

Synthesis of a new kind of carbohydrate-modified polysiloxanes and its morphological transition of molecular aggregates in water

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Abstract

Allylamides of gluconic acid were synthesized by the reaction of allylamine with lactones using dimethyl formamide as a solvent. In this reaction, hydroxyl groups were protected by trimethylsilyl groups via three different pathways that connect sugar units onto the polysiloxane chains. A series of well-defined polysiloxanes with pendent sugar units were prepared by hydrosilation of the trimethylsilyl-protected allylamides with hydric polysiloxanes in the presence of the Platinum dioxide as a catalyst. The catalytic activity and selectivity were discussed in detail. All products were characterized by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy, respectively. Furthermore, the shapes of molecular aggregates of target polymers in water were studied by transmission electron microscopy, which reveals that the transitions of micelles- morphologies from spheres to vesicles can be controlled by adjusting hydrogen content of primary materials or by changing initial solvents.

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Keywords: Carbohydrate-modified polysiloxanes; Hydrosilation; Molecular aggregates; Vesicles

1. Introduction

Several papers (Kobayashi, Sumitomo, & Ina, 1985; Laurence Bes et al., 2003; Matin, Ampofo, Linhardt, & Dordick, 1992; Nakaya, Nishio, Memita, & Imoto, 1993; Turnbull & Stoddart, 2002) have been published on polymers substituted with pendant sugar units, which could be used for cell immobilization, medical tubing, column materials, etc. Most of these research works focused on the polymers with C–C main chains bearing saccharide residues, with relatively few chemists paying attention to silicon backbone polymers. Compared with the carbon chain polymers, polysiloxanes have remarkable properties such as flexibility, low cohesive energy, and biocompatibility. Braunmühl and Stadler (1998) and Braunmühl, Jonas, and Stadler (1995) reported a synthesis route of hybrid polymer based on hydric polysiloxanes through

hydrosilation reactions. Hydroxyl groups in the allyl amide of gluconic acid (AAG) were protected by acetic anhydride, and all hydroxyl groups were changed to carbonyl groups. However, in the hydrosilation process of hydric polysiloxanes with AAG, not all hydroxyl groups have minus effects on Si–H. Therefore, it is not necessary to fetch in too many carbonyl groups. On one hand, the lead-in groups increase steric hindrance; on the other hand, the electrophilic effect of completely protected AAG with carbonyl groups accordingly induces double bond's electron atmosphere density, which is unfavorable to the hydrosilation. Furthermore, the side reactions between methanol and amido groups maybe occur in subsequent reactions of the carbonyl groups' cleavage. Therefore, new routes of protecting hydroxyl groups were introduced here. Trimethylchlorosilane (TMSCl) and hexamethyldisilazane (HMDS) are well known as the selective protector in sugar-chemistry field (Burchard & Schulz, 1995; Desjardins & Eisenberg, 1991; Gao, Desjardins, & Eisenberg, 1992; Mormann & Demeter, 1999; Mormann, Demeter, & Wagner, 1999; Schuyten, Weaver, Reid, &

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Jurgens, 1948) due to their easy preparation and selective attachment resulting in the formation of silyl ethers. In this research, highly substituted AAG was obtained via HMDS/hydrogen chloride (HCl) using DMF as a solvent.

Jonas and Stadler (1991) declared that the common catalysts such as Speier's catalyst and dicyclopentadienyl platinum(II) chloride had no catalytic activities to this kind of hydrosilation reactions because of the amide linkage in the *N*-allylaldonamides, which acts as a poison to the catalysts. However, bis-cyclooctadiene (Rh-COD) was reported to be capable of catalyzing this kind of reaction (Jonas & Stadler, 1994). Several transition metallic catalysts including Speier's catalyst were investigated in this paper. It was found that platinum dioxide was a powerful hydrosilation catalyst in the reaction between hydric polysiloxanes and trimethylsilyl-AAG. After an effective cleavage process of trimethylsilyl ether by using $\text{BF}_3\text{-Et}_2\text{O}$, some polysiloxanes with side sugar units were obtained.

As reported previously, the carbohydrate-modified polysiloxanes are obvious amphiphilic polymers (Honda, Sakaki, & Nose, 1994; Prochazka et al., 1992; Qin, Tian, Ramireddy, Webber, & Munk, 1994; Ramesh et al., 1991; Xu & Winnik, 1991) whose main chains are hydrophobic polysiloxanes and the side units are hydrophilic sugars. Thus, they are suitable to be applied in the biomedical field. As the volume of hydrophilic sugar units is much smaller than that of hydrophobic PDMS, micelles known as "crew-cut" micelles, which was proposed by Halperin, Tirrell, and Lodge (1992) and characterized by Zhang, Barlow, and Eisenberg (1995) and Zhang and Eisenberg (1995), can be obtained in water solution. There are several factors which affect the shapes of these polymers, such as their composition, solvent, pH value, metal ion, and so on. The vesicles obtained from the double compatible molecules are not only utilized to simulate the structures of biomembranes, but also applied in medicine as molecular carriers (Gao et al., 1992).

Various micelles created by the sugar-containing polysiloxanes in water were observed by transmission electron microscopy. One of the influential factors is the composition of the amphiphilic polymer. The ratio of hydrophilic groups (sugar) to hydrophobic groups (polysiloxane chains) can be adjusted indirectly by changing the content of hydrogen in hydric silicone oil. Another factor is the

polarity of initial solvents. It was found that the polymer with a lower amount of hydrophilic segments tends to vesicles during the decrease of the polarity of solvents.

2. Experimental section

2.1. Materials

δ -Gluconolactone, TMSCl , and HMDS were obtained from Aldrich Chemical Co. Ltd. 46.5% (wt) of Boron fluoride in ether was from Alfa Aesar Chemicals. THF was dried over solid KOH before use. Toluene was dried over sodium and distilled before use. Other reagents were commercially available in some chemical reagent companies in China, and were used with suitable methods after purification.

2.2. Measurements

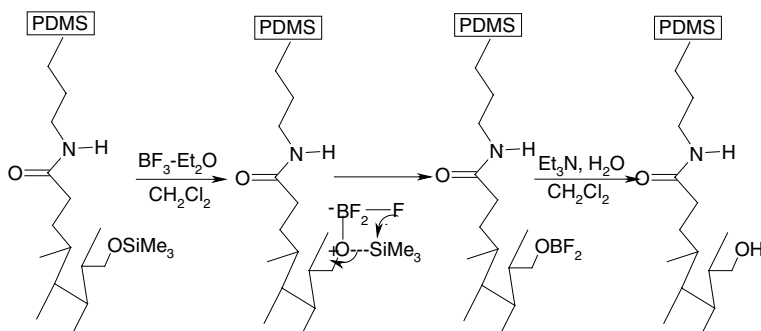
FT-IR was carried out on Nicolet FT-IR 20SX spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on AVANCE 400. The shapes of molecular aggregates were observed with JEM-100cxII at a voltage of 110 kV. Molecular weight of polysiloxanes was measured on Water 515 GPC under the standard of monodisperse polystyrene.

2.3. Synthesis of AAG

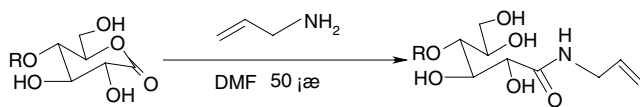
AAG was synthesized under the way as follows according to Scheme 2. Specifically, 3.64 g (20 mmol) δ -gluconolactone dissolved in 25 ml DMF. 2.85 g (50 mmol) allylamine was slowly added to this solution under stirring at 50 °C for 3 h. The excessive DMF was removed by reducing pressure. The remaining solid was washed with cyclohexane, recovered by filtration, and then recrystallized twice from isopropanol to obtain AAG, which appears as white powder. (Yield: 3.92 g (75%), $[\alpha]_D = 36.8$, m.p. = 120 °C.)

Spectral assignments were as follows:

IR (KBr) (cm^{-1}): 3400 (O–H, N–H), 2920 (C–H), 1665, 1648, 1642 (C=O, C=C), 1544 (N–H) ^1H NMR ($\text{DMSO}-d_6$): 7.33 (br s; 1H; NH), 5.88–5.68 (m; 1H; CH=), 5.34–5.08 (m; 2H, =CH₂), 4.06–3.88 (m; 2H; NH–CH₂), 3.79–3.32 (m; 11H; OH). ^{13}C NMR ($\text{DMSO}-d_6$): 172.99 (C=O), 134.55 (CH=), 120.88 (=CH₂), 73.32, 72.11, 71.23, 69.88 (C-2, 3, 4, 5), 63.70 (C-6), 41.76 (NH–CH₂).



Scheme 1. The mechanism of cleavage process via $\text{BF}_3\text{-Et}_2\text{O}$.



Scheme 2. Synthesis of AAG.

2.4. Synthesis of trimethylsilyl-AAG

To initiate reaction, 4.70 g (20 mmol) AAG and 32.2 g (200 mmol) HMDS were heated to reflux for 72 h under argon atmosphere. The “protection” of hydroxyl groups can be monitored by the change of ν -OH at 3400 cm^{-1} on IR spectroscopy. The excess HMDS was removed by reducing pressure. The residue was re-dissolved in *n*-hexane and purified under treatment with carbon black. The removal of *n*-hexane results in TMS-AAG as a faint yellow powder.

Yield: 10.6 g (79%); b.p.: 123–127 °C/0.005 mbar;

Spectral results as follows:

^1H NMR (CDCl_3): 6.21 (br s; 1H; NH), 5.88–5.73 (m; 1H; CH=), 5.42–5.24 (m; 2H; =CH₂), 4.30–2.44 (m; 8H; NH-CH₂, H-2, 3, 4, 5, 6, 6'), 0.21–0.04 (m; 54H; Si-CH₃). ^{13}C NMR (CDCl_3): 174.92 (C=O), 131.39 (CH=), 121.87 (=CH₂), 77.82, 75.55, 74.04, 72.64 (C-2, 3, 4, 5), 64.28 (C-6), 41.66 (NH-CH₂), 0.95, 0.81, 0.76, 0.49, 0.36 (Si-CH₃).

2.5. Synthesis of poly(DMS-co-TMSAAGMS)

A total of 3.5 g (Si/H 80/8) hydric silicone oil was dissolved in 25 ml dry toluene under argon atmosphere and platinum dioxide (120 ppm equiv.) was added under gentle stirring. Then 3 g (5 mmol, excess 5%) TMS-AAG in 20 ml toluene was added in dropwise slowly. Then, the reaction mixture was heated to 85 °C for 36 h. The conversion of Si-H groups was observed with the decrease of ν (Si-H) at 2166 cm^{-1} on FT-IR spectroscopy. After cooling to room temperature, the remanent catalyzer was filtered through charcoal. Sandy beige residue was purified by column chromatography (silica gel, eluent: toluene) to remove the unreacted raw materials. The eluent was distilled off under reduced pressure. 5.8 g of target products was obtained.

Spectral results are as follows:

^1H NMR (CDCl_3): 5.91 (br s; 1H; NH), 4.29–2.67 (m; 8H; H-2, 3, 4, 5, 6, 6', N-CH₂), 1.63–1.46 (m; 2H; Si-CH₂-CH₂), 0.52–0.44 (m; 2H; Si-CH₂), 0.00 (s; Si-CH₃). ^{13}C NMR (CDCl_3): 171.94 (C=O), 79.26, 78.01, 75.93, 72.54 (glu-C₂-C₅), 63.59 (C-6), 41.38 (NH-CH₂), 25.22–23.74 (Si-CH₂-CH₂), 18.36–16.05 (Si-CH₂), –0.36–0.90 (TMS-Si-CH₃), –2.28 (Si-CH₃).

2.6. Synthesis of saccharine polysiloxane

A total of 5.2 g (Si Pw/n = 80/8, poly(DMS-co-TMSAAGMS), with 25 mmol trimethylsilyl ether groups) was dissolved in 50 ml of dry CH_2Cl_2 under nitrogen atmosphere. The mixture was cooled to –10 °C and 4.62 ml of boron fluoride/ether (37.5 mmol) was added with gentle stirring over 12 h. The degree of cleaving of trimethylsilyl groups was monitored by decreasing of δ (Si-C) at 1265 cm^{-1} and ν (Si-O) at 1120 cm^{-1} on RT-IR spectroscopy with a corresponding increase of ν (O-H) at 3480 – 3030 cm^{-1} . Triethylamine (5 ml), water (5 ml), and dichloromethane (50 ml) was added in sequence to dilute the mixture. The resulting solution was washed twice using 50 ml of saturated sodium chloride solution. The organic phase was separated, dried over sodium sulfate. The CH_2Cl_2 was removed in a rotatory evaporator. The residue was purified by silica gel column chromatography with toluene as the eluent to produce 3.5 g of pure sugar siloxane: Yield 92%.

FT-IR (cm^{-1}): 3400 (ν (b), ν (-OH)), 2967 (s, ν (C-H)), 1658 (w, ν (C=O) amide I), 1548 (w, δ (N-H) amide II), 1260 (s, δ (Si-C)), 1085/1022 (b, ν (Si-O)/ ν (C-O)), 805 (s, ν (Si-C)). ^{13}C NMR (THF-d₅): 172.1 (C-1), 73.6–70.2 (C-2–C-5), 64.9 (C-6), 42.5 (–NHCH₂), 24.2 (–CH₂CH₂CH₂–), 15.3 (Si-CH₂–), 1.7–(–1.4)(–SiCH₃).

2.7. Preparation and observation of “crew-cut” molecular aggregates

Because the carbohydrate-modified polysiloxanes obtained has a very large weight fraction of hydrophobic polysiloxanes, it is impossible to gain stable solution by direct dissolution in water. Therefore, in order to prepare stable solution of Saccharine polysiloxane, DMF was selected as a solvent, which is a common solvent for both PDMS and AAG. The mass ratio of solute ranged from 0.5% to 4.0%, subsequently, distilled water was dropped

Table 1
Synthesis of trimethylsilyl (TMS)-protected AAG

Unsaturated compound	Silylating agent	Mol/mol –OH	Solvent	Temperature (°C)	Reaction time (h)	DS
AAG	TMSCl	2.6:1	Pyridine	110	72	2.4
	TMSCl	3:1	Pyridine/toluene	110	48	2.7
	HMDS/HCL	2:1	DMF	110	120	2.8
	HMDS	2.6:1	DMA/LiCl	80	48	2.8
	HMDS	2:1	—	75	72	2.7

into the polymer/DMF solution at a rate of 4 drops/min with high-speed stirring. After critical aggregative-density point, initial pellucid solution turned into lattices. The addition of water was continued until 45 wt%. The milksop was placed into dialysis bags for 4 days to remove the organic solvent. A glob of diluted solution (dilution ratio 10) was placed onto a copper grid (75 μm , coated with carbon), and then otiose water was blotted with bibulous paper. After the grid was dyed by a little glob of uranium acetate for 5 min, and then was dried in the air, the morphologies of aggregate were observed through TEM.

3. Results and discussion

3.1. Synthesis of carbohydrate-modified PDMS

3.1.1. The protection of hydroxyl groups

In the process of synthesizing carbohydrate-modified PDMS from allylated sugars and hydric polysiloxances, several hydroxyl groups of the sugars units must be protected before hydrosilation in order to avoid side reactions. The original method (Braunmühl & Stadler, 1998) was to use acetic anhydride as a protector. In the past 10 years, TMSCl and HMDS were well known as selective protecting materials in sugar chemical field that resulting in the formation of silyl ethers. In this research, five methods of protecting hydroxyl groups in the sugar units were studied. The extent of substitution of the hydroxyl groups could be quantitatively measured according to NMR method. The results are listed in Table 1.

It was found that highly substituted AAG can be obtained by using HMDS/HCl as protecting system and using dimethyl formamide (DMF) as a solvent. Through this method, not only were the sugar units protected from suffering some serious adverse reaction conditions that would have adversely affected the sugar's optical properties and biocompatibility, but also difficulties in the subsequent reactions were reduced. Moreover, side reactions between methanol and amide groups which occurred in the original deprotection process (Braunmühl & Stadler, 1998) can be effectively avoided; thus, the yield of final polymer can be increase considerably. Although a good degree of substitution, DS, can be also obtained from dimethyl acetamide (DMA)/lithium chloride (LiCl) in much shorter reaction time, we waived this method because the reaction was not easily controlled because of its severe speed, and LiCl was difficult to be removed as impurity.

3.1.2. Equilibrium of hydric silicone oil

The solution and surface properties of carbohydrate-modified PDMS in aqueous media mainly depend on the molecular weight and the content of sugar units. To obtain a great variety of target polymer, hydric silicone oils with different molecular weights and composition are essential primary materials. After equilibrating perhydrous silicone oil with octamethylcyclotetrasiloxane and hexamethyldisiloxane while sulfuric acid act as a catalyst. The hydrogen of silicone oil could be varied from 0% to 100%, and the molecular weight of the containing hydrogen silicone oil can also be varied from 3000 g mol^{-1} up to 12,000 g mol^{-1} ($\overline{M}_w/\overline{M}_n = 1.4 - 2.3$ according to GPC analysis). Some kinds of them were listed in Table 2.

3.1.3. Catalyst

Hydrosilation addition is the most important process for preparing carbohydrate-modified PDMS. But, it is difficult to find a suitable catalyst in this reaction because the amino groups do poison to the common Speier's catalyst. After testing large variety of Karstedt catalyst and complexes of transition metal ions such as $(\text{Et}_2\text{S})\text{PtCl}_2$, Platinum dioxide and bis(1,5-cyclooctadiene)dirhodium dichloride and others to prepare several kinds of aminopropyl polysiloxane-base polymer, it was showed that platinum dioxide was also an effective catalyst in the reaction with a yield almost one hundred percent (100%) according to the ^1H NMR of crude product, without induction period, and the remanent catalyzer could be easily reclaimed by filtration. This dioxide was also an effective catalyst to the addition of D_4^{H} with allylamine which had been reported in the previous paper (Chuanjian, Ruifang, & Shengyu, 2004).

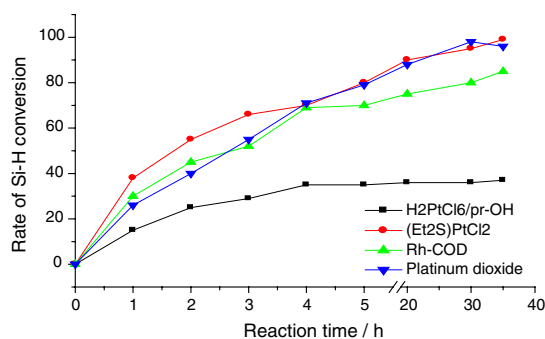


Fig. 1. Capabilities of various catalysts in the hydrosilation of TMS-AAG.

Table 2
silicone oils used by cationic equilibration

Silicone oil (Si Pw/n)	H content wt%	$\overline{M}_n/\text{g mol}^{-1}$ by GPC	$\overline{M}_w/\text{g mol}^{-1}$ by GPC	$M_w/\text{g mol}^{-1}$ by GPC	DC
40/4	0.137	1,800	3,100	2,918	1.7
80/4	0.068	3,020	6,080	5,878	2.0
80/8	0.137	3,290	5,900	5,822	1.8
160/4	0.034	5,190	11,900	11,798	2.3
160/8	0.068	8,400	11,780	11,742	1.4
160/16	0.137	7,220	11,500	11,630	1.6

Capabilities of some catalysts in this experiment were showed in Fig. 1.

From Fig. 1, it can be found that platinum dioxide and $(\text{Et}_2\text{S})\text{PtCl}_2$ are the suitable catalyzers for this kind of unsaturated monomer with amido link, while $\text{H}_2\text{PtCl}_6/\text{pr-OH}$ is inactive to this reaction.

3.1.4. Deprotection

Though trimethylsilyl group is widely used in the protection of hydroxyl groups, it is still difficult to keep conformations of the sugar units during cleaving the trimethylsilyl ether due to the coexisting of multiple functional groups. Three routes were studied in this research such as tetra-*n*-butyl-ammonium fluoride, potassium carbonate/methanol and boron fluoride/ether. Trimethylsilyl ether can be cleaved in dry CH_2Cl_2 in the presence of boron fluoride/ether under nitrogen atmosphere. It was a high selective reagent with a yield of 92%. The possible mechanism of this cleavage process was presented in Scheme 1.

3.2. Molecular aggregates of carbohydrate-modified PDMS

3.2.1. Influence of the polarity of solvent

Various molecular aggregates of $\text{PDMS}_{74}\text{-co-PAAGMS}_4$, which were achieved by adding water into initial polymer solutions in different solvents, were shown in Fig. 2. It can be seen that spherical aggregations are the main forms, when the initiative percentage concentration ranges from 0.5% to 3.0% (mass fraction) and the solvent is DMF. The diameters of sphere are 25–50 nm. It can be deduced from the composition of carbohydrate-modified PDMS that the hydrophobic PDMS is inside the sphere micelles while the surfaces contain hydrophilic sugar units. When the same polymer is dissolved in tetrahydrofuran (THF)/DMF (mass ratio 1:1) and the initial solvent (1.0–3.0, wt%) is added into water, rod-like micelles are the main forms, and the size of the rods is bigger than that of sphere micelles. When only THF is used as initiative solvent (1.5–4, wt%), the vesicles can be observed as the main forms. The diameters of cores are 80–120 nm and the thickness of the corona is 20–30 nm. Moreover, a small amount of spheres and rods remain the same. The rod-like micelles are the transitional forms during the transformation from sphere to vesicle.

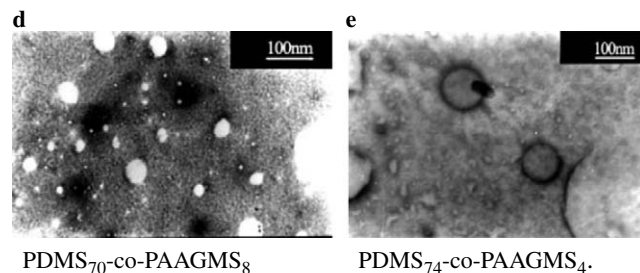


Fig. 3. TEM pictures of crew-cut aggregate of different PDMS-co-PAAGMS.

3.2.2. Influence of composition of polymer

By changing the composition of the carbohydrate-modified PDMS, the molecular aggregations can be transformed from spheres to vesicles in the same cosolvent, which are shown in Fig. 3. When THF is used as an initial solvent and the solution's mass concentration is 2.5 wt%, different "crew-cut" aggregates can be obtained from $\text{PDMS}_{70}\text{-co-PAAGMS}_8$ and $\text{PDMS}_{74}\text{-co-PAAGMS}_4$. The former copolymers (AAG content 10%) mainly form spheres, while the latter (AAG content 2.5%) results in vesicle micelles. With decreasing content of AAG segments, the morphology of the copolymer in solution changes from sphere to vesicle. When THF/DMF (mass ratio 1:1) is used as initial solvent, $\text{PDMS}_{150}\text{-co-PAAGMS}_8$ (AAG content 5.0%) in the solution is in forms of vesicles, while $\text{PDMS}_{34}\text{-co-PAAGMS}_4$ (AAG content 10.0%) in the solution presents spherical micelles by further verifying the regularity mentioned above.

4. Conclusions

In summary, the research showed that a kind of carbohydrate-modified PDMS can be easily synthesized by hydrosilation reaction after the hydroxyl groups of AAG were protected by HMDS. It was found that the morphological transition from spheres to vesicles for one specific sweet polysiloxane can be controlled by changing the initial solvent's polarities or changing the content of sugars units. In addition, this kind of novel polymers has interesting potential as functional system, such as surface modifiers or chiral templates. Furthermore, the size of these vesicles should allow us to obtain

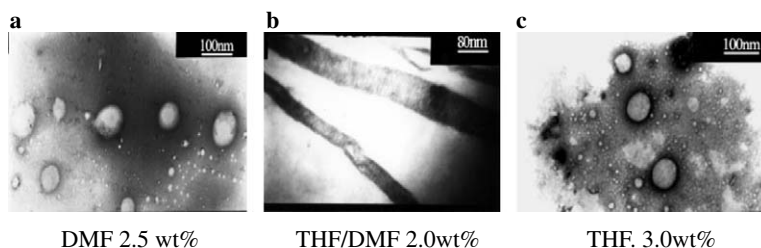


Fig. 2. TEM pictures of $\text{PDMS}_{74}\text{-co-PAAGMS}_4$ in different initial solvents.

micromechanical measurements such as bending modulus and maximal strain, which will be our further research area in the future.

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