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Preparation of Poly(acrylic acid) Nano-films by In-situ Polymerization of Acrylic Acid Macroclusters on Silicon Oxide Surfaces

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Summary: A new method for preparing poly(acrylic acid) (PAA) films on silicon oxide surfaces with smooth morphology has been developed. Acrylic acid (AA) was preferably adsorbed on silicon oxide surfaces in AA/ chloroform binary liquids and formed a hydrogen-bonded organized structure, which was called molecular macrocluster. AA macroclusters on silicon oxide surfaces were in-situ polymerized to obtain molecularly flat polymer films with thickness up to 10 nm. In-situ polymerizations were conducted by photo-irradiation in the presence of a photo initiator, 2,2-dimethoxy-2-phenyl-acetophenone (DPA). As a reference, the adsorption of PAA polymerized in the bulk solution was examined on silicon oxide surfaces. A series of techniques such as attenuated total reflection–FTIR (ATR-FTIR) spectroscopy, ellipsometry and atomic force microscopy (AFM) was utilized for characterizing two types of films. It was found that flat PAA films with linear hydrogen-bonded COOH could only be obtained by in-situ polymerization, which demonstrated this method was an effective way for preparing molecularly uniform polymer films. The surface morphology and thickness of obtained PAA films were found to be dependent on the monomer concentration, initiator amount and photoirradiation time. Molecularly uniform and flat PAA films were obtained after 5 min irradiation at 0.8 mol% AA in the presence of 5 wt% DPA.

Keywords: acrylic acid; films; macroclusters; photopolymerization

Introduction

Over the past thirty years, the modification of solid surfaces with polymeric materials has drawn much interest in a wide range of interdisciplinary fields, including chemistry, physics, biology and nanotechnology.[1–2] The self-assembled monolayer (SAM),[3,4] layer-by-layer technique (LBL),[5,6] Langmuir-Blodgett (LB) technique[7,8] and the spin coating process[9] are widely used methods for preparing thin films. However, these techniques suffered several drawbacks. The spin coating can only be applied to flat substrates, while others can be used for other substrates. For LB technique, the film quality depends on mechanical manipulation, and building up the film on a large scale and at a high speed may be impossible. Although the LBL technique can circumvent this shortcoming, it is not suitable for preparing molecularly flat films. Self-assembled monolayer is thought to be an important technique for forming films at the molecular level, but it is not favorable for preparing films with thickness in the range of tens of nanometers.

In order to solve these problems, a new method, in-situ polymerization of macroclusters formed on silica surface, has been proposed for fabricating nano-polymer films. This method is based on our recent finding, that alcohols and carboxylic acids are selectively adsorbed onto silica surfaces in a non-polar solvent and form hydrogen-

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bonded macroclusters in the thickness of more than several ten nanometers.[10,11] These surface macroclusters are in the ordered linear chain structure with the cluster axis aligned almost normal to the surface.[10,11] In-situ polymerization of macroclusters formed by polymerizable molecules (such as acrylic acid, amide) is supposed to prepare uniform, defect-free films with thickness more than several ten nanometers.

Polymerization of organized assemblies (LB films, vesicles, micelles etc) from designed reactive amphiphiles is a useful technique to convert them into more durable structures,[12–17] especially photopolymerization, as the free-radical process is initiated independent on polymerization temperature. For example, polymerized vesicles maintained their size and shape even in excess surfactant, indicating a two-dimensional strained polymerization can yield stable three-dimensional objects.[18,19] Polymerization of molecular organized assemblies could not only provide improved stability but fix the orientation of the molecules.[20]

The in-situ photopolymerization of surface macroclusters shows similar advantages. It allows a simple preparation process without complicated instrumentation, and is independent on substrate shape. Polymer films could be prepared by this method at a reasonable speed on an industrial scale. Moreover, the polymer films prepared by this method were reported to be defect-free at the AFM scale.[21] However, the polymerization process wasn't investigated in detail. Furthermore, the failure in preparing films on silicon oxide surfaces somewhat limited the applications of this method, since the modification of silicon oxide surfaces by various polymer films has gained considerable attention due to its important applications ranging from microelectronics to solar cells.[22–24]

In this study, we prepared PAA films with thickness of more than 10nm on silicon oxide surfaces by in-situ photopolymerization. From the comparison of films by in-situ polymerization and by adsorbed from polymerized AA solution, it revealed that the in-situ polymerization of macroclusters provides a unique method for preparing polymer films with smooth morphology. Conditions of polymerization, i.e. monomer concentration, amount of initiator and irradiating time were varied to optimize the reaction conditions in respect to the morphology and thickness.

Experimental Part

Materials

The acrylic acid monomer from Nacalai Tesque was distilled under reduced pressure (667pa) prior to use. Chloroform (Nacalai Tesque, 98%) was first washed with pure water and sodium hydroxide solution to remove any residual ethanol, then dried with anhydrous calcium chloride and distilled immediately prior to use. 2,2-dimethoxy-2-phenylacetophenone (DPA) was used as a photo initiator without any purification. The substrates used here were an oxidized silicon prism for ATR–FTIR, a silicon wafer for ellipsometer measurement and atomic force microscopy. The treatment of substrates was the same as described in previous papers.[10,11]

Adsorption and Polymerization of Acrylic Acid on Silicon Oxide Surfaces

The washed substrates were treated with water vapor plasma in order to ensure the existence of surface silanol groups, and immediately put into chloroform. Acrylic acid was added to the chloroform at the concentration of acrylic acid from 0.1 to 1.0 mol%. After equilibrating adsorption for 30 min, DPA (dissolved into chloroform) was added until 1-5 wt% with respect to AA concentration. The photopolymerization was carried out using a deep UV lamp with an intensity of 4 mw/cm^2 for 5-15 min. After polymerization, the films were washed thoroughly with chloroform to remove the unreacted monomer and adsorbed initiator. In other method, 0.8 mol% AA in chloroform was photo-irradiated for 15 min with deep UV lamp in the presence of 5 wt% DPA, and then adsorbed onto silicon oxide surfaces for 30 min. The adsorbed PAA films were obtained.

Characterization

The thickness of polymer films could be directly measured by an ellipsometer (MIZOJIRI-OPTICAL, DHA-XA/S3-T). The polymerization process was monitored by the attenuated total reflection –FTIR (ATR-FTIR) using a Perkin–Elmer FTIR system 2000, equipped with a ATR attachment from Grasby Specac and a homemade stainless steel liquid cell. ATR-FTIR spectra were measured using a silicon prism (Nihon PASTEC, 60 × 16 × 4 mm trapezoid) as a substrate. The surface morphology of PAA films on a silicon wafer was investigated by AFM (Digital instrument NanoScope IV) in the contact mode using Si_3N_4 cantilever (Olympus, OMCL-TR400PS). The root mean square (RMS) roughness of the surface modified by PAA films was calculated from the AFM images.

Results and Discussion

Polymerization of Acrylic Acid Macroclusters on Silicon Oxide Surfaces

To characterize the polymerization process of an acrylic acid adsorption layer on silicon oxide surfaces, ATR-FTIR spectra of adsorbed AA for each step of treatments, including the course of photoirradiation, were measured in AA-chloroform mixtures, as summarized in Figure 1 and Table 1. The spectrum of 0.8 mol% AA adsorbed onto a silicon oxide surface in chloroform shows a strong peak at 1702 cm^{-1} with a shoulder peak at 1730 cm^{-1}, which correspond to the C=O stretching of the hydrogen-bonded and the free COOH of AA, respectively.[25–27] The peaks at 1636 cm^{-1} and 1620 cm^{-1} are assigned to the C=C stretching vibration. A medium intensity peak at 1432 cm^{-1} is due to CH_2 deformation, and a peak at 1260 cm^{-1} is ascribed to C–O stretching coupled with O–H in-plane bending of the carboxyl group.[28]

After the addition of a photo initiator-DPA, two new peaks at 1594 cm^{-1} and

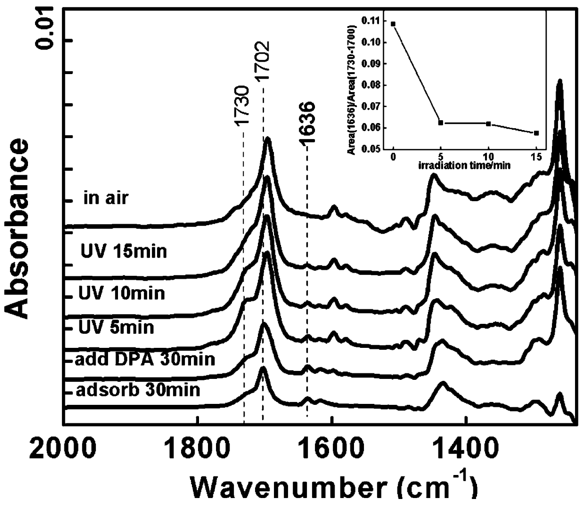

Figure 1.

ATR-FTIR spectra of 0.8 mol% AA in chloroform adsorbed on silicon oxide surfaces for 30 min, and during the course of UV irradiation from 0–15 min as well as the spectrum of PAA film measured in air. Inset figure is the dependence of relative intensity of adsorption band at 1636 cm^{-1} (Area (1636 cm^{-1})/Area (1700 cm^{-1}) on irradiation time.

Table 1.
Change in IR Frequencies (ν/cm^{-1}) of adsorbed AA for each step of treatments.

Adsorption 30 min	Add DPA	UV 5–15 min	In air	assignment
1730, shoulder	1730, shoulder	1730, decrease	No	C=O stretching of free COOH group
1702, strong	1702, strong	1696	1696	C=O stretching of hydrogen-bonded COOH group
1636	1636	1636,decrease	No	C=C stretching of AA
1620	1620	1620,decrease	No	
	1594, 1580	1594, 1580	1594, 1580	C=C stretching of phenyl ring of DPA
1432	1432	1448	1448	CH_2 deformation
1260	1260	1260	1260	C–O stretching coupled with O–H in plane bending

1580 cm^{-1} appear, which correspond to the phenyl ring of DPA. This indicates that the initiator can be incorporated in the AA adsorbed layer on silicon oxide surfaces, which is effective to initiate polymerization. In the process of irradiation, the peak of C=C stretching vibration (1636 cm^{-1}) decreases, a shoulder peak at 1730 cm^{-1} ascribed to C=O stretching vibration of free COOH group decreases gradually, and hydrogen-bonded COOH shifts to lower wavenumber, from 1702 cm^{-1} to 1696 cm^{-1}. The carbonyl peak at around 1700 cm^{-1} was used as an internal standard peak for investigating changes in vinyl group (inset figure). The ratio of integrated band area at 1636 cm^{-1} (C=C group) to that of 1700 cm^{-1} (C=O group) sharply decreases during the initial 5 min irradiation, which reflects that the polymerization takes place via the breaking of C=C group and the formation of C–C bonds.[29] At the irradiation time after 5 min, the C=C group doesn't remarkably decrease, indicating that the polymerization process could progress in short time under irradiation. The decrease in absorption band at 1730 cm^{-1} and the shift of absorption band from 1702 cm^{-1} to 1696 cm^{-1} may be also due to the polymerization. It is reported that in PAA system, the C=O stretching peak of the free carboxyl group appears at around 1730 cm^{-1}, and that of the cyclic hydrogen-bonded COOH in dimeric form appears at 1705 cm^{-1}, while the C=O group would continue to shift to a lower frequency at 1688 cm^{-1} if inner hydrogen bonding of the oligomeric formed.[29,30] According to that elucidation, the decrease in 1730 cm^{-1} and the shift of C=O band at 1702 cm^{-1} are both attributed to the inner hydrogen groups of the oligomeric COOH groups due to polymerization.

After 15 min irradiation, the solution was removed and the film was thoroughly rinsed by chloroform, subsequently, the spectrum was measured in air, all absorption bands should be from polymer film. It is obvious C=O stretching (1696 cm^{-1}), CH_2 deformation (1448 cm^{-1}) and C–O stretching(1260 cm^{-1}) still exist, which demonstrates the formation of PAA film. The disappearance of C=C bonding is due to all unreacted AA monomer being removed by rinsing. The peak at 1730 cm^{-1} disappears; indicating that non-hydrogen bonded carbonyl group is also removed by rinsing and only polymerized AA exist on silicon oxide surfaces.

Comparison of PAA Films Prepared by in-situ Polymerization of AA Macroclusters and by Adsorption from PAA Solution

The FT-IR spectrum of PAA film prepared by adsorption from PAA solution was recorded to compare with in-situ polymerized films (Figure 2). In the case of PAA film adsorbed from PAA solution, the spectrum shows much lower absorbance than that of in-situ polymerized. This means a thick polymer film was not formed on the surfaces by adsorption from PAA solution. Furthermore, the peak of C=O band is different from that of in-situ polymerized. As mentioned before, the C=O band of in-situ polymerized PAA film appeared at 1696 cm^{-1}, which could be attributed to

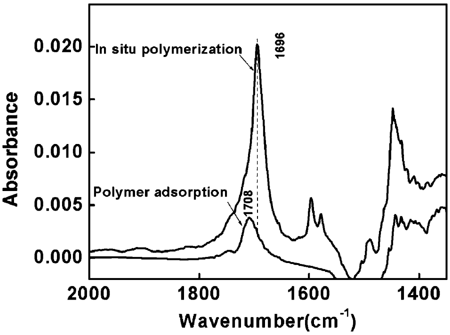

Figure 2.
ATR-FTIR spectra of PAA films prepared by in-situ polymerization and by adsorption.

the inner hydrogen groups of the oligomeric COOH group.[29] On the other hand, a peak at 1708 cm^{-1} for the adsorbed PAA film is assigned to the C=O stretching modes of the cyclic hydrogen-bonded COOH group in a dimeric form. Based on the detailed analysis of the IR spectra, we think that this difference is due to the chain structure, and the in-situ polymerization of surface macroclusters could result in PAA film with linear chains.

The ellipsometer data show that the thickness of PAA film prepared by in situ polymerization is 15.62 ± 4.1 nm, while that of adsorbed PAA film is only 2.1 ± 0.9 nm thick, agreeing well with ATR-FTIR spectra.

The morphology of PAA film obtained by in-situ polymerization was found to be significantly different from that of adsorbed film, as shown in Figure 3. In the case of PAA film formed by in-situ polymerization, quite smooth morphology appears in the scale of 2 × 2 μm. The root mean square roughness (RMS) directly calculated from AFM images is 0.248 nm. In contrast, there is no uniform film on the substrate for adsorbed PAA film. The surface shows a few domain structures with a size around 400 nm and with a height about 50 nm. The roughness (RMS = 4.732 nm) is more than an order of magnitude higher than that of in-situ polymerized film. The combination of above experimental results has led to important sight that the in-situ polymerization of surface macroclusters is responsible for the preparation of defect-free polymer films accompanied with an ordered structure. It is concluded that the surface macroclusters formed by hydrogen-bonding, which has an ordered structure, is essentially important to determine not only the structure of films but also the morphology.

Effect of Monomer Concentration on the Thickness of PAA Films

Preparation of PAA films by in-situ photo-irradiation was found to be significantly dependent on the monomer concentration. Figure 4 shows the thickness of obtained PAA films as a function of AA concentration at 5 wt% DPA (with respect to AA monomer). At monomer concentrations lower than 0.8 mol%, the PAA films formed on silicon oxide surfaces are rather thin, the thickness is below 5 nm. The thick films can only be obtained at concentrations

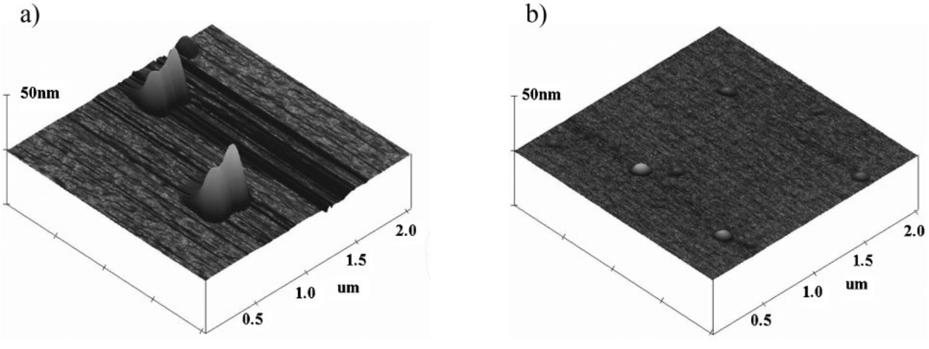

Figure 3.
AFM images of PAA films prepared by (a) adsorption PAA and (b) in-situ polymerisation.

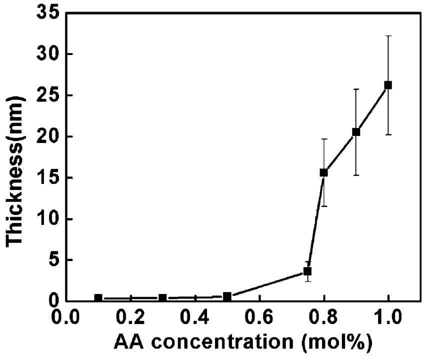

Figure 4.
Dependence of the thickness of obtained PAA films on AA concentration.

above 0.8 mol%. This is obviously different from the PAA films on glass surface. Molecularly flat PAA films with thickness of about 20 nm can be formed at a concentration of 0.1 mol%, as previously reported by our group.[21] This might be resulting from the difference in substrate that affects the formation of macroclusters. Recently, we have found that the macrocluster formation is rather delicate, and utterly relies on surface density of the OH group on a substrate.[31] However, the reason for it is still not so clear; more experiments are needed to be done to elucidate this problem. In order to avoid polymerization in bulk solution and diffusion of monomer onto surface, 0.8 mol% AA, which is the lowest concentration to obtain PAA films with thickness of about 10 nm, was used to prepare polymer films.

Effect of Initiator Concentration on the Thickness and Morphology of PAA Films

In order to investigate the effect of initiator amount on the morphology and thickness of PAA films, polymerization was carried out at varying amount of DPA ranging from 1–5 wt% when the monomer concentration was at 0.8 mol%. For the 1 wt%, 2 wt% and 3 wt% DPA, only thin PAA films with thickness of 0.8 ± 0.5 nm, 1.9 ± 0.9 nm and 1.6 ± 0.7 nm were prepared, respectively. With increasing the DPA ratio to 4% and 5%, the thickness of PAA films increased gradually from 7.3 ± 0.3 to 15.6 ± 4.1nm. It is supposed that initiator amount also plays an important role in polymerization.

Figure 5 shows the AFM images of PAA films on silicon wafer surfaces by photoirradiation at 4 wt% and 5 wt% DPA. For the 4 wt% DPA, the obtained image of the film surface is quite flat (RMS value is 0.134nm in a 2 × 2 μm scale). In the AFM image of PAA film initiated by 5 wt% DPA, roughness of surface (RMS = 0.248 nm) is little higher than that of with 4% DPA. Some domain structures appear, and their size range and average height are from 50 nm to 100 nm and 3 nm, respectively. These surface morphologies were highly reproducible in different sets of experiments, which confirmed that the formation of molecularly flat, uniform PAA films could be obtained by the in-situ photoirradiation of AA macroclusters on silicon oxide surfaces. Subsequent increases in initiator amount results in the increase of polymer film thickness, meanwhile roughness also increases with thickness. As stated previously, the goal of this work was to prepare the defect-free polymer films with certain thickness, so 5 wt% DPA was selected to initiate surface clusters. According to the previous work, the short irradiation time would be favorable for the smooth morphology, because this way could avoid the influence of the diffusion of monomer and /or polymer, formed in the bulk, to the surface.

Effect of Irradiation Time

To understand how irradiation time influences the morphology of polymer films, the AFM images of PAA films formed on

Table 2.
The thickness of PAA films prepared at 0.8mol% AA with DPA varying from 1% to 5% (wt%).

DPA concentration (wt%)	1	2	3	4	5
Thickness (nm)	0.8 ± 0.5	1.9 ± 0.9	1.6 ± 0.7	7.3 ± 0.3	15.62 ± 4.1

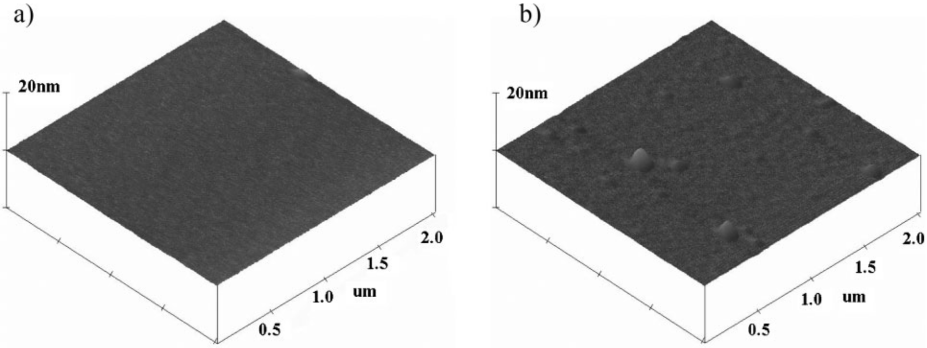

Figure 5.
AFM images of PAA films by in-situ polymerization of 0.8 mol% AA for 15 min at (a) 4 wt% DPA and (b) 5 wt% DPA.

silicon wafer surface by photoirradiation for 5 min, 10 min and 15 min were investigated, as shown in Figure 6. For the 5 min irradiation, the image of the film surface is flat (RMS = 0.119 nm), without any defect or domains. And the thickness is 10.0 ± 0.3 nm, which is a bit lower than polymerization for 15 min. This is accordance with the result of ATR-FTIR spectra, from which the polymerization seems to be equilibrium at the first 5 min. In an AFM image of the PAA film obtained by irradiation for 10 min, several domains appears on the surface and roughness (RMS = 0.149 nm) increases slightly than that of 5 min irradiation. The thickness is 9.3 ± 0.8 nm, which is similar with one prepared by the irradiation for 5 min and a little lower than that of 15 min irradiation. For prolonged irradiation to 15 min, as mentioned before, more domains appear. That is may be due to the influence of diffused monomer and / or polymer, formed in the bulk, to the surface. These results indicate that the low concentration of monomer, certain amount initiator and short irradiation time are essential for preparing smooth and uniform polymer film with thickness of about 10 nm. Under this condition, most of PAA films were made from the adsorbed acrylic acid layer rather than the effect of diffusion of polymer from bulk.

Conclusions

Preparation of PAA nano-films was successfully carried out by in-situ polymerization of AA macroclusters on silicon oxide surfaces. ATR-FTIR measurements were undertaken to understand the polymerization process and the formation of PAA

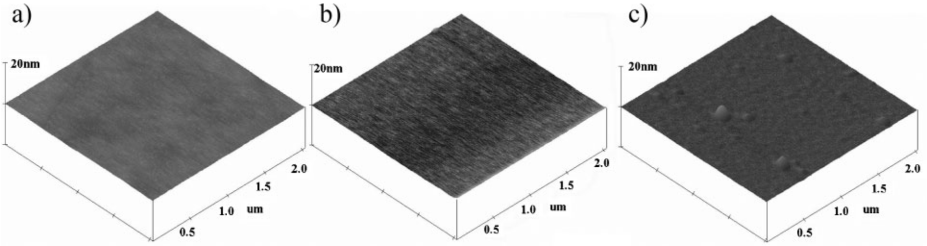

Figure 6.
AFM images of PAA films prepared by in-situ photoirradiation of 0.8 mol% AA for (a) 5 min (b) 10 min and (c) 15 min.

films. FT-IR spectra indicated the presence of linear hydrogen-bonded COOH species. The comparison of in-situ polymerization and adsorption of polymer shows the in-situ polymerization is an effective way to prepare uniform polymer films with smooth morphology. The thickness and morphology has been found to be dependent on polymerization condition. Polymerization at proper initiator ratio and short irradiation time are essential for obtaining molecularly flat and uniform surface with thickness of more than 10 nm.

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