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Formation dynamics of layer-by-layer self-assembled films probed by second harmonic generation

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We investigate the formation dynamics of self-assembled polyelectrolyte multilayers on glass substrates by *in situ* and *ex situ* second harmonic generation (SHG) measurements and atomic force microscopy (AFM). The time dependence of the SHG signal during the adsorption process is attributed to a time dependent surface potential of the polyelectrolyte film. The dynamics can be quantitatively understood using a random sequential adsorption (RSA) model for the buildup of a film consisting of polyelectrolyte disks with polydisperse sizes. Differences between wet and dry films are also investigated. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1495839]

I. INTRODUCTION

The study of layer-by-layer self-assembly of oppositely charged species has received increasing attention over the past decade.[1,2] The simplicity of this method for thin film preparation as well as the high quality and reproducibility of the films are very promising for various applications. In addition, the method also has a unique ability of combining monolayers of different types of materials such as inorganic nanoparticles,[3] dye molecules,[4] fullerenes,[5] proteins,[6] DNA,[7] and conducting polymers[8] into ultrathin film systems.

A deeper understanding of the film growth kinetics is a key the optimization of fabrication procedures. Several theories have been elaborated to model the adsorption of polymers and polyelectrolytes on solid substrates.[9–11] Only limited experimental information, however, is available on kinetic aspects of polyelectrolyte adsorption. From the theoretical point of view the description of the adsorption kinetics is a very challenging task due to the complexity of interactions and the nonequilibrium nature of the situation during the ongoing formation of the self-assembled film. It was shown recently that polymer as well as polyelectrolyte deposition occurs faster than surface structure equilibration.[12,13] From the experimental point of view only very few techniques can provide sufficient mass and time resolution. The techniques which have been used for the investigation of adsorption kinetics are the quartz crystal microbalance technique (QCM) and various optical techniques.[14,15] QCM is sensitive to mass changes and can resolve the adsorption of monolayers. It cannot be excluded, however, that the use of the QCM itself changes the adsorption and desorption kinetics. Among the optical techniques surface plasmon spectroscopy (SPS) is restricted to the use of metal substrates while Fourier transform infrared spectroscopy (FTIR) only provides a limited time resolution (≈ 40 s).[16–18] Another promising optical method relies on monitoring changes of waveguide modes during the adsorption process.[19] This technique was used to study the adsorption of proteins on flat surfaces[20] as well as the kinetics of multilayer formation out of polyelectrolytes.[21] The best time resolution achieved so far is limited by the need for mechanical rotation of the waveguide and reaches ≈ 30 s.[20]

Second harmonic generation (SHG) has been proven to be a useful method to analyze surface properties.[22–25] Surface SHG has recently been measured during the growth of polyelectrolyte multilayers with weak second order nonlinearities[26] as well as from dry multilayer films.[27] In this paper we use surface SHG to study the formation dynamics of polyelectrolyte multilayers with high time resolution. An analysis of the time-dependence of the SHG signals shows that the adsorption kinetics can be described within the framework of random sequential adsorption (RSA), in which the adsorption of monolayers is considered as a statistical process of irreversibly adsorbing species taking into account the time-dependent reduction of the surface density of available adsorption sites. This model is well suited to describe the nonequilibrium dynamics of polyelectrolyte adsorption and gives insight into the early stages of layer formation beyond equilibrium models.[10,9] While a smooth homogeneous film is formed at long deposition times (>10 min),[12] here we study the dynamics of the initial processes leading to the formation of a granular structure.

II. EXPERIMENT

The polyelectrolytes studied here [poly(ethylenimine) (PEI, 18,197-8, $M_w \sim 750\,000$, branched polymer), poly(methylacrylic acid) (PMA, 43,4507, $M_w \sim 5\,400$), poly(diallyldimethylammonium chloride) (PDDA, 40,901-4, $M_w \sim 100\,000$–$200\,000$), and polystryrenesulfonic acid (PSS, 24, 305-1, $M_w \sim 70\,000$)] have been purchased from Aldrich (see the inset of Fig. 1). The concentration (with respect to the repeat unit of the polyelectrolyte) of PEI is $5 \cdot 10^{-2}$ M and that of the other polyelectrolytes is 1

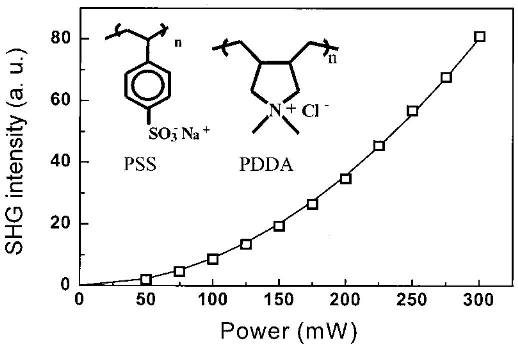

FIG. 1. Squares: Power dependence of SHG signal from a polyelectrolyte/water interface. Line: Quadratic fit with $y=Ax^2$, where A is the fitting parameter.

$\cdot 10^{-2}$ M. A dialysis tube from SERVA was used to remove the low molecular weight components ($M_w < 6\,000$) from the polyelectrolyte samples. PSS and PDDA solutions were subjected to a two day dialysis. In addition, all the solutions were filtrated using a 0.22 mm CM membrane filter from MERCK before being used in the sample preparation. Float glass and transparent walls of quartz cuvettes are used as substrates after being cleaned by an RCA cleaning procedure [immersion of the substrates in a mixture of $NH_3 \cdot H_2O$:H_2O_2:H_2O (1:1:5) for 20 min at 80 °C]. In the film preparation the substrates are immersed in the polyelectrolyte solution for 10 min (in the case of cuvettes, the solution is simply kept in the cuvette for 10 min) and subsequently immersed three times in Milli-Q water for 1 min (in the case of cuvettes, Milli-Q water is injected into the cuvette and kept there for 1 min; this procedure is run three times). By repeating the above procedures using positively and negatively charged polyelectrolyte solutions in an alternate fashion, films with various layer sequences are prepared. The adsorption kinetics is monitored by *in situ* SHG during the film fabrication. No drying process is introduced until the film preparation is completed.

SHG signals are measured using a modelocked Ti:sapphire-laser for excitation. The laser has a pulse duration of 150 fs and a repetition rate of 76 MHz. The p-polarized beam is focused with a 40 mm lens on the internal interface (quartz/solution) of a quartz cuvette. For minimization of reflection losses a small quartz prism has been fixed to the outside of the quartz cuvette using index matching fluid. The SHG signal is detected in reflection with a photomultiplier using photon-counting techniques. Several filters are used to block the light at the fundamental wavelength. The set-up has a time resolution of 3 s. A typical power dependence of the SHG-signal is depicted in Fig. 1. The signal intensity depends quadratically on the input power.

For the investigation of completed dry samples one series of samples consisting of different numbers of PDDA and PSS layers deposited on top of a precursor film of (PEI/PMA)*3/PEI is prepared. The chemical structures of these two polyelectrolytes are shown in Fig. 1. An automated dipping apparatus is used to prepare the samples. The adsorption time for all the polyelectrolytes is set to 10 min for each layer.

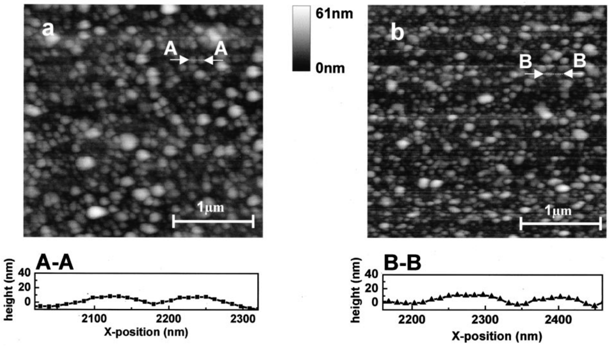

FIG. 2. Topography of a (3×3) μm area of a dry polyelectrolyte multilayer measured with an AFM. In the case of (a), a PSS layer was deposited on a PSS/PDDA bilayer which, in turn, is situated on top of a (PEI/PMA)*3/PEI precursor. In the case of (b), an additional PDDA layer was deposited on top of the uppermost PSS layer. For both images the rms roughness is determined to approximately 9 nm. Selected height profiles of some disklike grains (along the dashed lines) are shown below topographies.

In the SHG experiments on dry samples the incident light beam is focused onto the sample under 45° against the surface normal (lens with focal length of 40 mm). A clean glass wafer is used as a reference.

For a better understanding of the time dependent SHG signal it is important to know the morphology of the prepared films. Therefore the topographies of all samples in the dry state are measured with an atomic force microscope (AFM) in tapping mode. We use standard sharpened silicon tips (Olympus) with radii of typically 6.8 nm. The tips are coated with aluminum.

III. RESULTS AND DISCUSSION

A. Topography

Figure 2 shows the topographies of (3×3) μm^2 areas of two polyelectrolyte films. In the case of Fig. 2(a), a PSS layer was deposited on a PSS/PDDA bilayer which, in turn, is situated on top of a (PEI/PMA)*3/PEI precursor. The film shown in Fig. 2(b) differs from that in Fig. 2(a) in that an additional PDDA layer was deposited on top of the uppermost PSS layer. Example height profiles are shown in the lower part of Fig. 2 for selected grains. The diameter of the granules varies between 20 nm and 100 nm. The ratio of height and diameter of the granules lies typically between 1/10 and 1/7. In both cases the rms roughness is determined to approximately 9 nm. It appears, however, that the average granule size is slightly larger in the case of an uppermost PSS layer. For the number of polyions forming one typical disk we estimate a value of approximately 550. We note a similar granular structure is also observed on samples that contain additional PSS/PDDA bilayers. The observation of disklike granules is in agreement with recent experimental work. It was suggested that polyelectrolyte chains adsorb faster than the surface structure equilibrates via diffusion, and initially form granules each consisting of many coiled polyelectrolyte chains.[12] If the adsorption process is terminated before equilibrium is reached, the granular structure is

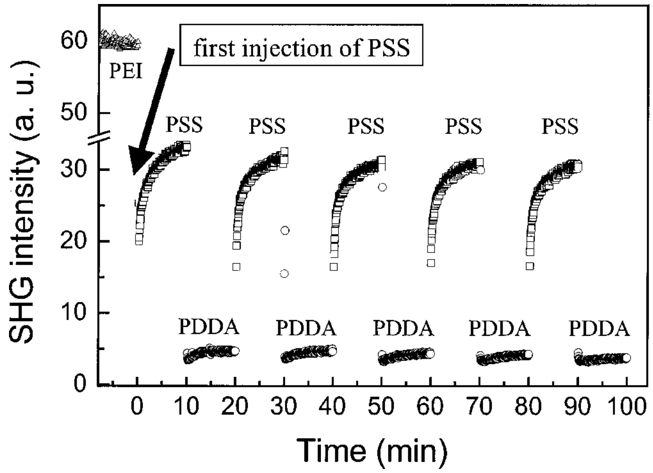

FIG. 3. *In situ* SHG signal taken during the layer-by-layer growth of a PSS/PDDA multilayer.

frozen in rather than forming the uniform films that are observed at longer times.[12,9] The granular structure of the adsorbed polyelectrolytes observed in Fig. 2 suggests describing the adsorption kinetics in terms of a random sequential adsorption (RSA) model, which considers irreversible adsorption of macromolecules in surface areas that have not previously been occupied by other units.[28–30]

B. Layer formation dynamics

Figure 3 shows the measured time-dependent SHG signal starting with the deposition of the first PSS layer on top of the precursor film. After the PSS solution is injected at time zero into the cuvette the SHG signal drops down from the value observed for the precursor film to a minimum within a few seconds (<10 s). In agreement with previous work by Goh *et al.*[26] the SHG signal increases again with ongoing polyelectrolyte adsorption. A similar time dependence has been observed recently by Xie and Granick[17] using fourier transform infrared spectroscopy in attenuated total reflection mode (FTIR-ATR). After 10 min the PSS solution is removed. After washing, a PDDA solution is added to the cuvette and the SHG measurement is started again. The signal drops again down to a minimum and, after passing it, increases to a value which is roughly a factor of 7 less than in the case of PSS. Film preparation and SHG measurements are continued by adding alternately PSS and PDDA. We repeatedly get SHG results very similar to those we find for the first adsorbed layers of PSS and PDDA.

For an analysis of the SHG signal two contributions have to be considered:[26,31] (i) a dc field independent and (ii) a dc field dependent term,

$$\mathbf{E}(\mathbf{2\omega})\propto\mathbf{P^{(0)}}(\mathbf{2}\omega)+\chi^{(\mathbf{3})}\mathbf{E}(\omega)\mathbf{E}(\omega)\varphi_{\mathbf{0}}. \tag{3.1}$$

Here $\mathbf{E}(\omega)$ is the applied optical field. $\mathbf{P^{(0)}}(\mathbf{2}\omega)$ is the second order nonlinear polarization which is independent of the surface potential. A bulk contribution from the polyelectrolyte layers is ruled out since the SHG signal does not increase with the number of layers, as shown in Fig. 3. Therefore only the electric dipole term $\mathbf{P^{(0)}}(\mathbf{2}\omega)=\chi_{\mathbf{S}}^{(\mathbf{2})}\mathbf{E}(\omega)\mathbf{E}(\omega)$ stemming from the substrate/film and film/solution interfaces contributes to the dc-field independent term.

The main changes in the SHG signal are caused by changes of the surface potential φ_0 due to the adsorption of new charged molecules. The dominating role of the surface potential is justified by an estimation of the magnitude of the dc field associated with it: The surface density of adsorbed polyions in our case can be estimated using the value of 10^{12} molecules/cm^2 determined by x-ray scattering[21] on a PSS film prepared under similar conditions. By multiplying the mean repeat unit number $\langle N\rangle\sim340$ of a PSS chain with the molecular surface density we get $6\cdot10^{14}$ subunits per cm^2. Since every subunit carries one elementary charge a density of $6\cdot10^{14}$ per cm^2 is calculated. This results in an large electrostatic field on the order of 10^6 V/cm.[32] It was shown in Ref. 31 that the SHG signal from a fused silica/water interface is caused by similarly large electrostatic fields near the interface. In our case additional changes in $\chi^{(3)}$ during the adsorption process have to be considered.

The time dependence of the SHG signal is attributed to a transient change of the surface potential φ_0. Immediately after injection of a new polyelectrolyte solution the polyions will adsorb very rapidly since all adsorption sites are unoccupied. The surface potential due to the previous polyelectrolyte layer will be neutralized very rapidly and φ_0 will drop to zero. After the sign change the potential increases again due to the ongoing adsorption of charged polyelectrolyte forming polydisperse disks on the substrate. More quantitatively, the time dependent potential $\varphi_0(t)$ is proportional to the surface charge density $\sigma(t)$,

$$\varphi_0(t)\propto\sigma(t)=n(t)e, \tag{3.2}$$

where $n(t)$ is the number of charges per unit area and e is the elementary charge. This density is also proportional to the surface density of adsorbed polyelectrolyte grains $n_{\mathrm{PEL}}(t)$. For modeling the adsorption dynamics of polyelectrolytes we apply the theory of random sequential adsorption (RSA).[28] In this theory the adsorption of monolayers is described as a statistical process of irreversibly adsorbing species taking into account the reduction of the surface density of available adsorption sites.[28–30] Our AFM images as well as previous work[12] indicates the formation of disklike granules during the adsorption process. During the ongoing adsorption of polyelectrolytes the chains reorganize such that granules consisting of many chains are formed. The total density of adsorption sites is gradually decreased leading to a slowing down of further adsorption.

Applying this model the time dependent surface density of polyelectrolyte disks is described by

$$n_{\mathrm{PEL}}(t)=n_{\mathrm{PEL},J}-\frac{c}{t^{1/d}}, \tag{3.3}$$

where $n_{\mathrm{PEL},J}$ is the jamming density, d is the number of degrees of freedom of the adsorbed species, and c is a constant. Computer simulations[33] and theoretical calculations[34] predict $d=3$ in the case of polydisperse disks.

For the calculation of the SHG signal according to Eq. (3.1) the time dependence of $\chi^{(3)}$ has to be considered as well. $\chi^{(3)}$ consists of different contributions from the (macro)molecules at the interface between film and solution,

$$\chi^{(3)}=n_{\mathrm{PEL}}(t)\cdot\gamma_{\mathrm{PEL}}+n_{\mathrm{H_2O}}(t)\cdot\gamma_{\mathrm{H_2O}}, \tag{3.4}$$

where $n_{\mathrm{H_2O}}$ is the surface density of water molecules. γ_{PEL} and $\gamma_{\mathrm{H_2O}}$ are the third order molecular hyperpolarizabilities of polyelectrolytes and water molecules, respectively. During adsorption of the oppositely charged polyelectrolytes $\chi^{(3)}(t)$ alternates between the extreme values $\chi^{(3)}_{\mathrm{PSS}}$ for a film with a PSS monolayer as the last layer and $\chi^{(3)}_{\mathrm{PDDA}}$ for a film fully covered with a PDDA monolayer. In both cases there is also a contribution from the water molecules near the film surface.[31] Thus, during the adsorption of a new polyelectrolyte layer $\chi^{(3)}(t)$ is, in a linear approximation, modified according to the following equation:

$$\chi^{(3)}(t)=n_{\mathrm{PEL}}(t)\cdot\gamma_{\mathrm{eff}}+\chi^{(3)}_{0}, \tag{3.5}$$

where $\chi^{(3)}_{0}$ is the third order nonlinear susceptibility prior to adsorption of the new layer. γ_{eff} takes into account contributions from polyelectrolytes and water molecules.

As seen in Fig. 3, at the beginning of adding a polyelectrolyte solution into the cuvette the signal from every layer drops down much faster than the time resolution of our setup (≈ 3 s). This drop can be explained by the rapid adsorption of polyelectrolytes. As long as the surface density of the resulting disklike granules is well below the jamming density the adsorption rate is very high. This leads to a fast compensation of the surface charges and thus a drop of the surface potential and hence the SHG signal. After neutralization of the surface charges the ongoing adsorption gives rise to an increase of the absolute value of the surface potential; this increase subsequently slows down due to the disk density approaching the jamming density.

We fitted the increase of the SHG signal using Eqs. (3.1)–(3.5) and determined $n_{\mathrm{PEL},J}/c=2.5\ \mathrm{s}^{-1/3}$ for PSS and $n_{\mathrm{PEL},J}/c=0.96\ \mathrm{s}^{-1/3}$ for PDDA as fit parameters. The fits are shown as solid lines in Fig. 4 together with the measured SHG data taken from the period $t=40-50$ min and 30–40 min, respectively, in Fig. 3. For easier comparison with theory the axes have been rescaled. Excellent agreement between the experimental curve and the fit using the RSA model is found for both polyelectrolytes. We have to conclude that the RSA model gives a very good description of the formation dynamics of self-assembled monolayers formed by polyelectrolyte disks.

We attribute the large difference (factor 7) of the SHG signal from PSS and PDDA to the difference of the hyperpolarizabilities γ_{PEL} and to residual water molecules between the substrate and the first polyelectrolyte layer. As outlined in Ref. 26 some charges at the quartz substrate might not be compensated by the first polyelectrolyte layer (PEI). This would give rise to an orientation of residual water molecules near the substrate in parallel to water molecules near the uppermost negatively charged PSS layer. As a result the nonlinear signals from both kinds of water molecules will add to each other. In addtion, it is expected that the aromatic ring of PSS gives rise to a higher hyperpolarizibility than in the case of the nonconjugated PDDA.[35] Therefore in our case $\beta_{\mathrm{PSS}}>\beta_{\mathrm{PDDA}}$ and $\gamma_{\mathrm{PSS}}>\gamma_{\mathrm{PDDA}}$ for the second and third order hyperpolarizabilities should hold.

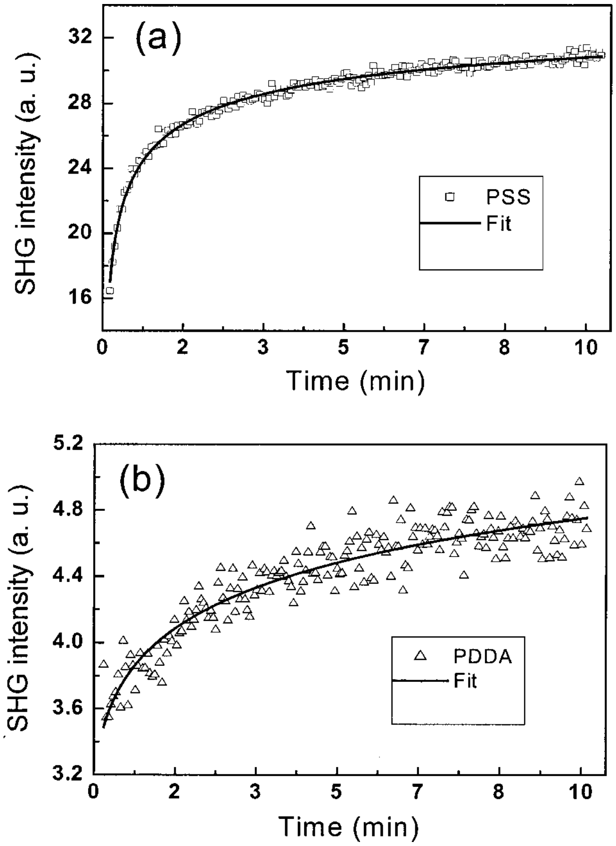

FIG. 4. Enlarged plot of the SHG signals from PSS (a) and PDDA (b) in the interval $t=40-50$ min and 30–40 min, respectively. The solid lines are fits using the RSA model as described in the text.

C. Built-in electric fields in dry samples

The drying process of the samples should lead to charge neutralization of the surface due to adsorption of counterions. The layer structure is expected not to be significantly changed upon drying.[36]

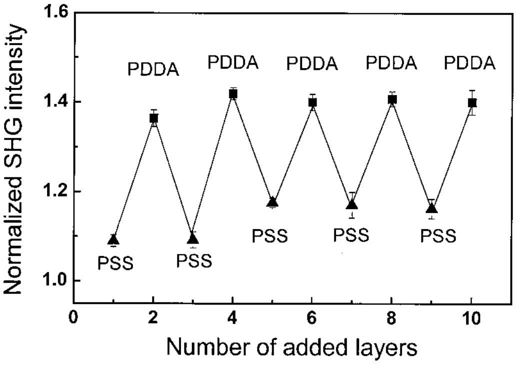

FIG. 5. SHG signals measured from a series of dry multilayer samples of PSS/PDDA deposited on a precursor film. The respective intensities have been normalized to the SHG signal observed on a glass surface under the same experimental conditions.

The SHG results of different multilayer structures measured in the dry state are shown in Fig. 5. Again, no continuous increase of the SHG signal with the number of adsorbed layers is observed. This rules out again a bulk contribution to the nonlinear polarization in the case of dry films. The signal from the films ending with a PDDA layer is always higher than that from films which exhibit PSS as the last layer. This is the reversed situation compared to the wet state. In comparison to the wet state (cf. Fig. 2), however, the difference between PSS and PDDA is very small. The surprising observation of a larger signal in case of an uppermost PDDA layer is in contrast to the expected smaller second and third order hyperpolarizibilities as compared to PSS.

We attribute this observation to the buildup of an internal DC field in the case of PDDA as the uppermost layer. It is known that the first layer does not fully compensate the surface charges of the substrate.[37] In our case the substrate charge is negative, therefore the positive counterions from PSS can additionally compensate or screen these charges by penetrating into the multilayer film when the film dries. We speculate that this process is most efficient for thin films leading to the smallest SHG signal in the case of only one or two PSS layers (see Fig. 5). In contrast the negative counter ions from PDDA do not compensate the negative charge on the substrate and a dc electric field is left. This additional field induces SHG for the samples with an uppermost PDDA layer. We note that we made similar observations when measuring the SHG signals from PEI (polycation) and PMA (polyanion) multilayers (not shown here). In this case films ending with PEI gave larger signals than films ending with PMA.

Recently it has been pointed out that the uppermost layer in a layer-by-layer self assembled film can influence the fractional ionization of an embedded weak polyelectrolyte.[17,38] This effect might also play a role in our measurements. A future more detailed investigation of the relation between the fractional ionization of embedded layers and the overall SHG signal should clarify this issue.

IV. CONCLUSIONS

We have presented a detailed *in situ* SHG study of the formation dynamics of polyelectrolyte multilayers using the self-assembly technique. The adsorption dynamics can be understood in terms of random sequential adsorption (RSA) of polyelectrolytes forming polydisperse disks that lead to a time-dependent surface potential. In the dry state the SHG signal is modified by electric fields caused by uncompensated substrate charges.

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