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"Chemistry in a spinneret" to fabricate hollow fibers for organic solvent filtration

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ABSTRACT

Organic solvent filtration (OSF) is a very efficient separation technique with high potential in many branches of industry. Currently the choice of the commercial membranes is limited only to a few flat sheet membranes and spiral wound modules. It is generally known that a membrane in hollow fiber form has several advantages, over a flat configuration, such as high surface to volume ratio and no need of spacers. Consequently more compact and simpler modules and easy to scale up can be built.

In this work we explore a new technique called "chemistry in a spinneret", to fabricate a hollow fiber (HF) for OSF. This technique combines the membrane formation and crosslinking reaction into a single step process. P84 polyimide was chosen as a membrane forming polymer and poly(ethylene imine) (PEI), dissolved in the bore liquid, as a crosslinking agent. In order to obtain a membrane with the best stability and low membrane MWCO, the composition of the bore liquid was systematically varied, including solvent/non-solvent ratio and PEI concentration.

The crosslinked membranes have MWCO in the range of $2500-3500 \text{ g mol}^{-1}$ and toluene permeance in the range of $0.2-1.1 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The most stable crosslinked membrane maintains 80% of its mass after 11 days immersion in *N*-methyl-2-pyrrolidinone. Due to crosslinking, the HFs become more hydrophilic and therefore attractive for separations in alcohol systems. Preliminary results are in fact presented here using an ethanol/polyethylene glycol model system.

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1. Introduction

Organic solvent filtration (OSF) is a simple yet effective, separation technique with high potential in many branches of industry. The already reported successful applications are ranging from petrochemistry [1] through pharmaceutical manufacturing [2–6], to catalytic processes [7–9]. The polymeric membranes described in the literature are generally either asymmetric integrally skinned made of polyimides (PI) [10] or thin film composites comprising a poly(dimethylsiloxane) (PDMS) separating layer on a polyacrylonitrile (PAN) [11–18] or PI porous support [19]. The asymmetric integrally skinned PI membranes are usually prepared by phase inversion from solutions in polar aprotic solvents [6]. Consequently this type of membranes cannot be used directly for separations in such solvents (e.g. *N*-methyl pyrrolidone (NMP), di-methyl sulfoxide (DMSO), di-methyl formamide (DMF) or di-methyl acetamide (DMAc)). This limitation can be surmounted by a diamine crosslinking step involving an imide-ring opening reaction [20]. The crosslinking can be accomplished either in post casting process [21] or during phase separation [22].

It is generally accepted that a hollow fiber (HF) membrane has several advantages over a flat sheet membrane. A higher surface to volume ratio of HF membrane enables building of more compact modules. The module design there is simpler since there is no spacer. Besides, scaling up of HF membrane module is easier comparing to the flat membrane configuration. Despite all these advantages there are no such membranes commercially available in the OSF field. The literature is also very scarce on this topic. Some of the first thin film composite HF membranes for OSN were reported by Korikov et al. [23] and Kosaraju and Sirkar [24]. These membranes were prepared by interfacial polymerization and successfully applied for filtration of ethanolic and methanolic solutions. Recently Loh et al. developed polyaniline (PANI) hollow fibers with good stability in dimethyl formamide and acetone [25]. Recently, we reported [26] a new HF fabrication method, called "chemistry in a spinneret", in which membrane formation and crosslinking are integrated into a single step process. By careful control of the interplay between the phase inversion and the chemical crosslinking one can influence the final

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morphology and chemistry of the HF making "chemistry in a spinneret" a very attractive method for preparation of membranes for OSF. Our previous work focused on understanding of membrane formation process and study of gas separations and filtration of proteins in aqueous systems. In this work we explore "chemistry in a spinneret" for fabrication of membranes for OSF. To this end P84 polyimide is used as a membrane forming polymer and poly(ethylene imine) (PEI) as crosslinking agent. The composition of the bore liquid was systematically varied, including solvent/non-solvent ratio and PEI concentration, in order to achieve the best membrane stability and low MWCO. The morphology of all HF membranes was methodically studied using SEM imaging and selected membranes were chosen for permeation experiments (permeance/ MWCO) using a high pressure cross flow set-up.

2. Experimental

2.1. Materials

Evonik Industries P84 polyimide (325 mesh, STD) was purchased from HP Polymer GmbH, Austria. N-methyl-2-pyrrolidinone (NMP, 99% extra pure) was supplied by Acros Organics (Belgium). Poly(ethylene imine) (PEI, $M_{\rm w} \sim 25,000 \text{ g mol}^{-1}$; $M_{\rm n} \sim 10,000 \text{ g mol}^{-1}$; containing 34% primary amines, 40% secondary amines and 26% tertiary amines; water-free) were supplied by Sigma-Aldrich (The Netherlands). Broad molecular weight polystyrene (PS) was synthesized according to procedure described in Ref. [27] and poly(ethylene glycol)'s (PEG) of molecular weights 200, 600, 1500 and 3000 g mol⁻¹ were supplied by Sigma-Aldrich (The Netherlands). Toluene, ethanol and glycerol all of analytical grade, were purchased from Merck (Germany). Technical ethanol and *n*-hexane, used for hollow fibers fabrication, were purchased from Assink Chemie (The Netherlands). Two component epoxy resin Araldite® 2014-1 (Viba, The Netherlands) was used as membrane potting material for membrane module fabrication. All chemicals were used as received without further purification.

2.2. Fabrication of hollow fiber membranes

Nine batches of the hollow fibers named B1-B9 were produced by wet immersion precipitation spinning using a triple orifice spinneret. P84 polyimide was dried overnight at 150 °C. The polymer dope solution was prepared by mixing NMP (66% w/w) with glycerol (10% w/w) in a glass flask followed by addition of P84 powder (24% w/w). The solution was stirred for 48 h at 55 °C, next it was filtered through a 15 µm mesh Bekipor ST 15 AL 3 metal filter (Bekaert) at 60 °C and kept in the spinning tank at 55 °C for 48 h for degassing. Before spinning the polymer solution was cooled down to 22 °C. Both bore and shell liquids were stirred continuously at room temperature for 24 h and left for degassing for 12 h. Coagulation bath (external coagulant) was filled up with tap water at room temperature. The dope and shell liquids compositions and spinning process parameters were kept constant and only the bore liquid composition was varied (for details see Table 1). The dope solution, the bore and shell liquids were simultaneously extruded through a triple spinneret. The extruded fiber, after a brief residence in the air gap, was immersed in a coagulation bath. The take-up velocity was regulated by a pulling wheel, rotating at an adjustable speed. The collected fiber was cut into approximately one meter long pieces and immersed in a flowing water bath for 72 h to remove residual solvents and excess of crosslinking agent. In order to prevent pore collapse upon drying the fibers were first immersed in ethanol for 24 h, next in *n*-hexane for 24 h and finally dried in the air at ambient conditions.

Table 1

IV	lembrane	preparation	parameters.	

Polymer dope: 24% (w/w) P84, 10% (w/w) glycerol, 66% (w/w) NMP Shell liquid: 75% (w/w) NMP, 25% (w/w) distilled water External coagulant: tap water						
Fibers	Bore l	iquid (%) (w/w)	Bore liquid NMP/		
	PEI	NMP	Water	water		
B1	20	68.5	11.5	6/1		
B2	20	66.7	13.3	5/1		
B3	20	64	16	4/1		
B4	20	60	20	3/1		
B5	20	57.1	22.9	2.5/1		
B6	20	53.3	26.7	2/1		
P7	20	40	40	1/1		

В/	20	40	40	1/1
B8	23	51.3	25.8	2/1
B9	15	63.8	21.3	3/1
Spinning parameters	Dope so speed	olution	ml/min	3.0
	Bore liquid speed		ml/min	1.4
	Shell lic speed	quid	ml/min	0.8
	Air gap	length	cm	2.5
	Take-up	o speed	m/min	2.2
	Temper	ature	°C	22
	Humidi	tv	%	40

2.3. Scanning electron microscopy

The HF were fractured in liquid nitrogen and mounted onto holders. After drying in a vacuum oven at 30 °C for 12 h, the samples were sputtered with gold (4 min, 13 mA) using a Blazers Union SCD 040 sputtering device. SEM images of the spun HF membranes were made using Jeol JSM5600LV scanning electron microscope (SEM) at a 5 kV accelerating voltage and working distance of 24 mm.

2.4. Module preparation and filtration experiments

Each module contained two randomly selected fibers (33 cm each) potted with Araldite epoxy resin. The resin was allowed to set for at least 24 h before the module was used for filtration. The permeation experiments were performed in a custom made cross-flow set-up in a total recycle mode. The detailed description of the filtration set up can be found elsewhere [27]. In order to ensure fully turbulent flow (Re \approx 11,700) and consequently minimize effects of concentration polarization, all measurements were performed at high cross-flow velocity of about 10 m s⁻¹. Before the first permeation measurement, each new membrane was pre-compacted for 4 h at 20 bar without permeate being collected. Prior to the first measurement, the system was stabilized at a desired pressure for 2 h. The toluene permeation was performed in the order 5, 10, 20, 15 and then 7.5 bar. In the case of ethanol the order was 20, 15, 10 and 5 bar. The permeance of membranes (P, $1 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) was calculated from the slope of the flux versus trans membrane pressure (TMP) plot.

2.5. Molecular weight cut-off (MWCO) measurements

The MWCO reported in this work was obtained from filtration experiments at 7.5 bar using PS in toluene (0.3% w/w, MW 300–15,000 g mol⁻¹) and PEG in ethanol solutions (0.3% w/w, MW 100–4000 g mol⁻¹) (Fig. 1).

For all collected PEG/ethanol samples a solvent swap was performed; ethanol was evaporated and exchanged for a mobile aqueous phase (aq. 0.05 M NaNO₃ and 0.05 g l^{-1} NaN₃). All samples of oligomers were analyzed using an Agilent Technologies 1200 Series GPC system with a Shodex RI-71 refractive index detector. For



Fig. 1. Chemical structures of (a) polystyrene, PS and (b) poly (ethylene glycol), PEG.



Fig. 2. FTIR spectra of P84 hollow fiber membranes (non-crosslinked and crosslinked).

PS separation a PSS SDV 1000 Å column and toluene as a mobile phase were used. For the PEG analysis, two PSS Suprema 100 Å columns were used. The mobile phase was aqueous solution of NaNO₃ (0.05 M) and NaN₃ (0.05 g l^{-1}). The detailed analysis

of PEG oligomers was done following the procedure described by Dalwani et al. [28].

2.6. Mass loss experiments

The stability of the crosslinked fibers in NMP was evaluated by quantitative mass loss analysis. Six fibers were used from each batch. Pieces of 5 cm pieces were cut from the middle of each fiber and dried in a vacuum oven at 150 °C for 24 h to remove water. Then, the samples were left in a desiccator to cool down and the weight of each fiber was obtained using analytical balance (Mettler Toledo AE240). After that, the samples were separately immersed in NMP for eleven days. The residual samples were rinsed first in water for 24 h and afterwards in ethanol for 5 days. After drying in a vacuum oven at 150 °C for 3 days, the samples were weighed again and the mass loss was calculated.

2.7. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

Changes between the crosslinked and non-crosslinked P84 membranes were analyzed using a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with universal ATR polarization accessory. The samples of crosslinked P84, were prepared by removing non-crosslinked part of a membrane in NMP followed by rinsing in water and ethanol. A P84 powder was used as the non-crosslinked samples. All samples before measurements were dried in a vacuum oven at 30 °C for 12 h. The FT-IR spectra were recorded over a scanning range of $650-4000 \text{ cm}^{-1}$ with a resolution of 1.0 cm⁻¹ at room temperature. The changes of typical imide and amide bands were used to identify the changes in polymer structure [22].

2.8. Contact angle measurements

In order to investigate influence of PEI crosslinking on the membrane hydrophilicity, water contact angles were measured. For



Crosslinked P84

this, flat membranes of non-crosslinked P84 membranes were prepared by casting the dope solution (24% w/w P84, 10% w/w glycerol. 66% w/w NMP) onto a silicon wafer followed by immediate immersion into a water bath at room temperature. The flat crosslinked P84 membranes were obtained by immersion of the cast polymer in a bath containing the bore liquid for preparation of B4 fiber (20% PEI, NMP/water = 3/1) for 30 s, followed by immersion in a water bath. After precipitation, the 200 μ m-thick membranes were kept in running water bath for 72 h to remove any residual solvents and excess of PEI. The membranes were then rinsed with Millipore water and air-dried. Prior to contact angle measurements, the membranes were kept in a vacuum oven at 30 °C for 2 h. The static contact angle measurements were performed on a Dataphysics contact angle system OCA 20 at room temperature. For this, 10 µl of deionized water droplets were placed onto the membrane surface by a computer controlled syringe. After 5 s, contact angle of the water drop was recorded and analyzed using SCA20 software. Measurements were repeated eight to ten times for every membrane.

3. Results and discussion

3.1. The formation of crosslinked P84

Fig. 2 shows the normalized, to the highest peak, FTIR spectra for the crosslinked and non-crosslinked P84. FTIR spectrum was recorded for each batch of HF. Since no significant difference in spectra among the crosslinked HF samples was observed, Fig. 2 presents spectrum of B6 as an example. For crosslinked P84 membrane, the typical imide peaks at 1778 cm⁻¹ (symmetric C=O stretching) and 1714 cm⁻¹ (asymmetric C=O stretching) decrease in comparison to non-crosslinked P84. Besides the typical amide peaks, a result of crosslinking reaction between P84 and PEI is increase of the peaks at 1655 cm⁻¹ (C=O stretching) and 1536 cm⁻¹ (C–N stretching). These results indicate that crosslinking reaction between imide groups of P84 and amine groups of PEI occurs, resulting in amide bonds formation (see in Fig. 3 the proposed crosslinked mechanism).

3.2. Water contact angle measurement

The water contact angle of non-crosslinked and crosslinked P84 membranes are $75 \pm 1^{\circ}$ and $61 \pm 2^{\circ}$, respectively, showing that crosslinking results in more hydrophilic membrane. This is probably due to the free amine groups (secondary and tertiary) of PEI introduced during crosslinking (see Fig. 3). As shown in Fig. 3, crosslinking reaction occurs between carbonyl groups of P84 imide ring and primary ($-NH_2$) or secondary (=NH) amine groups of PEI, resulting in the formation of amide bonds (NH-C=O). It seems that due to less steric hindrance, reaction of primary amine groups with an imide ring is preferable. These free amine groups besides increasing hydrophilicity of the membrane, also introduce positive charge at the membrane surface [26].

3.3. Organic solvent filtration hollow fibers fabrication and optimization

Fig. 4 shows the morphology of the produced HF and Table 2 presents the results of their characterization. All fibers have rather spongy, macrovoid free structure (Fig. 4a) with a well centered bore. The surface of the selective layer in case of fibers with high NMP/ water ratio (B1–B2) is smoother than that with low NMP concentration (B6–B7). The fibers where high NMP concentration in bore liquid was used (B1–B3), have two distinct layers: a dense inner layer and a porous sponge substructure. With decrease of NMP

concentration, the thickness of the inner dense layer decreases and already at the NMP/water ratio 3:1 it seems that the fiber is completely porous (Fig. 4, B4). The fibers B1, B2 and B3 dissolve almost completely in NMP (see mass loss, Table 2), leaving only a thin gellike green inner layer, suggesting that only this thin inner layer is crosslinked. Similar observations on the influence of NMP /water ratio in the bore liquid on the morphology of P84 – PEI crosslinked HF was recently demonstrated by Kopeć et al. [26]. They report that, the membrane formation on the bore side is controlled by the interplay of crosslinking and the phase separation. If the phase separation occurs faster than crosslinking, a porous structure is formed. If crosslinking is faster than phase separation, a dense inner layer is



Fig. 4. SEM images of all spun hollow fibers: (a) cross section of the inner selective layer, (b) surface of inner selective layer.





Fig. 4 (continued)

formed. On the shell side, the structure formation is a result of only phase inversion. The thickness of the inner dense layer is determined by the diffusion rate of these two fronts, coagulation from the outside and crosslinking from the inside of the fiber. The formation and the growth of the dense inner layer, stop at the point where these two fronts meet. In fact, a high NMP/water ratio in bore liquid generally results in a membrane structure with thin, crosslinked,

Table 2		
Characterization	of hollow	fibers.

dense inner layer, whereas a low NMP/water ratio results in a porous more crosslinked fiber. As the NMP/water ratio in the bore liquid decreases, phase inversion occurs faster. Consequently, the dense layer is not formed because the crosslinking reaction between PEI and unsolidified P84 becomes slow compared to coagulation. The porous inner layer does not hinder further PEI diffusion into already solidified porous polymer matrix and crosslinking reaction can still proceed. This secondary crosslinking is much slower, as reported by Vanherck et al. [22] and seems to have no impact on membrane morphology. Table 2 shows that, as NMP/water ratio decreases, generally the fibers become more porous (B6 and B7 are permeable for toluene) and better crosslinked (lower mass loss in NMP). It seems that the more porous the inner layer is the higher diffusion rate of PEI through the fiber wall and thus better crosslinking. After phase inversion and until the bore liquid is fully washed away from the fiber, diffusion of PEI through the crosslinked laver and hence secondary crosslinking may be possible. This might explain very good crosslinking of B6 (longer contact time with PEI in the washing bath). The clean toluene permeance of this fiber was 1.5 ± $0.1 \text{ Im}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, in the order of magnitude expected for nanofiltration membranes. However, measurement using PS/toluene solution show that its MWCO is around 3300 g mol⁻¹ (see Fig. 5). Interestingly, when the NMP/water ratio is raised to 2.5:1 the membrane becomes denser concerning permeance $(0.5 \pm$ $0.3 \ l \ m^{-2} \ h^{-1} \ bar^{-1})$ but its MWCO stays around 3300 g mol⁻¹ (see Fig. 5 and Table 3). It seems that in this case, the increase of NMP content in the bore liquid does not influence significantly the pore size distribution but results in decrease of the separation layer porosity. The MWCO of the crosslinked membrane decreases to 2500 g mol⁻¹ and its permeance to 0.2 \pm 0.1 l m $^{-2}$ h $^{-1}$ bar $^{-1}$ when 23% w/w PEI in the bore liquid is applied (fiber B8 in Fig. 5 and Table 3). In this case, it seems that both porosity and the average pore size of the membranes decrease and as a result lower crosslinking occurs (fiber B8 has higher mass loss $(43 \pm 6\% \text{ w/w})$ compared to B6 $(20 \pm 3\% \text{ w/w})$ w)). Finally, using lower PEI concentration in bore liquid slows down crosslinking leading to a more open membrane structure. In fact, the B9 membrane with NMP/water ratio 3:1 and 15% w/w of PEI has relatively high toluene/PS permeance of $1.1 \, \text{l} \, \text{m}^{-2} \, \text{h}^{-1} \, \text{bar}^{-1}$ (Fig. 5a). however its MWCO remains around 3300 g mol⁻¹ (Fig. 5b). There, PEI diffusion into polymer matrix is rapid and somewhat better crosslinking is achieved (mass loss of B9 fiber is around 61% and lower than that of B4 (83%, see Table 2).

3.4. Membrane performance in ethanol

Due to increased hydrophilicity of the crosslinked membranes, performance of two selected HF (B5 and B8) in a polar system was evaluated. As a model solvent ethanol was chosen because of its wide use in purification processes such as in food industry

HFcode	NMP:H ₂ O in bore liquid	PEI in bore liquid (%) (w/w)	Layer(s) (SEM)	Mass loss (%)	Permeance of toluene	Toluene/PS	
					(l m ⁻² h ⁻¹ bar ⁻¹)	Permeance $(1 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1})$	$\frac{MWCO}{(g mol^{-1})}$
B1	6:1	20	2	99 ± 0	0 ^a	n.m	n.m
B2	5:1	20	2	98 ± 2	0 ^a	n.m	n.m
B3	4:1	20	2	98 ± 1	0 ^a	n.m	n.m
B4	3:1	20	1	83 ± 1	0 ^a	n.m	n.m
B5	2.5:1	20	1	74 ± 3	n.m	0.5 ± 0.3	3300
B6	2:1	20	1	20 ± 3	1.5 ± 0.1	0.9 ± 0.2	3300
B7	1:1	20	1	64 ± 8	24.5 ± 1	n.m	n.m
B8	2:1	23	1	43 ± 6	n.m	0.2 ± 0.1	2500
B9	3:1	15	1	61 ± 4	n.m	1.1 ± 0.3	3300

n.m. - Not measured.

^a No toluene permeation observed at 30 bar over 8 h.



Fig. 5. HF membranes B6, B5, B9 and B8: (a) Flux of PS/toluene as a function of TMP, (b) PS retention at 7.5 bar.

Table 3

Comparison of the performances B5 and B8 fibers in $\ensuremath{\mathsf{EtOH}/\mathsf{PEG}}$ and toluene/PS systems.

	HF membrane System	B5		B8		
		Permeance $(l m^{-2} h^{-1} bar^{-1})$	Retention at 3300 g mol ⁻¹ (%)	Permeance $(l m^{-2} h^{-1} bar^{-1})$	Retention at 2500 g mol ⁻¹ (%)	
	Toluene/ PS	0.5 ± 0.3	90** (PS)	0.2 ± 0.1	90** (PS)	
	Ethanol/ PEG	13.9 ± 0.8	23* (PEG)	16.0 ± 0.9	14 [*] (PEG)	
	Ethanol	14.6 ± 0.2	-	17.2 ± 1.6	-	

* Obtained at 5 bar; no rejection at higher pressures.

** Obtained as the average of permeation at 7.5 and 15 bar.

for extraction of oils and valuable bio-active compounds from raw plant materials, xanthophylls from corn and polyphenols from green tea [6] and as a substitute extractant for other organic solvents, e.g. hexane [29]. Poly(ethylene glycol) (PEG) was selected as a model solute, since it is polar and hydrophilic. The MW range of PEG was restricted up to 4000 g mol⁻¹ due to limitation in solubility of higher fractions in pure ethanol [30].

Fig. 6a presents transport of ethanol and PEG/ethanol mixtures for those HF. The linear relation between flux and trans membrane pressure indicates that there is no membrane compaction within



Fig. 6. (a) Clean EtOH and EtOH/PEG permeance and (b) PEG rejection of B5 and B8 fibers.

this pressure range. For both membranes, the permeance of pure ethanol and PEG/ethanol are also very similar, indicating that there is no significant effect of concentration polarization. For both membranes the permeance of PEG/ethanol is very high in comparison to toluene/PS mixture, probably due to membrane hydrophilicity (see Table 3). The PEG retention however for both membranes is low, 14–23% over the whole studied MW range (300–4000 g mol⁻¹) (Fig. 6b). This may be due to higher interaction of the hydrophilic crosslinked membrane with ethanol causing membrane swelling and/or due to the shape of the PEG molecule itself. PEG has a linear structure and small chain diameter (see Fig. 1). This makes PEG flexible, easy to deform and to fit into smaller pores whereas the more rigid and bulky polystyrene due to the presence of benzene rings in its chain [31] may have higher retention.

4. Conclusions

In this study the concept of "chemistry in a spinneret" was explored towards fabrication of HF membranes for OSF. The HF were prepared using P84 polyimide as a base polymer and poly(ethylene imine) (PEI) as crosslinking agent. The interplay between crosslinking and the phase inversion during spinning process was studied by varying systematically the composition of bore liquid, i.e. (PEI), NMP and water concentrations. In general, the prepared HF membranes have MWCO (measured in the polystyrene/toluene system) in the range 2500-3500 g mol⁻¹ whereas toluene permeances are relatively low; ranging from 0.2 to $1.1 \, \mathrm{lm^{-2} \, h^{-1} \, bar^{-1}}$. The membranes are partially stable in *N*-methyl-2-pyrrolidinone (NMP), the most stable one maintains 80% of its mass after 11 days immersion in NMP. Due to crosslinking, the HFs become more hydrophilic and therefore have high ethanol/PEG permeance and low PEG retention. Future research in this field should focus on the development and characterization of P84/PEI membranes for polar organic solvents.

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