Preparation of Polymer Nano-Films by In-situ Polymerization of Hydrogen Bonded Clusters on Silica Surfaces

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Materials with a regulated structure on the nanometer or molecular scale are becoming important and are attracting much attention.   In this study, we present a method to prepare polymer nano-films which are molecularly flat and ordered.   This method was developed based on our recent findings, the hydrogen bonded cluster formation of alcohol and carboxylic acid selectively adsorbed onto silica surfaces in cyclohexane, which were revealed by surface forces measurements, ATR-FTIR spectroscopy and adsorption isotherm measurements. We utilized this phenomenon for preparing polymer nano-films by the in-situ photopolymerization of acrylic acid clusters formed on silica surfaces in cyclohexane.   The polymer film morphologies were investigated by varying the monomer concentration and photoirradiation time.   Molecularly uniform and flat polymer films were obtained after a 20 min photoirradiation at 0.1 mol% acrylic acid (highest asperity < 1.5 nm in 3 μm x 3μm, thickness $\approx$ 20–30 nm).   The ATR-FTIR spectra revealed that the films obtained had an ordered structure, reflecting the structures of the surface macroclusters of the monomer precursors.   This new preparation method has advantages such as simplicity and applicability to any substrate shape.

Key words: Polymer nano-film, Hydrogen bond, Cluster, Polymerization, Silica surface

1. INTRODUCTION

With the downsizing and the enhanced functions of devices, the development of materials with regulated structures at the nanometer or molecular level is becoming important.   For example, organic thin films are used for many devices such as optical guides, insulators, and conductors, because of their enormous diversity and fine tunability of shape.   For constructing the organic thin films, the self-assembling of monolayers [1], the Langmuir-Blodgett (LB) technique [2], the consecutive adsorption of polyelectrolytes [3], and the spin-cast method have been widely used.   The self-assembling technique can form rather stable monolayer films, but is not suitable for preparing films of several nanometer thicknesses.   In principle, the LB technique can prepare such nano-films, however, it requires special facilities and the manipulation is rather complicated.   The spin-cast method is not suitable for making films with a thickness less than 100 nm. Therefore, a complemental technique is desirable to fabricate organic films which are flat and uniform.

In this study, we present a novel method to form molecularly flat and uniform organic films with thickness of tens of nanometers.   Recently, we have found that alcohols (methanol and ethanol) and carboxylic acids (propionic acid and isobutyric acid) selectively adsorb onto silica surfaces in cyclohexane and form a hydrogen bonded macrocluster at concentrations below 0.5 mol% [4–6].

This phenomenon was utilized for making organic nano-films on a solid surface by the in-situ photopolymerization of a vinyl monomer which bears the carboxylic acid group. Here, we used acrylic acid which has a structure similar to propionic acid except for the double bond.   The adsorption layer of the acrylic acid monomer formed on glass and silicon oxide surfaces in an acrylic acid–cyclohexane binary mixture was in-situ polymerized by UV irradiation.   The obtained polymer films were characterized by an atomic force microscope (AFM) and Fourier transform infrared spectroscopy in the attenuated total reflection mode (ATR-FTIR).   In a 0.1 mol% acrylic acid solution, the polymer films, which were molecularly flat and uniform, were obtained.   A unique ordered structure of adsorbed carboxylic acids was maintained in these films.

2. EXPERIMENTAL
2.1 Materials

The acrylic acid monomer from Nacalai Tesque was distilled under reduced pressure (667 Pa) prior to use [7]. Cyclohexane from Nacalai Tesque was dried with sodium, then distilled immediately prior to use in order to avoid the strong effect of residual water in the solvent.   Azobis-isobutyronitrile (AIBN) from Nacalai Tesque was used as a polymerization initiator.   Poly(acrylic acid) purchased from Wako Chemical was also investigated as a reference.

2.2 Adsorption polymerization method

Glass plates (Matsunami, micro cover glass) were washed in a mixture of sulfuric acid and hydrogen peroxide (4:1, v/v), then thoroughly rinsed with pure water.   The washed glass plates were treated with water vapor plasma (Samco, BP-1, 20 W, 13.56 MHz rf source in 80 Pa of argon and water, 50 ml/min flow rate) for 3 min [8] in order to ensure the existence of silanol groups on the glass surfaces, then put in a glass vessel which contained cyclohexane.   Acrylic acid was added to the vessel and the concentration of acrylic acid was adjusted to 0.1–2.0 mol%.   After an equilibrating adsorption for 1 h, AIBN dissolved in benzene (0.1 or 0.4 M) was added until the molar ratio of AIBN:monomer reached 1:1000, then irradiated with a Hg lamp (HAMAMATSU, Model-C940) to initiate the polymerization.   After the irradiation for 20–180 min, the glass plates were removed from the vessel and dried in a vacuum desiccator.   For ATR-FTIR spectroscopy, a silicon oxide surface formed on the silicon crystal prism (Nihon PASTEC, 60 x 16 x 4 mm trapezoid) was used instead of the glass surface [9], and pretreatment and polymerization were performed in the same manner as for the glass plates.   A schematic illustration of the adsorption polymerization method is presented in Figure 1.
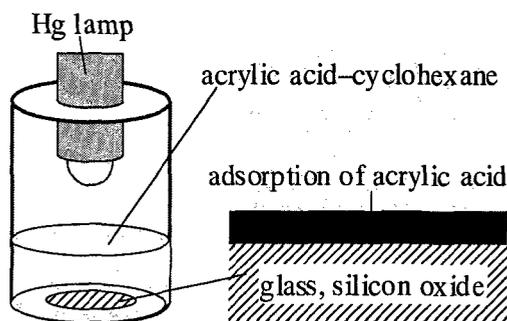

Figure 1.   Schematic illustration of the adsorption polymerization method.

2.3 Characterization of polymer films

An atomic force microscope (AFM, Seiko instruments, SPI3700–SPA300) was used to characterize the poly(acrylic acid) films obtained by the adsorption polymerization.   Surface topographic images were obtained in the contact mode using a V-shaped silicon nitride cantilever with a spring constant of 0.89 N/m (Olympus, OMCL-TR400PS-2).   The AFM was also used for evaluating the polymer film thickness by measuring the interaction forces between a polymer film and the silicon probe tip.   For the interaction forces measurement, a stiff rectangular-shaped silicon cantilever (Nanosensors, POINTPROBES S3G2T6-8L225) with a spring constant of 50 N/m was used to apply a high load (up to a few μN) to the polymer film.

The ATR-FTIR spectra of the poly(acrylic acid) film formed on the silicon oxide surfaces were recorded on a

Perkin-Elmer FTIR system 2000 using a TGS detector [10, 11].   Typically 200 scans were collected with a resolution of 4 cm^{-1} under the dry air condition.   The ATR attachment from Grasby Specac was used combined with a homemade stainless steel cell sealed with a Teflon O-ring which can also be used for measurements in liquids. The background spectrum was measured after the water vapor plasma treatment, then adsorption polymerization was performed.   As a reference, the transmission spectrum of the purchased poly(acrylic acid) dispersed in a KBr tablet was measured.

3. RESULTS AND DISCUSSION

3.1 AFM images of poly(acrylic acid) films

Figure 2 shows the AFM images of poly(acrylic acid) films formed on glass surfaces by photoirradiation for 20, 40, and 60 min at an acrylic acid concentration of 0.1 mol%.   For the 20 min irradiation, the obtained images of the film surfaces were extremely flat (peak to peak height was less than 1.5 nm in a 3 μm x 3 μm area) and practically no defect was detected (Figure 2(a)).   This surface morphology was highly reproducible in different sets of experiments.   This means that the formation of the molecularly flat, uniform and defectless poly(acrylic acid) film, with a thickness of more than 8 nm was obtained by the 20 min irradiation in a 0.1 mol% acrylic acid solution.   In an AFM image of the poly(acrylic acid) film obtained by irradiation for 40 min, several protuberances (about 3 nm in average height) in the 3 μm x 3 μm area appeared (Figure 2(b)).   After the irradiation for 60 min, a slight increase in the number of protuberances was observed (Figure 2(c)), but the major part of the surface remained flat.   For prolonged irradiation, the influence of diffused monomers and/or polymers, formed in the bulk, to the surfaces became significant and was attributed to the observed protuberances.

When the concentration of the acrylic acid increased, the structures of the obtained polymer films were quite different from those at 0.1 mol%.   Films obtained with a 40 min irradiation in 1.0 mol% acrylic acid solution exhibited many uniform protuberances (about 100 nm in diameter and 5 nm in height) on the surfaces.   The extremely uniform and flat surface was also obtained for films prepared by the irradiation for 180 min in a 1.0 mol% acrylic acid solution.   Its structure was similar to that obtained by the 20 min irradiation in 0.1 mol% acrylic acid (Figure 2(a)).   This could be explained by filling the spaces between the protuberances with a uniform height, however, good reproducibility was not achieved.   These results indicated that the low concentration of acrylic acid and short irradiation time are essential for obtaining molecularly flat and uniform polymer surfaces with good reproducibility.   Under this condition, the obtained polymer films were made only from the adsorbed acrylic acid monomer, and by avoiding the effect of diffusion of the monomers and polymers from the bulk.
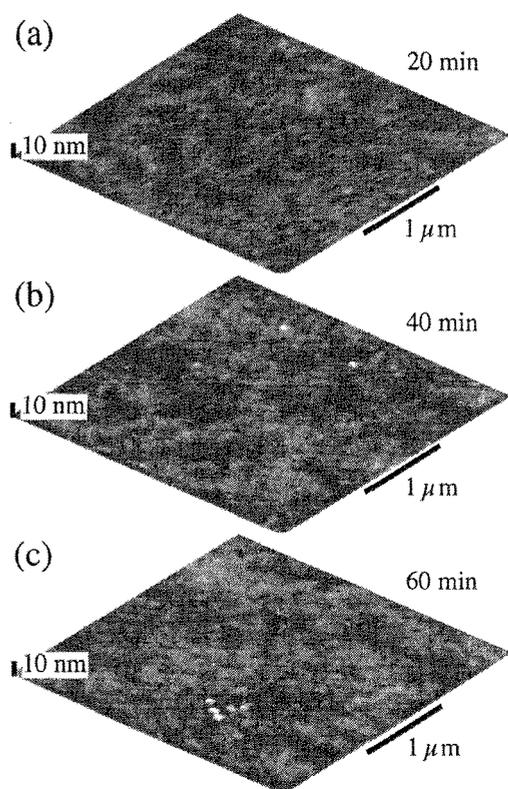
Figure 2.   AFM images of poly(acrylic acid) films obtained by the adsorption polymerization method for an acrylic acid monomer concentration of 0.1 mol% with the irradiation time of (a) 20 min, (b) 40 min, and (c) 60 min.

3.2 Characterization of the molecularly flat and uniform poly(acrylic acid) film

The molecularly flat and uniform poly(acrylic acid) film obtained at 0.1 mol% acrylic acid by the 20 min irradiation was further investigated by the forces measurement and ATR-IR spectroscopy.   Figure 3 shows force profiles between the poly(acrylic acid) film and silicon tip in air.   The zero of the surface distance was adjusted to the region where the extension of the piezo and the deflection of the cantilever were in a linear relation beyond the 2 μN load.   The repulsive forces appeared at distances of 16-25 nm.   This result indicated that the thickness of the poly(acrylic acid) film was around 16-25 nm.   However, the real thickness might be slightly larger than this value because there is no guarantee for the contact of the probe tip with the glass surface under the polymer film.

Figure 4 shows an ATR-FTIR spectrum of the poly(acrylic acid) film formed on the silicon oxide surface of the silicon prism and transmission spectrum of the commercial poly(acrylic acid) dispersed in a KBr tablet. The broad stretching band of the hydrogen bonded OH appeared around 3200 cm^{-1} in the ATR mode which was higher shifted compared with that observed in the transmission mode (around 3000 cm^{-1}).   The stretching

of the hydrogen bonded C=O was observed at 1654 cm^{-1} in the ATR mode which was lower shifted compared with that in the transmission spectrum (1719 cm^{-1}).   Additionally, the negative absorption peak of the free SiOH groups at 3700 cm^{-1} was observed in the ATR spectrum.   This negative absorption of SiOH indicated that the poly(acrylic acid) film was anchored through hydrogen bonding with surface silanol groups [12]

It is known that the oxalic acid forms two different anhydrous crystalline structures which are called α and β[13].   In the α form, the C=O and OH groups of a single COOH are associated with different oxalic acid molecules, exhibiting the OH stretching absorption at higher wavenumber (3114 cm^{-1}) compared with that of the β oxalic acid (2890 cm^{-1}) where the molecules are linked by the intermolecular cyclic form of hydrogen bonding. Therefore, the higher wavenumber shift of the OH stretching band (around 3200 cm^{-1}) in the ATR mode indicated the formation of hydrogen bonding in the non-cyclic form of the poly(acrylic acid) film.

This behavior was further supported by the shift in the C=O stretching band.   Dong et al. measured the temperature dependence of the IR spectra of the poly(acrylic acid) spin cast film [14].   They reported that the C=O stretching band was composed of a free C=O at 1742 cm^{-1}, a terminal C=O at 1725 cm^{-1}, a cyclic dimer C=O at 1705 cm^{-1} and an inner C=O of the linear form at 1680 cm^{-1}.   According to these assignments, the lower wavenumber shift in the C=O band (1654 cm^{-1} in the ATR mode) also indicated non-cyclic hydrogen-bonding formation between the carbonyl groups in the poly(acrylic acid) films.   A plausible structure of the poly(acrylic acid) film is schematically illustrated in Figure 5.

ATR-FTIR spectra of propionic acid in cyclohexane on a silicon oxide surface also exhibited a similar higher shift of the OH stretching band [4].   Therefore, the structure of a monomer adsorption layer was somewhat maintained after polymerization.   This adsorption polymerization method may allow one to incorporate specific structures into the polymer films.

4. CONCLUSION

In this study, we presented a novel, simple and universal method to prepare polymer nano-films, that is, the in-situ polymerization of the monomer adsorption layer formed on the solid surfaces.   By this method, poly(acrylic acid) nano-films (thickness of 20-30 nm),
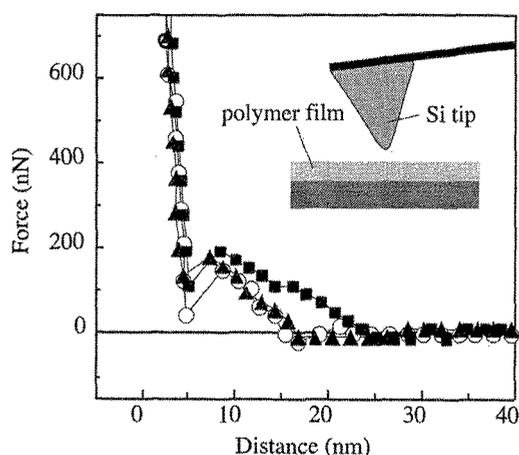
Figure 3.   Interaction forces between the silicon probe tip and a poly(acrylic acid) film formed by the irradiation for 20 min in a 0.1 mol% acrylic acid solution.
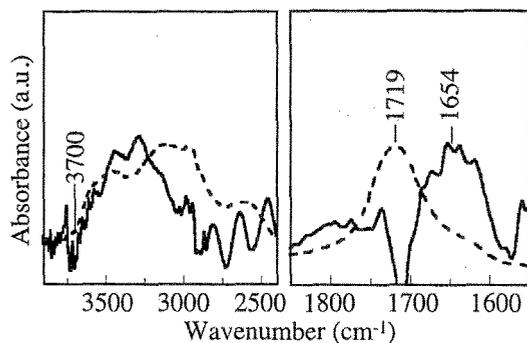

Figure 4.   IR spectra of poly(acrylic acid).   Solid line: ATR-IR spectrum of poly(acrylic acid) film formed on the silicon oxide by irradiation for 20 min in 0.1 mol% acrylic acid solution; broken line: commercial poly(acrylic acid) dispersed in a KBr tablet obtained in the transmission mode.
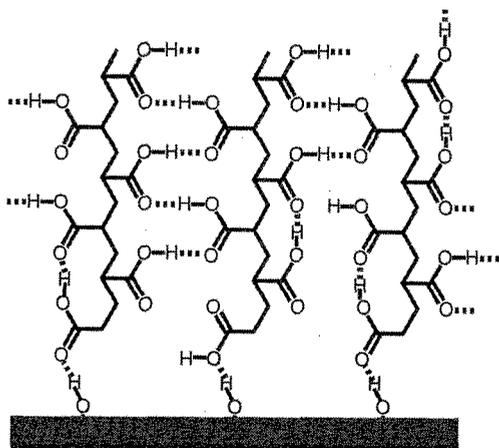

Figure 5.   Schematic structure of poly(acrylic acid) film obtained by the adsorption polymerization method.
which were molecularly flat, uniform and with no defect,

were obtained with high reproducibility.   Compared to the other popular methods such as the spin-cast and the LB method, the adsorption method is simple, low cost and highly applicable to different substrate shape. Preparation of uniquely ordered and/or structured films should be possible.   With these advantages, this method is quite unique, and should be applicable in many areas of material sciences.

5. REFERENCES

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