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SHORT COMMUNICATION

Surface modification of thin polystyrene films

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Abstract The sulfonation of polystyrene (PS) films with 50 and 96% sulfuric acid as a function of time is presented. In contrast to previous literature reports, we showed that the treatment of PS films even with dilute sulfuric acid yields sulfonated surfaces after reaction times of 30 s–1 h. The hydrophilicity of the modified PS increased considerably in comparison to the unreacted PS films. X-ray photoelectron spectroscopy yielded evidence for the sulfonation of PS at the surface. Unreacted spin-coated PS films were very smooth, while modified PS showed some clumps dispersed on a flat surface, as analyzed by atomic force microscopy. The surface morphology was identified as a phase-separated system composed of domains of unreacted PS and a matrix of sulfonated PS by fluorescence microscopy using the positively charged dye rhodamine B. The adsorption of the polycation diallyldimethylammonium chloride on the sulfonated PS surface could be detected. The thickness of the adsorbed polycation was 2.2 nm.

Key words Polystyrene – Sulfonation – Surface analysis – Adsorption – Wet modification

Introduction

The polymers most commonly used in technological applications have a very low surface energy and are hydrophobic. Polymer surface modifications are generally performed if the surface properties do not suit the desired applications. After modification the surface should carry the functional groups, while the bulk properties should remain unchanged. We will focus here on the surface modification of polystyrene (PS). This

polymer is frequently used in industry due to its low cost and easy processing.

The modification of the PS surface by applying dry processes of high-energy irradiation is well described in the literature. For instance, corona discharge, UV and γ radiation[1, 2], plasma treatment [3, 4] and glow discharge [5] have successfully modified PS. One disadvantage of these methods is the degradation of the polymer caused by the radiation. In addition wet modification processes of the PS surfaces have been reported in the literature [6–10]. Gibson and coworkers [8–10] reported the sulfonation of 80-μm thick PS films. The films were immersed in 100% H_2SO_4 for 2 min [8–10]. They obtained a sulfonated layer of 3.5 μm on top of the PS surface and reported that the rate of sulfonation dramatically dropped as soon as dilute H_2SO_4 was used. They reported that 96% H_2SO_4 was too unreactive; only very slightly sulfonated films were obtained after 16 h reaction. In this work we present a systematic study of the modification of PS surfaces by sulfonation for two concentrations of H_2SO_4 as a function of time. Moreover, a detailed investigation of the surface structure was performed.

Materials and methods

PS $M_w \sim 200{,}000$ g/mol, atactic) was kindly supplied by BASF, Ludwigshafen, Germany. It was dissolved in toluene at a concentration of 20 mg/ml and spin-coated on silicon wafers (3×3 cm^2). Reagent-grade toluene (Riedel-de-Häen) was filtered through a Millipore filter (0.2 μm) prior to use. The silicon wafers (purchased from CrysTec, Berlin, Germany; covered by a 2-nm SiO_2 layer) were cleaned prior to spin-coating using the following procedure. The wafers were kept in dichloromethane for 15 min, afterwards they were immersed in an oxidizing mixture of NH_3, H_2O_2 and distilled water (1:1:5) at a temperature of 70 °C for 20 min. After this, the wafers were washed with distilled water and dried under a stream of N_2. All polymer films were obtained from solutions spin-cast at approximately 3,000 rpm for 1 min.

Poly(sodium 4-styrenesulfonate) (PSS, $M_w \sim 70{,}000$ g/mol) was purchased from Aldrich. An aqueous solution of 5 mg/ml PSS was cast on Si wafers. Poly-(diallyl dimethylammoniumchloride) (DADMAC, $M_w \sim 150{,}000$ g/mol) was purchased from Aldrich. It was diluted with distilled water to a concentration of 1 mg/ml. Sulfuric acid (96 ± 1% H_2SO_4, Merck) was used without any pre treatment. A 50-μM solution of rhodamine B (Fluka) was prepared in ethanol containing 0.01 vol% acetic acid.

Surface modification methods

Spin-coated PS films were completely covered by a liquid film of H_2SO_4 either at a concentration of 96% for 30 and 60 s or at a concentration of 50% H_2SO_4 for 15, 30 and 60 min. Afterwards the samples were washed 10 times with pure water, dried under a stream of N_2 and characterized.

Ellipsometry [11]

A Rudolph Auto EL-II null-ellipsometer (New Jersey, USA) equipped with the He-Ne laser (λ = 632.8 nm) with the angle of incidence fixed at 70.0° was used to determine the thickness and the index of refraction of the PS films, assuming indices of refraction for Si of $3.858 - i\ 0.018$ [12] and for SiO_2 of 1.462. The incident laser beam covers an area of approximately 3 mm^2 and the samples were measured at several spots of the same sample. The results reported are averaged over 20 different samples. For the interpretation of the ellipsometric data a multilayer model [11] and Jones matrices calculations were used.

Contact angles

The contact angles of water drops (4 μl) were measured according to a standard method [13] before and after the surface modification at room temperature. Advancing and receding angles were obtained by increasing or decreasing the drop volume. The values reported are averaged over measurements performed at several spots for 20 different samples.

Atomic force microscopy

Atomic force microscopy (AFM) investigations were carried out with a commercial instrument (Park Scientific Instruments, Sunnyvale, USA) equipped with a homebuilt head with a laser deflection detection system. The measurements were performed in the contact mode in air at room temperature. V-shaped silicon nitride cantilevers with sharpened pyramidal tips and force constants between 0.03 and 0.1 N/m were applied. All AFM images represent unfiltered original data and are displayed in a linear gray scale. The total load force, which includes adhesion and capillary forces, did not exceed 15 nN during the measurements.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) experiments were performed with an ESCALAB-5 electron spectrometer (VG Scientific, East Grinstead, UK) in a UHV system with a base pressure of approximately 10^{-10} mbar. The photoelectrons are excited in a sample area of about 50 mm^2 by means of nonmonochromatized Mg Kα-radiation at a power of 100 W. The kinetic energies are measured by a 150° hemispherical energy analyzer operated in the constant analyzer energy mode using a pass energy of 20 eV for elemental spectra and a resolution of 1.2 eV for the Au $f^{7/2}$ photopeak. The photoelectron take-off angle was set to 0° with respect to the sample normal. The binding-energy scale was calibrated using a value of 285.0 eV for the contamination C 1*s* photopeak and controlled by means of the well-known photopeaks of metallic Cu, Ag, and Au, respectively. For the analysis of multiple peaks in the XPS spectra the VGX 900 software permits simultaneous fitting of up to six Gaussian components with adjustable Lorentzian line shape contributions and asymmetries.

Fluorescence microscopy

PS films treated with 96% H_2SO_4 for 60 s were immersed in the rhodamine B solution for 10 s. After this, the samples were washed with pure ethanol and dried under a stream of N_2. Fluorescence microscopy (FM) analysis of these samples was performed in air with a NORAN Odyssey XL (Middleton, USA) confocal microscope using an objective with a magnification of 40×.

Results and discussion

The untreated spin-coated PS films were characterized first by means of null-ellipsometry and contact-angle measurements. The mean thickness and index of refrac-

tion obtained for 20 samples amounted to 143 ± 6 nm and 1.583 ± 0.003, respectively, as shown in Table 1. These index of refraction values found at the wavelength of 632.8 nm agree well with the literature value of 1.582 [14, 15]. Contact-angle measurements with water drops reveal, as expected, a very high hydrophobicity. The mean advancing angle θ_a is 90° ± 2° and the mean receding angle θ_r is 88° ± 2°.

The samples treated with 96% H_2SO_4 for 30 and 60 s both have a mean thickness of 143 ± 3 nm and have mean indices of refraction of 1.588 ± 0.002 and 1.585 ± 0.003, respectively as presented in Table 1. These values are nearly identical to those measured for untreated PS and do not show any dependence on the reaction time. On the other hand the PS surfaces become very hydrophilic after surface treatment. A big decrease in the contact angles is observed. A mean advancing angle and a mean receding angle of 55° ± 3° and 36° ± 5°, respectively, are obtained for the treated samples, independent of the reaction time. The increase in the hydrophilicity of the surface after acid treatment and the similarity found in the indices of refraction for

Table 1 Thickness, indices of refraction and contact-angle measurements of water drops obtained for unmodified polystyrene (PS) films, PS films treated with H_2SO_4 and poly(sodium 4-styrene sulfonate) (*PSS*) films

Conditions	Thickness (nm)	Index of refraction (at λ = 632.8 nm)	Contact angle (°)		
			θ_{adv}	θ_{rec}	$\Delta\theta$
Untreated	143 ± 6	1.583 ± 0.003	90 ± 2	88 ± 2	2
95–97% H_2SO_4					
30 s	143 ± 3	1.588 ± 0.002	53 ± 2	29 ± 5	24
60 s	143 ± 4	1.585 ± 0.003	55 ± 3	33 ± 5	22
50% H_2SO_4					
15 min	141 ± 4	1.589 ± 0.004	58 ± 5	42 ± 5	16
30 min	142 ± 3	1.591 ± 0.005	54 ± 4	34 ± 2	20
60 min	143 ± 3	1.585 ± 0.003	57 ± 3	37 ± 3	20
PSS	45 ± 2	1.593 ± 0.002	–	–	

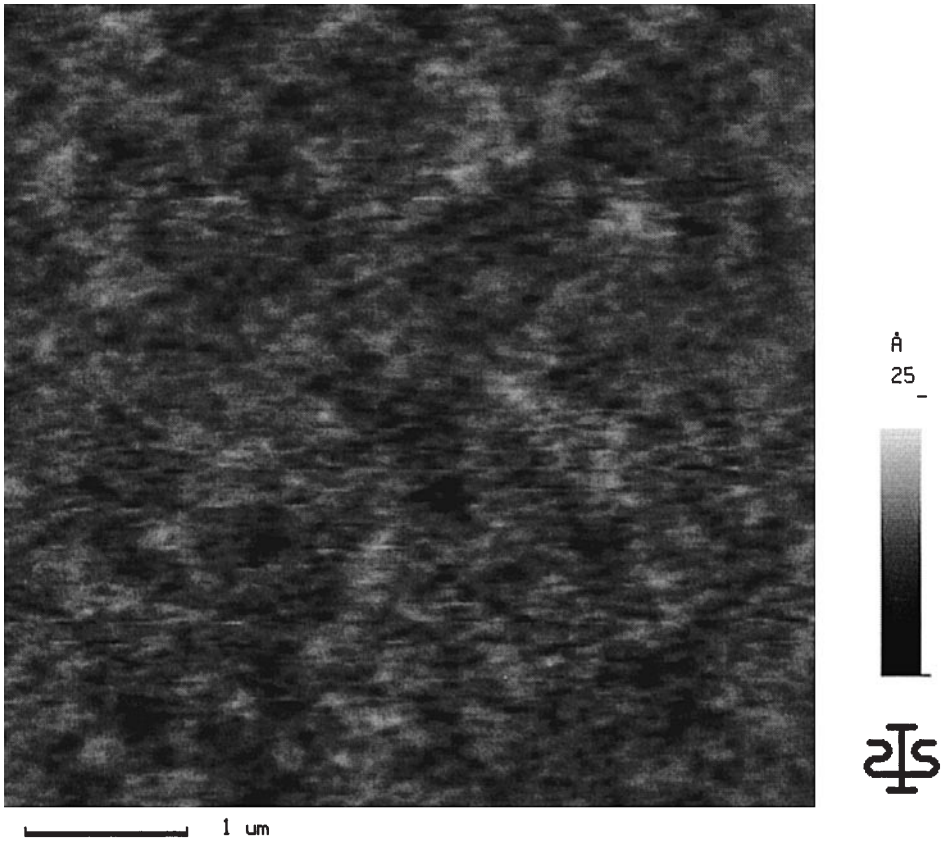


Fig. 1 Atomic force microscopy (*AFM*) image of untreated spin-coated polystyrene (*PS*) (143-nm thick)

treated and untreated PS surfaces indicate that a change in the chemical composition of the surface takes places very quickly. For comparison, we measured the index of refraction of spin-coated films (~45 nm thick) of PSS (Aldrich) on Si wafers. It amounts to 1.593 ± 0002 (Table 1) and is comparable to those measured for samples treated with 96% H_2SO_4 for 30 and 60 s.

Also under milder conditions we cannot observe any influence of the reaction time. Samples treated with 50% H_2SO_4 for 15, 30 and 60 min show similar values of thickness and index of refraction, as shown in Table 1. These values are comparable to those obtained for PS films treated with 96% H_2SO_4. The PS surfaces treated with 50% H_2SO_4 after 15, 30 and 60 min turn hydrophilic as well. In contrast to the results presented by Gibson [10], our findings show that a rapid reaction is also possible with more dilute H_2SO_4. Advancing and receding angles of contact of 54° ± 5° and 39° ± 5°, respectively, were measured. PS films treated with 50% H_2SO_4 for a period of time shorter than 15 min do not exhibit a significant increase in wettability.

In general the hysteresis in the contact angle $\Delta\theta$ ($\Delta\theta = \theta_a - \theta_r$) gives some indication about the surface roughness or composition [16]. The untreated PS films are very smooth and homogeneous, $\Delta\theta = 2°$, whereas the PS surfaces modified with 95–97% H_2SO_4 and 50% H_2SO_4 show average hysteresis of $\Delta\theta = 19°$ and $\Delta\theta = 15°$, respectively. These results are discussed later together with the results of microscopy.

AFM measurements reveal a very smooth untreated PS surface (Fig. 1), as expected from the $\Delta\theta$ values. The root-mean-square (rms) roughness obtained for a scan area of 25 μm^2 amounts to 1.86 Å. Films formed by spin-coating are generally very smooth [14]. In contrast, the PS films modified with 95–97% H_2SO_4 and 50% H_2SO_4 show rms roughnesses of 12.7 Å and 22.2 Å, respectively, for a scan area of 25 μm^2 and clumps dispersed over a flat surface, as shown in Fig. 2. The

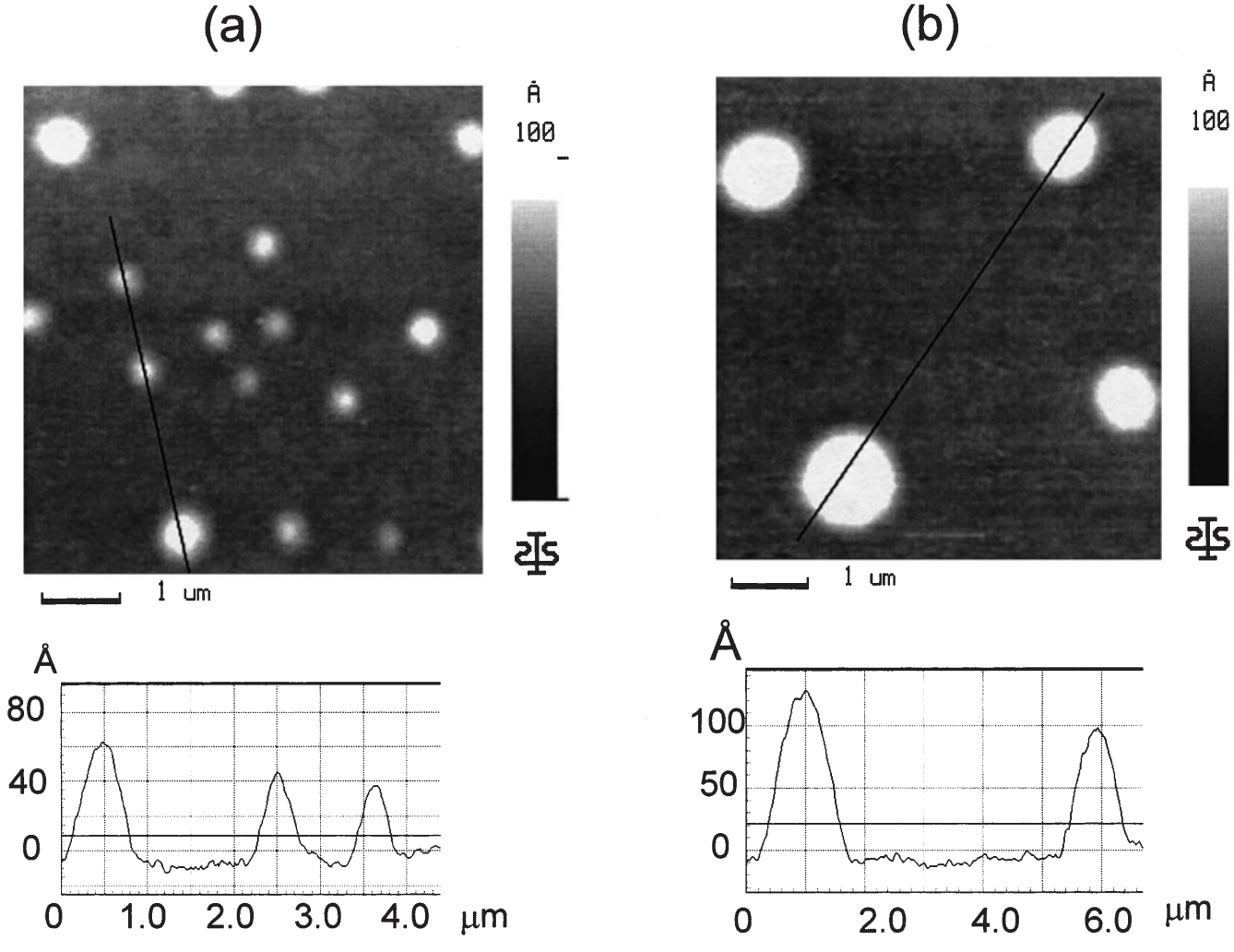


Fig. 2 AFM image of spin-coated PS (143-nm thick) after surface treatment with **a** 95–97% H_2SO_4 for 60 s and **b** 50% H_2SO_4 for 15 min, with the respective cross-section images

clumps observed on the PS films modified with 95–97% H_2SO_4 are found more frequently and on average they are smaller than those on the PS films modified with 50% H_2SO_4. The area in-between the clumps is homogeneous, showing an rms roughness of 2.6 Å (determined in a scan area of 4 μm^2). These structural features might be interpreted as a result of the surface reaction.

What really occurs on the PS surface when it comes in contact with H_2SO_4? Are the reaction mechanisms at the surface similar to those in solution? The sulfonation of aromatic rings in solution is known to be an electrophilic substitution [17]. In aqueous H_2SO_4 solutions the electrophile is a combination of H_2SO_4 and H_3O^+ ($H_3SO_4^+$) at concentrations below 80%; above it, the electrophile is a combination of H_2SO_4 and SO_3 ($H_2S_2O_7$). The reaction product is a ring with an SO_3^- or SO_3H group in the ortho or para position, as shown in Fig. 3. Assuming that this mechanism is also valid for surface reactions, the presence of SO_3^- or SO_3H substituents at the surface of PS would explain the increase in the PS wettability by water after acid treatment. In order to verify this, XPS measurements were performed for untreated and $H_2SO_4^-$ treated PS surfaces. For comparison commercial PSS cast from aqueous solution on Si wafers was investigated as well.

The XPS measurements performed on unmodified PS show only the photopeak corresponding to C 1*s* with the typical [8, 18] binding energy of 285.0 eV, as shown in Fig. 4. The surfaces of PS films treated with 95–97% H_2SO_4 for 60 s and PSS films show the photopeaks corresponding to C 1*s*, S 2*p* and O 1*s*, as presented in Fig. 4. The intensities are scaled relative to each other. The C 1*s* photopeaks measured for unmodified, modified PS films and PSS result in identical binding energies of 285.0 eV. We do not observe an extra photopeak corresponding to the C—S bonds because the energies for C—C and C—S bonds lie very close to each other and the tiny energy difference (ΔE = 1 eV) could not be resolved by the spectrometer used here.

The S 2*p* photopeak corresponding to the modified PS films and PSS films in Fig. 4 can be well-fitted as a spin-orbit doublet composed by the low-energy S $2p^{3/2}$

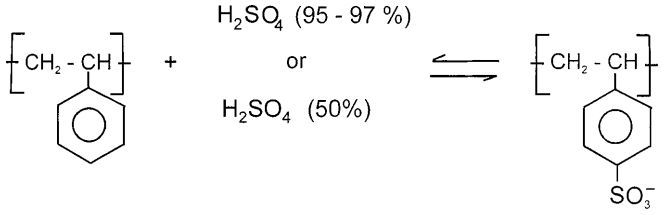


Fig. 3 Schematic representation of the sulfonation reaction of aromatic rings

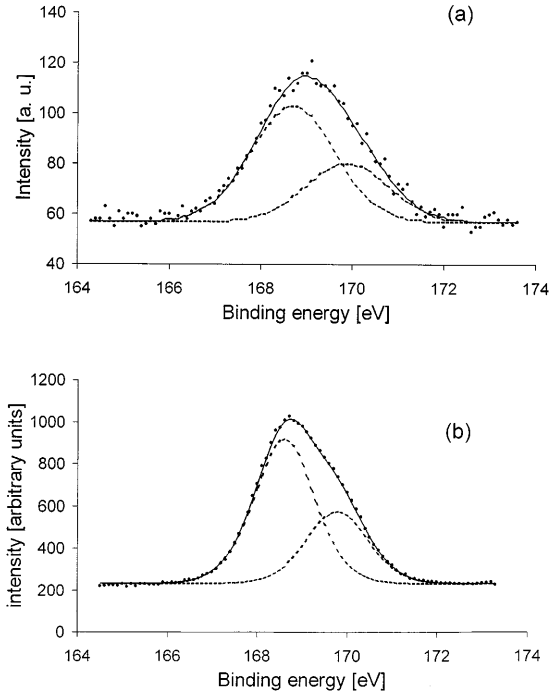


Fig. 5 S 2*p* spectral region of **a** modified spin-coated PS (95 – 97% H_2SO_4 for 60 s) and **b** cast PSS on a Si wafer. Experimental data (•) and fitted curves (*dashed lines*) for the spin-orbit doublet S $2p^{3/2}$ and S $2p^{1/2}$ at 168.7 and 169.8 eV, respectively, with an intensity ratio of approximately 2:1

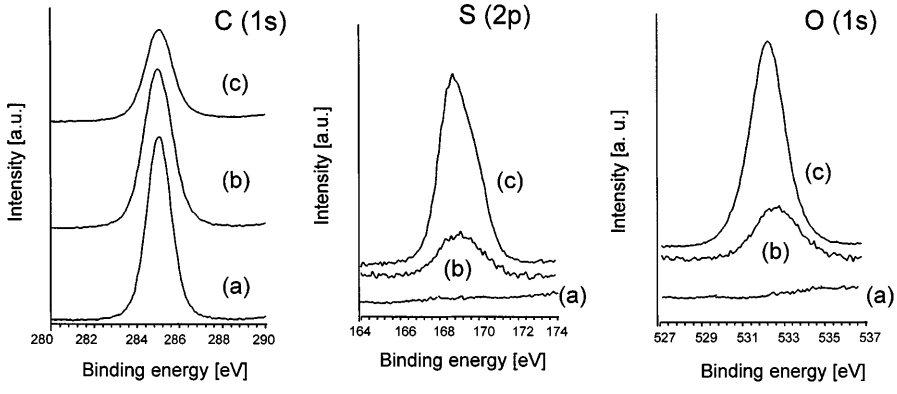
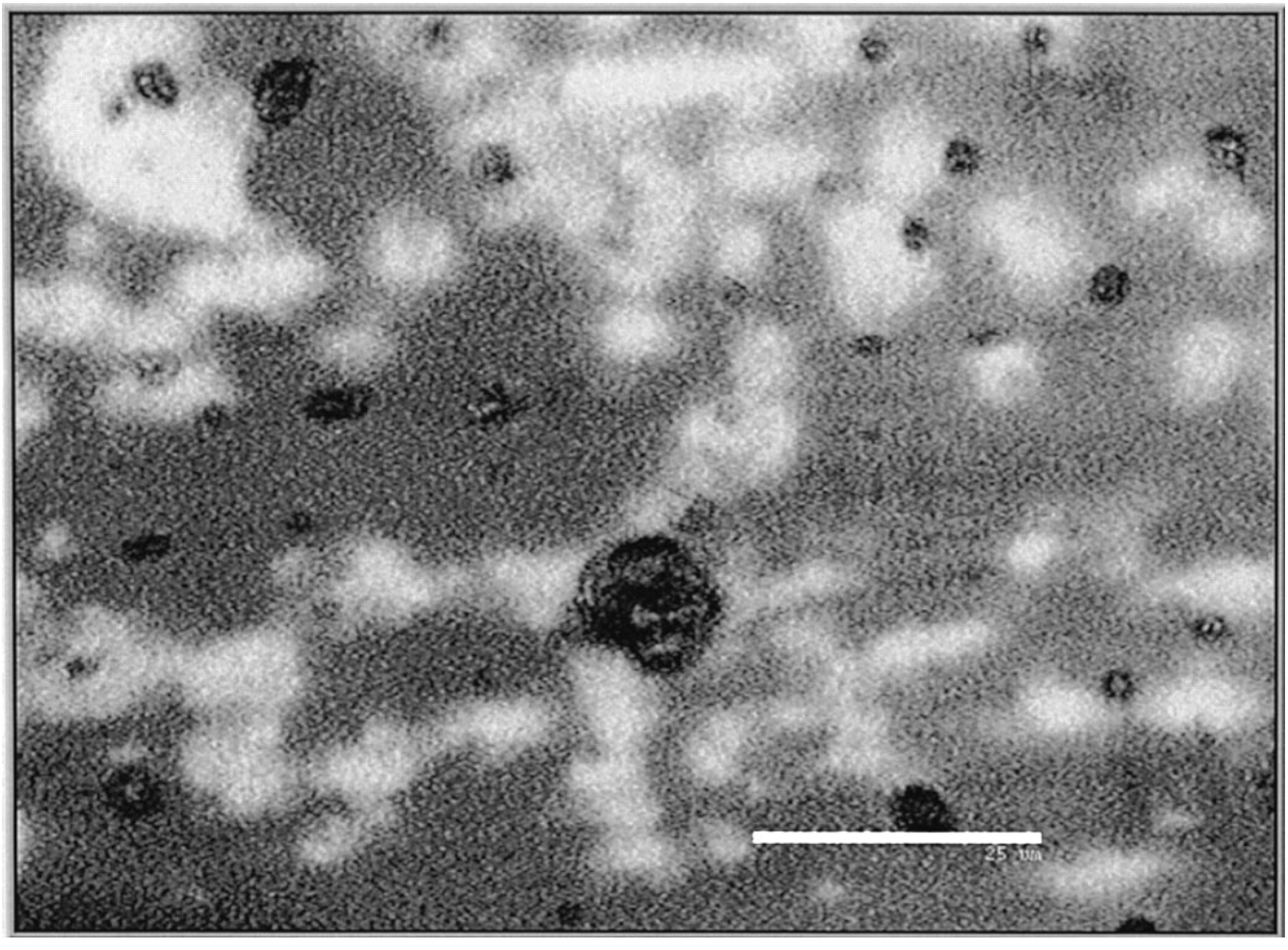


Fig. 4 X-ray photoelectron spectroscopy measurement of the C 1*s*, S 2*p* and O 1*s* core levels for **a** untreated spin-coated PS on a Si wafer, **b** modified spin-coated PS (95–97% H_2SO_4 for 60 s) on a Si wafer and **c** cast poly(sodium 4-styrene sulfonate) (*PSS*) on a Si wafer

and the high-energy S $2p^{1/2}$ components of sulfur at 168.7 and 169.8 eV, respectively, in an intensity ratio of approximately 2:1 (Fig. 5), as described in the literature [18, 19]. The O 1*s* photopeaks obtained for the PS films treated with H_2SO_4 and PSS films are practically identical (Fig. 4). They show binding energies at 532.7 and 532.3 eV, respectively. These results show that the reaction on the PS films with H_2SO_4 yields the same functional groups as those present in the PSS chains, namely, SO_3^-.

The spatial distribution of SO_3^- groups on the modified PS surface was investigated by means of FM. The electrostatic interactions between rhodamine B (cationic dye) and the SO_3^- groups on the surface account for a stable adsorption process. In Fig. 6 a typical FM image of the surface is shown. The light areas are attributed to the adsorption of rhodamine B and the dark islands to the absence of rhodamine B. The intensity of fluorescence in the light areas is not homogeneous: rhodamine B adsorbs more strongly in some regions than in others. This effect might be due to different degrees of sulfonation on the surface. The dark islands distributed on the surface have shape and diameters comparable to those observed in the topographic image obtained by AFM (Fig. 2). These findings indicate that the modified surface is composed of domains (dark islands) where sulfonation probably does not take place and a matrix functionalized with SO_3^- groups. The sulfonation reaction leads to a statistical distribution of SO_3^- groups along the PS chains [7]; however, some portions of the PS chains might carry no SO_3^- groups. Since PS and PS-SO_3^- are incompatible, the spherical shape of the dark domain (PS) might be the result of an attempt to minimize contact with the matrix (PS-SO_3^-). This heterogeneous composition leads to regions with different surface energies, which contribute to the increase in the contact-angle hysteresis discussed before.

Fig. 6 Typical fluorescence microscopy image of spin-coated PS (143-nm thick) surface treated with 95–97% H_2SO_4 for 60 s and stained with rhodamine B. The *scale bar* corresponds to 25 μm



Since we had PS surfaces charged by SO_3^- group, we were eager to know how polycations would adsorb on them. DADMAC is a polycation consisting of quaternary ammonium ions. We immersed the modified PS surfaces in a solution of DADMAC at neutral pH for 1 day. After this, the samples were washed with water, dried under a stream of N_2 and characterized by means of null-ellipsometry. The increase in thickness for DADMAC amounts to 2.2 ± 0.2 nm. The adsorption of DADMAC on the modified PS is driven by electrostatic interactions. The observed thickness of the DADMAC layer might be due to the formation of loops, tails and trains as is known from the work of Decher [20].

In order to check whether the increase in the film thickness after exposure to the DADMAC solution is due only to adsorption or if there is an additional swelling effect of the PS film, which might persist even after drying, the following control experiment was done. PS films treated with 95–97% H_2SO_4 for 60 s were dipped in pure water for 1 h. After that time the films were dried under N_2 and analyzed by ellipsometry. An increase of (3 ± 1) Å in the film thickness was measured. This thickness is much smaller than that measured after exposure to DADMAC solution; therefore, the influence of swelling on the increase in film thickness is very small in comparison to the effect observed.

Conclusion

We present a very simple method to turn PS surfaces from hydrophobic to hydrophilic, which is based on treatment with 95–97% or 50% H_2SO_4 for 30 s-1 h. XPS measurements provide evidence for the sulfonation of PS at the surface. The presence of SO_3^- groups on the PS surface is responsible for the increase in the wettability of the PS films. FM of a sample stained by rhodamine B reveals the presence of unmodified PS domains dispersed in a matrix of sulfonated PS. The modified PS films are negatively charged surfaces, which can serve as substrates for many applications; for instance, for the formation of multilayers.

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References

1. Onyiriuka EC, Hersh LS, Hertl W (1991) J Colloid Interface Sci 144: 98
2. Onyiriuka EC (1993) J Appl Polym Sci 47: 2187
3. Idage SB, Badrinarayanan S (1998) Langmuir 14: 2780
4. Keller D, Schröder K, Husen B, Ohl A (1997) Polym Prepr Am Chem Soc Div Polym Chem 38: 1043
5. Tamada Y, Ikada Y (1993) Polymer 34: 2208
6. Rao BS, Puschett JB, Matyjaszewski K (1991) J Appl Polym Sci 43: 925
7. Feng Y, Karim A, Weiss RA, Douglas JF, Han CC (1998) Macromolecules 31: 484
8. Gibson HW, Salaneck WR, Bailey FC, Pochan JM, Thomas HR (1978) Polym Prepr Am Chem Soc Div Polym Chem 19: 320
9. Gibson HW, Bailey FC, Mincer JL, Gunther WHH (1979) J Polym Sci Polym Chem Ed 17: 2961
10. Gibson HW, Bailey FC (1980) Macromolecules 13: 34
11. Azzam RM, Bashara NM (1979) Ellipsometry and polarized light. North Holland, Amsterdam
12. Edward D (1985) Handbook of optical constants of solids. Academic Press, New York
13. Adamson A (1982) Physical chemistry of surfaces. Wiley, New York
14. Siqueira DF, Schubert DW, Erb V, Stamm M, Amato JP (1995) Colloid Polym Sci 273: 1041
15 Burrell (1975) Polymer handbook. Wiley Interscience, New York
16. Garbassi F, Morra M, Occhiello E (1992) Polymer surfaces: from physics to technology, Wiley, New York
17. March J (1992) Advanced organic chemistry: reactions, mechanisms and structures. Wiley, New York, p 528
18. Moulder JF, Stickle WF, Sobol PE, Bomben KD (1992) Handbook of X-ray photoelectron spectroscopy. Perkin Elmer, Eden Prairie, Minn
19. Laibinis PE, Whitesides GM (1992) J Am Chem Soc 114: 9028
20. Decher G (1997) Science 277: 1232