Modification of Surfaces by Covalent Attachment of Polymer Micelles

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Abstract: Polymer micelles composed of polystyrene-*block*-poly(methacrylic acid) have been chemically attached to amino-modified SiO_2 surfaces by carbodiimide coupling. The density of coverage is very high (ca. 3 x 10^{10} micelles/cm^2) and fairly uniform. The diameter of the micelles is ca. 50 nm and the distribution of micelle sizes is essentially undisturbed by this coupling reaction. These modified surfaces might be of interest in surface modification because of the very high density of reactive groups that are associated with each micelle.

BACKGROUND

Diblock copolymers can exhibit self-assembly capabilities due to different solvent selectivity of each block (Ref. 1). As a result of this, spherical micelle structures can be assembled with the micelle core formed by the poorly solvated block and the micelle corona from the well-solvated block. Amphiphilic block copolymers in water have received attention lately because of their scientific interest and potentially useful industrial applications (Ref. 2). For example, the release kinetics of hydrophobic chemicals from water-soluble micelles has been studied as a model of hydrophobic drug delivery in medicine (Ref. 3) and the detergent-like behavior of these kinds of micelles has been used for removal of specific organic pollutants (Ref. 4).

If water or aqueous buffers dissolve the polyelectrolyte block and strongly precipitate the remaining nonpolar blocks, the micelles exhibit strong segregation of the hydrophobic core and polyelectrolyte corona (Ref. 5). In the case of polystyrene, the high glass transition temperature assures that the core will be rigid and dense (Ref. 5b). Most micellization processes in aqueous solvents are not carried out under equilibrium conditions and each step of micelle preparation is significant for the properties of resulting micelles once mass exchange between unimers and micelles ceases (Ref 5d) or if none of polymers exist as unimers. In some cases amphiphilic block copolymers can spontaneously form micelles (Ref. 5a). Stepwise dialysis from organic solvent-water mixtures to pure water or buffer is often employed to prepare these micelles. After a certain composition of solvent in the dialysis is achieved and there is no further change in the association number but the hydrodynamic

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diameter of a micelle, which is primarily determined by the stretching of the corona, is highly sensitive to solvent composition (Ref. 5b,f,h).

The objective of these studies is the chemical attachment of polymeric micelles onto solid surfaces. Multiblock copolymers on surfaces and interfaces have been investigated by theoretical calculations and experimental model systems and industrial applications have been explored in fields as diverse as aerospace and electronics (Ref. 6). The efforts in this field have contributed to technological developments in the stabilization of dispersed particles, characterization methods, and surface modification. An important aspect of understanding the behavior of polymeric micelles on surfaces lies in characterization of their fixation process onto surfaces. The research described in this report provides techniques and chemistry associated with covalent attachment of water-soluble polymeric micelles assembled from polystyrene-*block*-poly(methacrylic acid) (PS-PMA) on quartz surfaces. Similar studies have been carried out previously on absorption of micelles on polystyrene films (Ref. 7), surface micellization of block copolymers on quartz or liquid surfaces (Ref. 8) and micelle attachment on silicon nitride surfaces (Ref. 9).

EXPERIMENTAL

Copolymers

The detailed synthesis and characterization of the polystyrene-*block*-poly(methacrylic acid) copolymer has been reported (Ref. 10). The PS-PMA copolymer was prepared by a living anionic polymerization in tetrahydrofuran at -78 °C. The weight fraction of PS block (W_{PS}) is 0.64 from NMR analysis and the weight average molecular weights are 2.83×10^4 g/mol for PS block and 1.54×10^4 g/mol for PMA block, as determined by GPC and NMR analyses. The molecular weight of the PS-PMA micelle measured by static light scattering is 1.25×10^7 g/mol which corresponds to an aggregation number of 286 (Ref. 11).

Preparation of Micelles

1,4-Dioxane (99.0 %) was used as received from EM science. The PS-PMA copolymer was dissolved in a dioxane/deionized water mixture (80 volume % dioxane) to produce micelles directly. The solution underwent stepwise dialysis against a series of dioxane/water mixtures with 60, 40, and 20 volume % dioxane. A fifty-fold volume excess solvent mixture was used at each step for 4 h and typically a 20 % dioxane step was performed twice. PVDF filters (0.45 mm pore size, Gelman) were used to filter the micellar solution although there is no visible aggregation.

Preparation of Reactive Surface

Fused quartz discs (1" x 1/16") were obtained from Quartz Plus, Inc. The quartz surfaces were cleaned by dipping the discs in a series of acid solutions: 10% HNO_3 for 1-2 min, 50/50 concentrated HCl/methanol for 1-2 min, and concentrated H_2SO_4 for 30-60 s. The surfaces were rinsed thoroughly with deionized water after each dipping and air-dried.

A 5 vol.-% (3-aminopropyl)trimethoxysilane (APTMS, b.p. 91-92 °C/15 mm, Aldrich) solution was prepared by mixing APTMS with toluene (Fisher Scientific) which was passed through an alumina column to remove water. The vapor phase silanization reaction was performed by placing the acid-cleaned quartz discs (DS1, DS2) in a stationary open holder located above refluxing 5 vol.-% APTMS in toluene solution at 97 °C for 6 h. The amino-activated quartz surfaces were washed with toluene, air-dried, and stored in a vacuum desiccator. A xylene solution of {3-[(2-aminoethyl)amino]propyl}trimethoxysilane (b.p. = 140 °C/15 mm) which has two active amino groups was also tried, but it failed since there was not enough vapor pressure of silane at the boiling point of xylene. In order to improve the uniformity of amino groups on surfaces, a device for rotating the quartz discs (DR1, DR2) during the vapor-phase reaction replaced the stationary holder.

The reaction mechanism for this process is well known: hydrolysis of alkoxy groups of APTMS occurs either by absorbed H_2O on substrate surfaces or with OH groups of the surfaces. In the former case, the resulting silanols can form covalent linkages with the substrate by losing water. However, these silanols may condense with themselves to form oligomers on the surface. Therefore, the dryness of the equipment and the surfaces is a critical factor of the reaction. The surfaces and the apparatus including the rotary disc holder were dried in an oven at 120 °C for 30 min before the surface activating reaction.

Micelle Attachment

The PS-PMA micelles were attached to the aminated surface by the reaction of the carboxyl groups on the micelle coronas using a carbodiimide reagent. A dilute 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide methiodide (Aldrich) solution in a 80-vol.-% dioxane/water mixture was mixed with a micelle solution and the activated quartz disc was then immersed into the carbodiimide and micelle mixture (12.0 mL) for 6 h at ambient temperature. The samples denoted 1065-10, 1065-15, 1065-20, and 1065-25 were prepared from 1.0, 1.5, 2.0, and 2.5 mmol of the carbodiimide in the reaction mixtures, respectively. The concentration of micelles was 1.065 mg/mL, which is equivalent to 4.45 mmol of carboxylic acid groups. The surface micelle samples were rinsed with 80 % dioxane/water mixture and air-dried completely before measurements.

Characterization of Surface

Water Contact Angle Measurement

Water contact angles were measured with NRL C.A. Goniometer (Ramé-hart, Inc.). Deionized water droplets (maximum of 100 μL) were used in all measurements at room temperature. The final readings were taken approximately 1 min but no more than 3 min after setting the water droplet on the level surface. The surface was divided into several sectors and then at least 20 water contact angles were measured for a quartz surface.

X-Ray Photoelectron Spectroscopy

To study the availability of the amino groups on surfaces with XPS, the activated surfaces were submerged into a stirred 3.5 vol.-% trifluoroacetic anhydride (TFAA, 99+ %, Aldrich) solution in dichloromethane (EM Science) at room temperature for 6 h. TFAA can react readily with the amino groups and has a distinct fluorine peak in XPS, which allows an estimate of the fraction of amino groups that are reactive towards carboxylic acids.

The nitrogen and fluorine composition of the amino surface activated with TFAA was measured by XPS with Physical Electronics PHI 5700 ESCA System Model 10-610. Since quartz is an insulator, the sample became charged during the experiment. The survey scan over 0 - 1400 eV was performed at a pass energy of 93.900 eV and an energy step of 0.25 eV. The monochromatic Al Kα X-rays were used at a power of 300 W. The base pressure was 3.5 x 10^{-10} Torr when the data were acquired. Several points on a surface were measured to obtain statistical results.

Scanning Electron Microscopy

The SEM samples were prepared by taping the micelle-attached surfaces on the pin mount for SEM (1 cm in diam., Ted Pella, Inc.). A touch of colloidal silver liquid (Ted Pella, Inc.) was applied on each surface in order to assure electrical contact. The surfaces were then coated with Au in a Ladd bench-top sputter at 2.5 kV and 20 mA for 60 s, which produced ca. 15 nm thickness of Au on the surfaces. Electron micrographs were acquired on a Philips Model SEM-515 scanning electron microscope with a Polaroid Camera at 25.3 kV with a beam size of 10 nm.

Atomic Force Microscopy

The micelles on the surface were also studied by AFM with Auto Probe cp AFM (Park Scientific). Ultralevers from Park Scientific were used as the cantilever and tip. The sample was taped on a stainless steel sample support (2 cm in diam.) which was placed on a piezoelectric scanner with a maximum scan range of 100 mm x 100 mm. The non-contact image was acquired while the displacement of the probe was used as the feedback in the constant-force mode.

RESULTS

SiO_2 Surface After Silane Reaction

Contact angle measurements and XPS are well-known analytical tools to monitor the uniformity and completeness of surface modification reactions. The surface was divided into several sectors and then at least 20 water contact angles were measured for a quartz surface. The nitrogen of APTMS on the surface can be easily detected by XPS. The survey spectrum of the aminated surface shows the very distinct characteristic O1s, C1s, Si1s, and Si2p peaks, but the N1s peak is small due to its low concentration. In our chemical treatment, carbon impurities were unavoidable, so the carbon composition is not a reliable measure of the surface composition. The Si and O peaks are mainly from the abundant Si and O in quartz, so the ratio of silicon to nitrogen or oxygen to nitrogen cannot be used to find the absolute density of amino groups on the surface. The ratio of the distinct N1s and F1s peaks was used to find the availability of amino groups after reacting TFAA with surface amino groups.

The results for the rotated (DR1, DR2) and unrotated (DS1, DS2) samples are summarized in Table 1.

Table 1. Water contact angles and XPS of quartz-supported PS-PMA micelles

	H_2O contact angle (°)		XPS
Sample[a]	acid-cleaned	+ aminosilane	F/N
DS1	23.1 ± 0.7	68.8 ± 3.6	0.60 ± 0.09
DS2	24.5 ± 0.2	64.9 ± 6.0	1.07 ± 0.18
DR1	24.5 ± 0.2[b]	71.3 ± 2.7[c]	1.16 ± 0.12
DR2	---	69.2 ± 3.0[c]	0.84 ± 0.10

[a] DS - a stationary disk during silanization, DR - a rotated disk; [b] average over both disks; [c] after TFAA treatment the contact angle was (65.7 ± 4.6)°

Rotation reduced the deviations in contact angle readings and composition ratio for a given sample and also the values for the two disks were in better agreement. We conclude that the rotary holder did improve the uniformity of the amino-surface. Although an excess of TFAA was reacted for quite some time, the composition ratios were still far short of the theoretical value. Therefore we conclude that only ca. one-third of amino groups on the surface may participate in the amide bond formation reaction when the micelles are attached onto the surface. The contact angle of the TFAA-treated surface is slightly smaller than the initial silane surface (Table 1). This is certainly not what you would expect if the surfaces were uniformly covered by CF_3COO groups.

Characterization of micelle-attached surface

After TFAA treatment, the PS-PMA micelles were chemically attached onto the amino-activated quartz surface as described earlier. Four different carbodiimide concentrations in a range suggested in previous study (Ref. 9) were tried to characterize the effect of carbodiimide concentration on the size and polydispersity of the micelles on surface.

A typical SEM picture at normal incidence for the sample surfaces and the corresponding size distribution is given in Figure 1. The attachment process used in this study is highly efficient. The surfaces were densely covered by the micelles and in general the coverages were uniform. However, for *1065-25*, which has the highest carbodiimide concentration, the variation was larger (see Table 2). The statistics of particle size for each sample showed an almost perfect normal distribution (see Figure 2 for a typical example).

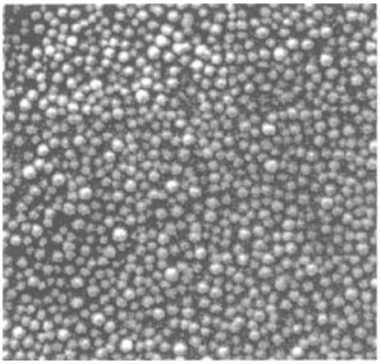

Figure 1. SEM image of quartz-supported PS-PMA micelles.

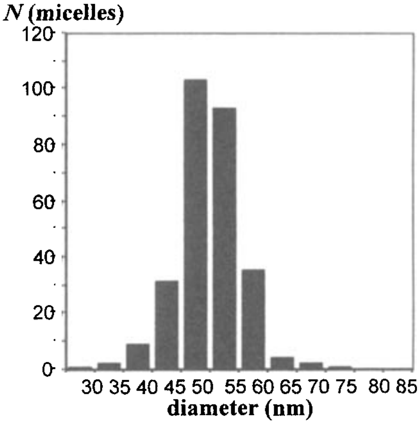

Figure 2. Size distribution of quartz-supported PS-PMA micelles. (Average = 50.1 ± 5.9 nm.)

It can be concluded from the variance that the polydispersity of the surface micelles is fairly small. The distribution analysis of SEM pictures is presented in Table 2. There is an increase in the surface density of micelles and the number of aggregates with carbodiimide concentration although the average size of the micelles was not dependent on the carbodiimide concentration. The aggregates are probably formed in the solution phase before the actual attachment reaction.

Table 2. Distributions in 1 μm^2 of SEM images of quartz-supported PS-PMA micelles

Sample	Average size nm	Number of micelles	Number of aggregates
1065-10	50.1 ± 5.9	281	4
1065-15	45.6 ± 5.4	313	2
1065-20	45.9 ± 5.9	346	11
1065-25A	51.7 ± 7.9	242	12
1065-25B	46.3 ± 6.2	378	16
1065-25C	45.1 ± 7.1	479	66
-25 series	46.7 ± 7.0	366	31

AFM was not successful in obtaining the height distribution of the micelles because the surface was too densely covered by PS-PMA micelles and a relatively large size AFM tip was used. Because the micelles on surface were presumed to be soft compared to other samples typically examined by AFM, a non-contact mode was used. A rough estimate of the height of the surface micelles was in the range of 10 - 20 nm.

The change in carbodiimide concentration did not influence the contact angle measurements of the micelle surface samples. The average contact angles for all samples was $(91.2 \pm 1.1)^\circ$ degrees, which was much higher than expected for a hydrophilic micelle corona (Ref. 7). We presume this is because of the excess carbodiimide on the micelle corona which reacts with the carboxylic acid to form a hydrophobic urea-like adduct. This adduct will cover that part of the micelle corona which was not used in the attachment reaction.

A rough calculation of the contact angle of the surface micelle may be carried out. Adamson gives the following equation for a composite surface (Ref. 12):

$$\cos \theta_{exp} = r \cos \theta_{true} = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (1)$$

where f_i is the fraction of area of type i, θ_i is the corresponding contact angle for i, and r is the roughness factor. Without consideration of r, Eq. 1 can be written

$$\cos \theta_{exp} = (1 - f_{mic}) \cos \theta_{amine} + f_{mic} \cos \theta_{mic} \qquad (2)$$

Taking the average density of micelles on the surface as N and $\pi(d_{mic}/2)^2$ as the geometric factor

$$f_{mic} = N\ \pi\ (d_{mic}/2)^2 \qquad (3)$$

The diameter of the micelles from QELS was ca. 54 nm and from the analysis of the SEM images a range from 45 to 52 nm is estimated. Combined with the value of N from Table 2, f_{mic} is calculated to be in the range 0.55 - 0.62. Since θ_{exp} and θ_{amine} are known (ca. 91.2° and 70.2°, respectively) and we have estimated f_{mic}, we solve Eq. 2. for $\cos\theta_{mic}$ and obtain θ_{mic} in the range 104 - 108°, which is very hydrophobic.

CONCLUSION

Chemical attachment of polystyrene-*block*-poly(methacrylic acid) micelles onto chemically modified quartz surface was accomplished by an amide-forming reaction with water-soluble carbodiimide. Water contact angles and XPS were measured to verify the siloxane modification reaction and to check the uniformity of resulting surface. The uniformity of amino-activated surface, which is essential to obtain homogeneous coverage of micelles, was improved by using a device for rotating the quartz discs during the vapor-phase reaction. The micelles in dioxane/water mixture were attached to the surface. The micelle surface was studied by SEM and AFM. The size and polydispersity of the micelles was not altered during the attachment process and the efficiency of the coupling process was high. The surface coverage tended to increase with carbodiimide concentration, but high concentration enhanced aggregation of the micelles. The average diameter of micelle obtained from the SEM pictures was very similar to the hydrodynamic diameter obtained from QELS.

This research suggests several future studies. The kinetics of the micelle attachment process can be studied since a technique to achieve a uniform surface was developed. Chromophores may be reacted with the micelle surface to produce samples appropriate for near-field scanning optical microscopy (NSOM). NSOM imaging could reveal if fluorescence tagging is uniform on the surface.

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