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Novel Azobenzene-Functionalized Polyelectrolytes of Different Substituted Head Groups 2: Control of Surface Wetting in Self-Assembled Multilayer Films

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A novel set of light-responsive polyelectrolytes has been developed and studied, to control and tune surface wettability by introducing various types of substituted R head-groups of azo polyelectrolytes in self-assembled multilayer (SAMU) films. As part of a larger project to develop polymer surfaces where one can exert precise control over properties important to proteins and cells in contact, photo-reversibly, we describe here how one can tune quite reliably the contact angle of a biocompatible SAMU, containing a photo-reversible azo chromophore for eventual directed cell growth. The azo polyelectrolytes described here have different substituted R head-group pairs of shorter-ionized hydrophilic COOH and SO_3H, shorter non-ionized hydrophobic H and OC_2H_5, and larger non-ionized hydrophobic octyl C_8H_{17} and C_8F_{17}, and were employed as polyanions to fabricate the SAMU onto silicon substrates by using the counter-charge polycation PDAC. The prepared SAMU films were primarily characterized by measurement of their contact angles with water. The surface wetting properties of the thin films were found to be dependent on the type of substituted R-groups of the azo polyelectrolytes through their degree of ionization, size, hydrophobicity/hydrophilicity, solubility, conformation, and inter-polymeric association and intra-polymeric aggregation. All these factors appeared to be inter-related, and influenced variations in hydrophobic/hydrophilic character to different extents of aggregates/non-aggregates in solution because of solvation effects of the azo polyanions, and were thus manifested when adsorbed as thin films via the SAMU deposition process. For example, one interesting observation is significantly higher contact angles of $\geq 79°$ for SAMU films of larger octyl R groups of PAPEA-C_8F_{17} and PAPEA-C_8H_{17} than for others with contact angles of $\leq 64°$ observed for non-polar R-groups of OC_2H_5 and H. Furthermore, lower contact angle values of $\leq 59°$ for SAMU films with polar R-groups of COOH and SO_3H relative to that of non-polar R-groups are in accordance with their expected order of the hydrophilicity or hydrophobicity. It is possible that the large octyl groups are more effective in shielding the ionic functional groups on the substrate surface, and contributed less to the water drop-molecule interactions with ionic groups of the PDAC and/or AA groups. In addition, higher hydrophobicity of the SAMU films may be due to the incorporation of bulky and hydrophobic groups in these polyelectrolytes, which can produce aggregates on the surfaces of the SAMU films. Through understanding and controlling the complex aggregation behavior of the different substituted R-groups of these azo polyelectrolytes, and hence their adsorption on substrates, it appears possible to finely tune the surface energy of these biocompatible films over a wide range, enhance the photo-switching capabilities of the SAMU films, and tailor other surface properties for the development and application of new devices in diverse areas of microfluidics, specialty coatings, sensors, and biomedical sciences.

Keywords: Azobenzene polyelectrolytes, biocompatibility, contact angle, hydrophilic/hydrophobic, self-assembled multilayer film, substituted head R-groups, surface energy, wettability

1 Introduction

In nature, structures and morphologies of many surfaces are uniquely optimized for their functional performance—for example, locomotive pond skating of insects, wetting of eyes, the wings of butterflies, etc. (1). But perhaps amongst the best examples is the sacred lotus flower leaf (Nelumbo Nucifera), which is known for its cleanliness due to the combination of chemical composition and physical texture, or the ability of the human eye to see, due to its Rohodospin molecules interconverting geometrically from one conformation to another when exposed to light. Although artificial approaches do not seem yet to reach such complex

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levels, one can mimic however, in part, such model systems by means of specially designed molecular assemblies. The motivation of the current research work originates from natural systems, such as those described above, by employing azobenzene photo-switchability in polymeric materials and using these to create self-assembled photo-reversible surfaces of controlled chemical composition and hierarchical micron- to nano-scale textures. The development of these precisely controlled photo-switchable surfaces may lead to an improved understanding of morphological structures, surface patterning and interfacial phenomena, including kinetics of droplet motion, surface tension gradients, super-amphiphilics, and self-cleaning mechanisms. The understanding of underlying switching mechanisms for such surface-based devices relies on the extent of control of their wettability/de-wettability characteristics, so is similarly important. These studies may enhance the performance of some tunable nano-mechanical and miniaturized fluidic systems, and are therefore capable of improving new devices in a broad range of areas from biosensors to new drug delivery systems, and on-chip microscale chemical process to microfluidics systems (2–4). Considering this, the current research attempts to provide insight into structures, functionalities, and compositions of thin films prepared by the technique of layer-by-layer self-assembled multilayers thin films (LBL SAMU) of photoresponsive azobenzene-functionlaized polymeric materials of varying wettability.

The LBL SAMU technique used in the present work presents advantages over other organic surface layer fabrication techniques based on self-assembled monolayers (SAMs) derived from alkyltrichlorosilanes on silicon/silicon dioxide, organo sulfur compounds chemisorbed on metals; or Langmuir-Blodgett mono- and multilayer and functionalized polymer surfaces (5–8). These techniques, relative to SAMU, encounter problems in controlling surface characteristics, and may demand difficult characterization, high yield surface reactions (because it is not possible to separate and purify the products), limitation with respect to the set of molecular components suitable for deposition, and the molecules are often not firmly trapped and frequently rearrange after or even during deposition. Due to this, in recent years, polyelectrolyte layer-by-layer (LBL) self-assembled multilayer (SAMU) deposition from aqueous solution has been extensively explored and shows promise in numerous applications (9–11). In a typical process, oppositely charged polymers are alternately adsorbed onto a substrate from dilute aqueous solution to produce multilayer thin films comprised of sequentially adsorbed layers of polycations and polyanions. This approach has the advantages that it is environmentally sound (typically all water-based processing), highly stable and robust, and is independent of the substrate size and topology. SAMU can be easily used to fabricate complex multilayer composite films with excellent control over molecular architecture, composition and functionality (9–13). In a recent communication (4), we demonstrated how surface energy could be photo-switched in a SAMU thin film, engineered to be biocompatible to neural cells, with the eventual goal of directed cell growth, and study of a synapse *in vitro*. An important part of this large project however, is being able to finely tune the initial surface energy (measured with contact angle) of the bio-films, as there is only a narrow window of acceptable surface energies for various cell types that permit normal cell function outside the body. Being able to produce bio-films with a predictable and controlled surface energy is thus key to these applications.

In the fabrication of LBL-SAMU films of PEL to date, including azo PEL, most of the work has been shown to control molecular organization and hence surface wetting by changing several solution processing variables including weak or strong PEL, ionic strength, temperature, post-processing and pH (14–16). However, to our knowledge, no systematic studies have been carried out to investigate the effect of substituents at the head and/or terminal groups of azobenzene on the characteristics, composition, interpenetration and wettability of the surfaces. Considering this, our approach has four main objectives. Firstly, we wish to employ azo PEL of efficient synthetic design which are the same except by the presence of different terminal head R-groups. For this purpose, azo polyelectrolytes with the substituted R-group pairs of shorter-ionized hydrophilic COOH and SO_3H, shorter-non-ionized hydrophobic H and OC_2H_5, and larger-nonionized hydrophobic octyl C_8H_{17} and C_8F_{17} were employed as polyanions to fabricate SAMU films onto glass and silicon substrates by using the counter charge polycation PDAC. The chemical structure of the azo PEL used in the work is presented in Figure 1. Possession of both self-assembly characteristics due to acrylic acid groups, and photoswitchability due to the azo monomer will enable the azobenzene functionalized polyelectrolytes to exhibit novel photo-reversible bio-applications. Secondly, we wish to explore in detail the role that the type of substituted head R-group plays in determining the surface composition, architecture and wetting of multilayer thin films with and without the effect of light. Thirdly, since many applications of surfaces involve contact with water, therefore, surfaces with different interactions offer an opportunity to separate phenomena occurring at a functionalized, hydrophilic surface from those reflecting non-functionalized surface behaviour or hydrophobicity with varying degrees of interpenetration (17). Finally, since water is used, results from aqueous studies of surface chemistry are thus important to practical problems both in life sciences and related ‘green’ industries (18). The work presented specifically here places particular emphasis on measurements of wettability of the pre-irradiated adsorbed films of azo PEL. More work is underway and will be submitted in future to investigate the effect of head R-groups on the photoresponsive switchability as well as others characteristics of these adsorbed films of azo PEL. Wet chemical methods of contact angle measurement are used here to characterize the fabricated films, but other

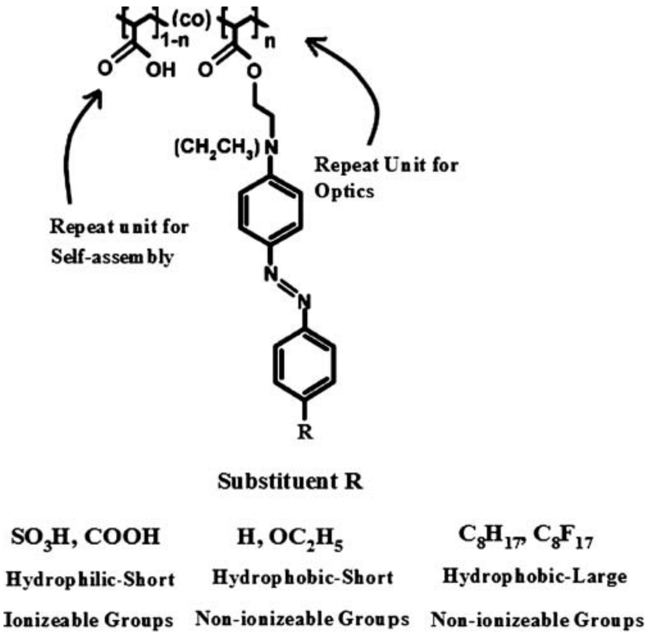

Fig. 1. General structure and classification of the polymers used to fabricate thin films by using the layer-by-layer self-assembled multilayer (SAMU) technique. Polymers are simply designated as PAPEA-R, where R is the substituted group on the para-position of the azobenzene chromophores. The different substituted R-groups present on the para position of the aromatic ring of the azo chromophores are also presented (19).

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commonly used microscopic and spectroscopic methods especially AFM, optical ellipsometry, and XPS, of course are also highly useful and will be the subject of future work. Surface wettability has been carried out because it is easily measureable, and has direct relevance to bio-medical applications that rely on surface energy for biocompatibility, for example for directed cell growth. One primary focus of our research is to understand how the wettability with water is affected by the molecular-level structure of azo head R groups. The surface wettability of adsorbed polyelectrolyte layers is dictated primarily by the first few angstroms of the outermost surface layer. As will be demonstrated in this paper, this can be accomplished via the creation of SAMU films by controlling the surface composition of the bilayers by changing the type of head R-group of azobenzene chromophore. The latter case represents a novel type of molecular level process to control wettability by introducing the type of head R-group of azo polyelectrolytes in a layer-by-layer adsorption process.

2 Experimental

2.1 Materials and Synthesis of Polymers

Chemicals were purchased from Aldrich and were used as such unless specified. The detail of the experimental work to synthesize and characterize the polymers is given elsewhere (19). Briefly, the precursor monomer, 2-(phenylethylamino)ethyl acrylate (PEA), was first synthesized by reacting acryloyl chloride with N-anilino ethanol followed by its copolymerization with desired molar concentrations of acrylic acid (AA). The post-azo coupling reaction was carried out by dropwise addition of diazonium salt of the amine derivatives to prepare copolymers designated as PAPEA-R.

2.2 Self-Assembled Multilayer Films (SAMU) Fabrication

Fabrication of thin films of azo PEL was carried out on polished silicon wafers (Wafernet) substrates. Prior to adsorption, silicon wafers were cleaned in a bath of 25% H_2SO_4 and 75% H_2CrO_4 for approximately 12 h followed by thoroughly rinsing with neutral Milli-Q water. An automatic slide stainer (Varistain 24-4, Shandon) was used to fabricate multilayer films by using Milli-Q water (resistivity >18 MΩ). Films were fabricated by alternate 20 min dipping cycles in the aqueous poly(diallyldimethylammonium chloride) (PDAC) solution and one of the azo polyanion solutions by the usual layer-by-layer technique. The concentrations of solutions were kept at 0.1 mmol/L. If required, the solubility of azo-functionalized polyelectrolytes was increased by pH adjustment, or the addition of salt such as $NaHCO_3$ and about 15 vol% of DMF. Three separate washing baths were used by dipping the substrate for 10 min each after each polycation or polyanion dipping step to remove any loosely-bound materials to the substrate. The prepared films were dried under vacuum at 60°C for about 12 h once the required number of layers adsorbed on the substrate.

2.3 Measurement of Surface Wettability

Surface wettability of the prepared SAMU films was investigated by the measurement of contact angle. The CCD camera and goniometer of an Optrel GBR Multiskop were used to measure the contact angle of liquids on the surfaces of the films. The standard sessile drop technique was employed to determine the static contact angle of H_2O and olive oil. A 10 μL syringe was used to push or suspend a liquid droplet on the tip of the syringe, and the platform on which the film was placed was raised until the film surface touched the droplet. In the case static contact angle, the platform then lowered-down, and the measurements were taken after about 15 sec. Average drop volume was kept at 1–1.5μL and an image of the droplet was obtained with a CCD camera. Contact angle software was used to obtain the average contact angle by calculating the contact angle of both the left and right-hand side of the droplet. The droplet profile was fitted using the Young-Laplace equation to obtain the surface energy, which was used to compute the contact angle using Young's Equation 1. The reported

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contact angles are an average of 5-8 measurements with an uncertainty of ±2.

3 Results and Discussion

3.1 Contact Angle Measurements and Surface Wettability on Ideal Surfaces

Wetting refers to the study of how a liquid deposited on a substrate interacts with it to spread out. In order to study the wettability of a film, contact angle measurements are routinely carried out. These measurements are made with water and other probe liquids, and are known to be very sensitive to the details of liquid-solid interfaces to the length scale of angstroms. The physical chemistry of wetting and the theoretical rationalization of contact angle measurements are the subject of a large amount of literature (1, 19). Thomas Young in 1805 was the first one to explain scientifically the wetting behaviour of liquid drops on solid surfaces (20). Young's law makes the basis of all wetting phenomenon and relates the wetting contact angle to the three interfacial tensions (or energies) to define the equilibrium shape of the drop as shown in Figure 2. Young's equation 1 gives a single value of contact angle exhibited by a given solid-liquid-vapor system on an ideal surface.

$$\cos\theta_E = (\gamma_{S,V} - \gamma_{S,L})/\gamma_{L,V} \quad (1)$$

Where θ_E is the equilibrium (or static) wetting contact angle, $\gamma_{S,V}$ is the solid-vapor interfacial surface tension, $\gamma_{S,L}$ is the solid-liquid interfacial surface tension, and $\gamma_{L,V}$ is the liquid-vapor interfacial surface tension.

According to Young's Equation 1, changes in Cos θ_E are linearly related to the changes in interfacial free energies. In practice, Cos θ_E is not linearly dependent on the composition of the surface and hence contact angle measurements cannot easily be used for quantification. Nonetheless contact angles do provide structural and composition information about the surfaces. For example, the contact angle of H_2O is sensitive to the polar functional groups of the surface and/or surface/air interface. These measurements thus reflect the extent of polarity order on the surface. The contact angle of water is more sensitive than the contact angle of oil to the presence of polar functional groups buried below as well as on the surface of the layer-liquid interface (21, 22). Considering this, measurements of the contact angles of water provide useful insight about the structures, compositions and functionalities of a layer.

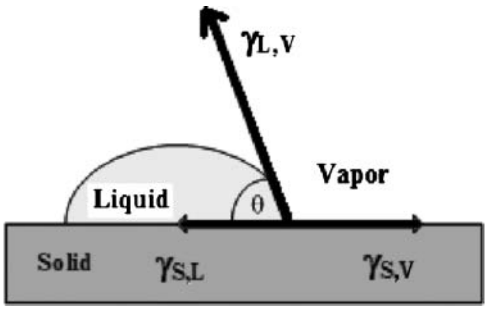

Fig. 2. Representation of the Young Equation (1) and equilibrium (or static) contact angle θ_E on an ideal surface.

3.2 Surface Wettability on Non-Ideal Surfaces

Young's Equation implies a single and unique contact angle on ideal surfaces which are perfectly homogeneous in terms of its texture, flatness, and composition. In practice however, surfaces are often heterogeneous due to variations in their roughness and composition. In general, it has been found that the experimentally observed apparent contact angle, θ^*, may or may not be equal to the Young contact angle, θ_E. Various models have been proposed to describe the thermodynamics and surface wetting on these heterogeneous surfaces. For the work described here, the Cassie-Baxter model can be used to explain the contribution of different surface components to determine the contact angles of the prepared SAMU films. Cassie-Baxter models of Equation 2 assume a physically smooth but chemical heterogeneous surface (23).

$$\cos\theta^* = \Phi_1 \cos\theta_1 + \Phi_2 \cos\theta_2 \quad (2)$$

Where Φ_1 and Φ_2 are the mole fractions of the two heterogeneous surfaces and θ_1 and θ_2 are their contact angles, respectively. The Cassie-Baxter state of a liquid drop on a surface assumes that the two constituents act independently to contribute to the wetting of that surface. The measurements of the contact angles of heterogeneous surfaces are very sensitive to the details of the individual and mixed constituents in the interfacial structure. The Cassie-Baxter model is therefore useful for the characterization of solid-liquid interfaces to account for thin films with mixed composition such as those typically fabricated by the layer-by-layer process of SAMU.

3.3 Surface Wettability of Water on the Adsorbed Azo PEL Films

The model surface behavior based on Young's Equation 1 puts emphasis on the thermodynamics or static contact angle only. In the present work, sessile drop equilibrium Young's contact angle θ_E of probe liquid droplets of H_2O was measured on the SAMU films. Table 1 summarizes the contact angle data and Figures 3, 4 and 5 represent the wetting characteristics of the SAMU film surfaces studied for different substituted R-groups. Figure 6 represents the effect of substituted R-groups of the PAPEA polymers on the contact angle and drop shape of water drops on the SAMU films of PAPEA-R.

The contact angle measurements of H_2O for various surface coatings of azo polyelectrolytes indicate significant differences in their wettability. Therefore, spreading of liquids

Table 1. Contact angle values of 5 bilayer pairs of PDAC/PAPEA-R self-assembled multilayer films (SAMU)

Substrate/ PAPEA-R Copolymer	*Contact angle (θ)/ Degree*	*Increase in contact Angle relative to Si Wafer (θ)/ Degree*	*Increase in Contact Angle relative to Si Wafer (%)*
Silicon Wafer	38	—	—
SO_3H	55	17	31
COOH	59	21	36
H	61	23	38
OC_2H_5	64	26	41
C_8H_{17}	79	41	52
C_8F_{17}	94	56	60

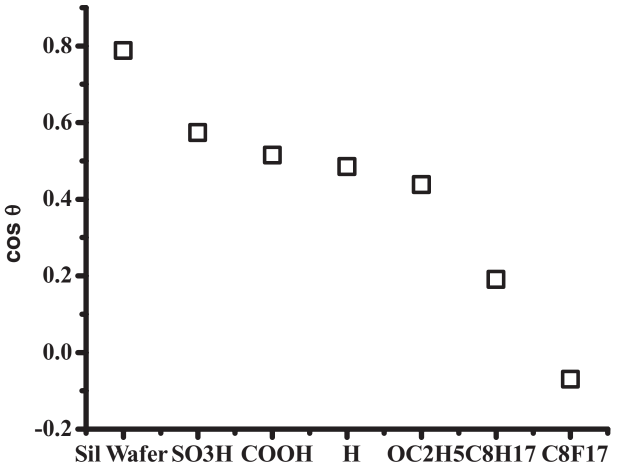

Fig. 4. Cosine of the contact angle of H_2O liquid droplet for the self-assembled multilayer films (SAMU) of azo polymers of PAPEA-R to exhibit the effect of different substituted R groups.

on these chemically and morphologically heterogeneous surfaces have numbers of useful characteristics, and can be discussed from the consideration of the growth of the SAMU films, interpenetration between neighboring layers, layers internal structures, layers composition, size of the substituted R-groups, and extent/nature of molecular interactions between the R-groups of PAPEA and water liquid droplets. For such characteristic heterogeneous surfaces, The Cassie-Baxter model of Equation 2 can be helpful to explain the observed variation in contact angle. If one assumes Φ_1 and Φ_2 represent the mole fractions of polycations PDAC and polyanion PAPEA-R, respectively, then consequently, a plot of Cos θ^* against Φ_1(mole fraction of polar repeat units) would be linear. As presented in Figure 4, the contact angles of water deviate from linearity for the surfaces containing mixed polar/non polar groups as expected to be present for the SAMU films. The observed deviations are plausible due to variation in the degree of ionization of the different PAPEA-R groups which influence the electrostatic interactions and hence the growth, structure and bilayers interpenetration. The presence of non-polar head R-groups, such as C_8H_{17} can surround the polar head COOH groups and result in poor hydrogen-bonding between protic head groups of the layer. Considering this, the suggested schematic of the formation of a 5-bilayer SAMU film of polyions pairs of PDAC/PAPEA-R can be presented schematically as in Figure 7. In principle, the adsorption of PEL allows for charge reversal on the surface, which has two important consequences: (i) repulsion of equally charged molecules and thus self-regulation of

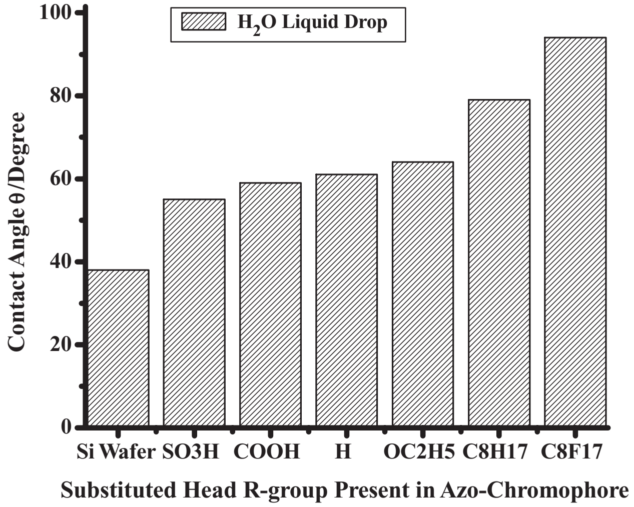

Fig. 3. Effect of substituted R groups on the contact angle of H_2O drop on the surface wettability of the self-assembled multilayer films (SAMU) of azo polymers. The contact angle values are within an experimental error of ±2°.

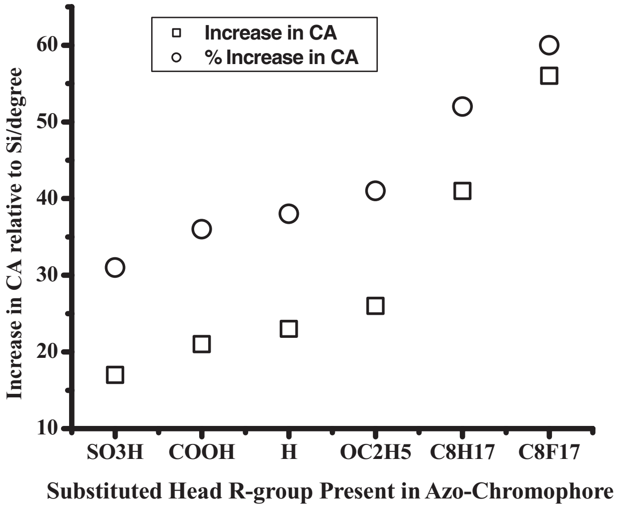

Fig. 5. Variation in surface wettability of H_2O liquid drops on the self-assembled multilayer films (SAMU) of azo polymers of PAPEA-R relative to that of the silicon substrate.

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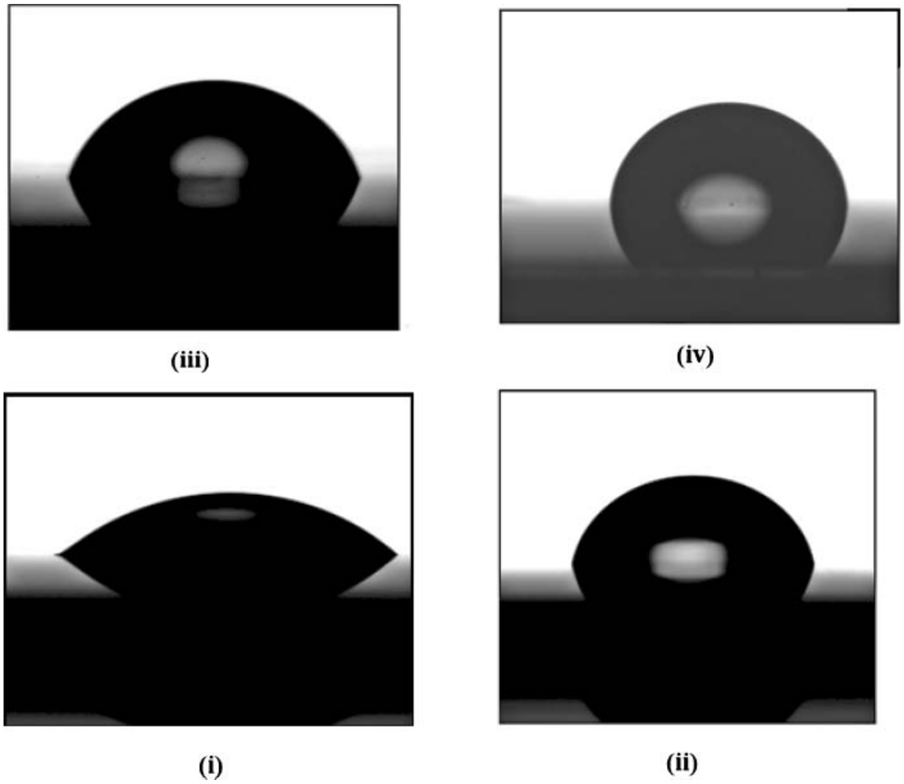

Fig. 6. Effect of substituted R-group of the PAPEA polymers on the contact angle and drop shape: lateral photograph of water drops on the surface of bare silicone wafer (i) SAMU films of PAPEA-COOH (ii), PAPEA-H (iii) and PAPEA-C_8F_{17} (iv).

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the adsorption and restriction to a single layer, and (ii) the ability of an oppositely charged molecule to be adsorbed in a second step on top of the first one. Cyclic repetition of both adsorption steps leads to the formation of multilayer structures.

Fabrication of SAMU films via the layer-by-layer technique provided the opportunity to tailor the macroscopic properties by control of the microscopic structure via appropriate choice of the molecular structure and the organization of the constituent units of the polyions pairs. The simple model commonly proposed is valid for films composed of flexible polyelectrolytes that can form 1:1 complexes such as that of polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH). For such cases, due to charge overcompensation, one layer can adsorb over the other (11). The apparent macroscopic characteristics of polyelectrolyte films can actually be of the nature of "fuzzy layered assemblies" because polymers are typically flexible molecules, and interpenetrate significantly. The classical, "fuzzy" multilayer model resulted in and internal structure with mobility and exchange, as well as interpenetration between neighboring layers. However, films adsorbed from polyions pairs of uneven charge density can exhibit even more complicated structures. The different level of growth, internal structure, functionality, and composition of the films for such complex systems have been reported to be controlled by the delicate electrostatic balance between polyions, diffusion of the polyions into the previously adsorbed film, and surface-constrained complexation between the polyanion and the polycation resulting from the mixing (9–16).

In the current work distinct pairs of different PAPEA-R were used to fabricate SAMUs. Due to variations in the charge density and sizes of the substituted R-groups in these polyelectrolytes, significantly different characteristics in terms of bulk and surface composition have been observed as indicated by differences in the values of contact angles. The contact angles were found to be increased by at least 17 degrees (31%) to 56 (60%) for the R-groups of SO_3H and C_8F_{17}, respectively, relative to that of Si substrate. Such variations have been reported to affect the layer thickness, the extent of neighboring layer interpenetration, and the surface composition of the number of functional groups contained within the films and on its surface to induce different wetting characteristics which can range from hydrophilic to hydrophobic (14). In addition, X-ray reflectivity measurements of the internal structures of the SAMU films indicated that the concentration of counterions present on each of the polyions directly affects the individual layer thicknesses, the roughness of interfaces, the material densities, and water and salt contents of the deposited film. Such studies have distinguished between three different interfaces of the substrate/film interface, the film/air interface and film/film internal interface (24, 25).

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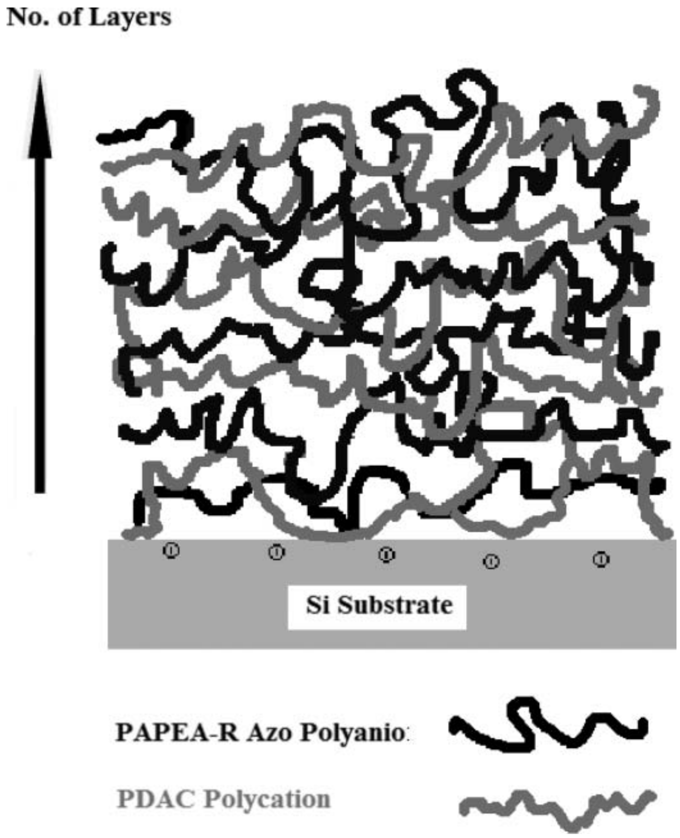

Fig. 7. Schematic of the buildup of the alternate 5 layer-by-layer SAMU film based on PDAC (polycation) and PAPEA-R (polyanion) on a Si substrate. For the sake of simplicity the counter-ions are not included in these schematic representations, where dark-gray lines present the adsorption of a polycation of PDAC and black lines the adsorption of a PAPEA-R azo polyanion.

The internal interfaces between the individual layers are reported to be of the largest roughness (24, 25). This was attributed to the possibility of the inter-chain digitation between molecules from adjacent layers. Considering the above, the observed results in the current work can be used to explain the interpenetration, composition and functionality of the prepared films of PAPEA-R from the consideration of the different substituted R-groups in terms of their ionization, size, and hydrophilic/hydrophobic characteristics as shown schematically in Figure 8.

As presented in Figure 8, the presence of a higher extent of polar COOH groups on the surface can promote H-bond formation with H_2O molecules which consequently results in the increase in surface wetting. The results summarized in Table 1 are in good agreement as the surface wetting increased with the increment of polar groups of COOH or SO_3H in the repeat unit of PEL. Since R-group of SO_3H of PAPEA-SO_3H are capable of participating in relatively more H-bonding interactions as compared to the COOH groups of PAPEA-COOH, and thus exhibited higher wetting. The higher wettability character of the PAPEA-COOH and PAPEA-SO_3H is an interesting observation. A principal difference between these two polyelectrolytes with polar R-groups relative to those with non-polar R-groups is that, in the former case, all the polymer repeat units are ionized and are capable of inducing the strong columbic interactions between the polyanions and oppositely charged polycation of PDAC. Under such circumstances, aqueous solutions of these polyanions are expected to be fully soluble. Furthermore, SAMU films of the PDAC polycations and the polyanions with all -COOH or -SO_3H repeat units are expected to be highly interpenetrated due to ionic interactions. Thus the main chains of the polymers are localized and closely-packed at the oppositely charged polyion film interfaces. The preliminary results suggest relatively lower film thickness observed from ellipsometry. The close packing as well as stronger ionic interactions of the polymer chains and polar azo chromophores with R-groups of -COOH and -SO_3H may produce different structural morphologies and structural transitions. The deposited bilayers are typically interpenetrated and that deposition is a surface charge dominated adsorption process resulting in higher surface wetting. For polyelectrolytes with non-polar R groups, however, it is likely that the polymer main chains of SAMU films have more free volume as found by thicker, less compact films with the possible existence of chain loops, and the absence of ionic azo chromophore interactions with PDAC (26).

In the case of PAPEA-R for H groups, the presence of polar COOH groups similar to that of Figure 8(i) is absent here. H_2O drops can participate in H-bond formation/interaction with the COOH groups of the repeat unit of acrylic acid, but such interactions are absent with this H group. Under such conditions, surface wettability is expected to decreases relative to that of R groups of COOH. The azo PEL of the PAPEA-R for octyl C_8F_{17} or C_8H_{17} groups are similar to that of PAPEA-H in terms of the degree of ionization and presence of COOH groups of the repeat units. There is again an absence of polar COOH groups similar to that of case (iii). However, as discussed more below, the presence of larger octyl groups as well as the possibility of their aggregation due to their hydrophobic character could have resulted in shielding of other polar groups present in both the polyanion and the polycation from H_2O drops. Due to this, H-bond interactions between the H_2O molecule drops and polar groups are reduced, and therefore resulted in the hydrophobic surface with a higher contact angle.

The relatively higher value of contact angle for the SAMU films of PAPEA-C_8F_{17} groups (contact angle of 94° with 60% increase relative to Si) can be attributed to the low surface energy of the floroalkyl group on the surface of such films. Similarly, the C_8H_{17} group also shows a significantly higher contact angle (contact angle of 79° with 52% relative to that of Si) than others non-polar R-groups of OC_2H_5 and H ($\sim$ contact angle of 60° with $\sim$40% relative to that of Si). Furthermore, lower contact angle values of SAMU films

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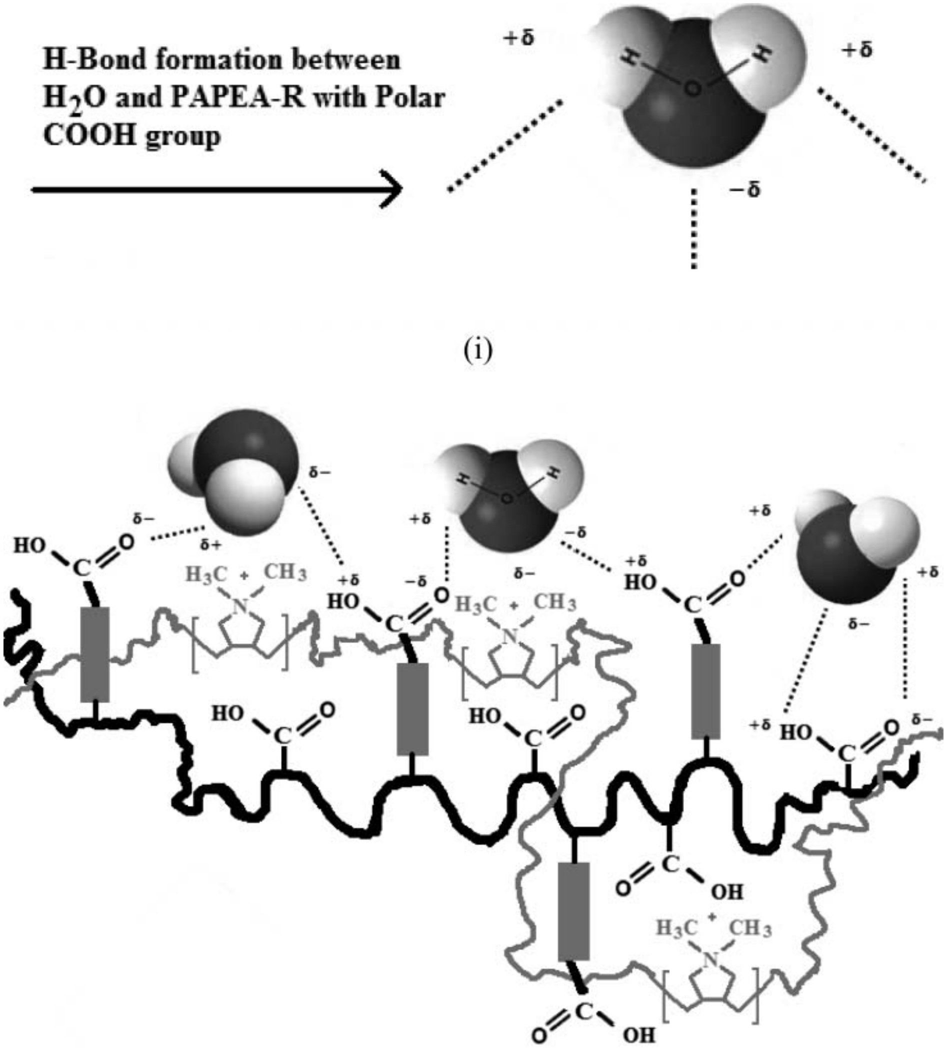

(i)

(ii)

Fig. 8. Suggested schematic of the molecular interactions of probe H_2O liquid drops with the top bilayer in thin films of polycation PDAC and polyanion PAPEA-R, where (i) depicts the formation of H-bonds between H_20 molecules and COOH groups from azo polyanions; (ii) depicts H_2O molecule interactions in the case of PAPEA-COOH; (iii) depicts relatively less H_2O molecule interaction in the case of PAPEA-H; (iv) depicts a further decrease of H_2O molecule interaction in the case of PAPEA-C_8H_{17} or C_8F_{17}. Also note the coverage or shielding of polar groups of the azo polyanion due to the presence of the larger octyl groups.

with polar R-groups of COOH and SO_3H relative to that of non-polar R-groups are in accordance with their expected order of the hydrophilicity or hydrophobicity. Comparison of the contact angle values for these SAMU films suggests that the long alkane type R-groups of C_8F_{17} and C_8H_{17} may have effectively hidden the underlining polar PDAC from counterion layers as well as acrylic acid groups from water drops as presented in Figure 8 (iv). The contact angles of the PAPEA-C_8H_{17} and PAPEA-C_8F_{17} films show a more dramatic increase than those of the PAPEA-H and PAPEA-OC_2H_5 films. It is possible that the large octyl groups are more effective in shielding the ionic functional group on the interfaces of internal and surface layers, and have contributed to the less sessile drop water molecule interactions with PDAC and/or AA groups. The longer octyl chains can pack and diffuse within the different interfaces of the SAMU films differently than shorter alkyl group of -H or -OC_2H_5 in the film internal as well as surface structure. The octyl groups can promote the coverage of relatively more ionic groups of COOH through diffusion at the air-film interface to suppress interaction between COOH groups and the H_2O molecule and thus reflect into the larger value in the contact angle. Another factor that seems to contribute to higher contact angle values is the possible presence of some forms of azo aggregation on the surface of these films. Blue-shifts were also observed in the UV-Vis spectra of the multilayer films, which strongly suggested the aggregation of the azobenzene chromophores in the multilayers (26).

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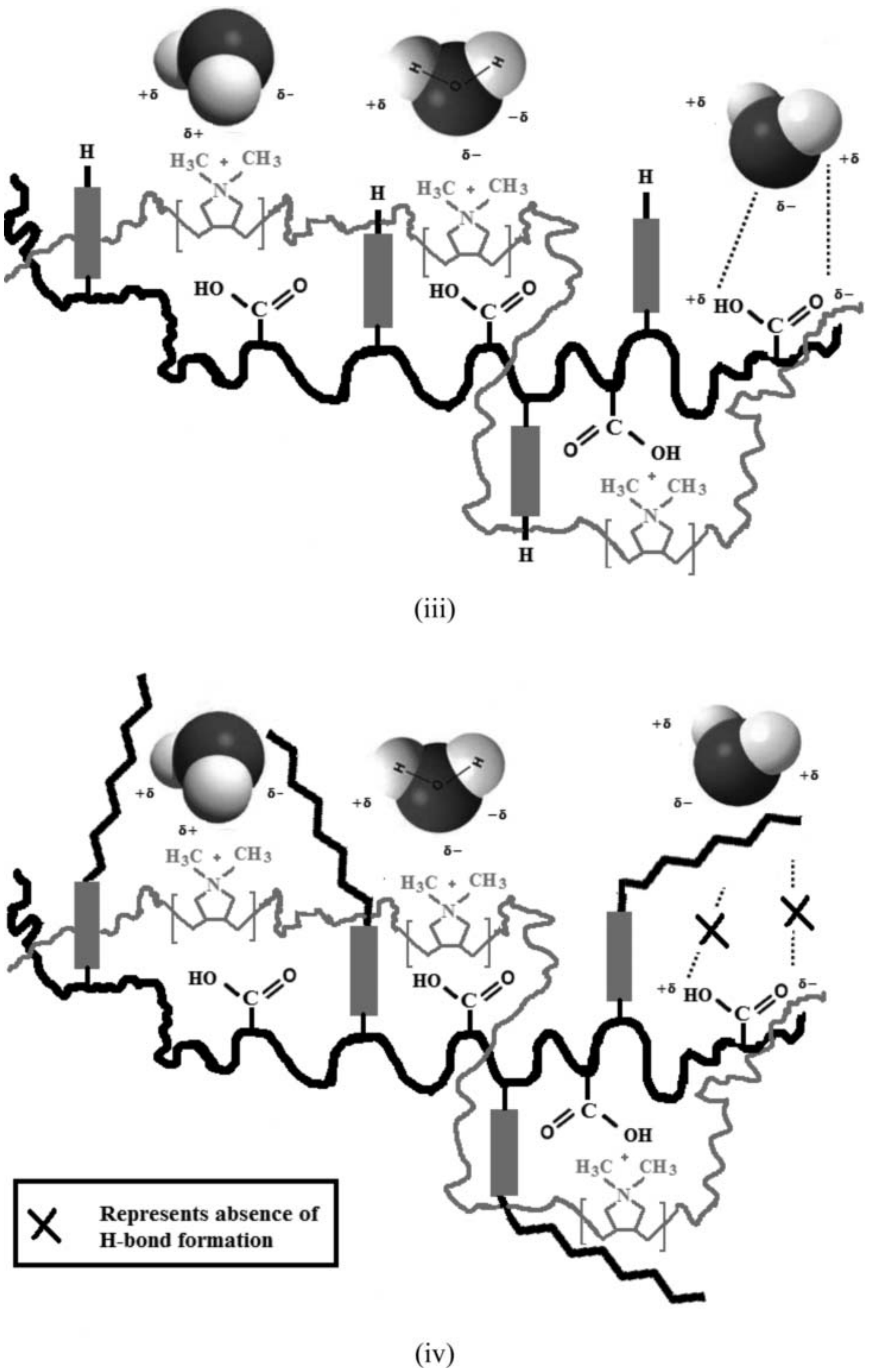

(iii)

(iv)

Fig. 8. (Continued)

Such aggregates formed for these multilayers were also observed from AFM analyses (26). An interesting property of the multilayers with aggregate particles on their surfaces is their particularly high hydrophobicity, which was evidenced by large contact angles with water. This observation is not unexpected due to the incorporation of bulky and hydrophobic groups in these polyelectrolytes, which can produce aggregates on the surfaces of the SAMU films. The design of functional polyelectrolyte films with bulky pendant groups such as that of C_8H_{17} or C_8F_{17}, may modify crucially the properties due to aggregation/clustering (17). The absence of polarity in the functional groups as compared to the ionic group support their aggregation or clustering in aqueous solution used for deposition of layers. This is due to both inter- as well as intra-polymeric association, which can subsequently effect the characteristics of the prepared films. In addition, the presence of aggregation in the solution used for deposition is possible as indicated by the blue shift in the spectra obtained in aqueous solution relative to that in pure DMF solvent. It is not clear how and to what extent such aggregates in solution can actually adsorb. Considering this, the employment of the PAPEA-C_8H_{17} or C_8F_{17} polyelectrolytes of uncharged, hydrophobic substituents bulky functional groups of octyl groups appeared to influence the regular film growth during sequential adsorption process. The presence of repeat units with charged groups of acrylic acid repeat units among these non-charged bulky azo repeat units do not necessarily suppress the extent of aggregation of azo functionalized groups. The distribution of the azo functional groups, their alignment and orientation on a given scale may be varied in the adsorption within the films and on air/films interface to modify the structure, density, composition, interpenetration and functionality of the films.

The above discussion suggested that the R-groups seem to affect the multilayer interpenetration and morphologies to different extents. Hence, the surface topography and wettability of SAMU films are likely to be influenced by the previously deposited PDAC polycation layers as well as the top azo polyanion layers. This interpenetration effect appeared to be more significant for all the short substituted R-groups studied in the current work as in such cases contact angle values do not differ significantly. The polycation PDAC and azo polyanion of PAPEAR-R with larger octyl groups, however, can produce varying extents of interlocked interpenetration in the film structure as well as appearing to shield the polar groups from H_2O to yield hydrophobic characteristics. Furthermore, the presence or absence of aggregates in these SAMU films seem to be a function of the charge balance and architecture of the azo PEL employed for layer-by-layer adsorption and can be exploited to tailor the important characteristics of the films such as surface-directed complexation between oppositely charged polyelectrolytes after diffusion in the film to determine the interchain digitations, compositions, functionalities, and characteristics of the type of hydrophilic, hydrophobics and surface energy.

4 Conclusions

The current study demonstrates a novel approach of employing various substituted head R-groups of azobenzene polyelelctrolytes to precisely control and tune the surface wettability of layer-by-layer self-assembled multilayer (SAMU) films, important for many biocompatibility applications, where only a narrow window of surfaces energies is suitable. Various types of R-group pairs such as shorter-ionized hydrophilic COOH and SO_3H, shorter-non-ionized hydrophobic H and OC_2H_5, and larger-nonionized hydrophobic octyl C_8H_{17} and C_8F_{17} were employed as polyanions to fabricate the SAMU onto silicon substrates by using the counter charge polycation PDAC. Measurement of the resultant water contact angle revealed relatively higher hydrophilic surfaces films for the COOH and SO_3H with contact angles around $\leq 59^\circ$, however, octyl pairs of C_8H_{17} and C_8F_{17} produced significantly hydrophobic surface films with contact angles $\geq 79^\circ$. Shorter-non-ionized hydrophobic H and OC_2H_5 wettability was found to be closer to that of films of COOH and SO_3H. Variation in the degree of ionization, size, hydrophobicity/hydrophilicity, solubility, conformation, and aggregation of the R-groups present in the solution of azobenzene polyelectrolyte seem to influence the interpenetration, organization and surface functionalities of the prepared films. These factors interrelate to each other and subsequently determine the interaction of a liquid with the film surface. The thin film materials reported here also incorporate light responsive azobenzene, for the eventual development of photo-reversible control of cells on these surfaces. Therefore, through careful synthetic design such as that described here, one can tune surface energies exactly for specific demanding bio applications such as directed cell growth, and enhance the capability to develop intelligent surfaces for applications in various biomedical nanotechnologies.

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