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## Temperature and Itaconic Acid Influences on Ba-Co-Mma Semi-Batch Process Emulsion Copolymerization and Copolymers

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**Abstract** This report analyzes the influence of itaconic acid and temperature on semi-batch emulsion copolymerization of butyl acrylate and methyl methacrylate and in properties of obtained copolymers. Reactions were made at two different temperatures (75 and 85°C), with or without itaconic acid. Resulting lattices were evaluated in their solids content, pH and average diameter particles. Besides, a sample of each lattice was coagulated with ethanol and the resulting solid was analyzed in elemental and gel content, viscosity at low shear stress rate, and thermal properties. Presence of itaconic acid reduced global conversion of the co-monomers, due to the reduction in polymerization rate, and increased the gel content of the polymers. It was observed that the presence of itaconic acid increased viscosity at low shear stress rate and slightly increased the copolymers glass transition temperatures, due to the presence of carboxylic acid groups, which increased the polymer chains polarity.

**Keywords** Emulsion polymerization, itaconic acid, renewable resources

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### Introduction

Emulsion copolymerization of butyl acrylate and methyl methacrylate has been studied by some researchers [1-5]. However, the demand for renewable monomers and polymer has increased among researchers in this field. Several monomers can be obtained from renewable resources [6], and one example is itaconic acid [7], an unsaturated dicarboxylic acid obtained from fermentation of rich in carbohydrates substrates using fungi of genus *Aspergillus* [8]. As other organic acids, it can be used as functionalizing agent in emulsion polymerization [9]. However, itaconic acid presence reduces initiator efficiency, leading to monomer conversion reduction. Interaction between itaconic acid and potassium persulfate resulted in a stable allylic radical formation, which is less effective to initiate polymerization. Its presence also increases final average diameter particle with increase on itaconic acid percentage, as consequence of lower formation of radicals during the initial stages [10,11]. Mendizabal et al. [12] studied pH influence on styrene-butyl acrylate core-shell polymers functionalization and their mechanical properties. Authors noted an increase in polymer functionalization when the pH was close to pKa of acid monomer. The results also showed which, with the increase of carboxylic acid groups on the functionalized polymer, its hardness and impact strength increased. Oliveira et al. [13] analyzed fumaric and itaconic acid influence on emulsion copolymerization of methyl methacrylate and n-butyl acrylate. In this report, it was observed that the lowest conversion level was obtained using itaconic acid as functionalizing agent and was also analyzed the distribution of these monomers on



the different phases of the emulsion system. In the case of itaconic acid, a small fraction remained inside the particle, as well as in the particle surface and in the aqueous phase. Liu et al. [14] used itaconic acid as functionalizing agent of (PBA)/P(MMA-ITA) core-shell particles, in a batch seeded emulsion polymerization. In comparison with same PBA/PMMA core-shell particles without itaconic acid, there was a little increase on T<sub>g</sub>, mainly due to the increase of intermolecular forces by the introduction of this co-monomer. Rabelero et al. [15] studied the influence of itaconic acid in the mechanical properties of PS/PBA and PBA/PS core-shell particles. According to the results, there is an increase on hardness, Young modulus, and tensile stress mainly with PS/PBA core/shell particles. Besides, T<sub>g</sub> also increased with itaconic acid content, suggesting that this component stiffens, by reducing the mobility of the polymer chains. There are few publications related to itaconic acid influence in emulsion polymerization. In order to reduce the gap of information, this report studied the influence of itaconic acid in the semi-batch copolymerization of butyl acrylate and methyl methacrylate, via comparison among the final properties of the lattices and the correlation of these properties with coagulated polymers properties.

## Materials and Methods

### Materials

Monomers, butyl acrylate (BA), methyl methacrylate (MMA) and itaconic acid (IA); initiators: persulfate sodium and ammonium persulfate, as well as the buffering agent, sodium acetate, were provided by Oswaldo Cruz Química LTDA. Surfactants employed were Hostapal BVQ-9, sodium alkylaryl polyglycol ether sulphate, from Clariant S.A.; and Sipomer COPS-1, sodium allyloxy-2-hydroxypropane sulfonate, from Rhodia S.A.. All reagents were used as received.

### Emulsion Polymerization and Characterization

Emulsion polymerizations were developed in a stainless-steel reactor, with capacity of 2.0 L. The reactor was equipped with an IKA RW 20 stirrer; a Gulterm 1200 type K thermocouple, from Gulton; a bubble condenser; a column with controlled feeding valve, in order to feed emulsion to the reactor, and a thermostatic bath from Marconi, model MA 159. Each emulsion, as shown in Table 1, was prepared in a 2000 mL becker with the aid of an IKA RW 18 S6 stirrer.

**Table 1:** Used formulations to obtain itaconic acid acrylate derivatives by emulsion polymerization.

	75IA4	85IA4	75IA0	85IA0
Temperature (°C)	75	85	75	85
Emulsion				
Water	264.98	264.98	264.98	264.98
Sipomer COPS 1	2.13	2.13	2.13	2.13
Hostapal BVQ-9	41.83	41.83	41.83	41.83
Butyl Acrylate	514.08	514.08	535.50	535.50
Methyl Methacrylate	90.72	90.72	94.50	94.50
Itaconic Acid	25.20	25.20	0	0
Solution 1				
Water	251.07	251.07	251.07	251.07
Sodium acetate	2.51	2.51	2.51	2.51
Sodium Persulfate	0.18	0.18	0.18	0.18
Solution 2				
Water	43.04	43.04	43.04	43.04
Ammonium Persulfate	1.97	1.97	1.97	1.97
Solution 3				
Water	17.93	17.93	17.93	17.93
Ammonium Persulfate	0.36	0.36	0.36	0.36



In the reactor, solution 1 was fed and heated until achieve the temperature to start the reaction. At this point, it started the emulsion feed simultaneously with the feeding of solution 2. The feed time was of 3.5 hours. After this period, in order to consume the residual monomers, it was added the solution 3, and the reaction temperature remained for 30 minutes. Next, the reactor was cooled up to room temperature.

Solids content evaluation of resulting lattices was performed according to the following procedure: small empty aluminum sample holders were weighed and after adding presence of five drops of each emulsion sample, they were weighed again. The weight difference before and after adding each sample emulsion was noted. Then, in order to evaporate water and residual monomers, they were placed in an oven at 145 °C for 20 minutes. After drying the small aluminum samples holders, they were weighted, and the values used in gravimetric analysis. The pH of the lattices was measured using an AJ Micronal AJX-522 pH meter. Average particle diameter and its distribution were evaluated by dynamic light scattering with the aid of a Mastersizer S machine. Water was used as the dispersing medium at room temperature. Resulting polymer properties were measured after the lattices being coagulated with the addition of ethanol, and the residues of water and ethanol being evaporated at room temperature, to avoid thermal degradation. After evaporation, the samples were characterized by elemental analysis, gel content, thermal and rheological properties. Elemental analysis was made in a Vario MACRO Cube CHNS Elemental Analyser, from Mettler Toledo, containing a MX5 microanalytical balance. The combustion temperature was 1150°C. In order to obtain the gel fraction of the final polymers, it was used Soxhlet extraction. It was weighted a filter paper, before and after adding 0.3 g of coagulated polymer sample, and the extraction was made under reflux with tetrahydrofuran (THF) for 24 hours, according to ASTM D2765-11 standard [16]. After this period, THF was evaporated from the paper filter with the remaining sample (insoluble polymer) at 70°C. When the total mass of the filter paper plus the sample remained constant, both were separately weighted, and their weights were recorded. The gel content was obtained through Equation (1):

$$\text{Gel Content (\%)} = \frac{W_s}{W_i} \times 100 \quad (1)$$

where  $W_s$  is the mass of insoluble fraction and  $W_i$  is the initial mass of the sample.

Rheological measurements were effectuated in steady-state system at low shear rates. The equipment used was an ARG2, from Rheometric Scientific, parallel plates rheometer. The measurements were made at following conditions: inert atmosphere ( $N_2$ ), temperature 240°C, plates' diameter of 25 mm and distance between the plates of 1.0 mm, scanning the shear stress rate between 0.01 and 1.0  $s^{-1}$ . Copolymers glass transition temperatures values ( $T_g$ ) were obtained via differential scanning calorimetry (DSC). Measurements were effectuated in a 2920 MDSC Mettler Toledo calorimeter, with the following conditions: inert atmosphere ( $N_2$ ), at flow rate of 50 mL/min, heating rate of 10°C/min, in a temperature interval between -100 and 160°C.

## Results & Discussion

Solid content values of each formulation are presented in Figure 1a. In all formulations, the level of solids content achieved more than 48%, indicating high level of co-monomers conversion. Furthermore, with the increase of polymerization temperature, the solids content moderately increases. In other words, the rate of the global conversion of co-monomers increases as a function of the reactor temperature. Besides, it was observed that the presence of itaconic acid in the formulations 75IA4 and 85IA4, caused a slight reduction on the solids content in comparison to the similar formulations without this component. This reduction can be attributed to the interaction between initiator and itaconic acid, which reduces initiator efficiency, as cited in [10]. The average particles diameter obtained for all formulations is shown in Fig. 1b. In emulsion polymerization, there is a conflict between the rates of chain growth and the rate of monomers diffusion inside the micelles. If polymerization is more effective than diffusion, it will have a reduction of free monomers inside the micelles and the final average particle diameter will be smaller. On contrary, if diffusion is more intense than polymerization, will occur monomers accumulation of inside the micelles and, as a consequence, the final average particle diameter will be larger [10,11, 17]. Regarding to the influence of itaconic acid, it was observed an increment of average particle diameter in its presence. Analyzing the data of average diameter particle together with solids content data, there is a correlation between these two parameters. With the presence of itaconic acid in the formulation, the initiator efficiency will reduce and the



diffusion of co-monomers will occur preferentially. Thus, there is an accumulation of monomers inside the particles where the polymerization occurs, and as a consequence, the particle became slightly larger.

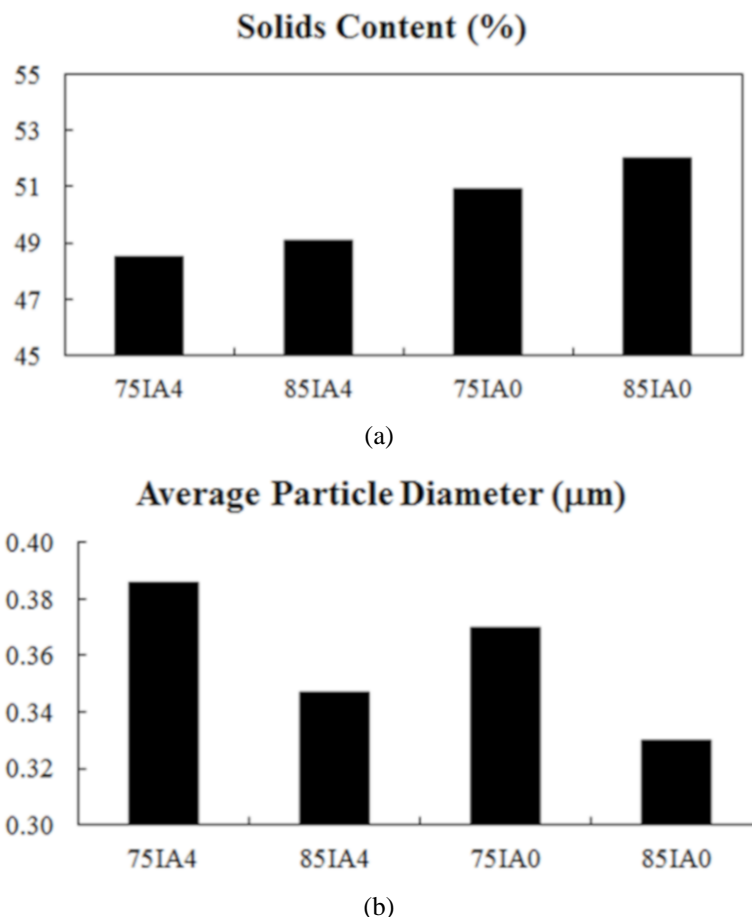


Figure 1: (a) Solids content and (b) average particle diameter of the used formulations.

pH values for the lattices are presented in Table 2. As seen, formulation 75IA4 showed the lowest pH value, while the highest value was obtained for formulation 85IA0. It is noted that in all formulations, the pH values exhibited acid characteristics and that the presence of itaconic acid in formulations 75IA4 and 85IA4, as expected, reduced the pH value of the lattices. Comparing formulations 75IA4 and 85IA4, as well as formulations 75IA0 and 85IA0, without itaconic acid, there is not significant variation on their pH values. Looking at the data in Fig. 1a and Table 2, formulation 85IA0 presented the highest pH value and highest solid content, i.e., the highest global co-monomers conversion level. Regardless of the presence of itaconic acid (in formulations 75IA4 and 85IA4) or absence (formulation 75IA0 and 85IA0), with the increase of temperature, the average particles diameter reduces. It occurs because the rate of polymerization also increases. In this case, the polymerization became more influent than diffusion of co-monomers inside the particles, in which the polymerization occurs, reducing the accumulation of monomers within them and, therefore, resulting smaller polymer particles.

Table 2: pH values of each formulation after polymerization.

Formulation	pH value
75IA4	2.7
85IA4	2.9
75IA0	4.3
85IA0	4.5



Co-monomers composition in each polymer synthesized was obtained via elemental analysis, based on Bakhshi *et al.* [18]. The oxygen percentages were calculated by subtracting the percentage of the total amount of C and N. With this procedure, it can be calculated the polymers compositions studied, in function of C, H and O mass percentages. In each butyl acrylate molecule, there are 7 C atoms, 12 H and 2 O and, similarly, in each methyl methacrylate molecule there are 5 C atoms, 8 H and 2 O. Itaconic acid has 7 C atoms, 12 H and 2 O in each molecule. Fig. 2 exhibits the molecular structure of the terpolymer.

The mass fraction of C% and H%, obtained via elemental analysis, can be correlated to the molecular structure of the copolymer, and number of mols of BA and MMA in formulations 3 and 4 (without IA) through Equations (2) and (3):

$$(7x + 5y)M_C = C\% \quad (2)$$

$$(12x + 8y)M_H = H\% \quad (3)$$

where x and y are, respectively, the number of moles of BA and MMA in 100 g of copolymer;  $M_C$  and  $M_H$  are molar mass of carbon and hydrogen, respectively. Solving the system in x and y, the obtained results are presented in Equations (4) and (5):

$$x = \frac{1}{4} \left( \frac{5H\%}{M_H} - \frac{8C\%}{M_C} \right) \quad (4)$$

$$y = \frac{1}{5} \left( \frac{C\%}{M_C} - 7x \right) \quad (5)$$

BA and MMA mass in 100 g of copolymers (mass percentage of each co-monomer) can be obtained using the multiplication of mol number x and y by molar mass of BA and MMA, respectively, with Equations (6) and (7):

$$MM_{BA} \cdot x = M_{BA} \quad (6)$$

$$MM_{MMA} \cdot y = M_{MMA} \quad (7)$$

With the Equations (8), (9) and (10), they have been calculated the monomers percentage, and the obtained values are presented in Table 3.

$$\%M_{BA} = MM_{BA} \cdot N_{BA} = MM_{BA} \cdot \frac{1}{4} \cdot \left( \frac{5 \cdot \%H}{MM_H} - \frac{8 \cdot \%C}{MM_C} \right) \quad (8)$$

$$\%M_{MMA} = MM_{MMA} \cdot N_{MMA} = MM_{MMA} \cdot \frac{1}{5} \left( \frac{\%C}{MM_C} - 7 \cdot N_{BA} \right) \quad (9)$$

$$\%IA = 100 - \%M_{BA} - \%M_{MMA} \quad (10)$$

**Table 3:** Mass percentages of C, H, O, and co-monomer composition in final polymers of all formulations, in %.

Formulation	C%	H%	O%	BA	MMA	IA
75IA4	63.55	9.01	27.44	76.29	22.52	1.19
85IA4	63.15	8.99	27.86	81.36	16.31	2.33
75IA0	64.33	9.13	26.54	83.58	16.42	0
85IA0	64.25	9.15	26.60	78.09	21.91	0

After obtaining the percentages of each element, it was obtained the mass percentages of the co-monomers in the final polymers, which are presented in Table 4. The modeling used to estimate the co-monomers percentage of each polymer is presented as following. The results of this model are the Equations (2) and (3) that follows: The values of mass percentages of C, H and O for each formulation are presented on Table 3.

It has been known that butyl acrylate copolymerization with methyl methacrylate tends to yield high percentage of gel content [3, 19]. Fig. 2 presents gel content values after Soxhlet extraction with THF. According to Kohut-Svelko *et al.* [20], in case of acrylates obtained by emulsion polymerization, it is expected a slight decrease on gel content with the increase of polymerization temperature. Authors used a Monte Carlo modeling and showed that, in lower temperatures, the insoluble fraction of polymer is higher and also the molar mass of the soluble fraction of polymer is too high. Thus, the solubility of the obtained polymer is reduced at lower temperatures. This occurs due to the combination of several factors, such as lower coefficient of intermolecular transfer chain; lower coefficient of chain termination by combination; lower monomers conversion at lower temperatures and reduced bimolecular termination rate, which leads to a drastic reduction in the number of particles having two or more radicals [20]. This fact may justify the results observed after comparing polymers from formulations 75IA4 and 85IA4, and formulations 75IA0 and 85IA0. It is noted that gel content formulations with itaconic acid are nearby 20% higher

than without itaconic acid, indicating that itaconic acid increases the chain transfer rate, leading to the crosslinking of P(BA-co-MMA). A possible cause is due to the possible interaction between itaconic acid and initiators, which reduces the efficiency of the polymerization rate.

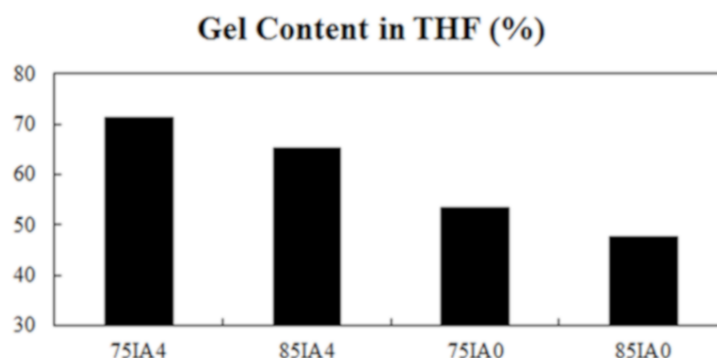


Figure 3: Final polymers gel content in THF

Comparing formulations 75IA4 and 85IA4, it was observed an increase of the itaconic acid percentage in the obtained polymers. According to previous reports [9,12], the maximum level of itaconic acid incorporation in the polymer chains occurs when pH inside the reactor is nearby the pKa of the unsaturated carboxylic acids. In formulation 85IA4, the value of pH measured is slightly higher and also slightly close to 3.85, i.e. the value of pKa for itaconic acid. Therefore, in formulation 85IA4, it was obtained a higher incorporation of this acid. If the pH increases significantly, the solubility of this acid in water must increase due to its capacity of salt formation, which is more soluble and less reactive. Furthermore, it was also observed that the behavior of the reactivity ratio changed in the presence of itaconic acid in the formulation. In formulations 75IA4 and 85IA4, the increase of temperature increases the mass percentage of butyl acrylate. On the other hand, in formulations 75IA0 and 85IA0, an increase in temperature increases the methyl methacrylate percentage in the final polymer. These results indicate that itaconic acid interferes with their reactivity ratios and allows obtaining copolymers with different monomers percentage and properties.

The influence of itaconic acid in the viscosity is seen in Fig. 4. As observed, the viscosity of polymer obtained with formulation 85IA4 increased nearby 100% in the maximum viscosity point, compared to the viscosity of the polymer obtained in formulation 85IA0. A possible justification is the higher gel content of formulation 85IA4, compared with formulation 85IA0, indicating higher crosslinking level. Besides, the higher presence of hydrogen bonds between chains due to the incorporation of itaconic acid on the polymer chains at polymer chains on formulation 85IA4.

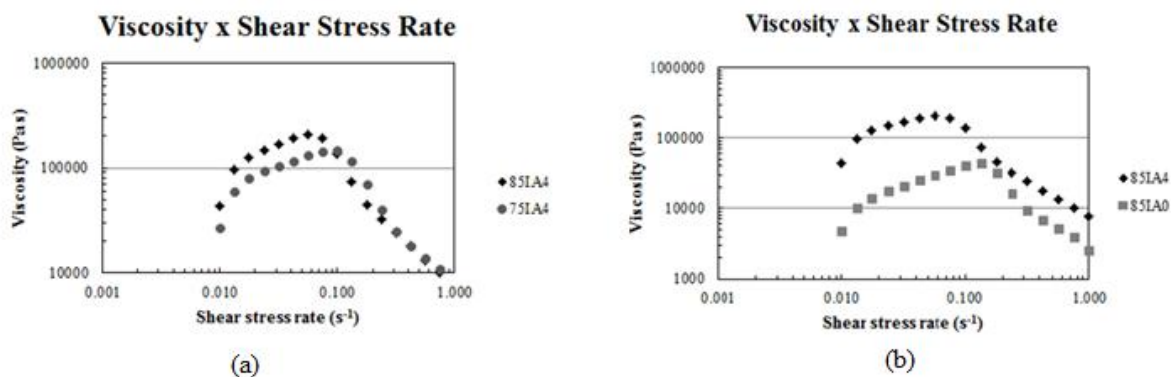


Figure 4: Viscosity at low shear stress rate of the resulting co polymers. (a) Influence of the temperature, (b) influence of itaconic acid presence



DSC thermograms of resultant polymers, as exhibited in Fig. 5, show their T<sub>g</sub> values. Two comparisons can be made with these results, i.e. the influence of temperature and the presence of itaconic acid. In the first comparison, it is seen a slight difference in T<sub>g</sub> values for formulations 75IA4 and 85IA4. According to elemental analysis, in formulation 85IA4, there is a little excess of itaconic acid in copolymer composition than in formulation 75IA4, even considering that there are higher mass percentage of methyl methacrylate in formulation 85IA4 than in formulation 75IA4, which would lead to a higher T<sub>g</sub>. The consequent increase on carboxylic acid groups on the chain also increases the presence of hydrogen bonds, which limits the polymer chains movements, therefore increasing the glass transition temperature.

In the case of formulations 85IA4 and formulation 85IA0, there is a slight influence of the presence of carboxylic acid co-monomer. Even with more mass percentage of butyl acrylate in formulation 85IA4, which would lead a lower T<sub>g</sub>, the value is two degrees higher than in formulation 85IA0. The possible cause also is the polarity increase, which resulted on more interaction among polymer chains, and consequent higher value of T<sub>g</sub>. These results agree with those presented by Rabelero *et al.* [15].

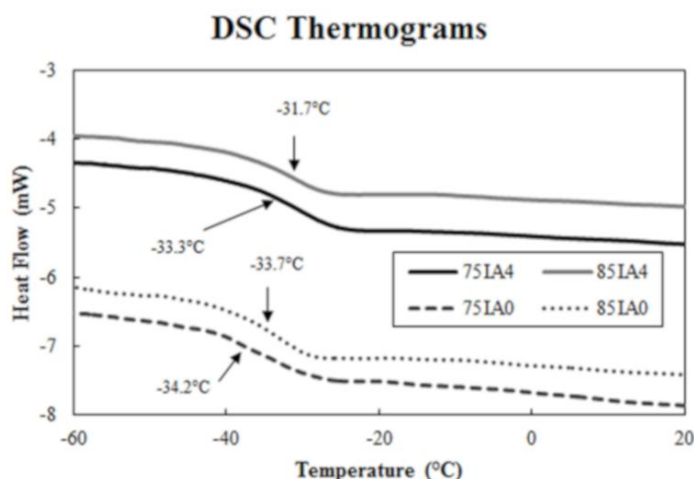


Figure 5: DSC thermograms of resulting copolymers

## Conclusion

According to the presented results, it became evident that using itaconic acid during copolymerization of butyl acrylate and methyl methacrylate reduces the global conversion of the co-monomers, increases the average particle diameter and level of gel content. Its presence increases the polarity of the polymer chains, increasing the values of T<sub>g</sub> and viscosity at low shear stress rate. Besides, the conversion of co-monomers has been reduced due to the efficiency's reduction of the initiator. The functionalization of acrylic polymers is essential to improve compatibility with other polymers, such as polyamides and polyesters. However, there is a necessity of optimizing the insertion of functional groups and the polymerization process parameters, in order to achieve the best conditions for each material, including the functional monomers.

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