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The effect of support material and conditioning on wettability of PAH/PSS multilayer films

Marta Kolasińska*, Piotr Warszyński[1]

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, 30-239 Cracow, Poland

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Abstract

An efficient method for characterizing wetting properties of heterogeneous surfaces produced by sequential adsorption of polyelectrolytes was developed. Three types of polyelectrolytes were used: polyallylamine hydrochloride (PAH), polyethyleneimine (PEI), both of a cationic type, and polysodium 4-styrenesulfonate (PSS), of an anionic type. Multilayer films were prepared by 'layer-by-layer' (LbL) deposition technique. Natural ruby mica, glass, titanium foil and silicon wafers were used as the support material for PE films. Wetting of polyelectrolyte films was determined experimentally by contact angle measurements, using technique of direct image analysis of shape of sessile drops. Periodic oscillations in contact angle values were observed for multilayers terminated by polycation and polyanion, respectively, and the variations in contact angle values strongly depended on the conditions of adsorption and multilayer treatment after deposition. Therefore, the influence of ionic strength of polyelectrolyte solution used for deposition on wetting of multilayer films was considered and also the effect of conditioning in different environments was investigated. It is usually assumed that film properties and stability strongly depend on the first layer which is used to anchor a multilayer at the surface of support material. To investigate influence of the first layer, PAH/PSS films were compared with more complex ones having PEI as the first layer with a sequence of PSS/PAH deposited on top of it.

Keywords: Support material; Conditioning; PAH/PSS films

1. Introduction

The sequential adsorption of oppositely charged polyelectrolytes by layer-by-layer (LbL) deposition technique is an efficient method for obtaining multilayer thin films. It has progressed significantly since Decher and Hong [1] demonstrated the basic principle of buildup of multilayer materials using alternating adsorption of PE. The technique allows controlling structure and the total film thickness on a molecular level [2]. Due to its versatility, such self-assembled polyelectrolyte multilayers have a great application potential. Possibility of the combination of different polyelectrolytes opens a wide range of different areas, where such materials can be used [3]. They can be applied as separation membranes for gases or dissolved species or for modification of surface properties, which has a special meaning in biomaterial area [4]. This technique can be efficiently used in the field of chemical and biochemical sensing [5–7]. Coating of colloidal particles and formation of hollow shell structures are of importance in case of encapsulation applications, e.g. in drug carrier systems or microreactors.

It is often assumed that the properties of polyelectrolyte multilayer films are independent of the underlying substrate. However, there should exist a minimal number of layers above which the properties of the system are governed to the greatest extent by the choice of polycation/polyanion pair. Type of polyelectrolyte used for deposition of the first layer plays an important role when stability of multilayer is concerned. The structure of the multilayer films is also strongly dependent on the deposition conditions and the

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* Corresponding author. Tel.: +48 12 6395128; fax: +48 12 425 1913.
E-mail addresses: nckolasi@cyf-kr.edu.pl (M. Kolasińska), ncwarszy@cyf-kr.edu.pl (P. Warszyński).

[1] Tel.: +48 12 6395121.

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most frequently used control parameters are ionic strength and pH of the solution. Also, the long time exposure to the conditions different than that encountered during deposition usually leads to change of polyelectrolyte multilayer structure.

The aim of our investigation was to determine the influence of the type of substrate, deposition conditions and pH of the conditioning solution on the wetting properties of the consecutive layers of PAH/PSS multilayer films and to compare obtained results of such structures with wettability of films having PEI as the first layer.

2. Experimental

Three types of polyelectrolytes were used in our studies (shown in Fig. 1): polyallylamine hydrochloride (PAH), polyethyleneimine (PEI), both of a cationic type, and polysodium 4-styrenesulfonate (PSS), of an anionic type. PAH and PSS having molecular weight of about 70,000 were purchased from Aldrich, PEI of average molecular weight 750,000—from Sigma, NaCl (99.5%) was obtained from Fluka, HCl—from P.O.Ch Gliwice, and NaOH—from Aldrich. Aqueous solutions of polyelectrolytes were prepared using four times distilled water. Adsorption of polyelectrolytes was performed from NaCl solutions of various concentrations (from 0.001 to 1.5 mol/l), with constant amount of polyelectrolyte (0.5 g/l). As a support material, natural ruby mica (from Dean Transted, England), glass (microscope slides), silicon wafers (generous gift of Prof. L. Lapcik, Thomas Bata University, Zlin) and titanium foil (from Good Fellow, England) were used. Mica was freshly cleaved before each multilayer formation process, glass was cleaned with chromic acid and washed with two times distilled water, titanium and silicon wafers were degreased with acetone and rinsed with ethyl alcohol and with water. Polyelectrolyte adsorption and contact angle measurements were carried out in temperature 295 K. Deposition lasted 30 min for every single step and rinsing between adsorption steps, about 1 min. After deposition of each PSS layer, the sample was rinsed with double-distilled water. Since PAH is a weak polyelectrolyte and its structure strongly depends on pH value (pK for PAH is around 7.5) [8,9], the deposited PAH layers were rinsed with HCl solution with pH value adjusted to pH value of PAH solution.

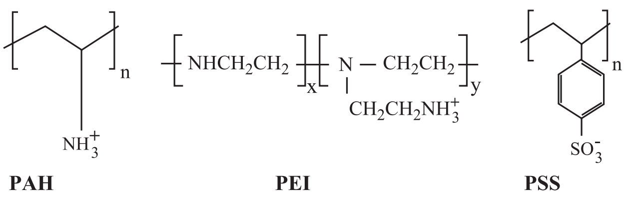

Fig. 1. Structural formulas of polyions applied in our studies.

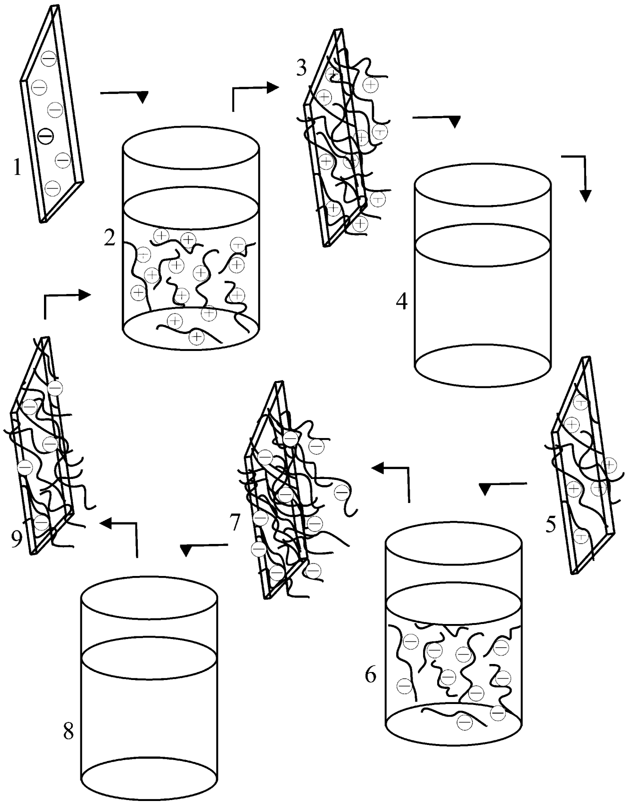

Fig. 2. Scheme of alternating adsorption cycle: (1) initial negatively charged substrate; (2) polycation solution; (3) first adsorbed layer with weakly bounded chains; (4, 8) rinsing solutions; (5) first irreversibly adsorbed layer; (6) polyanion solution; (7) two-layer film with weakly bounded chains; (9) two-layer film after rinsing.

Polyelectrolyte multilayer formation by 'LbL' technique is presented schematically in Fig. 2. It is carried out as follows: substrate with negatively charged surface is immersed into a polycation solution. Electrostatic interactions are the predominant driving force for deposition of the polyelectrolyte layer. Then the sample is rinsed with rinsing solution to remove weakly bounded polycation molecules in order to avoid their reaction with oppositely charged polyanions, which are deposited during the next adsorption step. Then the procedure is repeated until the required number of layers is obtained and rinsing is required after every single deposition step. In case of positively charged substrate, the sequence of adsorbed polyelectrolytes is reversed. Assembly of consecutive (oppositely charged) layer is possible due to charge reversal on a surface of the previous layer. Charge overcompensation can be observed by ζ potential measurements [10].

An efficient method for characterizing wetting properties of heterogeneous surfaces produced by sequential adsorption of polyelectrolytes was developed. The contact angle of a liquid drop on the substrate covered with polyelectrolyte multilayers was determined experimentally using technique of direct image analysis of shape of sessile drops. The experimental setup is schematically shown in Fig. 3a. Dried polyelectrolyte film deposited on support material (3) was placed in the thermostated chamber (2) of regulated humidity to prevent drop evaporation during the measure-

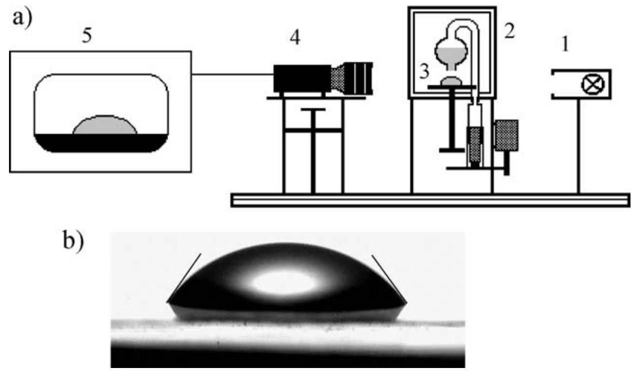

Fig. 3. (a) Experimental setup for direct image analyzing technique of sessile drop: (1) light source; (2) thermostated chamber; (3) substrate with polyelectrolyte film; (4) CCD video camera; (5) computer. (b) Image of water drop on the first PEI layer.

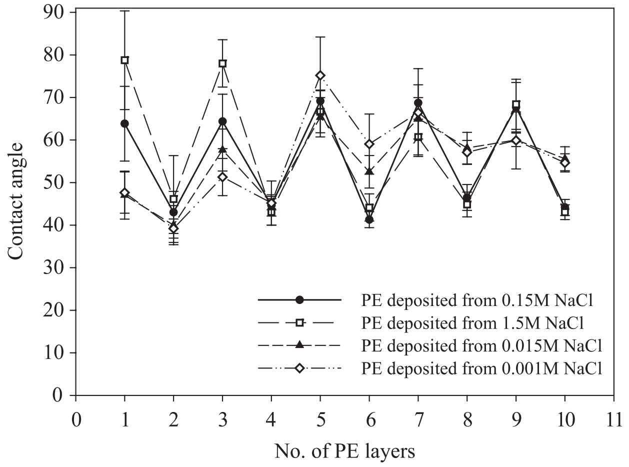

Fig. 4. Effect of electrolyte concentration in PE solution used for deposition.

ments. Droplets were created at the tip of the capillary of the quartz-glass stalagmometer by a precision gastight syringe and carefully placed on the polyelectrolyte multilayer surface. Volume of droplets was constant and it was equal to about 16 μl.

The video image of sessile drop was transmitted from CCD video camera (4) to the digital video processor (5), which performed the frame grabbing and digitization of the image. Then the solution of Young–Laplace equation was fitted to the digitized profile of the drop. Contact angle values are obtained by differentiation of this equation in the three-phase contact points. The example of a picture of water drop on PEI layer is presented in Fig. 3b. The mean value of contact angle measured on this layer was 57°.

3. Results and discussions

Periodic oscillations in contact angle values were observed for multilayers terminated by polyelectrolytes studied, PAH layers being more hydrophobic than PSS layers. However, the amplitude of contact angle variations was strongly dependent on electrolyte concentration of the polyelectrolyte solution used for deposition (see Fig. 4) and was the smallest for low ionic strength, suggesting significant inter-penetration of oppositely charged polyelectrolyte layers during their deposition. Surface of multilayers formed in 0.15 M NaCl seems to be more homogeneous than adsorbed from solutions of other salt concentrations, because the experimental scatter of contact angle values measured on a surface of given layer was the lowest. It was also found that generally PAH layers were more heterogeneous, regardless of the electrolyte concentration in the deposition solution.

When the effect of support material on polyelectrolyte adsorption was investigated, in all experiments with different substrates, the multilayers were adsorbed from 0.15 M NaCl polyelectrolyte solutions. The biggest differences among films formed at various substrates can be observed for first few layers, as it is shown in Fig. 5. For glass and unpolished silicon wafers, the influence of substrate is the strongest because irregular oscillations of contact angle values measured on consecutive layers were observed. Moreover, great scatter of the contact angle values measured at a given layer was noticed. This is in contrast to polyelectrolyte films on mica and titanium foil where much more uniform oscillations and lower scatter were observed. This effect can be due to inhomogeneity of glass and silicon substrates. Starting from the sixth layer, i.e. from third layer of PAH/PSS pair deposited, the wetting seems to become independent of the substrate.

Multilayer properties after conditioning in different environments were then investigated. Water (natural pH ≈ 6) and NaCl, HCl, NaOH solutions with concentration 10^{-3} mol/l were chosen to compare the influence of pH value of conditioning solutions, the last three having the same ionic strength of solutions. Effect of pH is particularly important in case of PAH, which is a weak polyelectrolyte so its degree of dissociation strongly depends on pH value. Duration of the conditioning process was the same for all

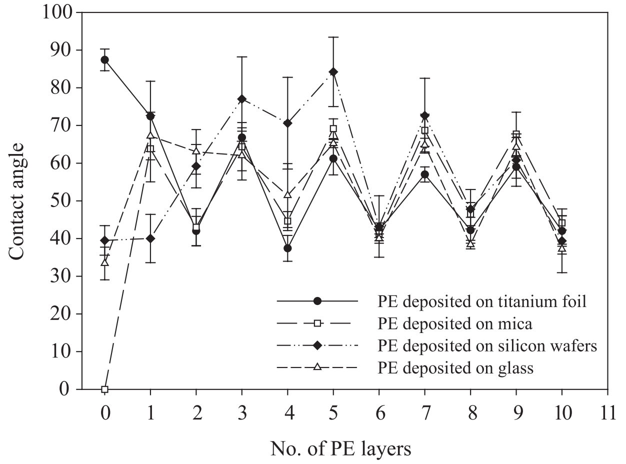

Fig. 5. Effect of support material.

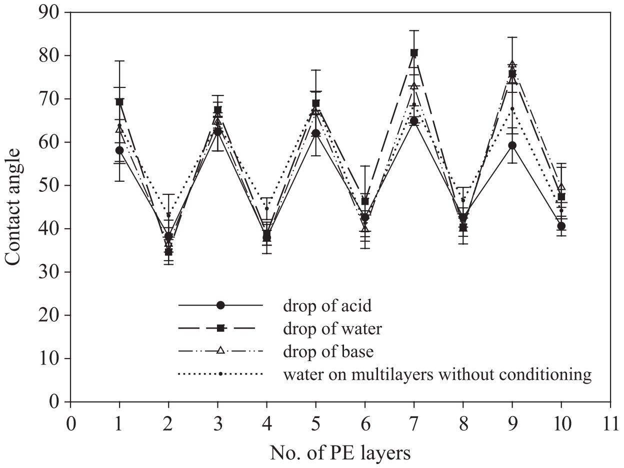

Fig. 6. PAH/PSS films conditioned in water (time of conditioning: about 48 h).

experiments (48 h). Effect of drop composition was also checked and wetting by water, HCl, NaOH solutions drops with the same concentration as for conditioning solutions were investigated. All PE films were formed on mica by deposition from 0.15 M NaCl solutions. The results are presented in Figs. 6–9.

Wettability of multilayers after conditioning in water is comparable to that of polyelectrolyte films without conditioning and there are no significant differences between contact angle values of drops with various composition especially at PSS layers (see Fig. 6).

In case of films conditioned in NaCl solution, such treatment makes multilayer surface more hydrophilic (see Fig. 7) with smaller oscillations in contact angle values measured on consecutive layers than as it was for multilayers after conditioning in water. One can assume that small ions interact with polyelectrolytes resulting in reconformation of the layers. Similarly as for water conditioned film, practically there is no dependence of the wettability of multilayers on drop composition.

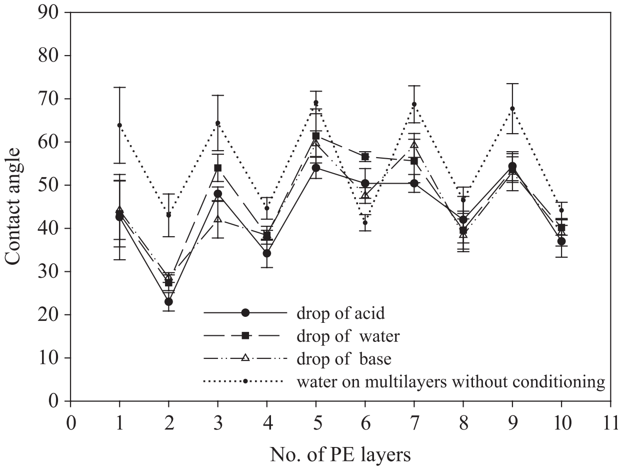

Fig. 7. PAH/PSS films conditioned in 10^{-3} M NaCl (time of conditioning: about 48 h).

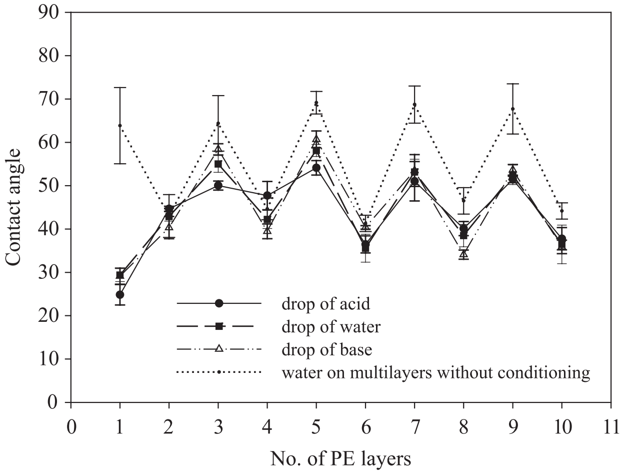

Fig. 8. PAH/PSS films conditioned in HCl solution (pH=3, time of conditioning: about 48 h).

The effect of pH of conditioning solution was investigated by measuring wetting properties of multilayers after keeping them for 48 h in 10^{-3} M HCl solution (pH=3) or in 10^{-3} M NaOH solution (pH=11) (see Figs. 8 and 9). The oscillations of the contact angle observed on the consecutive layers after the acidic treatment of the multilayer were similar as in NaCl solution of the same ionic strength (10^{-3} M). It can be expected that at respective pH values of the solutions used for conditioning (pH=3 and pH about 6) PAH is similarly charged and when the reconformation process is electrostatically driven, similar structure of the multilayer should be obtained. The hypothesis of reconformation of the multilayer, stronger when PAH is the topmost layer, is supported by the observation of gradual decrease of its zeta potential [11].

The entirely different picture can be observed when the multilayer films are conditioned in basic environment. In this case, practically no oscillations of the contact angles between consecutive layers can be observed. The films are much more hydrophilic than without conditioning. It

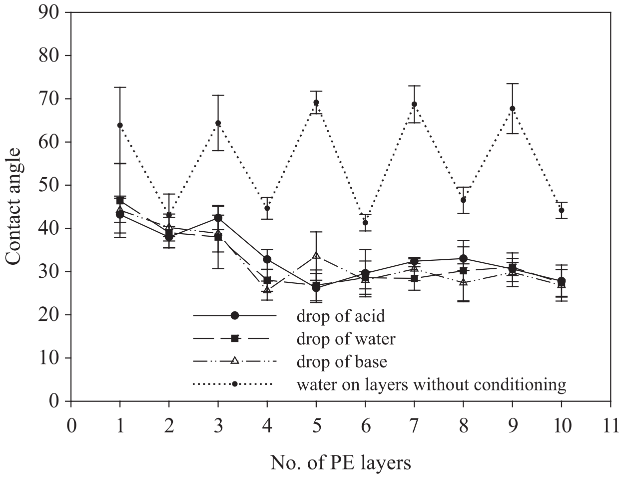

Fig. 9. PAH/PSS films conditioned in NaOH solution (pH=11, time of conditioning: about 48 h).

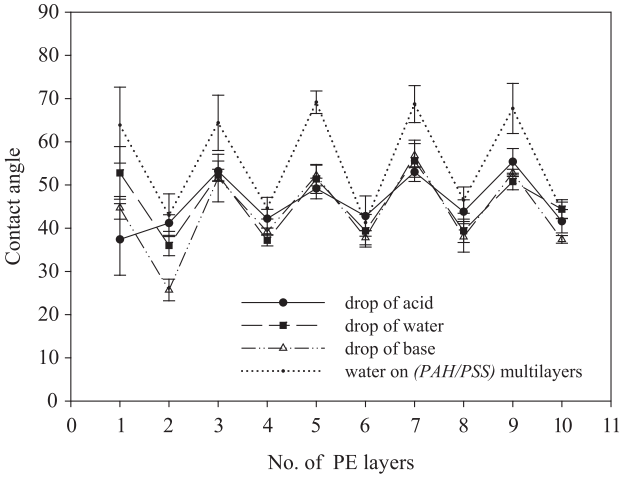

Fig. 10. PE films with PEI as the first layer in comparison with PAH/PSS films.

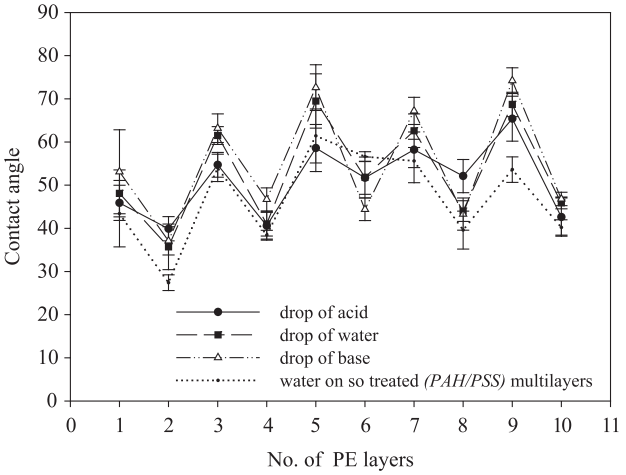

Fig. 12. PE films with PEI as the first layer conditioned in 10^{-3} M NaCl solution (time of conditioning: about 48 h).

suggests either the partial removal of the film (however, it is not supported by ζ potential measurements performed on so treated PAH/PSS films [11]), or some major structural changes within the film together with OH^- incorporation. It should be mentioned that in these conditions PAH is weakly charged. The composition of the drops had again practically no influence on wetting of multilayers.

We also investigated the influence of another polycation used as the first layer. PEI was chosen because of its ability to strongly anchor at the substrate surface. The oscillations in contact angle values measured on consecutive layers were smaller than in case of films consisting of PAH and PSS only, which is shown in Fig. 10. It means that usage of PEI as the first layer makes composition of films more uniform. Starting from the second layer, practically no differences are observed in comparison with wetting properties of PAH/PSS films, as far as PSS layers are concerned. PAH-terminated multilayers are more hydrophilic than previously. Taking into account the fact that the contact angle values for first PEI layer are lower than for first PAH layer, it looks like a high molecular weight PEI influences cationic layers by competing with PAH and this influence can be seen even in the most distant layer of PAH. Surfaces of particular multilayers seemed to be more homogenous because smaller scatter in contact angle values, measured on a given layer, was observed.

Effect of conditioning of multilayers containing PEI was investigated in the same way as for PAH/PSS films. All films were formed on mica, deposited from 0.15 M NaCl solutions of PE. The results are presented in Figs. 11–14. For films conditioning in water (Fig. 11), similar trends as for non-conditioned films are observed. Wetting of PSS layers is the same as for simple PAH/PSS films and PAH layers seem to be more hydrophobic becoming comparable with these layers in PAH/PSS films.

In case of conditioning in 10^{-3} M NaCl solution, the situation is reversed as it is demonstrated in Fig. 12. After conditioning PAH layers in the PEI(PSS/PAH) multilayers are more hydrophobic than the same layers in PAH/PSS films. Since the contact angle on these layers reaches one

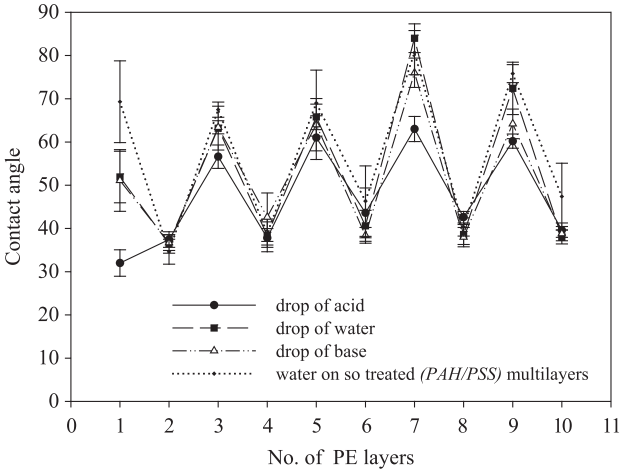

Fig. 11. PE films with PEI as the first layer conditioned in water (time of conditioning: about 48 h).

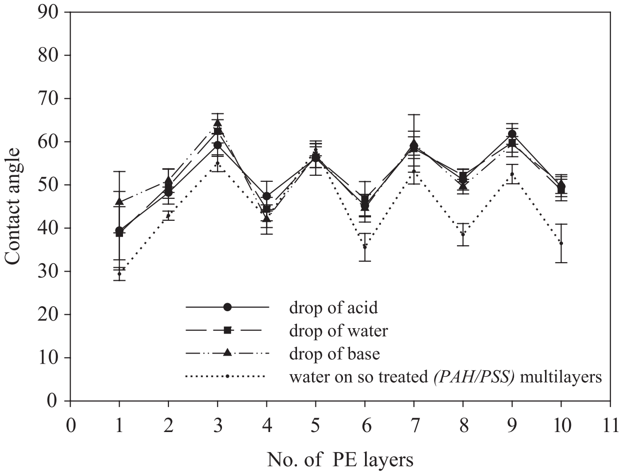

Fig. 13. PE films with PEI as the first layer conditioned in 10^{-3} M HCl solution (time of conditioning: about 48 h).

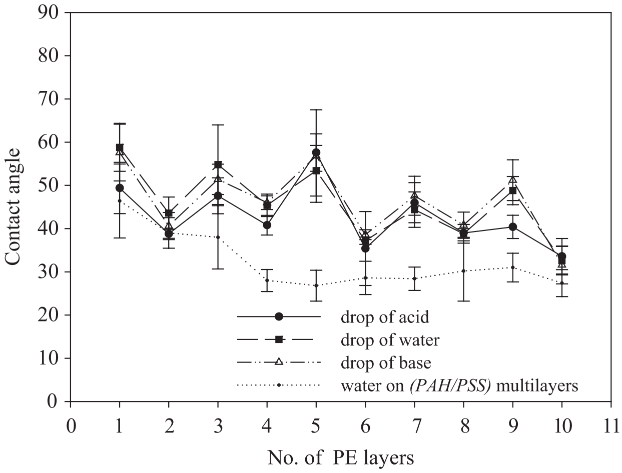

Fig. 14. PE films with PEI as the first layer conditioned in 10^{-3} M NaOH solution (time of conditioning: about 48 h).

observed at the first PAH layer deposited on mica, the effect can be explained as a preferential exposure of PAH after conditioning.

After acidic conditioning, the PEI(PSS/PAH) multilayers are slightly more hydrophobic than so treated PAH/PSS films with bigger differences for anionic layers. The acid-treated PEI containing multilayers are much more uniform than untreated ones. When films after NaOH solution treatment are considered, different results were obtained for multilayers containing PEI than for the simpler structures, built up only with PAH and PSS (see Fig. 14). The multilayers having PEI as the first layer are much more hydrophobic than PAH/PSS only films and slightly more hydrophobic than analogous, PEI(PSS/PAH) ones, without conditioning. In contrast to PAH/PSS films, there are distinct differences between contact angle values obtained for consecutive layers.

4. Conclusions

An efficient method for characterizing wettability of heterogeneous surfaces produced by 'layer-by-layer' adsorption of polyelectrolytes was developed. The contact angle of substrates covered by polyelectrolyte multilayers was determined experimentally using direct image analysis of shape of sessile drops. It was found that wetting properties of polyelectrolyte multilayers obtained by 'LbL' deposition technique strongly depended on deposition conditions. It was determined that for polyelectrolytes studied, the optimum ionic strength to obtain multilayers with congruent wetting properties and terminated with PE of a given sign corresponded to 0.15 M NaCl solution. Studying wetting properties of PAH/PSS on mica, glass, silicon wafer and titanium foil, it was found that starting from the sixth layer, i.e. from third layer of PAH/PSS pair deposited, the wetting seemed to become independent of the substrate. The post treatment with different conditioning solutions significantly influenced wetting of PE multilayers. The phenomenon was explained in terms of changes in film structure. The nature of these changes depends on the pH of the conditioning solution. Since PAH is weak electrolyte, whose degree of dissociation is pH-dependent, one can argue that the changes of the film structure occurring during multilayer conditioning are electrically driven. Nature of the structural changes is modified when highly molecular weight PEI is used as a first anchoring layer of PAH/PSS multilayer films.

Acknowledgements

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