

Adsorption Behavior of Polystyrene–Polyisoprene Diblock Copolymers with Zwitterionic Groups Using Quartz Crystal Microbalance: Effect of Different Microstructures

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Received May 6, 2002. In Final Form: July 27, 2002

The adsorption behavior of poly(styrene-*b*-isoprene) (PS-*b*-PI) copolymers functionalized with polar sulfobetaine zwitterionic groups at different positions along the backbone was investigated. Using dilute solutions in toluene, adsorption onto gold surface was investigated using a quartz crystal microbalance (QCM). ZwiS and ZwiSI, ZwiSZw, and SZwiI are PS-*b*-PI copolymers functionalized at the α -position (zwitterionic group is attached to isoprene or styrene), at the α,ω -positions, and at the junction-point in the chain, respectively. The copolymers showed interesting adsorption behavior according to the zwitterion position. The adsorption isotherms for the copolymers exhibited typical Langmuir isotherm behavior. They showed different adsorbing amounts, which was explained by possible conformational states of copolymers on the surface. It was found that the position of zwitterionic groups has a major role on adsorption kinetics despite similar molecular weight and composition for the copolymers.

Introduction

Block copolymers and end-functionalized polymers can adsorb on solid surfaces in the presence of selective solvents and selective surfaces.^{1–12} An insoluble block in copolymers or end-functionalized polymers adsorbs onto a surface via *physisorption*, allowing a soluble block to extend into solution in a “brushlike” conformation. The detailed polymer brush structure depends on the selectivity of the media, the length of each block, the interactions between blocks and the surface, and so forth. These polymer brushes are attractive candidates in applications such as colloidal stabilization, separation of colloidal mixtures, lubrication, adhesion, protein-resistant biosurfaces, and other related applications.^{1,2}

Several studies on the adsorption behavior of end-functionalized polymers have been reported. Fetters et al. studied adsorption and brush formation of end-functionalized polystyrene (PS) with zwitterionic groups and poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO) copolymers with a short adsorbing PEO block onto mica.^{9,10} Stamm et al. also investigated the adsorption behavior of functionalized poly(styrene-*b*-butadiene) (PS-*b*-PB) di- and triblock copolymers with randomly attached adsorbing positions in short PB blocks onto a silicon wafer.^{11,12} The adsorption kinetics showed a transport-limited regime at the beginning and a slower process after the formation of a dense surface coverage. They found that these systems largely behave like conventional block copolymers with selective adsorption of one block.

In our previous papers, the association and micellization of poly(styrene-*b*-isoprene) (PS-*b*-PI) copolymers functionalized with zwitterionic groups at various positions in two nonpolar solvents, CCl₄ and *n*-decane, were studied but not their adsorption behavior.^{13–16} Thus, adsorption studies of these block copolymers are of great interest from the viewpoint of structural characteristics as adsorbed “copolymer brushes”. In this study, PS-*b*-PI copolymers were synthesized and functionalized with zwitterionic groups at different positions along the backbone. The adsorption studies are performed in toluene, which is a good solvent for both blocks but a nonsolvent for the zwitterionic group.

Various techniques have been used to characterize the adsorption studies, such as ellipsometry,^{17,18} surface

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plasmon resonance spectroscopy,^{19,20} surface force measurements,^{9,10} dynamic light scattering,²¹ internal reflection interferometry,²² and total internal reflectance fluorescence (TIRF).²³ The quartz crystal microbalance (QCM) is known as a mass-sensing device with the ability to measure very small mass changes on a quartz crystal in real time. It is an ideal in-situ tool for studying adsorption processes and chemical sensing, since it has high sensitivity, defined by a relationship between mass and the frequency of the QCM.^{24–26} It has been applied mostly to measurements of mass adsorption or binding to the quartz surface in the gas phase. Recently, the QCM technique has been extended to liquid-phase measurements and the study of phenomena at solid–liquid interfaces.^{27–29} In this study, we have investigated the adsorption behavior of different PS-*b*-PI copolymers functionalized with polar sulfobetaine zwitterionic groups onto gold surfaces using the in-situ QCM technique.

Experimental Section

Polymer Synthesis. PS-*b*-PI copolymers functionalized with zwitterionic groups at different positions along the chain were synthesized by high vacuum anionic polymerization techniques with subsequent functionalization. Figure 1 shows the molecular structures of the various functionalized copolymers. Abbreviations of the copolymers were given according to the positions of zwitterionic groups. Complete details for the synthesis of these copolymers are given elsewhere.^{13–15} Briefly, for the synthesis of ZwIS and ZwSI (α -functionalized copolymer), 3-(dimethylamino)propyllithium (DMAPLi) was used as an initiator to introduce a dimethylamino group at the end of the chain. For the synthesis of ZwISZw (α,ω -functionalized copolymer), isoprene was polymerized first using DMAPLi as initiator followed by addition of the styrene monomer. After completion of the polymerization of styrene, excess 1-(4-dimethylaminophenyl)-1-phenylethylene (DMADPE) was introduced to the mixture. The capping reaction between the PSLi living ends and DMADPE was allowed to proceed for 3 days at room temperature to complete conversion of the chain end. For the synthesis of SZwI (junction-point-functionalized copolymer), styrene was polymerized first using *s*-BuLi as initiator. After completion of polymerization, a small excess of DMADPE was introduced to the reaction mixture and was left to react for 3 days at room temperature. Isoprene monomer was then added after 24 h. All polymerizations were terminated by addition of degassed methanol, and the resulting

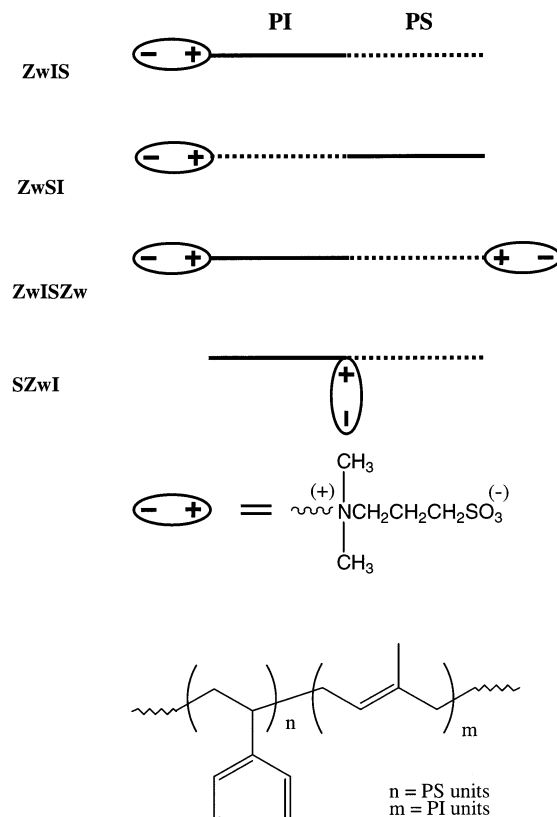


Figure 1. Molecular structures of PS-*b*-PI copolymers functionalized with zwitterionic groups.

copolymers were precipitated in methanol and dried under vacuum. Finally, all the dimethylamino groups were converted to sulfobetaine zwitterions by reaction with excess cyclopropanesulfone in THF at 70 °C for several days to ensure complete conversion.

Characterization of the Polymers. Number average molecular weights (M_n) were obtained using a membrane osmometer (Jupiter Instruments Company Model 231) with dry toluene. To determine the molecular weight distributions (MWDs), size exclusion chromatography (SEC) was performed using a Waters system composed of a Waters 600 pump controller, a set of four Styragel columns (continuous porosity range 10³ to 10⁶ Å), a Waters 410 differential refractometer, and a Waters 996 photodiode array UV detector at 30 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with linear PS standards. The average composition of the copolymers as well as functionality was determined by NMR spectroscopy using a Varian 200 MHz instrument at 30 °C.

Adsorption Measurements. The QCM apparatus, probe, and crystals are available from MAXTEK Inc. The diameter of the polished AT-cut QCM crystals (5 MHz) was 13 mm. The oscillation frequency was measured with a frequency counter (PM-740 Plating Monitor, MAXTEK, Inc.) and a PLO-10 phase lock oscillator, and the Data-Log Software (MAXTEK, Inc.) was used for data acquisition. The linearity of the phase lock oscillator was calibrated using a network analyzer over a wide frequency range and optimized for glossy films in the liquid phase. The gold electrodes were cleaned with a plasma etcher (Plasmod, March). To measure the polymer adsorption, the inert probe was first immersed in toluene until a stable frequency was obtained. After this, aliquots of the concentrated polymer solution (1 mg/mL) were added to make a desirable concentration in the range 0.0001–0.1 mg/mL. Measurements were recorded three times for each copolymer with a standard deviation within 1–3% of the average plot. We performed low-angle laser light scattering (LALLS) to verify the presence of micelles at the concentration range in which the adsorption experiments were performed. It was found that the PS-*b*-PI copolymers with zwitterionic groups do not aggregate in toluene.

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Data Analysis. The adsorbed amounts of copolymer per given area were calculated using the Sauerbrey equation:³⁰

$$\Delta F = \frac{-2F_q^2}{A_e \sqrt{\rho_q \mu_q}} \Delta m \quad (1)$$

where F_q is the fundamental resonant frequency of the QCM (5×10^6 Hz), A_e is the electrode area (1.327 cm^2), ρ_q is the density of the quartz (2.65 g/cm^3), and μ_q is the shear modulus of the quartz ($2.95 \times 10^6 \text{ N/cm}^2$). The equation is generally valid for measurements in air or in a vacuum. For the QCM crystals used in this study, $\Delta m \text{ (g)} = (-2.34 \times 10^{-8}) \Delta F \text{ (Hz)}$ when crystals operate in air. The amount of the adsorbed polymer A (in mg/m^2) can be calculated by dividing this equation by the electrode area (1.327 cm^2). Therefore, a value of $A \text{ (mg/m}^2\text{)} = -0.177 \Delta F \text{ (Hz)}$ was calculated. However, when the QCM is operating in the liquid phase, it also sensitively responds to the viscosity and density of the contacting solution as well as to the mass increase of the electrodes.²⁶ Recently, Caruso et al. calculated the QCM calibration factor in the liquid phase by a combined QCM/surface plasmon resonance spectroscopy (SPR) study.²⁴ Complementary SPR experiments of surfactant adsorption onto the gold surface suggest that the resonance frequency change of the QCM crystal in solution is 80% greater than that predicted by the Sauerbrey equation for air measurements.

In this study, we adopted the combined QCM/SPR method to calibrate the frequency changes of copolymer solution in toluene. A gold-coated glass substrate was immersed in ZwIS solution (0.01 mg/mL) in toluene for 2 h and then washed with toluene and dried with a light stream of dry N_2 . SPR measurements were performed using a Multiskop (Optrel, Germany). Details of the experimental setup have been reported elsewhere.³¹ The thickness of the adsorbed layer was calculated using a Fresnel calculation algorithm with a polymer layer dielectric constant of 2.359. The thickness of the adsorbed ZwIS layer on the gold substrate was determined to be 34.7 \AA .

The amount of the adsorbed polymer $A \text{ (mg/m}^2\text{)}$ was calculated using the following equation:

$$A = \frac{d(n_p - n_s)}{dn/dc} \quad (2)$$

where d is the calculated layer thickness, n_p is the refractive index of the adsorbed film, n_s is the refractive index of the pure toluene, and dn/dc is the refractive index increment of ZwIS in toluene. A $dn/dc = 0.0399 \text{ mL/g}$ of the polymer was determined using an Abbe refractometer. Thus, the QCM calibration factor required to obtain the same surface coverage from both SPR and QCM data for ZwIS adsorbed on gold from toluene is

$$A \text{ (mg/m}^2\text{)} = (-2.62 \times 10^{-2}) \Delta F \text{ (Hz)} \quad (3)$$

Since the compositions and molecular weights of the copolymers are generally similar, we used this relationship between frequency change and amount of copolymer absorbed onto gold substrate for the other copolymers.

Some parameters of the adsorbed layer can be obtained directly from the adsorbed amount, A . The surface density, σ , which is the inverse of the area per chain, is calculated using the following relation:

$$\sigma = \frac{A \text{ (mg/m}^2\text{)}}{M_w \text{ (mg/mol)}} N_A \text{ (chains/molecule)} \times 10^{-18} \quad (4)$$

where M_w is the molecular weight and N_A is Avogadro's number. Accordingly, the interchain spacing is found from $R = (1/\sigma)^{1/2}$.

Results and Discussion

The macromolecular characteristics of PS-*b*-PI copolymers functionalized with zwitterionic groups are listed in

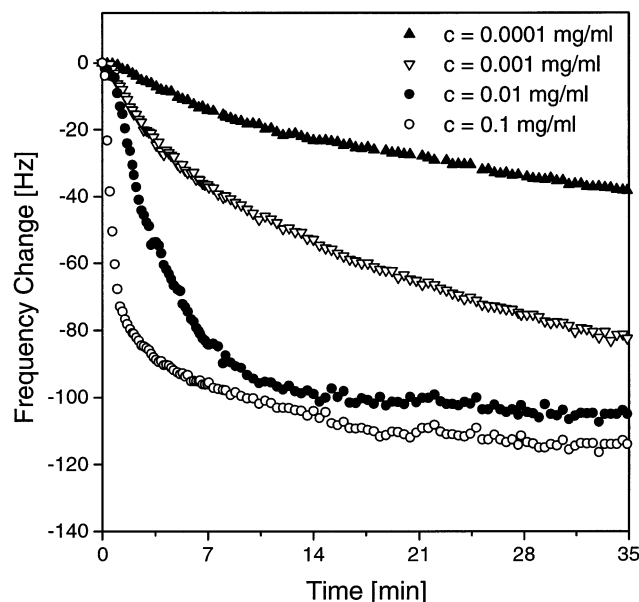


Figure 2. Frequency changes in the QCM for ZwSI in toluene at different concentrations.

Table 1. Macromolecular Characteristics of PS-*b*-PI Copolymers Functionalized with Zwitterionic Groups

copolymer	M_n	M_w/M_n	PS (wt %)
ZwIS	20 900	1.06	51
ZwSI	22 300	1.05	47
ZwISZw	24 300	1.06	54
SZwI	24 600	1.04	46

Table 1. They have almost similar molecular weight (M_w) and MWD, indicating that only the position of the zwitterionic groups should affect their adsorption behaviors.

Figure 2 shows the frequency changes of the QCM for a ZwSI solution in toluene at various concentrations, which are directly related to the adsorbed amount of copolymer. The frequency decreased with time, indicating ZwSI adsorbed on the gold electrode surface of the QCM. As the concentration of the copolymer solutions increased, the frequency change and the adsorption rate increased. Other functionalized copolymers also showed a similar general adsorption behavior with changing concentration.

To verify zwitterion group adsorption sites on the gold surface, the adsorption of PS-*b*-PI ($M_w = 36\,000$, PS wt % = 49.0) copolymers with *no* zwitterionic groups was investigated. As expected, there was no frequency decrease on the QCM in toluene. This result indicates that the sulfobetaine zwitterionic groups on the copolymers are responsible for adsorption on the gold surface. Note that these ionic groups are not soluble in toluene. The major driving force for adsorption is the difference between the solubility of the polymer blocks and the zwitterionic group in toluene. Therefore, polar zwitterionic groups can preferentially adsorb on gold surfaces. Smith et al. also reported the selective adsorption of a diblock copolymer of poly(vinyl-2-pyridine) and polystyrene from toluene on a silver surface.¹⁹ The image charge effects might be another driving force. Plunkett et al. investigated the adsorption and subsequent surfactant-induced swelling of a cationic polyelectrolyte on a gold surface by means of a QCM with dissipation (QCM-D). They suggested the mobility of electrons in the gold is high, which means that mobile negative charges may come close to the charged groups of the polyelectrolyte that contact the surface, and confirmed it with XPS investigation.³²

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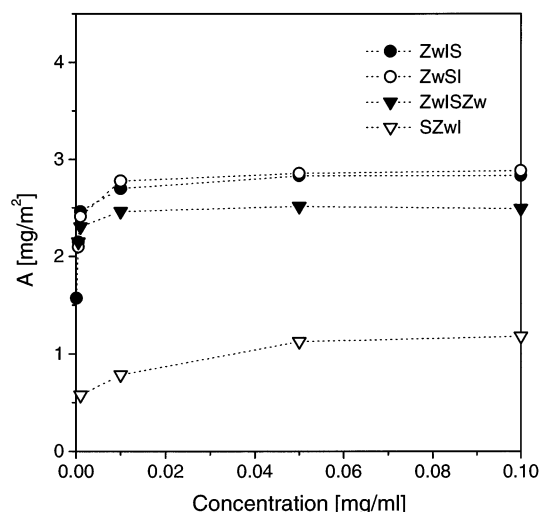


Figure 3. Adsorption isotherms for ZwIS, ZwSI, ZwISZw, and SZwI obtained from QCM measurements.

Adsorption Isotherms. Figure 3 shows the adsorption isotherms for all the copolymers according to concentration. It demonstrates a typical Langmuir isotherm behavior; the adsorbed amount of polymer increases as the concentration rises, reaching a plateau value where the adsorbed amount is independent of the polymer concentration. It is clear that Langmuir isotherms were significantly affected by the positions of the zwitterionic groups. The adsorbed amounts decreased in the order $\text{ZwSI} > \text{ZwIS} > \text{ZwISZw} > \text{SZwI}$. The plateau values for ZwSI (2.88 mg/m^2) and ZwIS (2.83 mg/m^2) are quite comparable to each other, if experimental error is taken into account. This suggests that the adsorbed amount of copolymer does not depend on whether the sulfobetaine zwitterionic group is attached to the end of polystyrene or the polyisoprene block. For the case of ZwISZw (2.52 mg/m^2) and SZwI (1.18 mg/m^2), the adsorbed amount was smaller than that of ZwIS and ZwSI. To explain these differences, possible conformational states of adsorbed copolymers on the gold surface were suggested in Figure 4. ZwIS and ZwSI can form a dense layer with brushlike conformations, and ZwISZw can form a layer with brushlike and loop conformations. Stamm et al.¹² investigated the adsorption of analogous PS–PB and PB–PS–PB block copolymers functionalized with urazole groups and found that the amount of absorbed PS–PB copolymer is about 50% larger than that of PB–PS–PB block copolymer, attributing it to their different conformational states. In their study, the adsorption amount of PS–PB copolymers was not dependent on the number of functional groups. However, in our study, the difference of adsorption was much smaller compared to that for PS–PB and PB–PS–PB copolymers, suggesting that ZwISZw adsorbed onto the gold surface had more brushlike conformations than loops because of the smaller zwitterionic groups at the end of the chain. In the case of SZwI, with zwitterionic groups located between two block polymers, the polymer behaves as a simultaneously adsorbed “two-arm brush” on the surface. This should occupy more area than copolymers, which have only one long arm. This is consistent with our observations on SZwI, resulting in a smaller adsorbed amount, ~40% compared to those of the other copolymers. Evers et al.³³ reported the use of self-consistent field theory

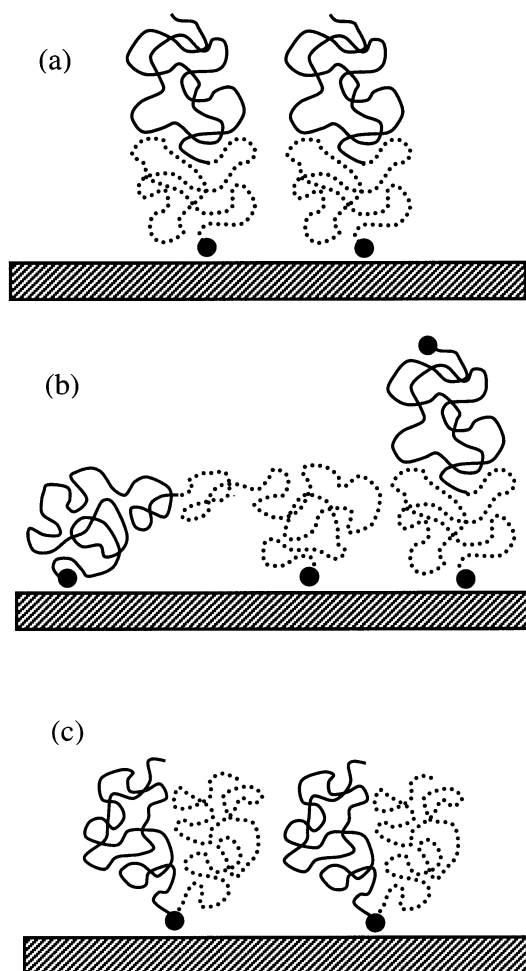


Figure 4. Possible conformational states of adsorbed (a) ZwIS (or ZwSI), (b) ZwISZw, and (c) SZwI.

to describe the adsorption of block copolymers. They found lower adsorbed amounts of BAB-triblock copolymers with adsorbing A-segments and nonadsorbing B-segments as compared to those of an AB-block copolymer with the same number of A- and B-segments.

Insight into the actual structure of the adsorbed layers formed may be gained by considering interchain spacing, R . Table 2 shows the grafting density and interchain spacing values for each copolymer at 0.01 mg/mL . For SZwI, where the zwitterionic group is located between the two blocks, R (5.9 nm) is higher compared to those for the other copolymers. Thus, it is clear that SZwI occupies more lateral space than other adsorbed copolymers, because of the two dangling styrene and isoprene blocks.

Adsorption Kinetics. The kinetics of adsorbed polymer layer formation can be separated into two stages: (i) a transport-limited regime and (ii) a brush-limited regime.⁶ In the transport-limited regime, the polymer adsorption is controlled by diffusion of polymer onto the solid surface with little interaction between polymers. In the brush-limited regime, after a dense surface coverage is achieved, adsorption of additional polymer can proceed by penetration of polymers through the potential barrier created by adsorbed polymers, that is, resulting in a significantly slower adsorption rate.

Figure 5 shows the adsorbed amount of the copolymers at the concentration 0.01 mg/mL versus $t^{1/2}$. The slow adsorption up to 1 min is due to the initial loading of the concentrated solution to solvent. The linear increase of the adsorbed amount with the square root of time is

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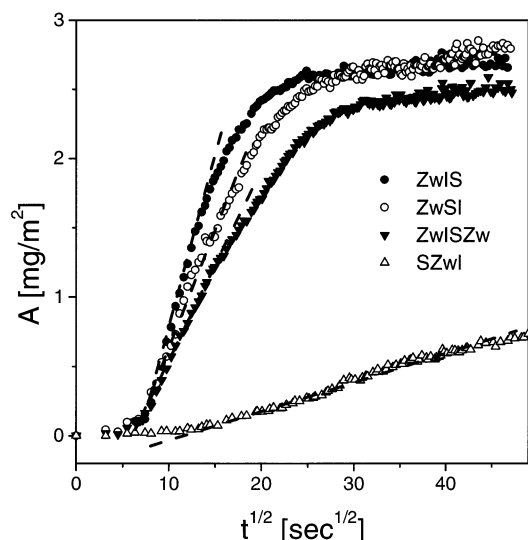


Figure 5. Adsorbed amount of zwitterionic group functionalized PS-*b*-PI copolymers as a function of adsorption time t .

Table 2. Diffusion Coefficients and Geometric Parameters of Adsorbed PS-*b*-PI Copolymers Functionalized with Zwitterionic Groups^a

copolymer	D (10^{-6} cm ² /s)	A (mg/m ²)	σ (chains/nm ²)	R (nm)
ZwIS	5.36	2.83	0.0815	3.5
ZwSI	2.73	2.88	0.0777	3.6
ZwISZw	1.58	2.52	0.0624	4.0
SZwI	0.0418	1.18	0.0289	5.9

^a D is the diffusion coefficient, A is the adsorbed amount, σ is the surface density, and R is the average distance between the anchoring blocks.

indicative of a transport-limited regime where simple Fickian diffusion to the surface is the rate-limiting step. An expression of the adsorbed amount at the surface as a function of time can be determined by integrating the flux of material to the surface:⁶

$$A(t) = \frac{2c_0}{\pi^{1/2}} (Dt)^{1/2} \quad (5)$$

where D is the diffusion coefficient of the polymer in solution and c_0 is the initial bulk concentration.

The calculated diffusion coefficients for each copolymer at 0.01 mg/mL are shown in Table 2. The functionalized copolymers showed different adsorption behaviors according to the position of their zwitterionic group. Interestingly, the values of D obtained for solutions of ZwIS, ZwSI, and ZwISZw are different, even though they have almost similar molecular weights and compositions. Stamm et al.¹² observed that PS-PB and PB-PS-PB block copolymers with randomly attached adsorbing positions in the short PB block had practically the same diffusion coefficients D even with comparable molecular weight. In our case, the position of the zwitterionic groups on the block copolymer plays a major role in the kinetics of adsorption behavior. Since toluene is a θ solvent for the polystyrene block but not for the polyisoprene block, polyisoprene should form a slightly more coiled "tangled" conformation than polystyrene in toluene. According to our results, when a zwitterionic group is attached to the more contracted polyisoprene (ZwIS), the copolymer diffused to the surface faster than ZwSI. For ZwISZw, since the zwitterionic groups are attached to both blocks, the diffusion rate is expected to be slower than that of ZwIS.

Equation 5 describes the time behavior of the adsorption correctly until a defined coverage is reached. The deviation of the A versus $t^{1/2}$ plot from linearity marks the end of the transport-controlled regime, and the adsorbed amount at this point, A_{diff} , can be obtained. Despite the different diffusion coefficients of ZwIS and ZwSI, the A_{diff} of ZwIS (1.47 mg/m²) is very similar to the A_{diff} of ZwSI (1.44 mg/m²). This is a very reasonable result, since both copolymers would have similar conformations on the surface because of their comparable molecular weights and compositions. The A_{diff} for ZwISZw (1.25 mg/m²) is smaller than those for ZwIS and ZwSI. This is because of the different conformational states between these copolymers on the surface, as we described in Figure 4.

In the case of SZwI, the copolymer diffuses to the surface very slowly compared to the cases of the other three copolymers. With this copolymer, the small zwitterionic group is located between the two polymer chains. Therefore, the zwitterionic group should have less accessibility to the surface compared to the case of copolymers with the zwitterionic group at the end of polymer. In other words, in order for the zwitterionic groups of SZwI to adsorb on the surface, this copolymer should undergo more macroconformation rearrangements, which slows down the rate of adsorption. The A_{diff} for SZwI (0.37 mg/m²) is also significantly lower than the others. Further investigation will be done on the mechanism and kinetics of adsorption for these copolymers using in-situ SPR techniques.

Conclusions

PS-*b*-PI copolymers of similar molecular weight and composition were functionalized with sulfobetaine zwitterionic groups at different positions along the backbone using anionic polymerization techniques. The adsorption behavior of the PS-*b*-PI copolymers in toluene was investigated using an in-situ QCM technique. Toluene is a good solvent for both blocks but is a nonsolvent for the zwitterionic group. The adsorption isotherms exhibited a typical Langmuir behavior and were dependent on the position of zwitterionic groups. The adsorbed amounts decreased in the order ZwIS, ZwSI > ZwISZw > SZwI. These differences were explained by possible conformational states of the adsorbed copolymers on the surface. ZwIS and ZwSI, where a zwitterionic group is attached to the end of PI or PS, form brush conformations, and ZwISZw, where zwitterionic groups are attached to both ends, forms a brush and loop conformation. When a zwitterionic group is between two blocks, SZwI, it occupies more lateral space than the other copolymers, because of two dangling polymer blocks.

The positions of the zwitterionic groups gave more significant effects on the adsorption kinetics. When the zwitterionic group is located at the end of PI (ZwIS), the copolymer diffused to the surface faster compared to the case of the copolymer where the zwitterionic group is located at the end of PS (ZwSI). The diffusion rate for the ZwISZw is found to be slower than those for ZwIS and ZwSI. In the case of SZwI, the diffusion coefficient is about 100 times smaller than those for other copolymers because of inherent macromolecular rearrangements³⁴ for adsorption, significantly affecting the diffusion process.

Acknowledgment. We acknowledge technical support from Maxtek Inc. and Optrel GmbH and helpful discussions with Dr. Kay Kanazawa.

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