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Preparation of PANI-coated poly(styrene-*co*-styrene sulfonate) nanoparticles

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Abstract

Poly(styrene-*co*-styrene sulfonate) (PS-PSS) latexes have been coated with thin overlayer of polyaniline (PANI) to produce electrically conductive 'core-shell' particles (PANI/PS-PSS) in the size of range 30–50 nm in diameter. PS-PSS core particles were prepared by radical emulsion copolymerization and PANI was oxidatively polymerized using ammonium peroxydisulfate (APS) on the surface of PS-PSS latex. PANI thin overlayer was observed in transmission electron microscopy (TEM) images indicating polymerization of aniline takes place preferably on the PS-PSS surface rather than in the aqueous bulk phase. Elemental analysis revealed that the weight percent of styrene sulfonate in PS-PSS copolymer was ca. 5.4% and the conductivities of PANI/PS-PSS pellets were greatly increased with the increase of nitrogen content. Thermal gravimetric analysis (TGA) thermograms showed two main degradation stages beginning at 360 and 460°C that correspond to the decomposition of PS-PSS and PANI, respectively.

Keywords: Polyaniline; Core-shell particle; Nanocomposite

1. Introduction

PANI dispersions, as one of the interesting ways to improve the processibility of PANI, have been studied by many research groups. Most of the works were focused on increasing the stability of PANI dispersions and controlling the size and morphology of the particles which are directly related to the properties of the PANI composites [1–3]. Usually, PANI dispersions are produced with suitable polymeric stabilizers such as poly(vinyl alcohol), poly(*N*-vinylpyrrolidone), cellulose ethers. An alternative approach involves coating latexes with thin overlayer of conducting polymers producing 'core-shell' particles. If the conducting overlayer is continuous and uniform, it can be expected to obtain relatively high conductivities even at very low conducting polymer loading and also give more facile route to prepare conducting polymer dispersions having desired particle size. In 1987, Yassar and co-workers reported that sulfonated and carboxylated polystyrene (PS) latexes of ca. 130 nm in diameter could be coated with polypyrrole (PPy) overlayers using $FeCl_3$ [4]. Similarly, Liu et al. used a H_2O_2/Fe^{3+} catalytic oxidation to coat 200 nm diameter styrene–butadiene–methacrylate latex particles with PPy [5]. As far as PANI is concerned, Armes et al. prepared micrometer-sized (1.6–2 μm) PANI-coated PS latexes and extensively studied their surface compositions with X-ray photoelectron spectroscopy (XPS) [6,7]. The thickness of PANI overlayer ranged from 2 to 30 nm and conductivity of the PANI-coated particles substantially increased with the increase of PANI loading. Maximum conductivity was 0.17 S cm^{-1} at 9.3 wt% of PANI loading. They reported that PANI overlayers on PS latexes typically have a nonuniform, inhomogeneous morphology in contrast to the relatively smooth morphologies obtained from the deposition of PPy.

In this study, we prepared PS-PSS latexes as core particles comprised of 30–50 nm in diameter. PSS groups on the particle surface were expected to act as anionic dopant for the PANI chains and enhance more uniform PANI deposition through electrostatic binding between the anilinium cation and the anionic sulfonate groups at the latex surface. Moreover, because coating is carried out with the latex containing nanoparticles (<50 nm) that have extremely larger surface area than micrometer-sized particles, it is anticipated that the polymerization would happen exclusively at the PS-PSS surface.

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2. Experimental

2.1. Materials

Styrene monomer (99%, Aldrich) was distilled at 55°C at reduced pressure. Aniline hydrochloride (97%, Aldrich), potassium peroxydisulfate (KPS, 99 + %, Aldrich), ammonium peroxydisulfate (APS, 98%, Kanto Chem), sodium dodecylsulfate (SDS, approx. 99%, Sigma) and 4-styrene sulfonic acid sodium salt (Aldrich) were used as received. Water (18.2 MΩ cm) was purified with Rios and Milli-Q system (Millipore). Amberlite IRA-410 (chloride form) and Amberlite IR-120Plus (sodium form) were thoroughly washed according to Vanderhoff and Hull [8] before used. All other chemicals used were reagent grade and used without further purification.

2.2. Preparation of PS-PSS core particles

Two-neck round bottom flask was charged with 20 g of styrene, 2 g of 4-styrene sulfonate sodium salt, 2 g of SDS, 0.2 g of KPS and 80 g of water. The reaction mixture was stirred over 1 h until it formed stable emulsion at room temperature and then placed into a thermostatted water bath maintained at 45°C. The polymerization proceeded for 24 h under nitrogen atmosphere. At the end of the reaction, small amount of diluted hydroquinone solution was added to stop polymerization and maintained at 80°C for 12 h to promote the hydrolysis of surface sulfate groups which arise from initiator fragments. Conversion in 24 h was assumed to be almost 100% because 85% conversion was achieved within 8 h in a separate experiment. Overall reaction scheme was referred to the recipe reported by Weiss et al. [9]. PS-PSS latex was washed three times with three or fourfold excess of mixed ion-exchange resin to exchange any cationic species with proton and remove other ionic species including PSS homopolymer molecules. Obtained PS-PSS latex was highly stable and precipitation was not observed even after centrifugation at 10,000 rpm for 30 min. PS-PSS latex was diluted with the appropriate amount of water to adjust solid content before washing with ion-exchange resin.

2.3. PANI coating

Aniline hydrochloride and 50 g of latex were mixed in a two-neck round bottom flask and stirred vigorously. PS-PSS latexes were sonicated (bath type) for 1 h before the coating experiments and the solid content was 5.6 wt%. The pH of PS-PSS latexes was around 3.0 and no external acid was added. APS was dissolved in 5 g of water and added dropwise into the reaction mixture. Reaction recipes are summarized in Table 1. The molar ratio of APS to aniline was kept to be 0.5 to avoid overoxidation. Polymerization was carried out for 4 h at 5 and 20°C under nitrogen atmosphere. After the polymerization was finished, PANI coated PS-PSS latexes were centrifuged at 3000 rpm. Supernatant was removed and the precipitates were washed with methanol. This centrifugation, decantation and redispersion cycle was repeated until the supernatant became clear and then, PANI coated PS-PSS particles were dried in a vacuum oven at 40°C over 6 h.

2.4. Characterization

Elemental analysis (Eager 200 model, C, H, N, S) was carried out to determine the composition of the PS-PSS copolymer and amount of PANI loading. Particle size and morphology were investigated by TEM (Jeol model, JEM2000-EX II). Samples were prepared by dropping highly diluted latexes on the carbon coated copper grid and dried in a desiccator at room temperature. The oxidation state and formation of polaron band were identified by UV–Vis spectroscopy (UNICAM 8700 SERIES UV–Vis spectrophotometer). FT-IR spectra (Nicolet, Magna-IR 760) were recorded and compared to that of PANI. TGA thermograms were recorded using Universal V2.6D TA Instruments. The programmed heating rate and N_2 flow rate were 10°C min^{-1}, 80 ml min^{-1}, respectively. Conductivities of PANI/PS-PSS pellets were measured by four-point probe connected to a Keithley voltmeter-constant current source system.

3. Results and discussion

3.1. TEM images

As shown in Fig. 1, the size of PS-PSS core particles are 30–50 nm in diameter. Relatively broad size distribution seems to arise from the low reaction temperature and consequently long nucleation period. A subtle, thin overlayer of PANI can be observed in Fig. 1(B) (PANI/PS-PSS-02) and more clearly in Fig. 2. During the reaction, no precipitation

Table 1
Reaction conditions, theoretical PANI loading, and conductivities of PANI/PS-PSS pellets

	Aniline–HCl (g)	Reaction temperature (°C)	Theoretically maximum PANI loading (wt%)[a]	σ (S cm^{-1})
PANI/PS-PSS-01	0.25	5	3.41	2.6×10^{-5}
PANI/PS-PSS-02	0.50	5	6.60	5.3×10^{-4}
PANI/PS-PSS-03	0.75	20	9.58	7.5×10^{-4}
PANI/PS-PSS-04	1.00	20	12.38	5.3×10^{-2}

[a] Calculated assuming 40% conversion of monomer.

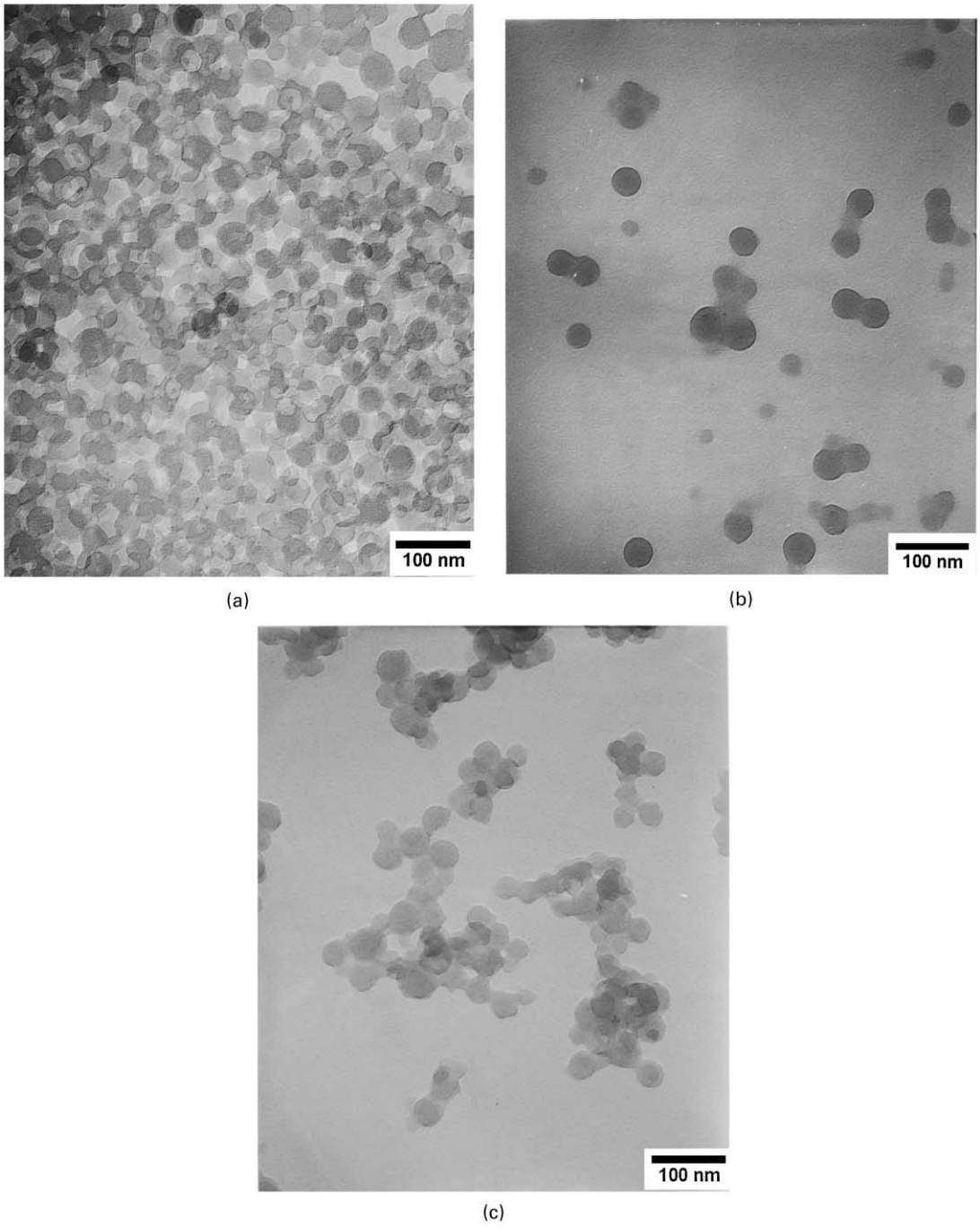

Fig. 1. TEM images of PS-PSS (a), PANI/PS-PSS-02 (b) and PANI/PS-PSS-04 (c).

of PANI indicating polymerization of aniline hydrochloride in aqueous bulk phase was observed. This can be thought that the most of the aniline hydrochloride monomers were polymerized at the PS-PSS surface forming PANI thin overlayer. The preference of polymerization at the PS-PSS surface can be explained by the electrostatic attraction between the anilinium cation and negatively charged PS-PSS particles. Since aniline has a known pK_a of 4.63, it was expected to be primarily positively charged at pH lower than 4.63 [10]. Thus, the initiation would happen at the surfaces of core particles. Furthermore, if the initiation was occurred around the core particles and the produced oligomers deposited on their surfaces, the further reaction would also mainly take place on the surfaces of core particles rather than in the aqueous bulk phase because the dimer and succeeding oligomers have lower oxidation potentials than aniline. The rapid increase in reaction rate is achieved by incorporating monomeric aniline–HCl onto the oligomeric species [11,12]. Although the solid content was lower than that used by Barthet et al. [7], many

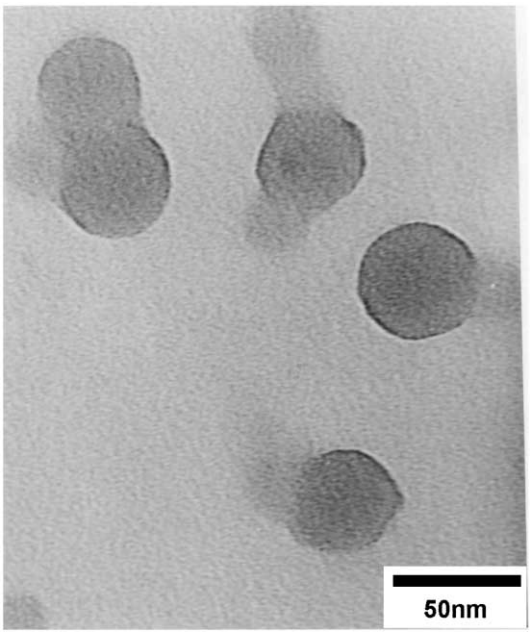

Fig. 2. Magnified TEM image of PANI/PS-PSS-02 showing PANI thin overlayer.

uncoated PS-PSS particles could be observed as shown in Fig. 1(C) (PANI/PS-PSS-04). This could be attributed to the much smaller particle size of used core particles.

3.2. Elemental analysis

Table 2 represents the composition of the uncoated and PANI coated particles obtained by elemental analysis. The weight ratio of PSS to PS-PSS was calculated approximately to 0.058 referring to the sample weight and weight percent of sulfur. Thus, the weight percent of styrene sulfonate in PS-PSS copolymer was 5.48%. Considering the monomer ratio of styrene sulfonate to styrene in weight was 0.1, about 58% of styrene sulfonate monomer was copolymerized with styrene producing PS-PSS particles. It seems that this low incorporation of styrene sulfonate resulted from the homopolymerization in aqueous phase because of the high initial styrene sulfonate concentration. The increase of PANI loading, nitrogen content, with the increase of aniline hydrochloride concentration is obvious as shown in Table 2. Exceptionally, PANI loading of PANI/PS-PSS-03 was decreased in spite of the increased amount of monomer. This unexpected result may be related to the reaction temperature. It is already well known that higher conversion and increase of molecular weight can be achieved by lowering the reaction temperature usually below 5°C [13,14]. Thus, this low PANI loading can be explained with the low conversion of aniline–HCl at relatively high reaction temperature.

Table 2
Element compositions of PS-PSS and PANI/PS-PSS (wt%) by elemental analysis

	C	H	S	N
PS-PSS	88.39	7.52	1.07	–
PANI/PS-PSS-01	87.98	7.56	1.01	0.94
PANI/PS-PSS-02	87.23	7.42	1.04	1.16
PANI/PS-PSS-03	86.15	7.42	1.06	1.04
PANI/PS-PSS-04	84.92	7.32	1.19	1.38

3.3. UV–Vis and FT-IR spectra

Dried PANI/PS-PSS powders were redispersed in water by sonication. Initially, very weak polaron bands were observed at 430 and 800 nm, but the intensity of the polaron band increased remarkably by adding small amount of HCl solution. We think this means the low doping levels of as-synthesized PANI/PS-PSS particles. In Fig. 3, all samples showed peak around 430 and 800 nm and both of them are related to the formation of polaron band. Only PANI/PS-PSS-01 showed a little blue-shifted weak polaron band around 780 nm. This is well consistent with the conductivity data and indicates the reduction of the conjugation length. This may be assigned to the too low PANI loading resulting in the low molecular weight and leaving most of the particles uncoated.

For comparison, the FT-IR spectra of the bulk PANI and PANI/PS-PSS-01 are represented in Fig. 4. Fig. 4(B) is the spectrum of PANI/PS-PSS-01 showing sp^3 C–H stretching bands at 2838 and 2920 cm^{-1} and several benzene ring sp^2 C–H stretching bands from 3000 to 3100 cm^{-1}. Peaks around 1000 and 1150 cm^{-1} could be assigned to the $-SO_3$ and $-SO_2$ stretching of styrene sulfonate unit [7,15]. Quinoid and benzenoid peak of PANI at 1490 and 1580 cm^{-1} in Fig. 4(A) was not shown in Fig. 4(B) due to overlapping with the aromatic C=C stretching bands ranging from 1400 to 1600 cm^{-1}. Only the peak at 1300 cm^{-1} from C–N stretching of a secondary aromatic

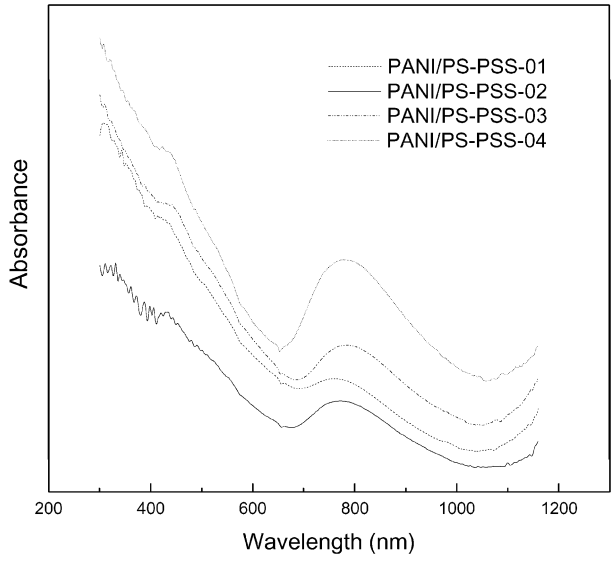

Fig. 3. UV–Vis spectra of PANI/PS-PSS.

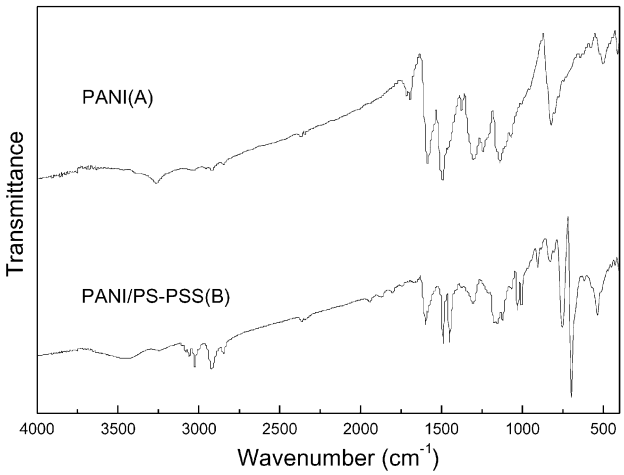

Fig. 4. FT-IR spectra of PANI and PANI/PS-PSS-01.

amine is observed in both figures [10,16]. All these features show the successful copolymerization of PS-PSS and followed PANI coating.

3.4. Thermal gravimetric analysis

Fig. 5 shows TGA thermograms of uncoated PS-PSS and PANI coated powders. Two distinctive degradation steps were observed in all other samples. From the comparison of the two thermograms, the first weight losses beginning at 370°C could be ascribed to the degradation of PS-PSS. The weight loss within the temperature range between 370 and 460°C is approximately 82%. As shown in Fig. 5, the onset temperature of coated PANI was ca. 460°C and it is higher by 30–40°C than that of the HCl doped PANI. Generally, the decomposition of HCl doped PANI begins at around 420°C under N_2 atmosphere [17] and the degradation temperature depends on the kind of counter-ion. Many authors have reported that the PANI doped with organic acid having long alkyl chain and polymeric acid shows increased thermal stability [17–20]. Thus, we concluded that this high thermal stability arises from the partial doping by the copolymerized styrene sulfonic acid or at least the formation of complex between PANI and PSS chain that become more resistant to thermal degradation than PANI, PSS itself. This also can be supported by the fact that the weight loss at the second degradation step is over 15%, which is not able to be explained with the maximum PANI loading, 12.38%.

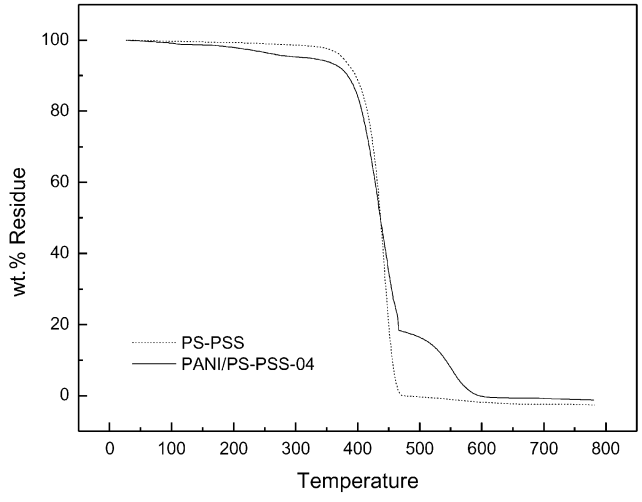

Fig. 5. TGA thermograms of PS-PSS and PANI/PS-PSS-04 (10°C min^{-1}, N_2).

3.5. Conductivity

Conductivities of the PANI/PS-PSS were greatly enhanced with the increase of PANI loading by three orders of magnitude. As PANI loading increased, color of powders became darker and white tint from the PS-PSS particles was noticeably reduced. Thus, more complete coating with PANI can be supposed at higher PANI loading. This was confirmed by TEM images showing coated PANI thin overlayer clearly. The two samples, PANI/PS-PSS-02, 03 that had the almost same PANI loading, showed the similar conductivity. Maximum conductivity, 0.05 S cm^{-1}, was obtained at 12.3 wt% loading of PANI (calculated assuming 40% conversion based on the amount of APS [21]). Although PANI loading was same or higher than that reported by Barthet et al. [7], maximum conductivity was lower by an order of magnitude. We conclude that more aniline–HCl monomer is required to coat all the core particles uniformly because PS-PSS core particles prepared in this study was much smaller (30–50 nm), consequently much larger surface area than those employed previously (100 nm–2 μm).

4. Conclusion

PS-PSS nanoparticles of 30–50 nm in diameter prepared by emulsion copolymerization were successfully coated with the PANI thin overlayer and it was confirmed by transmission electron microscopy (TEM). We think the PANI coating was facilitated by the negatively charged PS-PSS core particles. Although UV–Vis spectra showed characteristic peaks of HCl-doped PANI, the doping levels seemed to be low from the increases of peak intensities by addition of HCl solution. Elemental analysis data revealed the composition of the PS-PSS core particles and PANI coated particles. The weight percent of PSS in PS-PSS was about 5.4% and significant amount of styrene sulfonate seemed to be homopolymerized in the aqueous phase. To obtain more completely PANI coated PS-PSS, higher aniline concentration and lower reaction temperature were proposed. Thermal stability of coated PANI was enhanced by the formation of complex or doping with the copolymerized PSS. Conductivities were dependent on the PANI loading and significantly increased by three orders of magnitude as the PANI loading increased.

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