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Novel Azobenzene-Functionalized Polyelectrolytes of Different Substituted Head Groups 3: Control of Properties of Self-Assembled Multilayer Thin Films

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Novel azobenzene polyelectrolytes have been used to fabricate biocompatible self-assembled multilayer (SAMU) thin films of variable absorbance, thickness, organization, and morphology. The prepared SAMU films are useful for directed cell growth, and this application relies directly on control of contact and surface energy, and requires the ability to tune the surface characteristics which are critical to their development. The azo polyelectrolytes employed here were similar in their degree of polymerization and repeat unit composition of acrylic acid monomer and azo monomers, and only differ from each other due to the presence of different substituted head R-groups present on the p-position of the aromatic ring of the azo chromophores. Possession of characteristics of both the self-assembly due to acrylic acid groups, and photoswitchability of the azo monomer enable the azobenzene functionalized polyelectrolytes to exhibit novel photo-reversible applications. The 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 used as polyanions and counter charge PDAC used as polycation to fabricate the layer-by-layer SAMU films onto glass and silicon substrates. The fabricated SAMU films were also characterized by various techniques. The UV absorption maxima, $\lambda_{\max}p$ of the SAMU films move to lower wavelength relative to solution to exhibit a blue shift for the hydrophobic R-groups, while this behaviour was not observed for the hydrophilic R-groups. Similarly, the thickness, organization, morphology and other properties of the thin films were found to be dependent on the type of substituted R-groups of the azo polyelectrolytes due to the inter-related factors of ionization, hydrophobicity/hydrophilicity, solubility, and aggregation of azo PEL in the dipping solutions used for fabrication of the SAMU films. Understanding and controlling the adsorption characteristics of azo multilayer thin–film of switchable functionalities are vital to explore their potential for the development and application of new devices in diverse areas of biosensor, drug delivery systems, on-chip microscale chemical process and microfluidics systems.

Keywords: Aggregation, azobenzene-functionalized polyelectrolytes, biocompatible and bio-medical surfaces, hydrophilic, hydrophobic, self-assembled multilayer thin films

1 Introduction

One important and novel tool for creating thin films is via molecular self-assembly in combination with stimuli-responsive molecular function which can precisely switch some properties reversibly in space and time as demanded by certain applications (1–3). Considering this, such interplay is expected to provide wide opportunities for creating a new class of programmable materials and devices (4–7). Among various exploratory techniques, Langmuir-Blodgett (LB) and chemisorption methods have been employed widely in the past to fabricate thin films (8). These techniques have limitations such as requirements of special equipment, substrate size, and film quality. Considering this, in 1992, Decher and coworker extended the pioneering work of Iler to a new method using polyions to fabricate thin films via an electrostatic layer-by-layer self-assembled multilayer (SAMU) process (9–10). Since then, the SAMU film fabrication technique has attracted great attention in the past decades. This technique is based on physisorption from solution and utilizes the electrostatic attraction between opposite charges of polycation and polyanion. This simple approach enables micro/nano-achitecture control for each adsorbed layer from environmental friendly

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aqueous solution, and fabrication of films is largely independent of the nature, size and topology of substrates. Furthermore, the growth of single layers via this method offers the opportunity of controlling surface properties at the molecular level. Deposition of films can be carried out either by automatic dipping or manually by hand-dipping in glass beakers. The prepared films are known to be of good quality, stability, robustness and have excellent adhesion to wide variety of substrates including glass and silicon substrates. In addition to these advantages of the SAMU film, it also facilitates the incorporation of a wide variety of multicomponent materials and functionalities, including that of the polyelectrolytes containing photoresponsive azobenzene chromophores (azo) (9–12). The azo and its derivatives possess one of the most interesting characteristics due to their efficient photo-induced facile and reversible isomerization between *trans* and *cis* isomeric states (13). This photoisomerization effect can be manifested into the thin films containing the azo groups, and upon exposure to light, reversible changes in their mechanical, geometrical and electrical properties can be induced (14–17).

Considering the above, fabrication of SAMU thin films containing azo groups is a fascinating tool to control the characteristics of surfaces, and therefore, recent significant interest in this research area has been explored, such as nonlinear optical (NLO) thin film devices, specialty coatings exploiting hydrophilic or hydrophobic or amphiphilic properties, biocompatibility, antibacterial properties, molecular recognition, chemical sensing or biosensing, and microfluidic flow control (18–22). The optimized performance of many of such thin films is determined by the local structure of the polymeric matrix. Therefore, it is of paramount importance to understand their surface chemical composition, texture, morphology, and functional group dispersion on surfaces as well as interpenetrating within the films. There are several parameters which influence these properties such as the employment of weak or strong polyions, the pH, and the ionic strength (23–25) when deposited. In addition, one of the most important factors that can influences the properties of the thin films is the type of polyion used for film fabrication (26–27).

Our recent work has clearly demonstarted the significance of the type of azo polyion to fabricate SAMU film of stable photoswitchable surface energy (28). The primary goal of this large project is to engineer biocompatible surfaces of controllable surface characterstics with the eventual goal of directed neural cell growth, and study of a synapse *in vitro*. The precise control of properties is therefore critical, which allows the rational application of such bio-surfaces for cell function outside the human body. In view of the above considerations, we have synthesized novel azo PELs (29), and developed a new type of molecular level process to control sucrface wettability by introducing different type of head R-group of azo polyelectrolytes in a layer-by-layer adsorption process (30). The type of substituted head R-group of azobenzene was observed to determine the wetting characteristics, and hence quite reliably control and tune the surface energy of the SAMU films. The bilayer interpenertration, structures and composition was found to effect the surface wettability of adsorbed polyelectrolyte layers and is primarily controlled by the substituted R-group of the azo group. In the current work, further studies of the effect of type of substituted head R-groups of azo on the charcterstics of the adsorbed thin film properties fabricated via self-assembled layer-layer process have been investigated. The SAMU films were fabricated by using polyions based on PDAC as polycations and azo polyelectrolyte as polyanions. Synthesis of the azo polyanions used in the current work is described elsewhere (29). The azo polyanions only differ from each other due to the presence of substituted R-group at the para position on the aromatic ring of azobenzene. The substitution effect of R-groups of the azo polyanions on the properties of the SAMU films is investigated from the consideration of their charge density, hydrophilicity, hydrophobicity, and size. The thickness, organization, morphology and properties of the thin films are related to the type and size of substituted R-groups of azo being used through their degree of solubility, conformation, association and aggregation in the dipping solution used for the SAMU film fabrication.

2 Experimental

2.1 Materials and Synthesis of Polymers

Chemicals were purchased from Aldrich and used as such unless specified. The detail of the experimental work to synthesize and characterize the polymers is given elsewhere and Figure 1 presents the structures of the azo polymers used in the current work (29). 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 drop wise addition of diazonium salt of the amine derivatives to prepare copolymers designated as PAPEA-R.

2.2 Self-Assembled Multilayer Films (SAMU) Fabrication

Polished silicon wafers (Wafernet) and glass microscope slide (Fischerbrand) substrates were cleaned in a bath of 25% H_2SO_4 and 75% H_2CrO_4 for at least 12 h. This was followed by thoroughly rinsing with neutral Milli-Q water prior to polymer adsorption. Polyelectrolyte multilayer films were assembled on the substrates with the aid of an automatic slide stainer (Varistain 24-4, Shandon). For self-assembled layer fabrication, Milli-Q water (resistivity > 18 MΩ) was used. The 0.1 mmol/L concentrated solutions of poly(diallyldimethylammonium chloride)

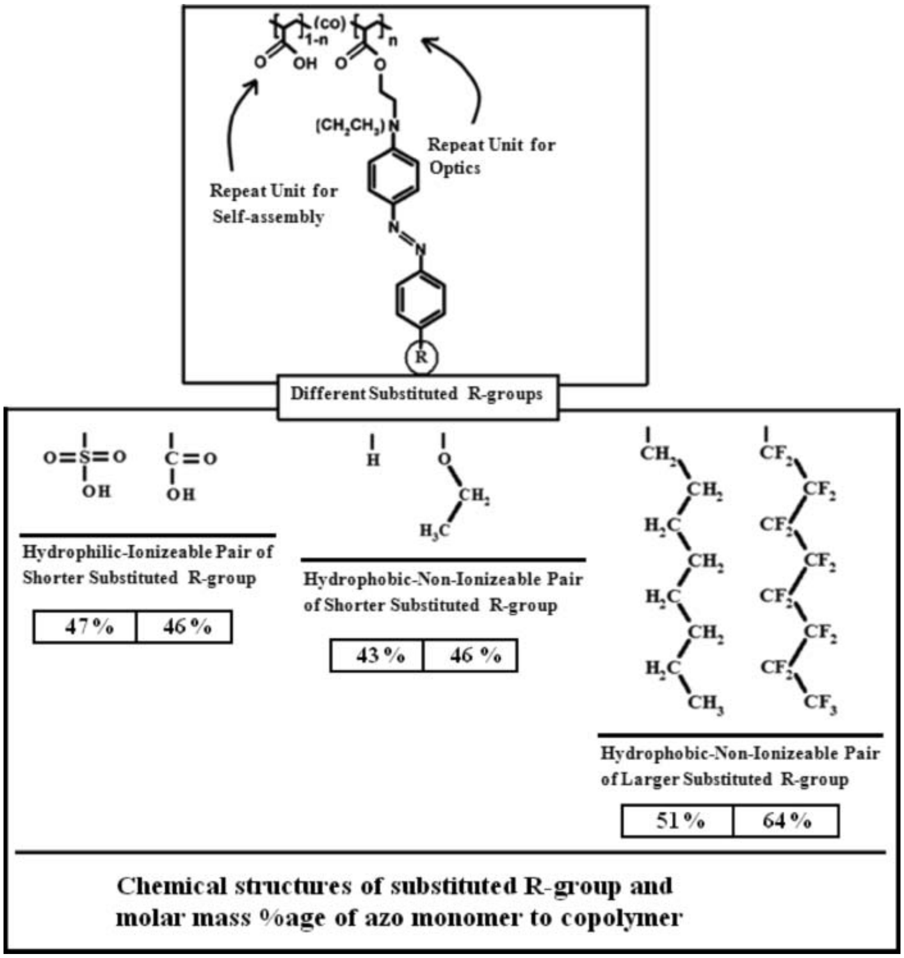

Fig. 1. General structure and classification of the polymers used to fabricate thin films by using the layer-by-layer self-assembled multilayer (SAMU) technique. Polymers are simply designated as PAPEA-R, where R is the substituted group on the para-position of the azobenzene chromophores. The molar mass %age of the azo monomer repeat units of different R-groups in the copolymer, which contain repeat units of 85 mol% AA monomer and 15 mol% of azo monomer are also presented (29).

(PDAC) and azo polyelectrolytes (with respect to azo repeat units) were used as polycation and polyanions, respectively. Films were fabricated by alternate 20 min dipping in aqueous PDAC solutions and one of the azo polyanion solutions by the usual layer-by-layer technique. If required, the solubility of azo-functionalized polyelectrolytes was increased by the addition of salt such as $NaHCO_3$ and about 5 vol% of DMF. After each polycation or polyanion dipping step, the slides were washed by dipping for 10 min into 3 separate washing baths. After the desired number of layers were deposited, the coated films were dried under vacuum at 60°C for about 12 h.

2.3 Characterization

Self-assembled multilayer films were studied by various techniques. UV-Visible absorption spectroscopy was used to study the absorption characteristics of the azo chromophore for the films deposited on the glass microscope slides. From these studies, absorption maxima, λ_{max}, values due to π to π^* electronic transition of the azo-polymers were determined. The thickness and refractive index of the fabricated and dried films were determined using a Gaertner Ellipsometer (Model L116C). The light source was a HeNe laser with wavelength at 633 nm and the angle of incidence was fixed at 70.0° with respect to the normal. The measurement necessary for the calculation of the film thickness consisted of the determination of two sets of polarizer and analyzer readings for the silicon substrates and of the corresponding values for the substrate coated with polyelectrolytes films. Thus, the ellipsometry determinations of total layer thickness are reported here as the statistical mean of at least 10 measurements after subtraction of surface oxide layer thickness (measured average of 22 Å±3 taken at different locations). The average errors associated with ellipsometry measurements were determined to be approximately ± 4%. Preliminary surface morphologies of the fabricated films were studied by using a Nanoscope's AFM, Version 3A, Digital Instrument. The AFM was operated in the contact mode using a standard silicon nitride cantilever in ambient air. The standard sessile drop technique was employed to determine the static contact angle of H_2O as described elsewhere (30). For this purpose, 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 reported contact angles are an average of at least 5 measurements with an uncertainty of ±2 degrees.

3 Results and Discussion

3.1 UV-Visible Absorption Spectroscopy Studies of the SAMU Films

Table 1 summarizes the characteristics of the self-assembled multilayer thin films. UV-Visible absorption spectra of the prepared self-assembled multilayers films of azo polyelectrolytes are presented in Figure 2. The prepared films appeared clear and uniform with good optical quality. Polyions used for the layer-by-layer process are expected to be fully ionized under the experimental conditions employed, and thus the charge density of the polyion pair was sufficient to proceed with charge overcompensation (reversal) during each subsequent adsorption steps (9–10). The λ_{max} values summarized in Table 1 and UV-Visible absorption spectra shown in Figures 2 and 3 indicate that SAMU films of azo PEL having hydrophobic R-groups, such as C_8H_{17} and C_8F_{17} exhibit the blue shifts or hypsochromic shifts. On the other hand, no noticeable shifts in the λ_{max} were observed for the R-groups of the hydrophilic or ionizeable COOH and SO_3H-based films. The observation of shift in the λ_{max} values for hydrophobic R-group in the SAMU film can be attributed to the interactions between neighbouring chromophores and their structural arrangements (31–32). It is interesting to consider the possible reasons for the aggregate formation and blue shift in the current SAMU film fabrication process. This observation is rationalized by taking into account the factors such as the hydrophilic or hydrophobic nature of the polyelectrolytes R-groups, solubility characters of PEL in the self-assembly solution, chromophore aggregation in solution, and degree of ionic repeat unit presence in the azo PEL chains. All these factors are inter-related to each other and influence the nature of localization of azobenzene chromophores on the surface of the thin films. A particularly interesting situation arises when the PEL undergos hydrophobic aggregation in dilute aqueous solution, but generally it is not clear how the associated character in solution influences the structure of adsorbed films, such as whether hydrophobic domains are preserved upon adsorption or not (12).

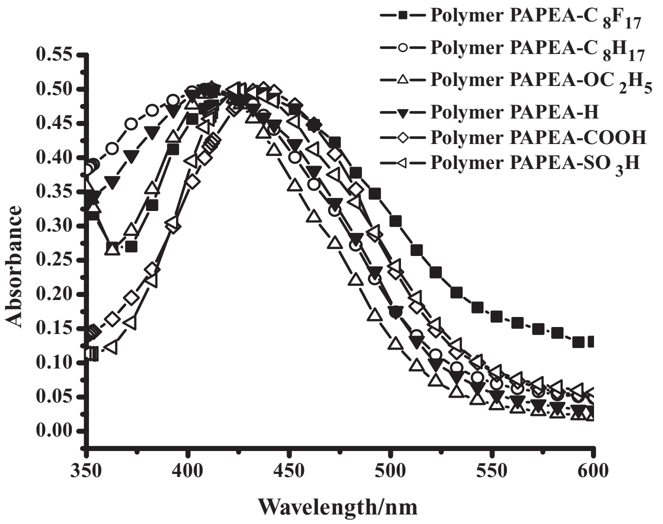

Fig. 2. UV-Visible absorption spectra of the 5-bilayers SAMU films of the PAPEA-R fabricated on glass slides, where R-substituent designates a group which is present on the p-position of the aromatic ring of the azobenzene chromophores.

3.2 Azo Chromophores Aggregation and Shift in Absorption Maxima λ_{max}

As mentioned earlier, the λ_{max} value of azobenzene chromophores depends significantly on the mutual orientation,

Table 1. Characteristics of the azobenzene polyelectrolytes PAPEA-R and their 5 layer-by-layer self-assembled multilayer films (SAMU)

	Molar mass		*Absorption Maxima λ_{max} (nm)*				
R-Group	*Azo monomer g/mole*	*Azo monomer % (w/w)**	*Polymer In DMF*	*SAMU*	*Shift Type/ value difference#*	*Thickness Å*	*Contact Angle H_2O θ*
SO_3H	388	47	419	423	No shift	165	55
COOH	352	46	439	440	No shift	162	59
H	308	43	418	407	Blue/11 nm	159	61
OC_2H_5	352	46	422	412	Blue/10 nm	188	64
C_8H_{17}	420	51	423	410	Blue/13 nm	242	79
C_8F_{17}	726	64	445	414	Blue/21 nm	258	94

*Molar mass calculations based on PAPEA-R copolymer composition, which contain repeat units of 85 mol% AA monomer and 15 mol% of azo monomer.

#Difference between DMF solution and SAMU film.

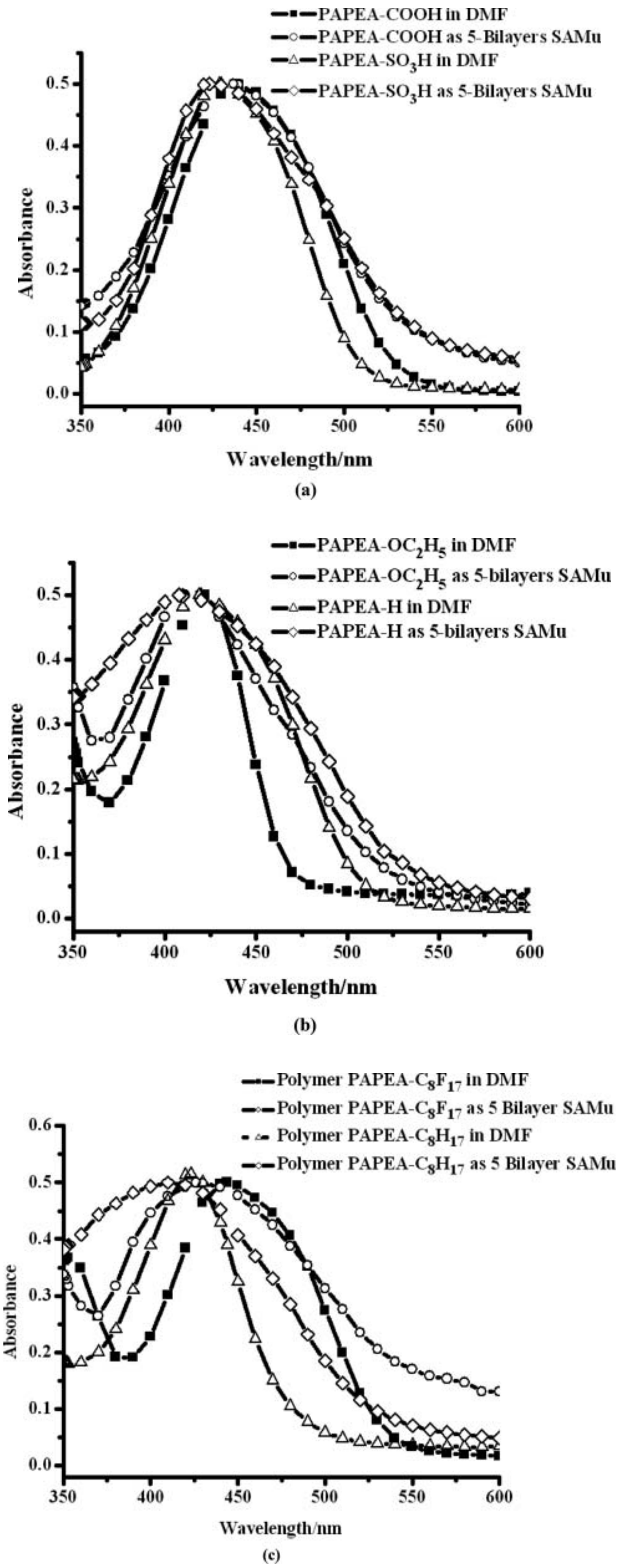

Fig. 3. UV-Visible absorption spectra of (a) PAPEA-COOH and PAPEA-SO$_3$H; (b) PAPEA-H and PAPEA-OC$_2$H$_5$; (c) PAPEA-C$_8$H$_{17}$ and PAPEA-C$_8$F$_{17}$ in DMF and as self-assembled multilayer (SAMU) films. Note the shift of λ_{max} to lower wavelength (blue shift) in the SAMU relative to that of in the DMF solvent.

distance, and aggregation numbers of the chromophores. Aggregates of the azobenzene chromophores are formed normally only in condensed media such as monolayer and Langmuir-Blodgett films, where these are densely packed to form contacts with each other. In contrast, in the present system, the aggregates appeared to be present in the SAMU films (33). According to the molecular exciton model proposes by McRae and Kasha, the aggregation of molecules into ordered structures (with corresponding dipoles) results in splitting of excitation energy levels (34). This results in a shift of the absorption spectra, which depend on the mutual orientation of the interacting dipole moments. The blue shift from the absorption band is indicative of linear chromophore aggregates with their transition moments parallel to each other and ordered perpendicular to the stacking direction (so called H-aggregates). On the other hand, the red shift is produced by the chromophore arrangement with their transition moments parallel to each other but greatly inclined from the normal to the stacking direction (so-called J-aggregates). The aggregation of dye molecules in an ordered structure (with corresponding dipoles) results in the splitting of the excitation energy levels. As a consequence, shifts in the absorption spectra are observed, depending on the mutual orientation of the interacting dipole moments. The amount of the wavelength shift depends on the degree of aggregation, which is determined by the mutual orientation, distance, and aggregation numbers of the chromophores (35–37). In-line and parallel aggregation are two ideal extreme cases, and generally, the mutual orientation of the interacting dipoles may be at some angle, resulting in more complex spectral changes. Further due to layer interpenetrations, aggregation and orientations of the chromophores can also vary from layer to layer or even within layers (38–39).

The spectral shifts observed in the current work can thus be explained by considering the above factors. Azo PELs with ionizeable head R-groups of COOH and SO$_3$H groups are hydrophilic, while H, OC$_2$H$_5$, C$_8$H$_{17}$ and C$_8$F$_{17}$ are hydrophobic, as well as non-ionized. All these PELs show good solubility in pure DMF or can be solubilized to variable degrees in H$_2$O:DMF mixed solvent systems. It is reasonable to expect that for the DMF:H$_2$O mixture solution used for SAMU films fabrication, azo PELs with hydrophobic R-groups form aggregates. This is supported by the observation of a blue shift in λ_{max} value of 28 nm for the PAPEA-C$_8$H$_{17}$ in DMF:H2O (8:2 volume ratio) mixed solvent systems as compared to pure DMF solvent. Contrary to this, for PEL with hydrophilic R-groups on the azo as COOH and SO$_3$H, however, shifts in the λ_{max} have not been observed because aggregate formation in solution used for self-assembly is less likely since these groups are highly water soluble. Furthermore, the presence of ionizeable groups in the azo PEL structures can render polymer chains with all repeat units fully ionized. This in return may have affected the way the PEL adsorbed onto previously deposited polycations. Under such conditions, acrylic acid repeat units as well as anionic groups on the azo chromophore are capable of undergoing electrostatic interactions with PDAC polycations. This results in relatively even distributions of chromophores and suppression of their interactions on the surface to such an extent that no shift was observed. In addition, the repeat unit's similar charge ionization of the polyelectrolyte chains result in their expansion due to ionic repulsion forces (40). On the other hand, PAPEA-R with hydrophobic R-groups on the azo chromophores are not ionizeable, and therefore, not expected to undergo ionic interactions with oppositely charged PDAC. In this case acrylic acid repeat units of the azo copolymer involve interactions with PDAC, while observation of aggregate formation is not unexpected. The extent of the spectral shifts observed suggests the presence of aggregates of varying sizes for the azo PEL used to fabricate the thin films. It is likely that the local concentrations of the azobenzene on the surface are high enough to form aggregates to produce the blue shift in the λ_{max} due to the formation of H-aggregates in the prepared films. This effect directly influences the variable hydrophobic/hydrophilic character of the PEL in the dipping solutions, and is manifested when adsorbed as thin films via the SAMU deposition process to influence the chracterstics of the thin films.

3.3 Surface and Thickness Characteristics of the SAMU Films

Both AFM and ellipsometry studies of the SAMU films have been carried out to further support the presence of azo aggregates, and observed shift in λ_{max}. Figure 4 represents the AFM image of a 5-bilayer SAMU film surface of PAPEA-C_8H_{17} and thicknesses of the prepared films are given in Table 1. Detailed AFM and Ellipsometry analysis including transmission electron microscopy (TEM) and dynamic light scattering (DLS) studies will be presented in future. However, initial results indicate the presence of aggregates of globular particles or micelle-like structures. PAPEA-C_8H_{17} has a polyamphiphilic structure with hydrophilic acrylic acid main chain segments (85 mole %) and partially functionalized hydrophobic repeat units with azo side chains (15 mole %). The micron/nano size micelle like particles have been reported to present in the SAMU films fabricated from PEL which contain hydrophobic/bulky substituents (41–42). The blue-shift observed in the UV-Visible spectra of both the solution and of the multilayer supported the presence of aggregation of the azobenzene chromophores in solution and also in the multilayers. Furthermore, as shown in Table 1, studies of the contact angles measurements of water on the SAMU films of these azo polyelectrolytes indicated significant differences in their wetting, chemical and surface characteristics, layer interpenetration, and topography. Comparison of the contact angle values for these SAMU films suggested that surfaces with long alkane type R-groups of C_8F_{17} and C_8H_{17} may have formed aggregates in the form of micelle particles and resulted in significantly higher hydrophobicity relative to shorter R-groups of H and OC_2H_5. The thicknesses of the SAMU films measured via ellipsometry also exhibit a dependence on the extent of hydrophobic or hydrophilic character of the azo polymers and showed correlation to that of the absorption shift in the spectra as demonstrated in Figure 5.

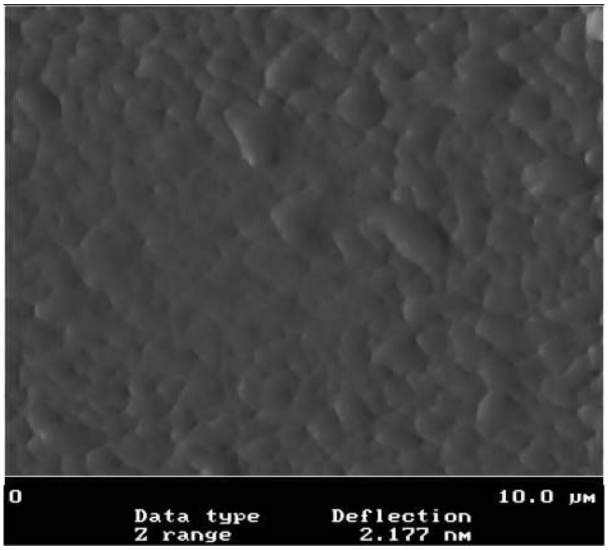

Fig. 4. AFM image of self-assembled multilayer thin films fabricated with polyion pairs of PDAC/PAPEA-C_8H_{17}. The outermost layer of PPEA-R-AA of C_8H_{18} indicates the presence of aggregates on the surface.

3.4 SAMU Film Properties of Azo PEL with Hydrophobic Head R-groups

The thickness of the SAMU films of the PAPEA-C_8F_{17}/PDAC or PAPEA-C_8H_{17}/PDAC were found to be 25 ± 5% thicker than films formed by other azo PEL substituents of H and OC_2H_5, and COOH and SO_3H. This difference in the thickness caused by the azo variation is fairly high, and appears to be attributed to the type and extent of aggregation in these polyelectrolytes. As given in Table 1, an increase of the weight percentage of the hydrophobic anionic azo polymers for the non-polar substituents H, OC_2H_5 and C_8H_{17} and C_8F_{17} leads to a higher amount of polymer being adsorbed, and the adsorbed amount increases more by increasing the hydrophobic content. This is an interesting observation since the charge density of these four anionic PEL with the non-polar and hydrophobic substituents are identical. Though the absorption shifts due to aggregation are comparable, the hydrophobic contents however are very different (Table 1). The azo PEL of PAPEA-C_8H_{17} and PAPEA-C_8F_{17} have long oily tails that could have influenced the way the aggregate structures

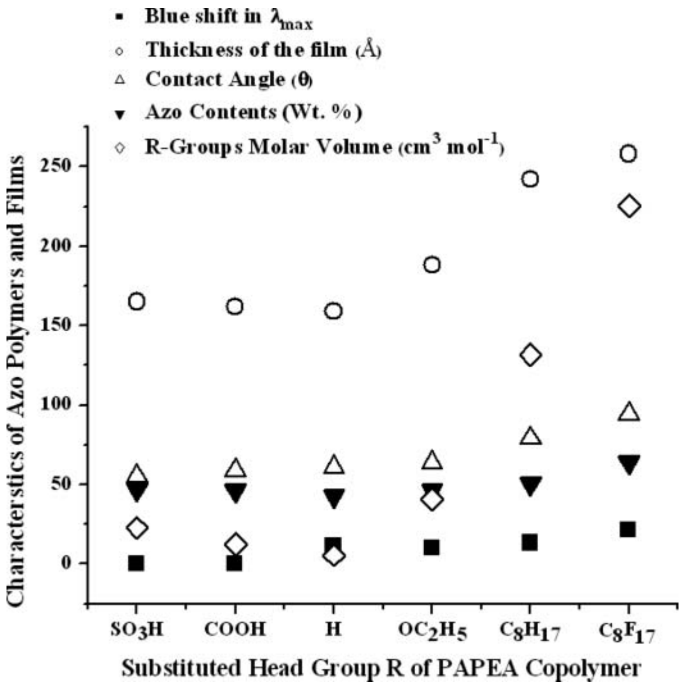

Fig. 5. Correlation between the substituted R-groups of azobenzene polyelectrolytes of PAPEA-R, and characteristics of the self-assembled multilayers thin films.

and their sizes formed on the film surface. The relatively higher thickness is explained from the consideration of the type of dipping solutions (i.e. solubility character of the azo PEL) being employed for the SAMU film fabrication. An increase in the hydrophobic contents is known to result in aggregation in solution, which may have influenced the multilayer formation and organization through interpolymeric association and intrapolymeric aggregation. If aqueous solvent quality decreased due to increase in hydrophobic contents, the electrostatic attraction between polyelectrolytes segment increased. Such attractive forces between the nearest repeat units cause the polyelectrolyte complex to contract, collapse, and coagulate. Due to such rearrangements, the polyelectrolyte chains in a solution induce the formation of aggregates in the film, as supported by the AFM image and blue shift data. Since the aggregation degree is significantly dependent on solubility, the conformation of the PEL chains of PAPEA-C_8H_{17} and PAPEA-C_8F_{17} within the assembly solution can therefore form a globular micellar structure and are subsequently adsorbed to the multilayer surface as the aggregates. The surface morphology that forms during the layer-by-layer assembly process thus likely originates from a hydrophobic attraction among alkyl chains of these PEL in the aqueous environment. In some ways, the effect is similar to that which causes a thickness variation of weak polyelectrolyte multilayer films through adjusting the pH of the preparation solution.

3.5 SAMU Film Properties of Azo PEL with Hydrophillic Head R-groups

It is also interesting to discuss the thin film properties of the azo PEL with hydrophilic R-groups of COOH and SO_3H. In this case, the solvent effect on the layer thickness was observed to be much less significant and different surface morphologies are possible as these molecules existed in solution in the non-aggregating form. There is high static repulsion force of the ionizing anionic carboxylic acid or SO_3H groups. Further, in this case chain segments are fully ionized, i.e., 15 mol% of azo monomer repeat units and 85 mol% of AA repeat units. This results in a 15 mol% higher charge density relative to other azo PEL of non-ionic substituents. Thus, both the higher charge density and repulsion between similarly charged repeat units can lead to thinner layers after adsorption. This means that these molecules can adopt a more stretched conformation. During the fabrication of the SAMU films of PAPEA-COOH and PAPEA-SO_3H, the molecules appeared to adsorb onto the substrate in a monomolecular form. On the other hand PAPEA-C_8H_{17} and PAPEA-C_8F_{17} form aggregates in solution, and accumulate during the LBL process. The increase in the adsorption from producing thicker films can be related to various interactions such as the between oppositely cationic charge PDAC layer and anionic AA of PAPEA, and a strong hydrophobic association. It is reasonable to expect that the different azo PEL molecules produce different morphologies. This is evident from the variation in the values of the contact angles, films thicknesses, and absorption shift. These properties of the SAMU films are attributed to the variation in their surface morphologies, roughness and textures of the films.

The above discussion suggests that through controlling the solution aggregation behaviour of amphiphilic polymers and hence the adsorption behaviour of the polymer, surface morphology, film organization, and hydrophilicity/hydrophobicity of the SAMU films can be tailored to varying extents as demanded by their uses and applications. More work is underway and will be reported to describe the studies of the photo-induced reversible switching of wettability by controlling composition and morphology of the SAMU thin films. Such studies of the thin films are necessary to explore new opportunities to control important surface-based processes such as for biosensors to new drug delivery systems, and on-chip microscale chemical process to microfluidics systems.

4 Conclusion

In the present study, various parameters which are important to control the characteristics of photo-responsive thin films of novel azobenzene polyelectrolytes (azo PEL) prepared via the SAMU process have been investigated. The SAMU films were fabricated by using PDAC as polycation and polyanion of the azo PEL, PAPEA-R. The PAPEA-R structure contained the repeat units of acrylic acid (AA) and 2-(phenylethylamino)ethyl acrylate (PEA) monomers functionalized with azobenzene chromophores, with R being the substituent group present on the para-position of the aromatic ring of the azobenzene chromophores. The solution properties and their subsequent adsorption on the substrates are highly dependent on the type of R-groups present in the azo PEL. For example, blue or hypsochromic shift in the UV-Visible absorption in the $\lambda_{\max}$ of the SAMU films were observed for azo PEL with hydrophobic non-ionized shorter R-groups of H and OC_2H_5 and larger octyl groups of C_8H_{17} and C_8F_{17}. On the other hand, no noticeable shifts were observed for shorter R-groups of COOH and SO_3H. Similarly, thicknesses of the SAMU films with larger R octyl groups of C_8H_{17} and C_8F_{17} determined by ellipsometry were significantly higher relative to that of other groups and were related to the shift in $\lambda_{\max}$. These observations are explained from the consideration of the solution characteristics of the R-groups of azo PEL in terms of their charge density, size, hydrophobic/hydrophilic contents, and interpolymeric association and intrapolymeric aggregations. These factors are found to be inter-related and manifested themselves during adsorption of the azo PEL from the dipping solution used to fabricate thin films via the SAMU deposition process to control the characteristics of the thin films. The SAMU thin film work reported here provides insight into the significance of the structures and solution characteristics of R-groups of the azo PEL, which can be adjusted to control the thickness, morphology, and functionality of these films. Such studies are important to understand, optimize and promote the applications of the photo-responsive thin films, whose functionalities can be precisely controlled and thus used as an enabling technology in multidisciplinary areas of reversibly switched surface science.

Acknowledgments

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References

1. Lahann, J., Mitragotri, S., Tran, T.N., Kaido, H., Sundaram, J., Choi, I.S., Hoffer, S., Somorjai, G.A. and Langer, R. (2003) *Science,* 299, 371–374.
2. Huber, D.L., Manginell, R.P., Samara, M.A., Kim, Byung-Il. and Bunker, B.C. (2003) *Science,* 30, 353–354.
3. Wang, R., Hashimoto, K., Fujishima, A., Chikuni, M., Kojima, E., Kitamura, A., Shimohigoshi, M. and Watanabe, T. (1997) *Nature*, 388, 431–432.
4. Zhao, B., Moore, J.S. and Beebe, D.J. (2001) *Science*, 291, 1023–1026.
5. Ichimura, K., Oh, S-K. and Nakagawa, M. (2000) *Science*, 288, 1624–1626.
6. Jiang, W., Wang, G., He, Y. and Wang, X. (2005) *Chem. Comm.,* 28, 3550–3552.
7. Sawodny, M., Schmidt, A., Stamm, M., Knoll, W., Urban, C. and Ringsdorf, H. (1991) *Polym. Adv. Tech.*, 2, 127–136.
8. Tredgold, R.H. (1987) *Rep. Prog. Phys.*, 50, 1609–1656.
9. Decher, G. , Hong, J.-D. and Schmitt, J. (1992) *Thin Solid Films.,* 210/211, 831–835.
10. Decher, G. and Schlenoff, J.B., Eds. *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials;* Wiley-VCH Verlag GmbH & Co. KGaA: Weinham, 2003.
11. Lee, S.H., Balasubramanian, S., Kim, D.Y., Viswanathan, N.K., Bian, S., Kumar, J. and Tripathy, S.K. (2000) *Macromolecules.*, 33, 6534–6540.
12. Wang, H., He, Y., Tuo, X. and Wang, X. (2004) *Macromolecules*, 37, 135–146.
13. Rau, H. Photoisomerization of Azobenzene., In *Photoreactive Organic Thin Films*, Sekkat, Z. and W. Knoll, Eds. Elsevier Science: New York, p. 3–39, 2002.
14. Natansohn, A. and Rochon, P. (1997) *ACS Symp. Seri.*, 672, 236–250.
15. Yager, K. G. and Barrett, C.J. (2006) *J. Photochem. Photobiology A: Chem.*, 182, 250–261.
16. Siewierski, L.M. , Brittain, W.J. , Petrash, S. and Foster. M.D. (1996) *Langmuir*, 12, 5838–5844.
17. Wu, L., Tuo, X., Cheng, H., Chen, Z. and Wang, X. (2001) *Macromolecules*, 34, 8005–8013.
18. Wang, X. , Balasubramanian, S., Li, L., Jiang, X., Sandman, D.J., Rubner, M.F., Kumar, J. and Tripathy, S.K. (2003) *Macrmol. Rap. Comm.*, 18, 6451–6559.
19. Oosaki, S., Hayasaki, H., Sakurai, Y., Yajima, S. and Kimura, K. (2005) *Chem. Comm.*, 28, 5226–5227.
20. Ishihara, K., Okazaki, A., Negishi, N., Shinohara, I., Kataoka, K. and Sakurai, Y. (1982) *J. App. Poly. Sci.*, 27, 239–245.
21. Yang, D., Piech, M., Bell, N.S., Gust, D., Vail, Park, C-D., Hayes, M.A. and Picraux, S.T.S., Garcia, A.A. and Schneider, J. (2007) *Langmuir*, 23, 10864–10872.
22. Akiyama, H. and Tamaoki, N. (2004) *J. Polym. Sci., Part A: Poly. Chem.*, 42, 5200–5214.
23. Shiratori, S.S. and Rubner, M.F. (2000) *Macromolecules*, 33, 4213–4219.
24. Arys, X., Laschewsky, A. and Jonas, A.M. (2001) *Macromolecules,* 34, 3318–3330.
25. Shi, X,. Shen, M. and Moehwald, H. (2004) *Prog. Polym. Sci.*, 29, 987–1019.
26. Dubas, S.T. and Schlenoff, J.B. (1999) *Macromolecules*, 32, 8153–8160.
27. Schonhoff, M. (2003) *Curr. Opin. Coll. Inter. Sci.*, 8, 86–95.
28. Ahmad, N.M., Lu, X. and Barrett, C.J. (2010) *J. Mater. Chem.,* 20, 244–247.
29. Ahmad, N.M., Saqib, M. and Barrett, C.J. (2010) *J. Mac. Sci., Part A: Pure and Appl. Chem.* 47(2), 106–118.
30. Ahmad, N.M., Saqib, M. and Barrett, C.J. (2010) *J. Mac. Sci., Part A: Pure and Appl. Chem.*, 47. Accepted.
31. Advincula, R.C."Polelectrolytes layer-by-layer Self-Assembled Muliayers Containing azobenzene Dyes", in: *Handbook of Polyelectrolytes and their Applications*, Vol. 1, Tripathy, S.K., Kumar, J.,and Nalwa, H.S., Eds., Amercian Scientific Publishers: Los Angeles, p. 65–97, 2002.
32. Sekkat, Z. and Knoll, W. "Photoisomerization and photo-orientation of azo dye in films of polymer: molecular interaction, free volume, and polymer structural effects", In *Photoreactive Organic Thin*

Films, Sekkat, Z., Knoll, W., Eds. Academic Press: San Diego, Calif., p. 107–143, 2002.
33. Hafiz, H.R. and Nakanishi, F. (2002) *Int. J. Polym. Mat.*, 51, 955–966.
34. Kasha, M., Rawls, H.R. and El-Bayoumi, M.A. (1995) *Pure Appl. Chem.,* 11, 371–392.
35. Sato, T., Ozaki, Y. and Iriyama, K. (1994) *Langmuir*, 10, 2363–2369.
36. Advincula, R.C., Fells, E. and Park, M-K. (2001) *Chem. Mater.*, 13, 2870–2878.
37. Labarthet, F.L., Freiberg, S., Pellerin, C., Pezolet, M., Natansohn, A. and Rochon. P. (2000) *Macromolecules*, 33, 6815–6823.
38. Decher, G., Ivov, Y. and Schmitt, J. (1994) *Thin Solid Films*, 244, 772–777.
39. Lösche, M., Schmitt, J., Decher, G., Bouwman, W.G. and Kjaer, K. (1998) *Macromolecules,* 31, 8893–8906.
40. Dobrynin, A.V. and Rubinstein, M. (2005) *Prog.Polym. Sci.*, 30, 1049–1118.
41. Laschewsky, A., Mallwitz, F., Baussard, J.-F., Cochin, D., Fischer, P., Habib-Jiwan, J.L. and Wischerhoff, E. (2004) *Macrom. Symp.*, 211, 135–156.
42. Morishima, Y., Kobayashi, T. and Nozakura, S. (1989) *Polym. J.*, 21, 267–274.