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Transparent Polystyrene Substrates with Controllable Surface Chlorosulfonation: Stable, Versatile, and Water-Compatible Precursors for Functionalization

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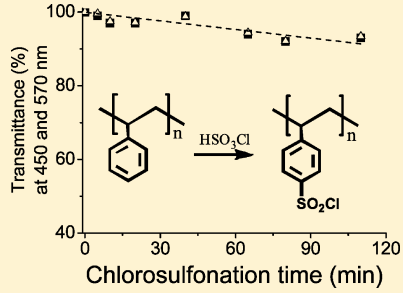
ABSTRACT: A simple and economic method is presented that allows the preparation of transparent polystyrene (PS) substrates activated with chlorosulfonyl groups. Chlorosulfonation has been analyzed by ATR-FTIR. Linear PS chains with different degrees of chlorosulfonation have been synthesized as model compounds in order to analyze the modification quantitatively. After chlorosulfonation the activated surfaces can be quantitatively converted in aqueous solution at room temperature to sulfo or sulfonazide groups or react with bifunctional aliphatic amines of different length via formation of sulfonamide linkages. In this way, surfaces with a huge variety of functionalities like amines, carboxylic or sulfonic groups, sulfonazides, esters, etc. may be obtained in a selective way controlling their density at the surface. In all cases, functional surfaces with excellent optical transparency are obtained. Aminated surfaces have successfully been probed for ELISA assays.



INTRODUCTION

Polystyrene is one of the most used polymer materials in the bioanalytical sector because it has excellent optical clarity, is easy to mold and relatively inexpensive. Slides and multiple-well plates from this material have gained widespread acceptance in part because pipetting, washing, and signal detection are easily automated.

A significant drawback of this polymer is its hydrophobic nature to which cells and other biomaterials have difficulty attaching. To overcome this problem, PS is often modified by chemical or physical methods. Typical surface treatments of polystyrene use corona discharge and chemical vapor deposition as well as gas phase ozonation under irradiation of UV light.[1,2] Other conventional methods used to modify polystyrene surfaces with amino groups are plasma polymerization of allylamine or plasma treatments in the presence of N_2 or NH_3.[3] A disadvantage of this type of physical surface modification techniques is the lack of selectivity and control of the reactions and usually a large number of different functional groups are created on the surface. This problem may be circumvented when wet-chemical surface treatments are used. A suitable reaction for the preparation of preactivated PS is the classical chlorosulfonation of aromatic rings using chlorosulfonic acid. This reaction on PS is being carried out for more than 50 years and many applications of the obtained products have been studied. In numerous work,[4−15] chlorosulfonation and subsequent sulfonamidation is carried out on cross-linked PS beads or PS in powder. In a patent from 1968, chlorosulfonation has been tried for the first time on PS surfaces using a hexane−HSO_3Cl emulsion.[16] However, nowadays it is known that this medium does not lead to chlorosulfonated surfaces but rather to the formation of SO_3H groups. Furthermore, the reactive solution is deactivated after short time as chlorosulfonation of the alkane cosolvent takes place as a secondary reaction. In fact, the first successful chlorosulfonation of plane transparent PS surfaces has been described very recently by Bicak et al.[17] who used this reaction for an improved metal deposition of copper on PS substrates. Because of the aim followed in this work the authors used relatively harsh reaction conditions that lead to the loss of transparency of the substrates and strongly opaque surfaces were obtained.

In the present work, we show for the first time the feasibility of obtaining "transparent" chlorosulfonated PS substrates. The method described here allows a facile control of the extension of chlorosulfonation on the surface, where up to 100% of the present aromatic rings may be activated. The activated surface is stable and water compatible. The utility of this activated material for subsequent functionalizations with amine or carboxylic groups maintaining the transparency of the substrates is demonstrated. Transparency is an indispensable condition for the subsequent use of the material in bioanalytical assays.

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EXPERIMENTAL PART

Materials. Transparent polystyrene sheets of 1 mm thickness and a surface of 8.0 cm × 2.5 cm were purchased from Resopal S.A., Madrid, Spain. Chlorosulfonic acid, concentrated sulfuric acid, Orange II, Toluidine blue O, α,ω-aminoacids, alifactic diamines, styrene, and sodium *p*-vinylphenylsulfonate were purchased from Sigma-Aldrich. Chlorosulfonic acid was distilled under reduced pressure prior to use.

96-well plates of PS from Sarstedt and the interleukin 6 detection ELISA set from eBioscience were used for the ELISA experiments

Methods. *Chlorosulfonation of PS Substrates.* In a thermostatable reactor reactangular transparent PS samples (dimensions 2.5 × 8.0 × 0.1 cm^3) or multiple-well plates are brought in contact with freshly distilled chlorosulfonic acid at temperatures between −15 and 0 °C. At different time intervals, the sample is taken with Teflon coated tweezers, washed for 15 s in cold (0 °C) concentrated sulfuric acid and finally for 30 s in an ice/water mixture. Then the samples are dried at ambient temperature.

Functionalization of PS Substrates. In a thermostatable reactor reactangular chlorosulfonated PS substrates with different amounts of chlorosulfonyl groups are immersed in aqueous solutions of α,ω-functionalized amines of different concentrations at temperatures between 0° and 70 °C. At different time intervals the samples are taken out, washed with warm (40 °C) water and dried at ambient temperature.

a. Synthesis of Chlorosulfonated PS by Polymerization. Preparation of Monomer (S-SO_2Cl).[18] A 15 g sample of sodium *p*-vinylbenzenesulfonate is suspended in 70 mL of *N*,*N*-dimethylformamide (DMF). The suspension is cooled to 0 °C and 30 mL of thionyl chloride are added dropwise. After the addition a pale yellow solution is obtained. The mixture is stirred for further 24 h at room temperature and then poured into ice. The organic phase is extracted twice with 100 mL of diethyl ether and dried with $MgSO_4$. Finally the solvent is eliminated and the crude product purified by chromatography using silica gel and CH_2Cl_2 as the eluent. Yield 85%.

b. Preparation of Homopolymer (PS-SO_2Cl). The desired polymer is obtained by classical radical polymerization in a 1 M solution of toluene using as the initiator AIBN (azobis(diisobutyronitrile)) in a 0.015 molar concentration. The polymerization is carried out at 60 °C for 48 h. The formed polymer precipitates during the polymerization and is isolated by filtration, washed twice with hexane, and dried as a fine white powder.

c. Preparation of Copolymers. Copolymers between 4-vinylbenzenesulfonyl chloride and styrene of different compositions are prepared in analogous conditions to those used in the homopolymerization. The obtained copolymers are precipitated in hexane−ether (1:1) and purified by three cycles of solubilization/precipitation in THF/hexane−ether.

Bioanalytical Application, ELISA Assay. Interleukin 6 (IL6) ELISA set (eBioscience) was used to evaluate the bioanalytical application of the modified surfaces. Previously, the new aminated plates were exposed to glutaraldehyde pretreatment (10% of glutaraldehyde solution for 20 minutes) to facilitate the covalent bond to the antibody. Then, the recommended protocol given in the ELISA set was carried out on new modified surfaces and a reference surface.

Characterization of Modified Substrates. ATR-FTIR measurements are carried out using an FTIR spectrometer Spectrum One of Perkin-Elmer equipped with a single reflection ATR device using as internal reflection elements diamond/ZnSe. This setup allows studying the samples with a penetration depth of around 2 μm.

To determine quantitatively the relative degree of modification of the functionalized films the bands at 1450 and 1370 cm^{-1} are used that correspond to the polymeric main chains of PS and the O═S═O valence bond of the SO_2Cl groups, respectively.

H NMR spectra of the compounds were recorded at 25 °C on a 300 MHz Varian spectrometer operating at 300 MHz using deuterated acetone or deuterated dimethyl sulfoxide as the solvent.

Colorimetric Determination. For the determination of amine (primary, secondary, and ternary) concentration at the surfaces a method described by P. Hamerli et al.[19] has been used: samples were immersed into a 500 mmol/L Acid Orange II (AO) solution dissolved in water with pH 3, set by HCl. After overnight shaking for at least12 h at room temperature, samples were washed twice with the acidic water. In order to dissolve the adsorbed AO, they were shaken for 15 min at room temperature in water with pH 12, set by NaOH. The AO concentration (which is similar to the amine concentration of the surfaces) of the solution was colorimetrically determined with an optical spectrometer at 485 nm.

Carboxylic groups were determined by an analogue procedure using Toluidine Blue O (TBO) as the dye. Its concentration after extraction from the surface is determined by measuring the absorbance at 697 nm.

AFM. Data about the surface roughness of the simples has been obtained using the atomic force microscope NANOSCOPE A/M-AFM-2 1556EX from Digital Instruments in tapping mode.

RESULTS AND DISCUSSION

Preparation. The main aim of this work is to prepare transparent PS substrates selectively functionalized with chlorosulfonyl (−SO_2Cl) groups. The challenge in the modification reaction between chlorosulfonic acid and transparent PS materials is to control the extremely high reactivity of this acid and overcome the problem of washing the surfaces after modification has taken place without loosing the transparency of the polymeric material. For this washing procedure a medium must be chosen that has to be a solvent for the acid, should not give a strong exothermic reaction with it and should neither interact with polystyrene as its surface would loose smoothness and transparency. Apolar organic solvents do usually interact with polymers and are furthermore immiscible with chlorosulfonic acid. On the other hand, most of the polar media like water or alcohols react violently when brought in contact with the acid. For this reason, we have carried out a two-step cleaning procedure using cold concentrated sulfuric acid in the first step and a water/ice mixture in the second one. The samples can then be dried and analyzed with respect to the achieved content of functional groups, transparency and surface reactivity.

The chemical analysis of the modified surfaces was carried out by ATR-FTIR spectroscopy. A series of spectra of PS samples exposed to chlorosulfonic acid for different periods of time is shown in Figure 1b. The IR spectrum of unmodified PS (Figure 1a) shows mainly three significant bands in the studied range: two at 1600 and 1490 cm^{-1} corresponding to the

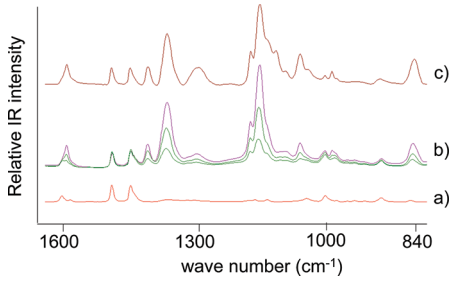

Figure 1. ATR-FTIR spectra in the range of 1650−800 cm^{-1} of (a) a pure PS film (yellow), (b) films modified for 10 min (green), 20 min (red), and 40 min (violet) with chlorosulfonic acid at −10 °C and (c) poly(styrene-*co*-4-vinylbenzenesulfonyl chloride) 50:50. Spectra are normalized with respect to the band at 1450 cm^{-1}.

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aromatic rings, and one at 1450 cm^{-1} proceeding from the C−H deformation of the polymeric alkyl main chain.

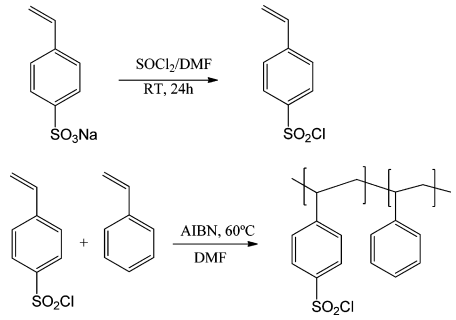
Upon chlorosulfonation, the IR spectrum changes significantly and new strong bands due to symmetric (1370 cm^{-1}) and asymmetric O═S═O valence bonds (1170 cm^{-1}) proceeding from the chlorosulfonyl group can be observed. Furthermore, a new band arises at 830 cm^{-1} due to the formation of *para*-substituted aromatic rings. After normalization of the spectra with respect to the band at 1450 cm^{-1} that is not affected by the modification reaction and remains constant, a relative conversion for the chlorosulfonation reaction can be determined using the increase of the band intensity at 1370 cm^{-1}.

The preparation of linear PS model compounds with different chlorosulfonation degrees has been faced in order to create a calibration curve and obtain absolute values for the degree of modification of the functionalized PS surfaces. Two approaches have been tried: the first one consisted in the chemical modification of PS in solution and the second one in a bottom-up approach by copolymerization of styrene and 4-vinylbenzenesulfonyl chloride.

Chlorosulfonation of PS in solution was not successful, because even under highly diluted conditions and low reaction temperatures cross-linked products were obtained that did not allow analysis by conventional H NMR. Probably, the electrophilic aromatic substitution with chlorosulfonyl groups takes place via activated transition states (like radicals) that recombine with radicals from other chains. The impossibility to obtain soluble chlorosulfonated PS in this way had also been observed by other authors.[17]

An alternative way to prepare model systems for chemically modified PS substrates is a bottom-up approach copolymerizing styrene with chlorosulfonated styrene monomer (Scheme 1).

Scheme 1. Synthesis of 4-Vinylbenzenesulfonyl Chloride and Its Copolymerization with Styrene



The latter compound is obtained by chlorination of commercially available sodium p-vinylbenzenesulfonate (see details in the Experimental Part).

The chemical structure of these copolymers and the percentage of sulfonyl chloride moieties have been checked by H NMR.

The ATR-FTIR-spectrum of poly(styrene-*co*-4-vinylbenzenesulfonyl chloride) 50:50 is compared in Figure 1 with the spectra of chemically modified PS substrates. One can see that the spectra of 1b and 1c are virtually identical showing that the structures of chlorosulfonated surfaces and model compounds are very similar. The IR-band intensity at 1370 cm^{-1} of model copolymers of different compositions were measured and used for calibration of the band intensities.

Figure 2 shows the degree of modification of chlorosulfonated PS surfaces as a function of reaction time for three

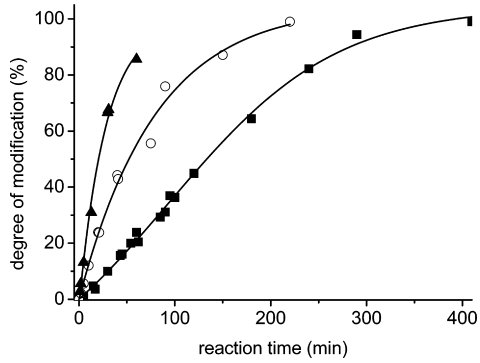


Figure 2. Degree of modification as a function of the chlorosulfonation time of PS at −10 (■), 0 (○), and +10 °C (▲).

different temperatures. According to this data even at the lowest temperature (−10 °C) complete conversion of all aromatic groups present in the subsurface area detectable by ATR takes place.

Surface Properties. One of the most important reasons for using PS in many bioanalytical assays like ELISA, is its excellent transparency necessary for the optical detection of for example color intensities. We have measured the transmittance of chlorosulfonated PS substrates as a function of the time samples had been exposed at −10 °C to the chlorosulfonating agent. The test has been carried out using two different wavelengths typically used in ELISA assays. As can be seen in Figure 3, the transmittance is independent of the wavelength

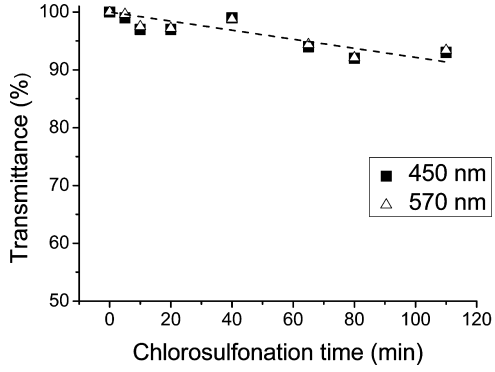


Figure 3. Transmittance of PS substrates as a function of chlorosulfonation time.

and decreases slowly and linearly with the time of functionalization. Even after 2 h of exposition to the acid the transparency of the substrate is maintained to more than 90%. The reasons for these excellent optical properties are on the one hand the high selectivity of the chlorosulfonation reaction at low temperatures and on the other hand the washing procedure in cold sulfuric acid and ice/water that eliminates the chlorosulfonic acid from the surface without producing a strongly exothermic reaction.

In order to analyze the surface morphology of chlorosulfonated PS substrates and study to which extent the surface roughness is influenced by the treatment with the modifier solution AFM images of pure and modified PS samples were recorded. These images together with the corresponding

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roughness profile obtained from AFM are shown in Figure 4. AFM images of both probes are qualitatively similar. The

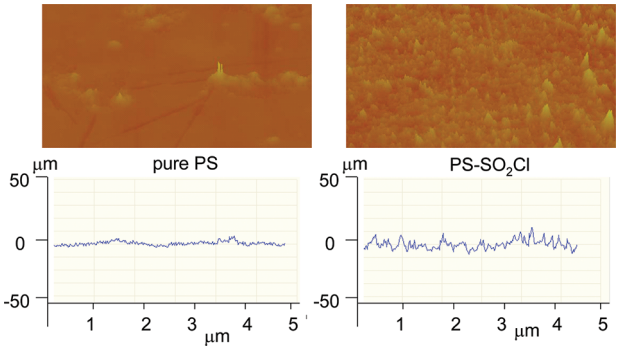


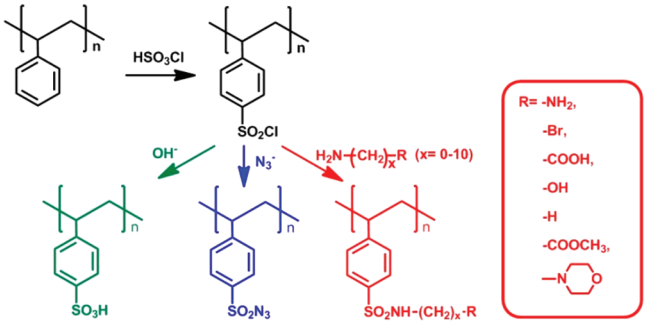
Figure 4. AFM images and corresponding roughness profile of a PS surface before and after modification for 10 min with chlorosulfonic acid at −10 °C.

characteristic surface roughness parameter R_q slightly increases from 1.8 to 2.6 μm when the surfaces are exposed to the acid. However, this increase in roughness does hardly affect the transparency of the samples.

Reactivity. Chlorosulfonated PS samples are stable and can be stored for long periods of time under ambient conditions without loosing their activity. FTIR-ATR analysis shows that freshly prepared samples and substrates stored for one year at room temperature in air exhibit identical spectra and reactivities toward nucleophiles. This is in contrast to many plasma modified materials that have generally to be used within a few months because they loose their activity due to reorientation processes of the functional groups on the surface.

The chemical reactivity of the activated surfaces has been tested exposing them in aqueous solution at room temperature to different nucleophiles that are shown in Scheme 2. Reactions

Scheme 2. Preparation of Functionalized PS Substrates



of the reactive groups with these nucleophiles have been followed by FTIR-ATR. Figure 5 shows that the chorosulfonyl moieties can be easily converted quantitatively to SO_3H groups when immersing the substrates in aqueous solution of pH = 11. The corresponding $-SO_3H$ bands indicated by black arrows appear at 1013, 1029, and 1127 cm^{-1} (spectrum c) while the band at 1370 cm^{-1} has completely disappeared and the second SO_2Cl band at 1170 cm^{-1} has broadened. The resulting spectrum in this case is very similar to that of pure commercial PS-SO_3H. It should be mentioned that the surfaces after this reaction remain as transparent as before.

Of further interest, is the fact that the hydrolysis of chlorosulfonyl groups that works very well at basic pH is

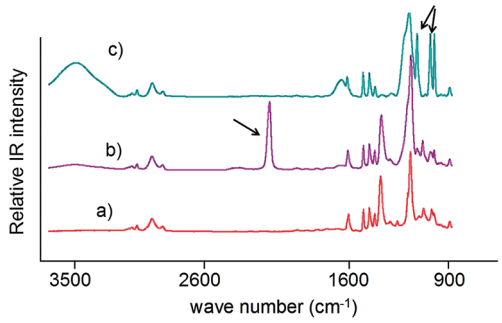


Figure 5. Polystyrene substrate modified with (a) SO_2Cl groups, (b) SO_2N_3 groups, and (c) SO_3H groups.

slow under neutral or acidic conditions. This allows carrying out modification reactions with other nucleophiles in water without the uncontrolled formation of sulfo moieties. In fact, immersion of the chlorosulfonated substrates into an aqueous sodium azide solution leads selectively to the formation of sulfonazide bonds as indicated by the formation of a strong band at 2132 cm^{-1} corresponding to the N_3^- units on the surface (spectrum b in Figure 5) while no peaks corresponding to SO_3H groups are observed. Also in this case the transparency of the samples is maintained.

Of special interest is the reaction of chlorosulfonated PS surfaces with bifunctional aliphatic amines allowing the amine group the linkage to the surface while the second functionality remains available for further reactions. In this way PS substrates with free amine, carboxylic, hydroxyl, halogen, morpholine, or ester groups can be prepared controlling their surface density. The number of functional groups on the surface is in all cases predetermined by the number of chlorosulfonic groups created previously. A further advantage of this approach of surface functionalization is the possibility to choose the appropriate length of the alkyl spacer x of the modifier. The possibility to vary this length is of special interest when biomolecules of demanding geometry shall be linked to the substrate.

Particularly interesting for bioanalytical assays are surfaces with amine and carboxy groups which may form covalent links to proteins or other biomolecules. In Figure 6 the change of the FTIR-ATR spectrum of chorosulfonated PS is shown when the substrate is immersed for 20 min in an aqueous solution of an aliphatic diamine (for example propane diamine): the

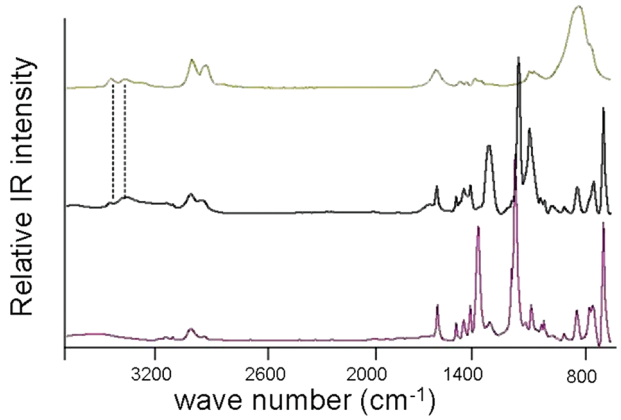


Figure 6. IR spectra of PS-SO_2Cl sample before (violet) and after (black) the amination reaction with propane diamine. For comparison the IR spectra of pure propane diamine is also shown (yellow).

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symmetric O═S═O band at 1370 cm^{-1} disappears completely and appears at 1315 cm^{-1} in the sulfonamide compound; the asymmetric O═S═O band at 1170 cm^{-1} is slightly shifted to 1152 cm^{-1}. Additionally new bands appear at 1094 cm^{-1} due to C−N valence bonds and at 3368 and 3279 cm^{-1} which proceed from associated and nonassociated N−H valence bonds respectively (broken lines).

In an analogue way carboxylated surfaces can be obtained reacting chlorosulfonated PS substrates in aqueous solutions with α,ω-aminoacids (for example β-alanine). Also in this case the characteristic shift from both SO_2Cl bands at 1370 and 1170 cm^{-1} to lower wave numbers is observed upon the formation of SO_2NH-units (Figure 7). Furthermore, a strong

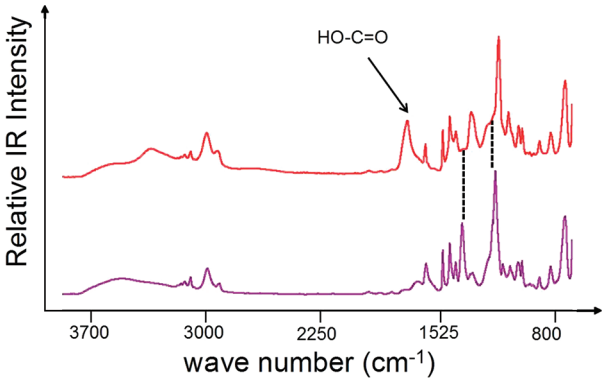

Figure 7. IR spectra of PS-SO_2Cl sample before (violet) and after (red) the carboxylation step using β-alanine.

carbonyl band appears at 1726 cm^{-1} and a broad carboxylic O−H valence bond around 3300 cm^{-1}. It has to be emphasized that the carboxylation reaction should be carried out at a pH that corresponds to the pK_s of the amine group. At lower pH the concentration of free active amine groups is reduced due to salt formation with the carboxy protons and at higher pH hydrolysis of SO_2Cl to SO_3H units may take place as a secondary reaction.

The number of available functional groups on the surface has been determined by colorimetry using Orange II for amine groups and Toluidine O for COOH groups. The method consists in the reversible formation of a salt complex between the functional group and a dye. When the complex is formed on the surface, excess dye can be washed off. Then the adhered dye is extracted by immersing the substrate in a known volume of basic water for amine groups and acidic solution for acid groups. Finally the dye concentration can be determined photometrically. In the case of aminated surfaces one detects between 2 and 10 nmol/cm^2 functional groups, in the case of carboxylated substrates between 50 and 400 nmol/cm^2 what is around 1−3 orders of magnitude larger than the amount in commercial plasma functionalized PS substrates. The difference in the functionalities density of aminated and carboxylated surfaces is probably due to different penetration depths of the corresponding dyes used in the colorimetric determination. A detailed study of this phenomenon is actually in progress.

ELISA. An ethylendiamine modified multiplate was studied for its bionalytical application as ELISA substrate. Because of the fact that the aldheyde groups react satisfactorily with amine groups of antibodies a glutaraldehyde treatment is applied on the aminated surface. The immunoassay was performed in the gluatraldehyde-ethylendiamine modified surface and in the reference ELISA set plate.

A standard curve with different concentrations of IL6 in the new surface is carried out to study the viability of the system. In Figure 8, the standard curve of the new modified multiplate is

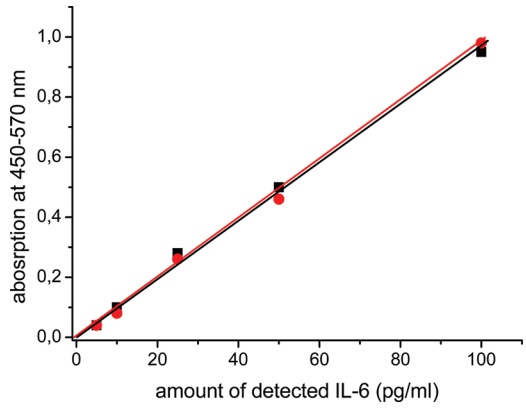

Figure 8. Standard curves for the determination of human IL-6 using ethylendiamine modified plate (black) and reference ELISA set plate (red).

presented and compared with the standard curve of the ELISA set multiplate. Obtained data result in similar curves showing that the new modified multiplate has the same high efficiency than the reference ELISA set multiplate.

According to the specifications of the IL6 ELISA set, whose detection limits are established in the range of 2−200 pg/mL, the sensitivity of the new modified multiplate is studied introducing a sample of 2 pg/mL of IL6. Using the standard curve previously obtained, the system quantified 2.08 pg/mL (DS 0.19, n = 5) demonstrating a sensitivity similar to the reference ELISA set multiplate and the potential applicability of the new surface for ELISA assays.

■ CONCLUSIONS

PS substrates can be activated by a simple and economic wet-chemical treatment in chlorosulfonic acid at low temperatures providing the surface selectively with a tunable number of chlorosulfonic groups that can be used to create or anchor a great variety of functional groups or biomolecules to the surface without loosing its transparency. The preactivated chlorosulfonated substrates are hydrolytically stable in ambient conditions and can be stored for months without loosing their activity. Surfaces homogeneously covered with a required number of amine or carboxylic groups may be created in a simple, cheap and reproducible way. The first ELISA assays carried out with 96-well polystyrene plates aminated according to the method presented here have shown that these materials can be used as an alternative to conventional materials.

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Notes

The authors declare no competing financial interest.

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