Synthesis of Poly(styrene-*co*-methyl methacrylate)-Based Ionomers and Their Langmuir and Langmuir−Blodgett (LB) Film Formation

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Poly(styrene-*co*-methyl methacrylate) (PS−PMMA) ionomers with several degrees of sulfonation were synthesized and characterized by infrared, UV−vis, and NMR spectroscopies, elemental analysis, and differential scanning calorimetry (DSC). Stable Langmuir films could be produced with PS−PMMA with 3 and 6 mol % of sulfonation, while PS−PMMA 8% exhibited material loss to the water subphase, probably due to its higher solubility. Surface pressure and surface potential isotherms with PS−PMMA 3% spread onto salt-containing subphases pointed to a film behavior characteristic of the polyelectrolyte effect, where charge repulsion governs the film properties. The Langmuir−Blodgett films of this ionomer were successfully transferred onto various substrates, as confirmed by UV−vis and FTIR spectroscopies. Using cycling voltammetry, we show that LB films from PS−PMMA 3% can be applied in selective sensing of dopamine, even in the presence of interferents such as ascorbic acid.

Introduction

Ionomers are ion-containing polymers with a small number of ionic groups, typically up to 10−15 mol %, randomly distributed in nonionic backbone chains.[1−3] They differ from polyelectrolytes in having a backbone with low polarity, being therefore insoluble in water. In nonpolar solvents, the ionic groups are not ionized and aggregation due to dipolar attractions of ion pairs occurs.[4−6] In polar organic solvents, e.g., dimethylformamide and dimethyl sulfoxide, ionomers behave like polyelectrolytes,[4,5,7] as the dissociation of ionic groups on the backbone leads to macroions and Coulombic repulsive forces. With interaction among the pendent ionic groups, either in solution or in solid films, the properties of ionomers may be varied widely, thus allowing a variety of applications.[8] Because ionomers are insoluble in water, they may be used to fabricate ion-containing Langmuir−Blodgett (LB) or Langmuir−Schaefer (LS) films. With these techniques nanostructured films can be fabricated with controllable thickness, high homogeneity and some degree of organization.[9] LB films from ionomers may form complexes with small moieties, analogously to some polyelectrolytes used as complexation agents for metals.[10] This feature can be exploited in sensor electrodes, where the ultrathin nature and layer-by-layer order of the LB film coating the electrode may lead to high sensitivity and selectivity. In this context, ionomers have been employed in electrodes since 1980 with the use of Nafion, which is a perfluorinated polymer.[11] In a recent paper,[12] Langmuir−Schaefer films of Nafion were employed in electrochemical and photoelectrochemical experiments with methyl viologen.

The motivation for our work has been the identification of ionomers amenable to LB film transfer, which can be used to modify electrodes in different ways, including changes in electrochemical activity and in the charge injection and transport characteristics in electroluminescent and photovoltaic devices.[13] This requires a fully fleshed characterization of Langmuir films and LB films, as the ionomer properties depend on a number of factors, such as ion concentration and the characteristics of the backbone, e.g., chemical nature, polarity, and flexibility.[1−3,14] Furthermore, electrostatic repulsion between ionic groups may govern the structure of the Langmuir film, which will depend strongly on the pH and ionic strength of the aqueous subphase. For the choice of the ionomers, we decided to employ copolymers of sulfonated polystyrene (SPS) and poly(methyl methacrylate) (PMMA). SPS is noncrystalline and has been well-characterized,[3−7,15−17] but it is brittle and adheres poorly to solid substrates, which may be critical for the fabrication of ultrathin LB films. PMMA has excellent optical transparency and better tenacity and adhesion compared to PS. It is also noncrystalline with the added advantage of possessing a glass transition temperature T_g close to that of PS (ca. 100 °C). Copolymers of methyl methacrylate and styrene were proven to be an even more interesting choice because they can be sulfonated in the same way as polystyrene and comparison with SPS is possible. This comparison allows investigation into the effect from the backbone chain polarity and flexibility on the final properties of ionomer films. In this paper, we report on the Langmuir and Langmuir−Blodgett properties of PS−PMMA ionomers with various degrees of sulfonation. Surface pressure ($\pi \times A$) and surface potential ($\Delta V \times A$) isotherms and Brewster angle microscopy (BAM) were used to characterize the Langmuir films at the air−water interface, while the deposited LB films were characterized by ultraviolet−visible (UV−vis) and Fourier transform infrared (FTIR) spectroscopies. It is also demonstrated with cyclic voltammetry that LB films from these ionomers can be used to detect dopamine selectively.

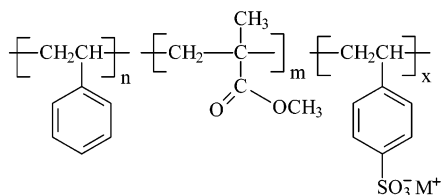† Universidade de São Paulo.
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Figure 1. Structure of the copolymer ionomer.

Experimental Section

Random copolymers of styrene and methyl methacrylate (PS−PMMA) with 50% of styrene and 50% of methyl methacrylate units and pure polystyrene were obtained by suspension polymerization of the purified monomers using benzoyl peroxide as initiator. The composition of the copolymer was confirmed by ^{1}H NMR to within 2% of accuracy. The molecular weight (M_w) of polystyrene and its copolymer with PMMA were 100 000 and 115 000 g/mol with polydispersity index (M_w/M_n) of 2.0, determined by size exclusion chromatography in tetrahydrofuran using polystyrene standards. The ionomers of polystyrene (PS) (3% of sulfonation) and poly(styrene-*co*-methyl methacrylate) copolymers (PS−PMMA 50:50) with several levels of sulfonation (3%, 6% and 8% in mol, Figure 1) were synthesized by sulfonation of the parent copolymers with acetyl sulfate in dichloroethane.[17] The sulfonated and the parent polymers were characterized by UV−vis (Hitachi 2001) and FTIR (ThermoNicolet Nexus 470) spectroscopies, elemental analysis (Carlo Erba), and ^{1}H NMR (Bruker 400 MHz in deuterated chloroform solution at 10 wt % concentration). The sulfonation degrees were estimated from the sulfur content determined by elemental analysis. Differential scanning calorimetry (DSC) experiments were carried out in a Shimadzu TW-50 system, at a heating ratio of 10 °C/min under N_2.

The Langmuir and LB films were produced with a KSV5000 Langmuir trough, housed in a class 10 000 clean room. All the polymer samples were dissolved in chloroform at a typical concentration of 0.2 mg/mL and spread onto water obtained from a Millipore ultrapure water system (resistivity 18.2 MΩ cm). The influence from different cations in the subphase was studied by using subphases containing various salts at 10^{-3} mol/L: NaCl, LiCl, and KCl. The experiments were conducted at room temperature, approximately 22 °C. Langmuir film compression was carried out at a barrier speed of 10 mm/min. A Wilhelmy plate and a Kelvin probe, both provided by KSV, were used to measure surface pressure and surface potential, respectively. Stability tests were performed by keeping the surface pressure at 26 mN/m while the time evolution of the area per molecule was recorded. A BAM2 plus by NFT (Göttingen, Germany) mounted on a Nima (U.K.) trough, equipped with a 30 mW laser emitting *p*-polarized light at a wavelength of 632 nm, was used to visualize the morphological features of monolayers as the light beam was reflected off the air−water interface at the Brewster angle. The light reflected from the surface was collected by two achromatic 10× long-distance objective lenses and detected with a charge-coupled device (CCD) connected to the microscope, which converts the reflectivity signal from the sample into a video image. Pictures were recorded directly in the computer memory via an image processor.

LB films were produced by transferring the Langmuir films onto ITO (indium−tin-oxide)-coated glass (Asahi Glass Co., Japan), quartz or silicon wafers (Aldrich). The typical dipping speed was 3 mm/min, with 30 min elapsing between the first and the second layer and 5 min for the subsequent layers when
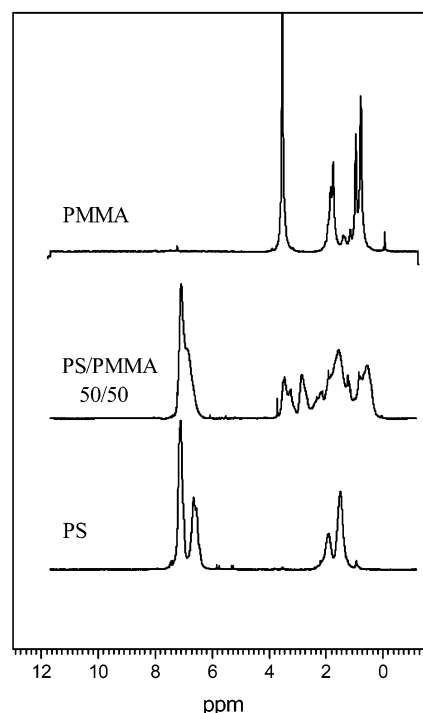

Figure 2. ^{1}H NMR of the parent polymers, polystyrene and copolymer of polystyrene and poly(methyl methacrylate) and poly(methyl methacrylate).

the substrate was out of the aqueous subphase. The LB films were produced keeping the surface pressure at 26 mN/m during deposition. The first 10 layers yielded Y-type films and Z-type LB films were produced in subsequent layers. All the films analyzed here contained 31 layers. The transfer ratio (TR) for the copolymer PS−PMMA 3% was ca. 0.5 in the upstrokes and 0.4 in the downstrokes, while it was 0.6 in Z-type films. These values are averages calculated from all TR values found for each one of the 31 layers. The LB films on silicon wafers were characterized by FTIR spectroscopy using a ThermoNicolet Nexus 470 FTIR, in the 4000−300 cm^{-1} range with 4 cm^{-1} resolution. UV−vis absorption measurements were carried out in a HITACHI U-2001 spectrophotometer in the range between 180 and 350 nm, for the LB films deposited onto quartz substrates.

Cyclic voltammograms were obtained with LB films deposited onto ITO using a potentiostat/galvanostat model 283 from EG&G Instruments and a three-electrode electrochemical cell with 10 mL volume. The reference electrode was Hg/Hg$_2$SO$_4$/K$_2$SO$_{4(sat.)}$ (MSE), a 1.0 cm^2 platinum foil was used as auxiliary electrode and the working electrode was the LB film onto ITO. The experiments were conducted in HCl 0.01 mol/L solution at room temperature (22 °C). Voltammograms were recorded for 31-layer LB films from PS−PMMA 3% at scan rates of 50 mV/s with dopamine (DA) and effects from the interferent ascorbic acid (AA) were also studied. The concentration of DA used was 5×10^{-5} mol/L, and the concentration of AA was 15×10^{-5} mol/L. After the measurements, the films tested were well washed with electrolytic solution and the reproducibility was investigated, with the LB films shown to be stable in all experiments.

Results and Discussion

Polymers Characterization. ^{1}H NMR spectra are presented in Figure 2 for pure PS, for PS−PMMA before the sulfonation reaction, and for PMMA for comparison. The peaks from 0 to
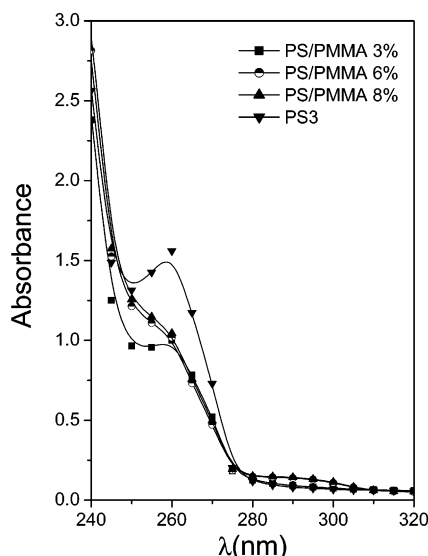
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Figure 3. UV−vis spectra for solutions of ionomers in chloroform.
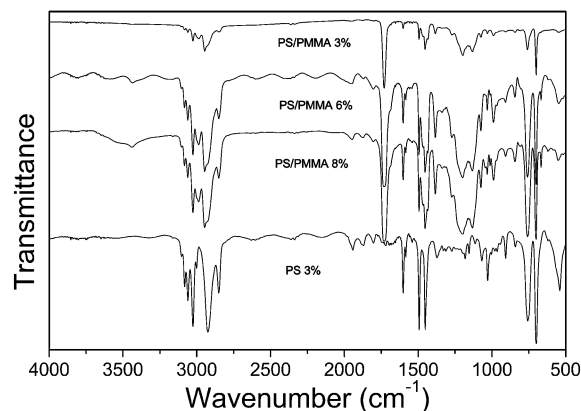
Figure 4. Infrared spectra of cast films from the ionomers.

Figure 5. Differential scanning calorimetry thermograms from PS and PS/PMMA ionomers and their parent polymers. The heating rate was 10°C/min.

TABLE 1: Data for Glass Transition Temperatures, T_g, Taken at the Middle Point between the Onset and the End of the Transition, and Energy Change in the Transition, Cp

material	T_g (°C)	Cp change (mW/mg)
PS	93.0	−0.054
PS3%	103.4	−0.058
PS:PMMA	97.7	−0.049
PS:PMMA3%	105.0	−0.052
PS:PMMA6%	108.7	−0.048
PS:PMMA8%	not detected	

4 ppm correspond to aliphatic protons while those from 5 to 8 are from aromatic protons of polystyrene. The ratio between aromatic and aliphatic protons yields a copolymer composition of 50%:50% for PS and PMMA in weight, as expected. The ^{1}H NMR spectral values for PS−PMMA are as follows (CDCl$_3$, δ ppm): 0.61−1.25 (3H, CH$_3$ PMMA), 1.25−2.3 (2H, CH$_2$, PMMA), 3.1−3.9 (3H, OCH$_3$, PMMA), 1.15−1.18 (2H, CH$_2$ PS), 1.8−2.4 (1H, CH PS), 6.25−6.9 (2H, Ar 2, 6) 6.9−7.4 (3H, Ar 3, 4, 5). The changes in profile seen in Figure 2 are consistent with the expected copolymerization.

Figure 3 shows similar UV−vis spectra for the pure polymers and copolymers at a fixed concentration in chloroform solutions (0.3 mg/mL), with maximum absorption at ca. 260 nm. A slightly higher absorbance is seen for pure PS due to a larger number of aromatic groups. There is also a small change with increasing sulfonation degree from 3 to 6 and 8%, with the absorption at 260 being less pronounced and a weak absorption peak appearing at 290 nm for the higher degrees, probably due to substituted aromatic rings.

Figure 4 shows similar FTIR spectra for cast films of the ionomers PS 3%, PS−PMMA 3, 6, and 8%. The spectra of the copolymers exhibit absorption bands characteristics of both PMMA and PS. In summary, bands appear at 2950 (C−H stretching), 1743 (C=O of the ester group of PMMA), 1190 (C−O stretching of the ester group), 1375 cm^{-1} (methyl groups of PMMA), 3023 (−CH− stretching from benzene rings of PS), 1670 (conjugation in PS), and 1190 cm^{-1} (asymmetric stretching of O−S−O). The latter is difficult to observe in the copolymers
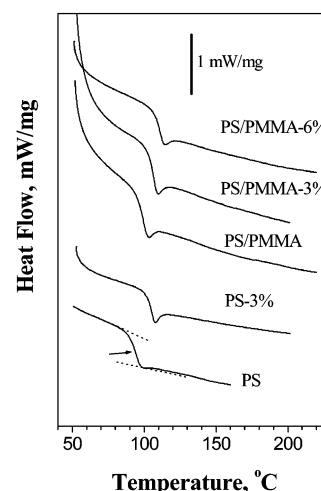
due to the absorption from PMMA in the same region. Therefore, the FTIR characterization serves only to show the groups from PMMA and PS, while copolymerization has been confirmed with the NMR data discussed above.

Differential scanning calorimetry thermograms are shown in Figure 5, from which glass transition temperatures, T_g, were determined in the half of the transition and are given in Table 1. T_g increases with the sulfonation degree as a consequence of the ion pair aggregation. The energy change in the transitions corresponded to approximately 0.05 mW/mg and seems to be independent of the sulfonation degree.

Langmuir Films. The surface pressure−area isotherms of the ionomers PS−PMMA with 3, 6, and 8% of sulfonation spread on pure water subphase are shown in Figure 6A, which also includes the isotherm of pure PS 3% for comparison. The area per molecule for pure PS in the condensed phase, extrapolated to zero pressure, is ca. 3 Å^2, which is much smaller than expected for the molecule as the cross section for PS according to the CPK model using the Hyperchem program is ∼30 Å^2. This indicates the formation of nonmonomolecular structures, since PS molecules are unlikely to dissolve in water to any great extent. For the copolymers, the area per molecule in the condensed phase is ca. 18 Å^2 for PS−PMMA 8%, 21 Å^2 for PS−PMMA 6% and 29 Å^2 for the film with PS−PMMA 3%. The area per molecule for PS−PMMA according to the CPK model using Hyperchem program is ∼35 Å^2, assuming that C=O is on the water. The decrease in area per molecule with increasing degree of sulfonation may be due to loss of material, since the copolymer tends to be more water-soluble for higher sulfonation degrees. Indeed, stability experiments showed that within 3 h, the area per molecule of the film with the ionomer PS−PMMA 8% decreased by 50%. However, the stability of the films from copolymers with 3 and 6 mol % of sulfonation was rather good, with a decrease of only 5% in area
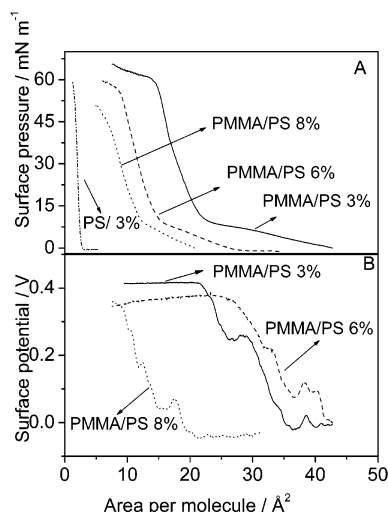
Figure 6. Surface pressure and surface potential isotherms for the ionomers.
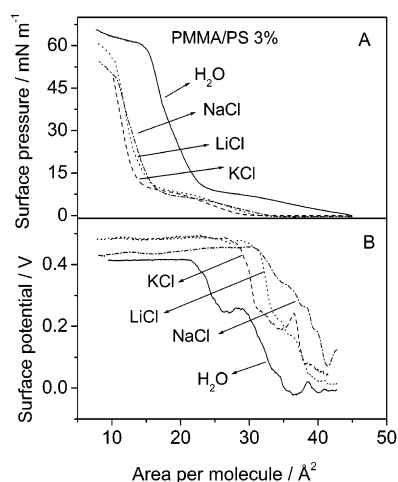

Figure 7. Surface pressure and surface potential isotherms of PMMA: PS 3% using different subphases.

as the film was kept at 26 mN/m for 3 h. Therefore, the smaller area for the latter films must also be attributed to the formation of nonmonomolecular structures. These results show that PS−PMMA-based ionomers are the best choice for the LB film fabrication, especially the lowest sulfonated copolymer, with 3 mol % of ionic groups.

The surface potential-area isotherms are shown in Figure 6B, which does not include data for pure PS since the surface potential was very low, varying from −0.05V in the gas phase to −0.15V in the condensed phase. The maximum surface potential for condensed monolayers is approximately 400 mV for the PS−PMMA monolayers, being slightly higher for PS−PMMA 3%. Another worth noting feature is the shift of the isotherm for PS−PMMA 8% toward lower areas, which actually reflects the loss of material as mentioned in the discussion of the surface pressure isotherms.

Because the stability of pure PS and PS−PMMA 8% was poor, subsequent experiments were conducted only with the ionomer PS−PMMA 3%. Isotherms of the PS−PMMA 3% using various electrolytes as subphases are shown in Figure 7A. The presence of ions in the subphase should decrease the solubility of the ionomer in the subphase[18] and consequently increase the area per molecule compared to those obtained on pure water, if some solubilization of the material occurred. However, adding salts to the subphase caused the area to

decrease for the ionomer PS−PMMA 3%. It is possible that the presence of salt screened the electrostatic repulsions between sulfonated groups, thus leading to more coiled polymer chains, analogously to polyelectrolytes or ionomers in polar solvents with added salts.[7] This result is evidence of the polyelectrolyte 2D behavior of ionomer films on the water subphase. In this context, a possible rationale for understanding the formation of Langmuir films of these ionomers is as follows. In a Langmuir film, the ionic groups will be immersed in water and dissociate, similarly to polyelectrolytes. An important parameter for polyelectrolyte solutions, which can be applied for ionomers in polar solvents, is the Bjerrum length, Q,[19] defined as the distance between two elementary charges when the electrostatic energy equals the thermal energy, $k_b T$.

$$Q = \frac{q_e^2}{\epsilon_o \epsilon k_b T} \quad (1)$$

where q_e (1.6×10^{-19} C) is the charge of the electron, ϵ_0 is the vacuum permittivity, ϵ is the solvent dielectric constant ($\epsilon_{H_2 0} = 80.4$) and $k_b T$ is the Boltzmann term ($k_b = 1.38 \times 10^{-23}$ J K^{-1}). For water at 25 °C, the Bjerrum length is 7.14 Å, which will be the shortest distance two ions can have to start ion condensation according to Manning's theory[20] for counterion condensation. For ionomers in polar solvents below the limit of ion condensation, the macroion diameter at zero polymer concentration, determined by low-angle light scattering[21] and intrinsic viscosity,[7] increases linearly with the ion content, thus indicating the effect from repulsion forces. In a two-dimension system such as a Langmuir film, even for low ionic content the repulsion force is expected to increase as the ionic groups come close together. These repulsion forces can also help organize the film. Considering a mean area for PS or PMMA monomers of 15 Å^2 (calculated by the CPK model using Hyperchem program) and each charge in a circular domain, the mean distances between charges in the copolymers with 3, 6, and 8% sulfonation are 25, 18, and 15.5 Å, respectively. These distances are larger than the Bjerrum length, and no ion condensation should occur in the Langmuir film.

Note in Figure 7A that there is no influence of the size of the cation, since Li, Na or K have the same effect, which again points to the importance of the electrostatic (or polyelectrolyte) effect. Figure 7B shows that the surface potential increases with the ions in the subphase (maximum at ca. 480 mV) in comparison with the monolayers on a pure water subphase. This may be due to a decrease in the negative contribution of the double-layer as the ionic strength is increased.[22]

BAM images of pure PS 3% and PS−PMMA 3% are shown in Figure 8. The images of pure PS show agglomerates even in the gaseous phase and upon compression the film is formed with the coming together of these agglomerates, consistent with the formation of thick nonmonomolecular structures inferred from the small areas per molecule in the surface pressure isotherms. For the copolymers, almost no domains appeared in the gaseous phase. For pressures higher than 1 mN/m, BAM images were very similar for all the surface pressures until the films collapsed. The images of copolymer present less aggregates and the film covers almost the whole water surface without noticeable defects. Therefore, incorporation of polar groups (carbonyl groups) in the polymer backbone of the copolymers contributes to a more homogeneous spreading of the molecules at the air−water interface, in comparison with the hydrocarbon backbone of pure PS.

Langmuir−Blodgett Films. The charged groups on the 2D arrangement of the Langmuir film will be separated by the
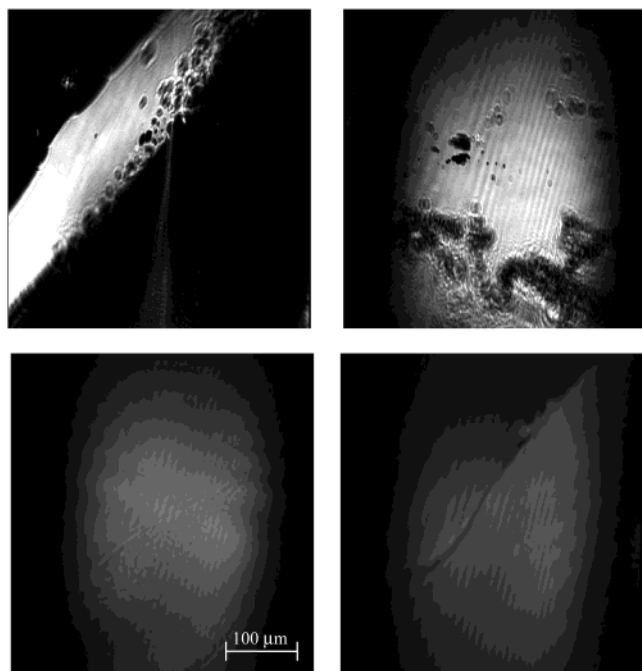
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Figure 8. BAM images for Langmuir films from pure PS 3% and PS:PMMA 3%.

Figure 9. UV−vis spectra of PS:PMMA 3% films (cast and LB) and in solution.

Figure 10. FTIR spectra of the PS:PMMA 3% LB film.

maximum possible distance, leading to a uniform distribution on the surface and minimizing the free energy of the system. This condition leads to self-organization of the charged groups on the Langmuir film that can be maintained after transfer of the LB film onto a solid substrate, since after drying the ion pair will be separated and no interaction between them is expected. As mentioned before the distances between charges in the Langmuir film are larger than the Bjerrum length and no ion condensation should occur in the first layer of deposited film. However, ion condensation may occur in subsequent layers due to the proximity between the layers leading to distances between charges to be less the Bjerrum length (7.14 Å), the limit for ion condensation. Therefore, as additional layers are deposited, charge repulsion is expected to hamper film transfer. Indeed, we noted that the values of transfer ratios (TR) for the immersion of the substrate decreased steeply and after 10 layers had been deposited for the PS−PMMA 3%, the TR values were less than 0.5. Therefore, we considered that after 10 layers, the film transfer was changed from Y-type (transfer on both withdrawal and immersion of the substrate) to Z-type, with transfer only on withdrawing the substrate. Nevertheless, tens of layers could be deposited as transfer did not cease completely, probably because repulsion had reached a limit. Such a limit is defined by counterion condensation, as observed in experiments where the viscosity at low polymer concentration of SPS ionomers remained almost constant in THF/H$_2$O solutions when the distance between charges was already shorter than the Bjerrum length.[7] It should be mentioned that LB films can also be produced with PS−PMMA 6 and 8 mol %, but they are not discussed here as we concentrate on the results obtained with the more stable Langmuir films for the PS−PMMA 3%.

Figure 9 shows the UV−vis spectra for a chloroform solution, a spin-coated film, and a 31-layer LB film (both on quartz substrates) for the PS−PMMA 3% sample. The wavelength of maximum absorbance in all cases is at 260 nm, characteristic of polystyrene backbones, with no evidence of aggregation in the LB film. Figure 10 shows the FTIR spectrum of a 31 layer-LB film of PS−PMMA 3%, which contains practically the same bands as the cast film depicted in Figure 4. This demonstrates
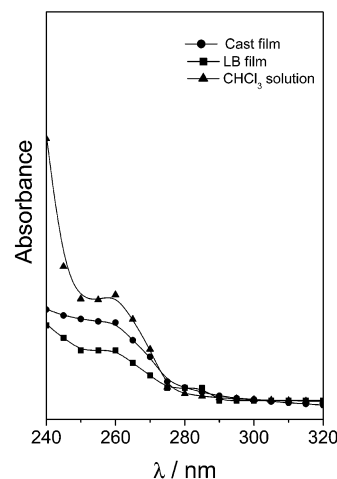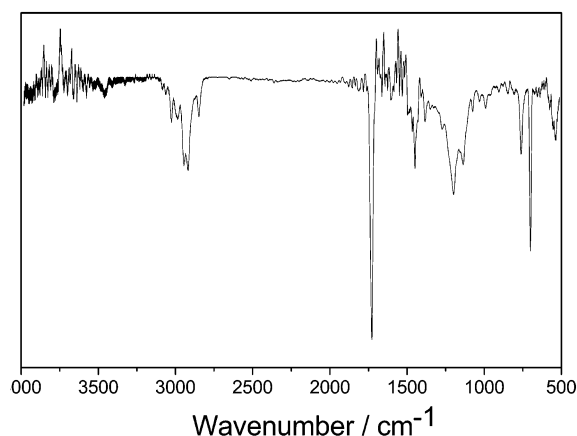
the successful transfer of the LB film. The absorptions due to the PMMA backbone appear more clearly in the LB films than that of PS (mainly C=O band at 1743 cm^{-1}) probably due to some degree of orientation of the carbonyl groups in films produced by the LB technique.[23,24]

It is well-known that films of Nafion and other ionomers and polyelecrolytes can incorporate cations by ion exchange. If the ionomer is used to coat an electrode, it can be used as a selective sensor for electroactive cations without interference from anions.[12] To investigate whether ionomers LB films display the capability of ion exchanging and selective sensing for cations, the electrochemical behavior of dopamine (DA) in LB films was studied by cyclic voltammetry (CV). We have chosen DA because it has been widely studied owing to its importance as a neurotransmitter in mammalian central nervous systems.[23] By way of illustration, it could be mentioned that the loss of DA-containing neurons may be associated with diseases such as Parkinson's disease.[25] Detection of DA is usually carried out with electrochemical methods since DA is electroactive. All curves in Figure 11 are for the third cycle of cyclic voltammo-grams, and the CV curves were reproducible after the third cycle in all cases. Figure 11A shows the electrochemical response of bare ITO substrate in the presence of DA, with oxidation/reduction peaks at ca. +680 and −330 mV. The bare ITO substrate has no electrochemical response if only the electrolyte solution HCl is present.[26] Figure 11B shows the cyclic voltam-mograms for the PS−PMMA 3% in the presence of 5 × 10^{-5} mol/L DA at 50 mV/s. The redox pair associated with DA, ca. +310 and −380 mV, respectively, is attributed to oxidation/

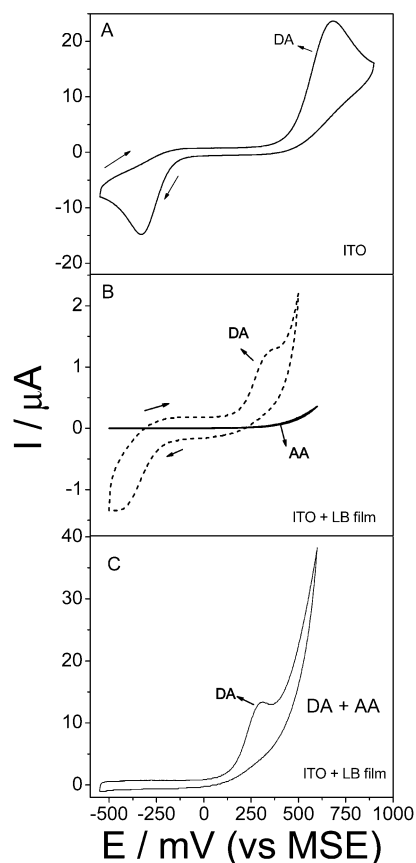**7038** *J. Phys. Chem. B, Vol. 108, No. 22, 2004*

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Figure 11. Cyclic voltammograms of dopamine in HCl 0.10 M: (a) bare ITO electrode; (b) ITO electrode covered with a 31-layer LB film of PS:PMMA 3% (also shown is the response for pure AA); (c) ITO electrode covered with a 31-layer LB film of PS:PMMA 3% in the presence of AA. The reference electrode was Hg/Hg$_2$SO$_4$/K$_2$SO$_{4(satd)}$ (MSE).

reduction of dopamine to dopaminequinone[27,28] with participation of two electrons. Note that the DA peak appears at a lower potential than for bare ITO. Therefore, PS−PMMA 3% in the LB films is an electrocatalytic agent for dopamine oxidation. Furthermore, since DA oxidation occurs at lower potentials, interferences from other organic compounds may be minimized. This is important because the voltammetric response of DA may be affected by interferents such as ascorbic acid (AA), which usually coexists in vivo with DA as anions.[29] Figure 11B shows that when ITO coated with a 31-layer LB film of PS−PMMA 3% is dipped in a solution containing AA, the cyclic voltammogram has no peaks in all cycles. For the bare ITO AA does display peaks under the same conditions, but only for the first cycle.[26] Figure 11c shows the third cycle of a voltammogram with the LB electrode immersed in a sample containing both AA and dopamine in a molar ratio of (3/1, AA/dopamine), all the other conditions remaining the same as in Figure 11b. Although the electrode is not sensitive to AA, the reduction peak of dopamine is modified when both substances are present in the sample, and the oxidation peak appears at a slightly lower potential. This can be due to the interaction between dopamine and AA.

These CV results confirm that PS−PMMA LB films are perm selective since they repel anions while incorporating cations. We recall that Nafion has been used to modify electrodes and eliminate AA interference.[30] The ionomer film used here can therefore be an alternative to Nafion in modified electrodes for this application.

Conclusions

PS−PMMA ionomers with several degrees of sulfonation have been synthesized and characterized by spectroscopies techniques, which confirmed the copolymerization. These ionomers have been proven to be amenable to the spreading of Langmuir films and transfer of Langmuir−Blodgett (LB) films, especially at low degrees of sulfonation (3 and 6 mol %). The poor stability of the Langmuir film with PS−PMMA 8% was attributed to its higher solubility in water. An analysis of Brewster angle microscopy data indicated that the incorporation of polar groups in the PS−PMMA copolymer improved spreading considerably, in comparison with films from pure PS. The area per molecule in Langmuir films of PS−PMMA 3% decreased with increasing ionic strength of the monovalent salt-containing subphase because charge repulsion was minimized and the ionomer chains were probably more coiled at higher concentrations. No effect could be noted when the salt was changed from NaCl to LiCl or KCl. These results are consistent with the polyelectrolyte effect known to occur in ionomers interacting with polar solvents. FTIR and UV−vis spectroscopies were used to verify the successful transfer of LB films onto different types of substrate. As a proof of concept, we demonstrated that LB films from ionomers can be used to modify ITO electrodes that are perm selective, repelling anions while incorporating cations. Cyclic voltammetry was employed to show that a 31-layer LB film from PS−PMMA 3% can detect dopamine, with no interference from ascorbic acid.

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