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Surface Initiated Living Cationic Polymerization of 2-Oxazolines

Rainer Jordan and Abraham Ulman*

Contribution from the Department of Chemical Engineering, Chemistry and Materials Science, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

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Abstract: A self-assembled monolayer on a planar gold substrate has been used to initiate the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline. The polymer chain end was functionalized with an alkyl moiety by means of the termination reaction in order to form an amphiphilic brush-type layer. The resulting layer ($d \sim 10$ nm) of linear poly(*N*-propionylethylenimine) (PPEI) is of uniform thickness and was found to be very stable.

Introduction

The preparation of polymer "brush-type" layers on solid surfaces is of specific interest due to their potential applications in a variety of technological fields.[1] Their intriguing properties are based on the fact that all polymer chains are confined into a small volume near an interface, and sterical restrictions force them to stretch away from the grafting point to the polymer layer edge. The theoretical descriptions of polymer brushes developed by Alexander[2] and de Gennes[3] best described the difference between a free polymer chain system (e.g., dilute solution) and a chain in a grafted brush.[4]

Due to their confinement, polymer brushes responding to an environmental stimulus such as solvent quality, ion strength, temperature, pressure, etc. in a collective, and hence uniform, way, along with a change of the surface properties. This behavior can be used to construct functional devices on a nanometer scale.[5−8]

To obtain a homogeneous polymer brush, first the surface grafting density has to be uniform as well as high with respect to the radius of gyration, second the polydispersity index (M_w/M_n) should be near to 1,[9] and finally all chains should be linear and only terminally grafted onto the surface. The latter requirements can easily be met by preparing end-functionalized polymers by, e.g., living anionic polymerization techniques. However, the preparation of polymer brushes with high grafting densities remains an experimental challenge.[1]

Beside the commonly employed technique to form a stable irreversible grafted polymer layer, which is to chemically graft a preformed functionalized polymer onto a solid substrate[10] or the selective adsorption of diblock copolymers,[11] they can be prepared via a direct surface initiation of the polymerization reaction. This approach is expected to result in considerably higher final grafting densities. Here, the grafting densities are not limited by a sterical barrier imposed by the already bonded chains, since the smaller monomer can readily access the initiator site or the propagating chain end. Taking full advantage

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of a living polymerization reaction mechanism, chain ends will propagate at the same rate over the entire surface, resulting in a uniform, steady increase in layer thickness.

Surface initiated polymerization techniques have been employed for a variety of monomers and different polymerization types, including radical polymerization[12] and cationic living polymerization[13] as well as anionic polymerization of styrene.[14]

In this paper, we present the surface initiated cationic ring-opening polymerization of a 2-substituted 2-oxazoline resulting in poly(*N*-acylethylenimine). This type of monomer is of particular interest due to the broad variety of polymerizable 2-oxazolines.[15] The resulting linear polymers are of narrow polydispersity and can be tailored with respect to their hydrophobicity[16] and crystallinity.[17] The highly living character of the ring-opening polymerization allows an easy way to prepare block-copolymers by means of consecutive addition of different 2-substituted monomers,[18] and terminal functionalities can be easily introduced by the termination reaction using nucleophiles such as primary or secondary amines.[19] To demonstrate the versatility of our approach, we focus on the polymerization of 2-ethyl-2-oxazoline, initiated at self-assembled monolayers (SAM) on gold.

Experimental Section

Materials. Dry THF (EM Science) was deoxygenated by nitrogen. Chloroform was obtained from EM Science, freshly distilled in a nitrogen atmosphere, and stored over molecular sieve (4A). Trifluoromethanesulfonic anhydride (Aldrich) and *N*,*N*-dioctadecylamine (Fluka) were used as received. 2-Ethyl-2-oxazoline (Aldrich) was purified by refluxing (2 h) over KOH and a subsequent distillation under an atmosphere of dry nitrogen.[20]

Preparation of Gold Substrates. Gold substrates were prepared by thermal evaporation of gold onto microscope glass slides (2.5 × 5 cm, Fischer). The glass slides were cleaned with ethanol in an ultrasonic bath for 15 min, dried, further cleaned for 15 min by argon plasma treatment (PLASMOD, March Instruments Inc.), and transferred into a UHV evaporation setup (Key Vacuum, Inc.). At a base pressure of no more than 10^{-6} Torr the substrates were baked at 300 °C for 16 h using an UV-halogen lamp. This promotes the adhesion of the gold directly onto the glass slides and an adhesive layer of chromium or titanium is no longer necessary. A layer of 100 nm gold (99.99%) was evaporated onto the bare glass at the same temperature with a constant rate between 0.15 and 0.2 nm/s. The deposited gold film was further annealed at 300 °C for another 16 h to increase the crystal size of the polycrystalline gold and decrease the roughness of the crystals. Substrates prepared in this manner feature large Au(111) crystals (approximately 0.5 μm^2) with typical roughness values of 0.2−0.1 nm (rms).

Monolayer Formation. Self-assembled monolayers of 11-hydroxyundecanethiolate (HUT) were prepared by immersing clean gold substrates (freshly prepared and subjected to Argon plasma treatment for 30 s) into a 10 μM solution of HUT in dry THF for 16 h under a nitrogen atmosphere. The final thickness (1.4−1.5 nm (±0.2)) as well as recorded ER FTIR spectra were in full agreement with previous results and correspond to the formation of a complete HUT monolayer.[21]

Preparation of Grafted Amphiphilic Poly(*N*-propionylethylenimine). Freshly prepared HUT monolayers on gold substrates (approximately 1 × 2.5 cm) were rinsed with THF, dried, and transferred into a reaction flask equipped with a condenser and a three-way stopcock. The air was exchanged with dry nitrogen gas by repetitive evacuation and purging with nitrogen. The substrates were exposed to a constant stream of trifluoromethanesulfonic anhydride vapor for about 1 h. The conversion of the HUT hydroxyl groups to the triflate functional group was allowed to complete overnight in the sealed reaction vessel. The reactor was again purged with nitrogen and, using airtight syringes and septa, 40 mL of dry chloroform and 2 mL of freshly distilled 2-ethyl-2-oxazoline were added at 0 °C. The reaction mixture was heated and allowed to react for 7 days under reflux. The polymerization was terminated by adding a solution of 0.2 g of *N*,*N*-dioctadecylamine in 2 mL of dry chloroform at 0 °C. After stirring for 1 day at room temperature, the substrates were taken out and immediately washed with 5 portions of 50 mL acetone.

Preparation of $PPEI_{10}$−OH. Hydroxyl terminated poly(*N*-propionylethylenimine) $PPEI_{10}$−OH was synthesized by means of living polymerization of 2-ethyl-2-oxazoline in dry CH_3CN using methyl tosylate as initiator and aqueous workup to introduce a terminal hydroxyl function.[22] The polymerization degree was controlled by the initial monomer/initiator ratio of 10/1.[23] Characterization of the final product by matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) and ^{1}H-NMR spectroscopy gave $n = 13$, $M_w/M_n = 1.14$.[10,24]

Ellipsometry. Ellipsometric data were obtained on an AutoEL Rudolf Research ellipsometer with a He−Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70° (Null-ellipsometry). For the calculation of the layer thickness, a refractive index of $n = 1.462$ for the HUT monolayer and $n = 1.591$ for the polymer layer was used. The in situ ellipsometry measurement (swelling experiment) was performed as follows: The sample substrate was placed on the ellipsometer stage, and two stripes of filter paper were placed ∼1 mm apart to allow the laser beam to reflect from the surface. The filter papers were covered with glass slides to minimize the evaporation rate as well as temperature fluctuations during the experiment and then soaked with the solvent. Ellipsometric data were collected throughout the experiment. The time resolution of collected data points was typically 40 s. Given values are averaged from consecutive measurements showing a stable reading for a minimum time interval of 15 min. Although a “swelling kinetic” can be recorded in this manner, repeated experiments showed that the time dependency of the swelling step was not reproducible due to a strong influence of the homemade setup (solvent diffusion rates through the filter paper).

A control sample of a deuterated poly(styrene-*block*-4-vinylpyridine) ($n = 220$), anchored to a silicon substrate[25] by the poly(4-vinylpyridine) block ($n = 20$) was tested using this method. The swelling of the layer from 10.4 nm in air as a poor solvent to 25.4 nm in toluene as measured with this setup is in excellent agreement with the height

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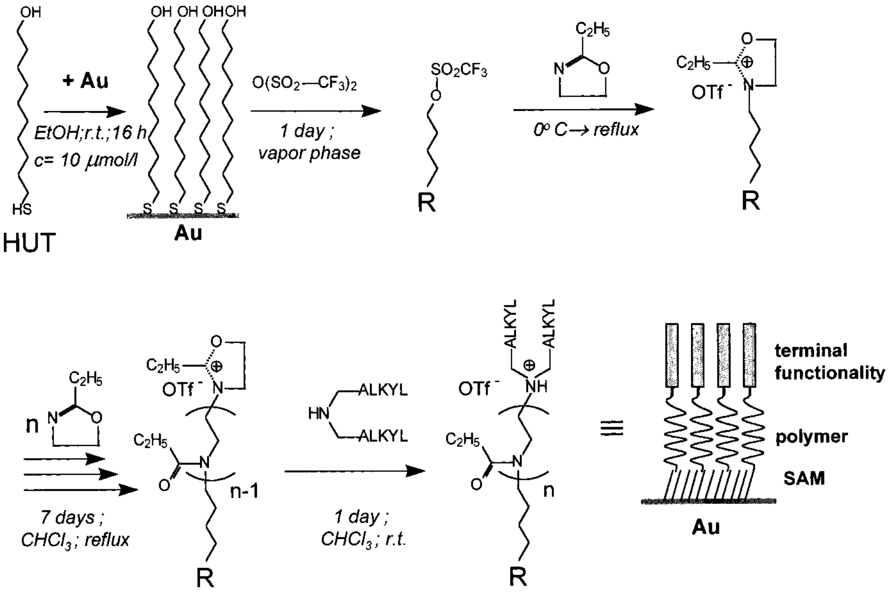

Figure 1. Reaction scheme for the preparation of PPEI films by means of surface initiated cationic ring-opening polymerization of 2-ethyl-2-oxazoline.

measured by AFM and neutron reflection in toluene liquid of ~24 nm.[26] The accuracy of all thickness values are typically within a ±0.2 nm error.

Contact Angle Measurements. Water contact angles were determined by using a Ramé-Hart goniometer equipped with a CAD camera and computer aided image analysis. For static contact angles, the angle at both sides of the free-standing droplet was measured at four different spots of the same substrate. Given results are average values of all measurements. As outlined in the Discussion section, the static contact angles of the amphiphilic polymer layer are strongly affected by a fast respond of the layer, resulting in quick change of the initial contact angle and therefore subject to a relatively large error. Advancing and receding angle measurements were found to be most accurate and reproducible if the tilting plate method were used.

FTIR Spectroscopy. ER FTIR spectra were recorded using a Magna 760 IR spectrometer equipped with a grazing angle setup (fixed angle of 80°, FT-80, SpectraTech), a polarizer (p-polarization) and a MCT-A detector cooled with liquid nitrogen. 2000 scans were accumulated at a spectral resolution of 2 cm^{-1} for the ER FTIR spectra. The bulk spectrum of PPEI (500 scans) was recorded with a Nicolet 5 SXB equipped with a SpectraTech IRplane microscope setup at a spectral resolution of 4 cm^{-1}.

Results and Discussion

To induce a homogeneous growth of polymer chains on a planar surface by means of living cationic polymerization, the starting reaction has to be fast ($k_{\mathrm{initiation}} \gg k_{\mathrm{propagation}}$) and highly efficient. It is well-known that the polymerization mechanism of 2-oxazolines strongly depends on the reaction conditions, solvent polarity, initiator/gegenion characteristics, and the kind of substitution at the 2-position of the monomer. Especially, the choice of the initiator determines if the propagating end is mainly a covalent species or an ion pair. Reviewing the literature,[18,27,28] and from our own experience, triflate groups attached to *n*-alkyl chains are ideal candidates for our purpose. The highly living character of the resulting onium/triflate ion pair as the active propagating species was demonstrated by Saegusa et al.[29] Our recent experimental results[23,24] demonstrated the usefulness of the "fast initiation technique", resulting in end functionalized PPEIs obtained in high yields, narrow molecular weight distribution, and absence of side products. Most of the reported polymerizations of 2-oxazolines were performed using acetonitrile as a polar solvent, which favors the propagating ion pair structure. We used chloroform, because the terminating agent, *N*,*N*-dioctadecylamine, is insoluble in acetonitrile but can be dissolved in chloroform even at 0 °C. This ensures a homogeneous exposure of the terminator to the living polymer chain ends throughout the entire substrate surface.

Figure 1 outlines the reaction pathway for the preparation of poly(*N*-propionylethylenimine) (PPEI) brush-type layers.

The layer thickness as measured directly after the last washing step at different spots across the entire substrate was 9.1 nm. The scattering of the thickness values of only ±0.3 nm is presumably due to a homogeneous initiation, polymerization, and termination reaction.[30]

Figure 2 displays the external reflection (ER) FTIR spectra of the thin film along with a typical bulk spectrum of an analogous $PPEI_{10}$−OH.

The similarity of both FTIR spectra confirms a successful reaction as outlined in Figure 1. In particular, the pronounced amide I band at 1650 cm^{-1} is characteristic for the presence of a tertiary amide group,[31] which is created upon the ring-opening polymerization of 2-oxazolines. In the fingerprint region, several bands appear at the same or only slightly shifted positions. Differences in the positions and relative intensities for, e.g., the CH_x deformation bands (δ CH_x), and in the CH_x-stretching (ν CH_x) region are to be expected due to the presence of the underlying SAM and the differently functionalized polymer chain ends in the spectrum of the grafted PPEI.

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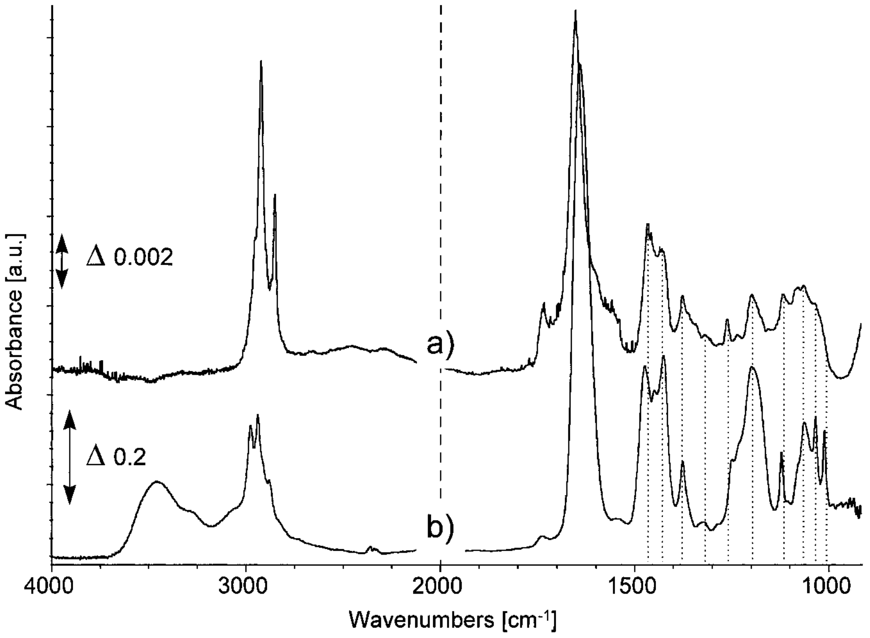

Figure 2. Comparison of FTIR spectra for identification: (a) ER FTIR spectrum of grafted PPEI and (b) bulk spectrum (transmission) of PPEI recorded as a casted film on a KBr crystal.

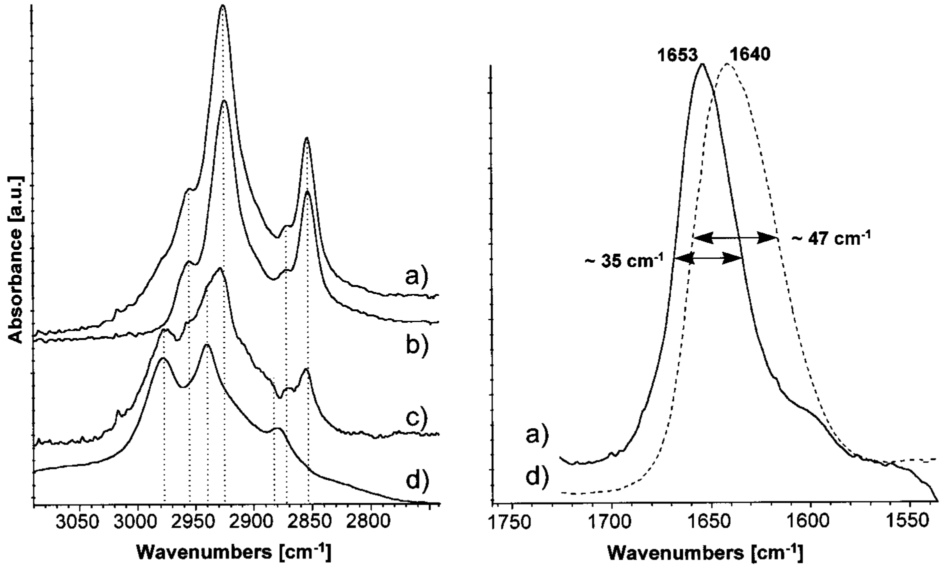

Figure 3. Analysis of the CH-stretching region (3000−2800 cm^{-1}) and the amide I band around 1650 cm^{-1}. (a) ER FTIR spectrum of PPEI as grown on the triflate functionalized HUT SAM. (b) ER FTIR spectrum of HUT SAM. (c) Subtraction result of (a)−(b). (d) Bulk spectrum of PPEI.

A direct comparison of the ER FTIR spectrum of the HUT monolayer with the grafted PPEI indicate an almost quantitative conversion of the primary alcohol function of the HUT to the triflate and its subsequent reaction leading to the grafted polymer. Considering the sterical requirements of a grafted polymer chain at its final length, it is unlikely that all functional sites successfully initiate a polymerization reaction. The fate of the unused initiator could not be determined by FTIR, due to the complexity of the resulting PPEI spectrum. However, the characteristic bands for the HUT monolayer around 3570 cm^{-1} (ν OH, broad) and 1258 cm^{-1} (δ_{ip} OH, strong) could not be identified in the polymer spectrum (Figure 2a); therefore, hydrolysis of unreacted triflate may be ruled out.

We emphasize that the total amount of grafted PPEI appears to be considerably higher, if compared to the "grafting onto" approach, using a similar amphiphilic PPEI.[10,23] There, we end-grafted an amphiphilic silane functionalized PPEI (n = 10 and 20) onto planar silica substrates. Analysis of X-ray reflection data gave a resulting total thickness of 3.25 nm ($(C_{18})_2$−PPEI$_{20}$−Si) composed of a polymer sublayer thickness of 1.75 nm and a polymer supported alkyl superficial layer of 1.5 nm. These values were obtained from water-swollen layers with induced spontaneous organization in terms of a phase separation of the amphiphilic ligands into a hydrophilic polymer layer and a layer of the tethered alkyl moieties. Although an optimized silanization reaction was employed to ensure maximum grafting densities, the integral adsorption for the amide I band of the corresponding ATR FTIR spectra is significantly lower than in the ER FTIR spectrum presented here (Figures 2 and 3).

To compare thickness values of both systems, we performed similar swelling experiments with the PPEI system on gold. The substrate was stored in water for 24 h, dried with a jet of nitrogen, and mounted onto the ellipsometer stage. The layer thickness increased from 9.1 nm (as-synthesized) to 11.3 nm. This increase in thickness can be explained by the stretching of the polymer chains to increase polymer solvent interactions.

After rinsing the substrate several times with ether as a poor solvent, the thickness decreased to 8.4 nm at the same spot. The whole experiment was cycled several times, and almost identical values were obtained.

Assuming a similar supramolecular arrangement for the swollen amphiphilic PPEI on gold, we can estimate the approximate thickness of the PPEI layer. Allowing ~1.3 nm for the SAM and ~1.5 nm for a loosely organized superficial layer of the terminal alkyl moiety leaves us with 8.5 nm for the polymer interlayer. A completely stretched PPEI chain ($n = 10$) is approximately 3.0−3.2 nm long,[32] that means that it would take 26−28 monomer units to span this distance. This crude estimation has to be considered as the lowest possible number for the polymerization degree. If we assume a similar grafting density of this system as obtained with $(C_{18})_2-PPEI_{20}-Si$ on silica, the polymerization degree calculates to ~1390 as the "upper limit". Considering the change in layer thickness upon swelling by a factor of only 1.35 the grafting density has to be much higher and therefore the polymerization degree lower.

To estimate the efficiency of the termination reaction, the CH_x-stretching area of both spectra was analyzed (Figure 3). Subtraction of the HUT monolayer spectrum (Figure 3b) from the grafted PPEI spectrum (Figure 3a) reveals an overall higher integral adsorption for the complete CH_x-stretching area (Figure 3c). The characteristic bands for the CH_3/CH_2−stretching modes of the propionyl side group, appearing at 2978, 2940, and 2880 cm^{-1},[17] could be unambiguously identified by comparison with the PPEI bulk spectrum (Figure 3d). Furthermore, stronger adsorption at 2926 and 2854 cm^{-1} indicate the presence of additional long *n*-alkyl chains. This suggests a successful termination reaction of the polymerization by the *N*,*N*-dioctadecylamine (Figure 1). Even though no final conclusions can be drawn regarding the stochiometry of this reaction step, water contact angle measurements indicate the presence of bonded alkyl moieties on the surface of grafted PPEI chains. If the substrate was immersed in water and then air-dried, an initial contact angle (sessile drop) of 80−75° was measured. This value decreased rapidly to a stable value of 60−62°. Advancing and receding angles (tilting plate) showed a pronounced hysteresis of approximately 30°. This has been observed earlier with similar amphiphilic PPEI modified surfaces[10,23] and appears to be characteristic for polymer supported alkyl monolayers.[33] A straightforward explanation is a dynamic rearrangement process of the interface, in which the tethered but not laterally immobilized alkyl moieties are exposed to the layer-air interface in order to minimize the surface free energy. However, the alkyl chains are probably buried in the layer, if contacted with water to increase polymer water interactions.

In the second spectrum section in Figure 3, a significant shift to higher wavenumbers and decrease of the half width of the amide I band in the ER FTIR spectrum of the grafted PPEI (a) can be observed.[34] This can be explained by a different conformational freedom and/or intra- and intermolecular interactions between polymer chains in the grafted PPEI when compared to the bulk phase.

It is well-known that SAMs of shorter *n*-alkyl thiols suffer from stability problems at elevated temperatures[35] or in boiling solvents. Especially, HUT and similar ω-functionalized monolayers tend to reorganize in order to reduce the surface free energy[36] or partly desorb when subjected to more drastic conditions. To test the stability of the grafted PPEI layer and to ultimately verify that the probed amount of the polymer is indeed irreversibly chemisorbed, one part of the substrate was washed by means of Soxhlet extraction with chloroform for 1 day. However, no significant differences in thickness values, wetting behavior, or in the FTIR spectrum could be detected. The synthesized monolayer/PPEI layer is surprisingly stable under extreme conditions such as a continuous extraction procedure with a hot good solvent.

In conclusion, we demonstrated a novel and efficient approach to immobilize polymers of 2-ethyl-2-oxazolines via surface induced polymerization using SAMs as surface bonded initiation sites.

The presented reaction can be readily applied to the broad variety of 2-oxazoline monomers to form corresponding homopolymers, as well as block-copolymers of poly(*N*-acylethylenimines) of different hydrophilic lipophilic balance and supramolecular structures. Stable, surface bonded polymer layers can therefore be prepared for different applications demanding a precise tailoring of their properties with respect to their adsorption behavior. In this context, PPEI modified surfaces are of great interest due to the low toxicity and denaturing potential toward numerous proteins[37] as well as significant reduction of protein adsorption on PPEI modified surfaces.[38] Related studies are currently ongoing in our laboratories.

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