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

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
polymers 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% H₂SO₄ 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 H₂SO₄ was used. They reported that 96% H₂SO₄ 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 H₂SO₄ 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 ($3 \times 3$ cm$^2$). Reagent-grade toluene (Riedel-de-Haën) was filtered through a Millipore filter ($0.2 \mu m$) prior to use. The silicon wafers (purchased from CrysTec, Berlin, Germany; covered by a 2-nm SiO₂ 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 NH₃, H₂O₂ 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 N₂. 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% H₂SO₄, 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 H₂SO₄ either at a concentration of 96% for 30 and 60 s or at a concentration of 50% H₂SO₄ for 15, 30 and 60 min. Afterwards the samples were washed 10 times with pure water, dried under a stream of N₂ and characterized.

Ellipsometry [11]

A Rudolph Auto EL-II null-ellipsometer (New Jersey, USA) equipped with the He-Ne laser ($\lambda = 632.8$ nm) with the angle of incidence fixed at 70° 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 SiO₂ of 1.462. The incident laser beam covers an area of approximately 3 mm² 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 ($4 \mu l$) 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 mm² 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 12 eV for elemental spectra and a resolution of 1.2 eV for the Au ⁷/₂ photopake. 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 1s photopake and controlled by means of the well-known photopakes 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% H₂SO₄ 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 N₂. 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-