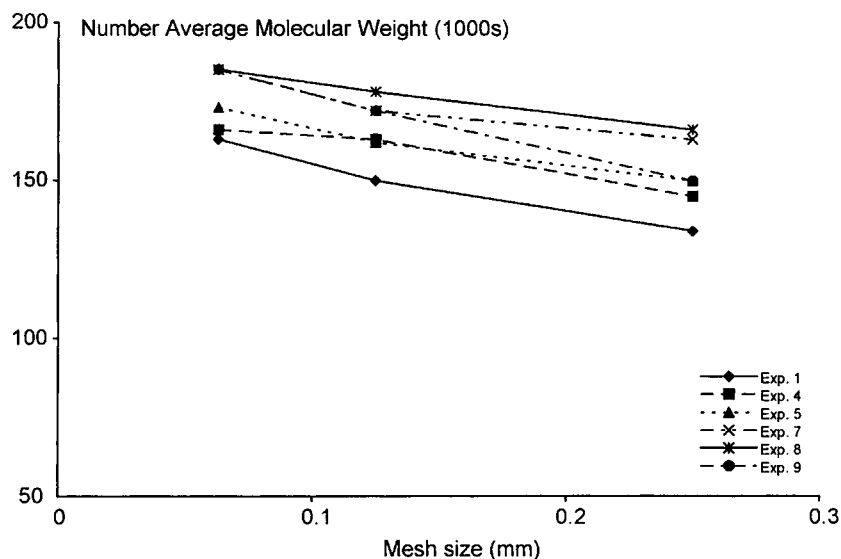
Figure 7 Molecular weights of different experiments (most and least viscous of each series) as a function of particle size.

polydispersity of the molecular weight distribution. Some experimental variation can be seen, but this is relatively small; and it can safely be said that the polydispersity varies from experiment to experiment. This also argues against the presence of any mass transfer resistance since, if concentration gradients were to form in more active polymerizations, this would have the effect of increasing the global polydispersity of the final product.

The dependence of molecular weight on particle size seen in Figure 7 might, at first glance, suggest that the larger particles were mass-transfer-limited. It is true that, if concentration gradients were present, they would be more significant in the larger particles than the smaller ones, and that this would be reflected by a decrease in the number and weight-average molecular weights. Nevertheless, it should be recalled that all experiments were performed on the same batch of catalyst and that they all had the same initial particle size distribution. Therefore, if the functionality evident in Figure 7 could be explained by monomer mass transfer resistance in the particle pores, the molecular weight of the larger particles of the more active polymerizations would

have lower molecular weights than the same cut in the less active polymerizations. This is clearly not the case. For example, if one compares experiment 9 to experiments 4 and 1, the molecular weight obtained in the highly active, viscous slurry of experiment 9, where molecular weight would be the lowest, is actually higher than the molecular weight of experiment 4, which in turn is higher than that of experiment 1.

Also, diffusion control of the polymerization would lead to a decrease in the ratio of the molecular weight of the small particles to the molecular weight of the bigger particles as a function of activity. Since diffusion resistance would lead to the establishment of concentration gradients in the particles, the monomer concentration, and thus the molecular weights, would be lower in the larger particles. However, as shown in Table III, this is not exactly the case. In fact, there is no really discernible difference between the various experiments analyzed.

It is most likely, therefore, that the reduction in molecular weight as a function of particle size is due to the method used to synthesize the catalysts, perhaps caused by diffusion limitations, but of the rel-

Table II   Melt Flow Indices for Different Experiments

Experiment No. →	1	4	5	7	8	9
I_2	0.25	0.14	0.23	0.35	0.43	0.46
I_5	0.89	0.64	0.85	1.2	1.49	1.83
I_5/I_2	3.56	4.57	3.70	3.43	3.47	3.98

Table III Ratio of Molecular Weights of Small to Large Particles as Function of Experiment Number

Experiment No. →	1	4	5	7	8	9
$M_{w_{small}}/M_{w_{big}}$	1.23	1.12	1.13	1.15	1.14	1.21

atively large molecules of cocatalyst, and not of the monomer. This point is worthy of future exploration but will not be discussed any further here and will be the object of a future publication.

CONCLUSIONS

The work presented here represents one of the first experimental studies on the evaluation of mass transfer resistance in the pores of highly active, heterogeneously catalyzed olefin polymerizations in the liquid phase.

Simultaneous variation of both activity and monomer diffusivity showed that, even when the diffusivity of ethylene is effectively reduced by an order of magnitude, no diffusion limitations are observed for activities up to almost 40,000 grams of polymer per grams of catalyst per hour. Decreasing the monomer diffusivity by increasing the viscosity of the slurry with an inert copolymer did not lead to a reduction in either the observed maximum rate of polymerization or in the time it took to achieve the initially elevated rates of reaction.

This conclusion was supported further by an analysis of the molecular weight of the polymer obtained as a function of particle size. It was shown that the reduction in molecular weight as a function of increasing particle size is due to chemical differences between large and small particles rather than diffusion limitations and concentration gradients in the growing polymer particles.

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