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Polyaniline and polypyrrole prepared in the presence of surfactants: a comparative conductivity study

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Abstract

Polyaniline and polypyrrole have been prepared by chemical oxidative polymerization of the corresponding monomers in an aqueous medium containing an anionic surfactant—sodium bis(2-ethylhexyl) sulfosuccinate, dodecylbenzenesulfonic acid and its sodium salt, and sodium dodecyl sulfate. Determination of the yield, elemental composition and density proved, and FTIR spectroscopy confirmed, that the anionic surfactants become incorporated in the conducting polymers. The polymerizations in the presence of a cationic surfactant, tetradecyltrimethylammonium bromide, were carried out for comparison. While the conductivity of polypyrrole became enhanced after the introduction of an anionic surfactant, the changes in the conductivity of polyaniline were marginal. The conductivity changes in both polymers during thermal ageing were measured at 175 °C. The electrical stability of polyaniline was better than that of polypyrrole. The presence of a surfactant improved the stability of conductivity of polypyrrole but reduced the electrical stability of polyaniline.

Keywords: Conducting polymer; Polypyrrole; Polyaniline

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1. Introduction

Surfactants have been used as additives in the polymerization of aniline and pyrrole for two reasons: (1) to affect the locus of polymerization by using the emulsion [1,2] or inverse emulsion [3–5] pathways, and thus to modify the molecular and supramolecular structure of the resulting polymers, and (2) to improve the properties of the polymers with respect to conductivity, stability, solubility in organic solvents, and processibility. The latter approach implicitly expects that a surfactant becomes incorporated into a conducting polymer.

The surfactants affect the preparation of conducting polymers, like polyaniline (PANI) and polypyrrole (PPy), in three ways: (1) the presence of surfactant micelles controls the distribution of the reactants between the micellar and aqueous phases, thus altering the locus and the course of polymerization [3,6], (2) anionic surfactants may act as counterions for conducting-polymer polycations, and (3) the hydrophobic part of the surfactant molecules may adsorb on the produced conducting polymer, a surfactant thus becoming a part of the resulting material. The surfactants used in these studies of the conducting polymers were mainly of the anionic type, and both the acids and their salts have been used. The acids are represented by dodecylbenzenesulfonic acid [7–13] and naphthalenesulfonic acid and its substituted derivatives [1,14–18], while typical salts are sodium dodecylbenzenesulfonate [7,19–23] and sodium dodecyl sulfate [4,5]. Papers investigating the role of non-ionic surfactants, e.g. those based on poly(ethylene oxide), are less frequent [24,25] and those dealing with cationic types are rare [3,23].

The presence of surfactants improves the colloidal solubility of conducting polymers in organic solvents [15,16,18] and, consequently, also the processibility [6, 26]. The production of nanocolloidal forms has been a frequent goal. Here, most success was achieved with PANI, when its synthesis had been carried out in the

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presence of an acid, such as dodecylbenzenesulfonic acid [8,10,12,13], and surfactants of cationic type like hexadecyltrimethylammonium bromide [3]. There are only a few reports on the formation of colloidal PPy stabilized with surfactants [27,28]. The occurrence of non-spherical morphologies in the presence of surfactants, like nanowires and nanotubes, has been observed for both PANI [17,23,29] and PPy [16].

It had been reported in the literature that the introduction of a surfactant during the preparation of PANI and PPy leads to an increase in the conductivity [5,19]. Wan et al. [16] claimed a conductivity of 27 S cm^{-1} for PPy prepared in the presence of 2-naphthalenesulfonic acid, while PANI prepared under the same conditions had a conductivity of 4 S cm^{-1}. A conductivity exceeding 100 S cm^{-1} was found for films prepared from PANI in combination with a surfactant [1,15,30]. Kudoh [19] obtained PPy having a conductivity as high as 40 S cm^{-1} when the polymerization was carried out in the presence of sodium alkylsulfonate, the result being strongly dependent on the oxidant used. In a preceding study [25], we have also noticed that PPy prepared in the presence of various surfactants had enhanced conductivity which, however, had never exceeded 10 S cm^{-1}. The introduction of a hydrophobic component into the conducting material is expected to reduce the sensitivity of conducting polymers to moisture and against subsequent hydrolysis and deprotonation. An increase in the thermal stability of conductivity may be anticipated and is indeed observed [19,25]. On the other hand, the sensitivity of electric response towards vapours of organic compounds may be conveniently used in the design of sensors and actuators [22].

It has recently been shown that anionic surfactants become incorporated in PPy, while cationic and non-ionic surfactants affect the properties of PPy prepared in their presence only marginally [25]. Such behaviour is understood because surfactants of the anionic type act as counterions for the PPy polycation. We have therefore decided to prepare PANI and PPy in media containing various anionic surfactants and to check (a) whether the anionic surfactants interact with both polymers and, in a positive case, (b) if this fact is reflected in the improved level of conduction and the thermal stability of conductivity as reported in the literature for PPy [19]. This study concentrates preferentially on PANI and on a comparison of its conductivity with PPy prepared under similar conditions.

2. Experimental

2.1. Preparation of polyaniline

Aniline hydrochloride (purum, Fluka; 2.59 g, 20 mmol) and a surfactant (2 g) were dispersed in water to 50 ml. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT; Fluka), dodecylbenzenesulfonic acid (DBSA; Fluka), sodium dodecylbenzenesulfonate (DBSNa; Fluka), sodium dodecylsulfate (SDS; Aldrich) and tetradecyltrimethylammonium bromide (TTAB; Sigma) have been used as surfactants in the preparation of both PANI and PPy. Ultrasonic treatment was used when a precipitate was formed after mixing the monomer and the surfactant. Ammonium peroxydisulfate (purum, Fluka; 5.71 g, 25 mmol) was dissolved in water also to 50 ml of solution. Both parts of the reaction medium were then mixed in a beaker, briefly stirred, and left at rest to polymerize. The course of exothermic polymerization was monitored by measuring the temperature of the reaction mixture [31]. Next day, the PANI precipitate was collected on a filter, washed 3 times with 100 ml portions of 0.2 M HCl, and similarly with acetone. The green PANI (emeraldine) powder was dried in air and then in vacuo at 60 °C.

2.2. Synthesis of polypyrrole

Pyrrole (Merck-Schuchardt) was distilled under reduced pressure and stored in a refrigerator at about 4 °C before use. An oxidant, anhydrous ferric sulfate (Merck; 16.2 g, 0.1 mol) and 0.01 mol of surfactant, if added, were dissolved in 200 ml of distilled water in a reaction vessel containing a magnetic stirring bar. Pyrrole (0.05 mol, 3.45 ml) was dispersed in 50 ml of water and then added dropwise into the stirred oxidant solution. The reaction was carried out for 4 h at room temperature with moderate stirring. The precipitated PPy was filtered off and washed with distilled water. The black PPy powder was dried in vacuo at 60 °C for 8 h.

2.3. Conductivity measurement and thermal ageing at 175 °C

Polymers were compressed into pellets, 13 mm in diameter and about 1 mm thick, and the conductivity was measured by the four-point method using a current source Keithley 238, a scanner Keithley 706 with switching cards, and a Solartron-Schlumberger 7081 Precision Voltmeter. The sample holder was placed in a chamber Heraeus–Vötsch VMT 07/35 operating with a temperature stability of ± 1 °C. The atmosphere in the chamber had a low humidity. Measurements of the conductivity were made simultaneously with four pellets. The temperature of the pellets, recorded with a thermocouple and a digital multimeter Keithley 195A DMM, was checked before and after each conductivity reading. The energy dissipated in the sample during measurement was kept as low as possible in order not to elevate the temperature of the sample due to Joule heating.

The temperature of the sample was elevated during 2–3 h from 16 to 175 °C. Then the ageing time was set to zero and the conductivity was recorded at the latter temperature as a function of time. The temperature of 175 °C was selected so that the ultimate loss of the conductivity of most samples took place within the 500 h allocated for the experiment.

2.4. FTIR spectra and density

Infra-red spectra were taken with a Nicolet IMPACT 400 FTIR spectrometer in a moisture-purged environment. All spectra in the range of 400–4000 cm^{-1} with a 2 cm^{-1} resolution were obtained from compressed KBr pellets in which PPy and PANI powders were dispersed. Two hundred scans were recorded for each FTIR spectrum. The Archimedes method based on weighing of polymer pellets prepared for the conductivity measurements in air and in decane at 20 °C with a Sartorius Research R16P balance was used to determine the densities.

3. Results and discussion

3.1. The course of polymerization

The fact the PANI constitutional units are able to interact with anionic surfactants is already indicated at monomer level. When aniline and surfactant solutions are mixed, a bulk precipitate forms. This means that the sulfoxy group of the surfactant had reacted with the anilinium cation to produce an insoluble salt. After some time, reduced by ultrasonic treatment, the suspension converts to a milky emulsion.

All syntheses produced polymer precipitates and the formation of colloids has not been observed except for the polymerization of aniline in the presence of DBSA, which afforded a partly colloidal form of PANI.DBSA, currently reported in the literature especially at higher surfactant concentrations [8,12].

Han et al. [13] observed that the aniline polymerization was faster in the presence of DBSA and attributed this fact to the increased acidity of the medium. Also, Kudoh [19] noted that the oxidation of pyrrole proceeds faster in the presence of anionic surfactants. On the other hand, Gill et al. [20] reported the retardation of aniline polymerization when DBSNa was added to reaction mixture. Our results indicate that the effect of the presence of SDS, DBSA and DBSNa on the rate of PANI formation is marginal (Fig. 1). A reaction mixture containing aniline hydrochloride is obviously sufficiently acidic to mask the higher acidity provided by DBSA compared with DBSNa. Retardation has been observed with AOT, possibly as a consequence of the limited miscibility of monomer and surfactant solutions. The presence of the cationic surfactant, TTAB, on the contrary, provided acceleration on aniline oxidation. Xia and Wang [3] have also noted the faster oxidation of aniline in the presence of the cationic surfactant, hexadecyltrimetylammonium bromide. This means that the role of the surfactants in the progress of aniline polymerization is not completely understood and a future systematic study of the reaction kinetics would be desirable.

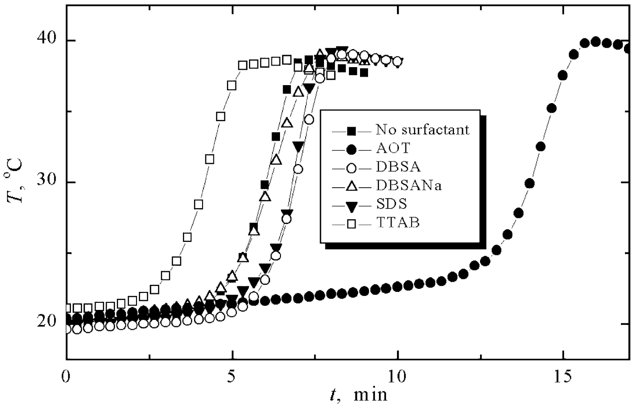

Fig. 1. Temperature profile of the exothermic oxidation of aniline in the presence of various surfactants. 0.2 M aniline hydrochloride, 0.25 M ammonium peroxydisulfate, 2 wt% surfactant. Mixing the solutions of reactants at 20 °C started the reaction.

3.2. Incorporation of anionic surfactants

Organic compounds that act as anionic surfactants in the polymerization of aniline and pyrrole can be divided from the formal point of view into two groups: (1) acids, like DBSA [7–10,12,13] or 2-naphthalenesulfonic acid [16], and (2) classic surfactant salts, like DBSNa [7,19] and SDS [4,19]. The presence of acids provides sufficient acidity in the medium and conditions suitable for the efficient of protonation of conducting polymers. The interaction of surfactant salts with polymers is expected to be more complex, because some acid is usually added [4] to convert aniline to the anilinium cation and to maintain the acidic reaction of the mixture needed for the production of conducting polymer.

The incorporation of a bulky surfactant anion into both PANI and PPy is demonstrated by the increase in the polymer yield. The yield is more than two times higher in the presence anionic surfactant compared with the case when the polymerization has been carried out in its absence (Table 1). Higher PPy yields, indicating the incorporation of the anionic surfactant, have been reported in the literature [9,19]. Also, Ichinohe [6] observed a considerably higher yield of PANI when the polymerization was carried out at the presence of anionic surfactant, and concluded that the surfactant becomes a part of the product.

On the other hand, the introduction of a cationic surfactant into the reaction mixture led to only a marginal increase in the mass of the produced PANI (Table 1). This means that the ionic interaction between the polycations and the surfactant moiety during polymerization is crucial for the incorporation of the surfactant into the polymer product. The cationic surfactant even inhibited the polymerization of pyrrole (Table 1).

Further support for the presence of surfactants in the

Table 1
The yield of conducting polymers and density of PANI at 20 °C

Surfactant	Yield (g per g of monomer)		Density (g cm^{-3})
	PANI	PPy	PANI
None	0.82[a]	0.52[b]	1.33
AOT	1.63	1.54	1.23
DBSA	1.97	1.17	1.20
DBSNa	1.69	1.51	1.19
SDS	1.57	1.27	1.18
TTAB[c]	1.06	0.14	1.31

[a] Stoichiometric expectation at 100% conversion of 1 g aniline hydrochloride is 0.84 g PANI hydrochloride. Data taken from Ref. [31].

[b] Polypyrrole sulfate.

[c] The only cationic surfactant used for the comparison with anionic surfactants.

products comes from the density measurements. It is expected that the incorporation of the bulky surfactant anion containing a hydrocarbon chain into the rigid-chain nitrogen-containing polymer would reduce the density, compared with the inorganic counterions. This is indeed well documented for PANI (Table 1). The change in the density is negligible in the case of TTAB, indicating that the content of cationic surfactant in the product is low, if any. The density of PPy could not be determined in a similar manner, because the compressed PPy pellets partially swell in decane and other solvents used in the Archimedes method.

Finally, the presence of anionic surfactants in the products is documented by the reduced content of nitrogen with both PANI and PPy (Table 2). Also, the higher content of sulfur corresponding to sulfoxy group in surfactants provides the same indication in the case of PANI. In PPy, the sulfur content also reflects the presence of sulfate counterions that are derived from the ferric sulfate used as an oxidant.

Table 2
Elemental composition (wt%) of polyanilines and polypyrroles prepared in the presence of surfactants

Surfactant	C	H	N	S
Polyanilines				
None[a]	59.7	4.9	10.6	1.0
AOT	57.9	4.9	7.7	4.9
DBSA	64.6	6.9	7.5	4.3
DBSNa	64.3	6.9	7.5	4.2
SDS	62.3	7.0	8.0	4.8
TTAB[b]	55.6	4.6	10.4	3.8
Polypyrroles				
None[c]	50.6	3.3	14.5	5.0
AOT	60.7	7.5	6.5	5.7
DBSA	65.7	7.1	7.4	5.2
DBSNa	64.4	7.4	6.0	5.7
SDS	62.3	7.2	7.5	5.5
TTAB[b]	52.4	3.2	14.8	3.9

[a] Polyaniline hydrochloride [31].

[b] The only cationic surfactant used for comparison.

[c] Polypyrrole sulfate.

The presence of anionic surfactant in the products is also confirmed by a comparison of the infrared spectra of PANI hydrochloride and PPy sulfate prepared in the presence and absence of a surfactant (Fig. 2). The peaks at about 1036 and 1011 cm^{-1} belonging to neat DBSNa are observed also in the spectra of polymers prepared in presence of this surfactant. A slight red shift of these peaks by comparison with their position in the spectrum of neat surfactant (at about 1041 and 1015 cm^{-1}) illustrates a more intimate interaction between the polymers and DBSNa.

3.3. Conductivity and thermal stability of conductivity

There is no significant effect of the presence of a surfactant on the conductivity of PANI (Table 3). The conductivities only differ within the experimental error; in the repeated preparations of PANI hydrochlorides the conductivity of the samples was 4.4 ± 1.7 S cm^{-1} [31]. On the contrary, with PPy, the positive effect of an anionic surfactant on the conductivity is marked (Table 3). It has to be noted that this is rather due to the poor conductivity of PPy sulfate prepared in the absence of surfactants. Kudoh [19] reported a higher conductivity of 1.3 S cm^{-1} for PPy prepared under similar conditions with the same oxidant.

The surfactant, if incorporated into conducting polymer, is likely to affect the thermal stability of conductivity. If large surfactant counterions constituted a part of the polymer, such materials might be less prone towards deprotonation and their electrical stability at thermal ageing might be thus improved. Rao et al. [4] found that the thermogravimetric stability of PANI was better when SDS was included in the reaction mixture and our results have indicated similar trends with PPy [25].

The annealing of the polymers at 175 °C demonstrates that the conductivity stability of PANI is higher than that of PPy. Over a period of about 1 day, the conductivity of

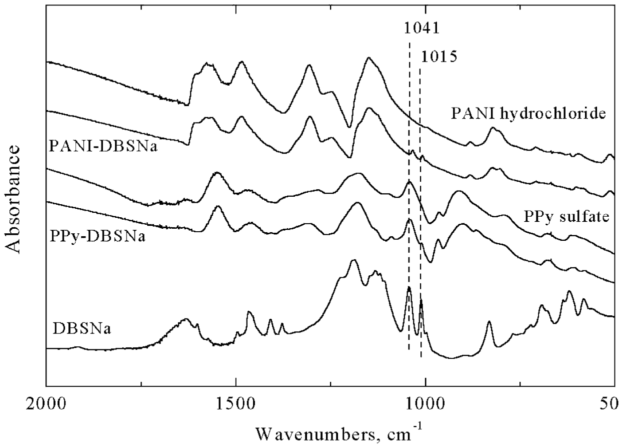

Fig. 2. Infrared spectra of polyaniline hydrochloride and polypyrrole sulfate prepared in the absence and in the presence of DBSNa, and the spectrum of neat DBSNa.

Table 3
Conductivity at 20 °C, σ, and relative conductivity decrease, σ_t/σ_0, measured at 175 °C after time $t = 5$, 25 and 125 h

Surfactant	σ (S cm^{-1})	σ_5/σ_0	σ_{25}/σ_0	σ_{125}/σ_0
Polyanilines				
None[a]	4.4	0.56	0.24	3.4×10^{-2}
AOT	2.1	0.18	[b]	[b]
DBSA	5.9	0.52	9.4×10^{-2}	2.5×10^{-4}
DBSNa	1.7	0.22	1.2×10^{-2}	1.8×10^{-4}
SDS	3.3	0.30	1.1×10^{-2}	[b]
TTAB[d]	5.6	0.52	[b]	[b]
Polypyrroles				
None[c]	0.049	6.8×10^{-3}	7.7×10^{-6}	[b]
AOT	7.3	1.3×10^{-2}	[b]	[b]
DBSA	9.9	7.5×10^{-2}	2.1×10^{-5}	[b]
DBSNa	8.3	0.14	2.6×10^{-5}	[b]
SDS	5.5	[b]	[b]	[b]
TTAB[d]	0.13	[b]	[b]	[b]

When the temperature of the sample reached 175 °C, the conductivity was σ_0 and the ageing time was set to $t = 0$.

[a] Polyaniline hydrochloride [31].

[b] The conductivity was lower than 10^{-10} S cm^{-1} or good electric contact with the sample could not be maintained because of the sample deformation.

[c] Polypyrrole sulfate.

[d] The cationic surfactant used for comparison with anionic surfactants.

polyanilines decreases by 1–2 orders of magnitude, while the drop in the conductivity of polypyrroles amounts to 4–7 orders over the same timescale (Fig. 3, Table 3). The PANI maintains the level of conductivity acceptable to many applications even after 500 h exposure to elevated temperature (Table 3). The presence of a surfactant in PANI reduced the stability of conductivity in all the cases under investigation (Fig. 3, Table 3). In the case of PPy, an improvement of both the conductivity and stability has been observed when the synthesis was carried out in the presence of anionic surfactants, at least for short annealing times. After long-term annealing, PPy sulfate shows an indication of better performance (Fig. 3). The enhanced thermal stability of PPy prepared in the presence of surfactants has earlier been demonstrated by Kudoh [19] who noted a marked improvement of this parameter when the ageing was performed at 85 and 125 °C, i.e. at temperatures lower than that used in the present study.

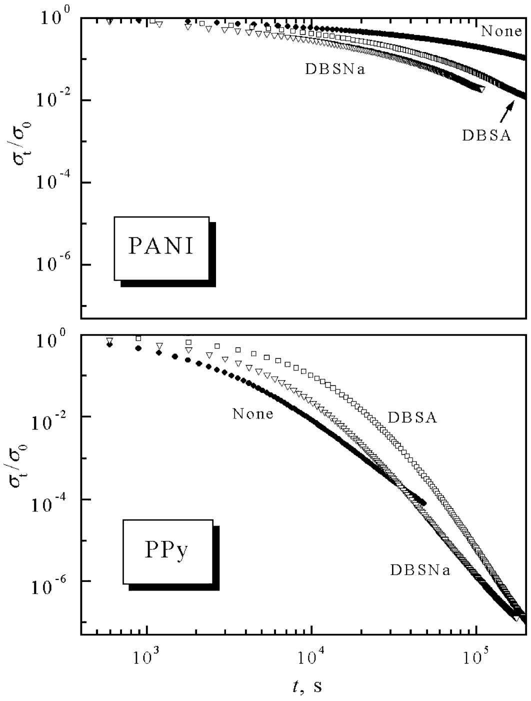

Fig. 3. The decrease in the conductivity of polyanilines (top) and polypyrroles (bottom) prepared in the presence of DBSA (squares) and DBSNa (triangles) and in the absence of surfactants (full circles) during ageing at 175 °C.

With both polymers, the presence of DBSA provided samples of better stability than in the case of its sodium salt, DBSNa (Fig. 3). This is intuitively expected, as an acid participates directly in the protonation of conducting polymers, while the salt does so only by reprotonation reactions.

3.4. Comments on the thermal stability of conductivity

PANI prepared by the oxidation of aniline hydrochloride in water has a typical conductivity of 4.4 S cm^{-1} [31]. When a similar polymerization was carried out in 1 M HCl, the conductivity of the PANI is improved to 11.9 S cm^{-1} [31]. Despite the higher conductivity after preparation, the thermal stability of the conductivity of the latter sample is worse (Fig. 4). When we discuss the effect of surfactants, the assessment of their role is relative. The introduction of an additive, like DBSA, leads to lower thermal stability of conductivity (Fig. 4). On the other hand, this stability of the product is much better than if a mineral acid, like HCl, had been introduced instead of DBSA.

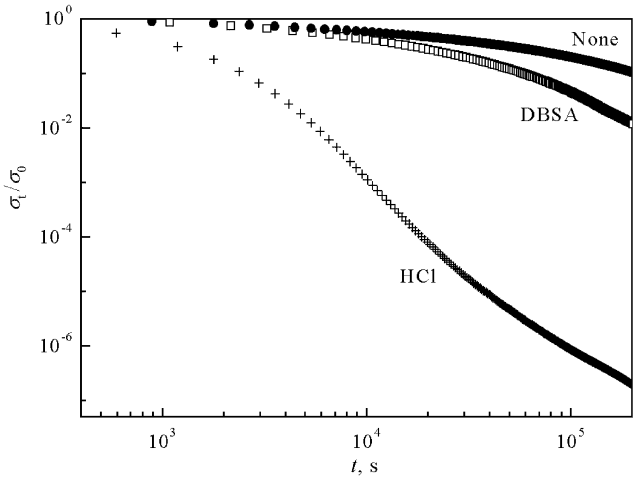

Fig. 4. Time dependence of the conductivity at 175 °C of polyanilines prepared in the presence of HCl (crosses), DBSA (squares), and in the absence of either of these additives (full circles).

4. Conclusions

Polyanilines and polypyrroles were prepared in the presence of four anionic surfactants. Determination of polymerization yield and density, elemental analysis, and FTIR spectroscopy prove that the anionic surfactants become incorporated into the conducting polymers. The similar inclusion of a cationic surfactant into conducting polymers was not observed.

The thermal stability of conductivity at 175 °C was significantly higher for PANI than for PPy. During about 1 day, PANI conductivity was reduced by 1–2 orders of magnitude, while 4–7 orders reduction was observed for PPy. The presence of surfactants in PANI does not enhance either the conductivity or the thermal stability of conductivity. In the case of PPy, however, an improvement in the electric parameters was noted. The samples prepared with dodecylbenzenesulfonic acid had better electric properties than those synthesized in the presence of sodium dodecylbenzenesulfonate.

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