Molecularly Ordered Low Molecular Weight Azobenzene Dyes and Polycation Alternate Multilayer Films: Aggregation, Layer Order, and Photoalignment

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Received February 2, 2001. Revised Manuscript Received June 25, 2001

Although the incorporation of small-molecule azobenzene dyes in polymer thin films has been investigated in the past, the application of the layer-by-layer adsorption technique has enabled incorporation of molecularly ordered dye layers without applying the Langmuir−Blodgett methodology. A problem with small-molecule dyes is their tendency to aggregate and even phase separate in polymer matrixes. With the alternate layer-by-layer technique, we have found that the aggregation properties of a charged chromophore are self-limiting and are promoted by adsorption to oppositely charged surfaces. The molecular assembly process of the dye−polycation pairs was investigated by a number of surface-sensitive spectroscopic and microscopic techniques. Comparison of the layer thickness with the molecular dimensions of the dyes suggests the formation of well-packed monomolecular layers depending on the size, spatial orientation, and aggregation limit of each pair. The polycation charge density and salt concentration play an important role in influencing aggregation both before and after adsorption to surfaces. Initial studies with the dye Direct Red 80 showed interesting photoalignment properties with linearly polarized UV−vis light. This method allows the preparation of functional ultrathin films of small-molecule azobenzene dyes for various optical applications.

Introduction

Recently, there has been great interest in molecularly organized ultrathin films prepared by the alternate layer-by-layer adsorption of linear polyions or electrostatic self-assembly (ESA).[1] Decher and co-workers extended the pioneering work of Iler et al.[2] by first reporting the assembly of bolaform amphiphiles.[3] Alternate adsorption of a polycation and a polyanion is readily achieved by overcompensation of polyelectrolytes adsorbing on oppositely charged surfaces. This technique has several advantages compared to the Langmuir−Blodgett method[4] for preparing ultrathin films. In general, it is a simpler technique involving simple equipment and procedures and has the capacity to prepare ultrathin layers. A large variety of water-soluble macroions or polyions can be used. The individual layers or pair layers can have distinct molecular thicknesses. And last, any charged surface can be employed and reversed by charge compensation. Many polymeric materials from biopolymers such as proteins to inorganic macromolecules such as clay have been assembled and investigated using this technique.[5] Surfaces of other geometries and colloidal particles have been coated with alternate layers of polyelectrolytes.[6] By applying the alternate assembly to low molecular weight species (dyes, amphiphiles, nanoparticles, etc.), this method is expected to become even more versatile as a means of preparing organized ultrathin films.

Recently Kunitake and co-workers have shown that low molecular weight chromophoric dyes are also capable of spontaneous assembly in aqueous solutions, where suitable charged surfaces are formed on the substrate.[7] Cooper and others demonstrated that anionic Congo Red and copper phthalocyanine tetrasulfonic acid dyes could be assembled with a cationic polymer.[8] Rubner has demonstrated small-molecule dye-to-dye assemblies of oppositely charged pairs.[9] Others have also reported dye-containing layer-by-layer assemblies for various potential optical and sensor applications.[10] It is therefore important to examine in detail the behavior of charged small-molecule dyes as components for alternate assembly. In particular, it is important to correlate the dimension, charge density, solubility, nature of aggregation, etc. of these molecular

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10.1021/cm0101172 CCC: $20.00

species on a class basis. For example, bolaamphiphiles tend to aggregate in solution,[11] yet they have been found to assemble as molecular layers in combination with oppositely charged polyions.[12,23]

Small-molecule azobenzene dyes have long been used as colorants, stains, and markers.[13] Their potential as optical materials has been widely investigated.[14] For practical reasons, spin-coated blend films have been widely used to prepare films for investigating their optical properties.[15] Understanding the aggregation and phase behavior of dyes in these blend films can be complicated but is important for proper interpretation of optical behavior. With the possibility of control at the molecular level, the utility of the layer-by-layer technique to incorporate azobenzene dyes with functional polymer films is expected to gain importance.[16] The main advantage of the layer-by-layer method over spin-coated systems is that the concentration and the layer order of the dye aggregates can be well characterized prior to optical studies. It is important to distinguish the aggregation nature of this class of small molecules during the adsorption from solution and as layers on a flat substrate. Thus, the technique opens the way for the use of polyelectrolytes as a class of polymers for ultrathin film preparation, with material combinations not possible for spin-coating.[1]

In this study, we have examined the alternate multilayer adsorption of charged azobenzene dye molecules with polycations.[17] The low molecular weight chromophoric azobenzene dye derivatives were chosen to have sufficient charge density to allow charge compensation for the adsorption of polycations. Two types of polycations were used mainly on the basis of charge density and the effect of pH. The molecular assembly process of the polyion−dye pairs was investigated by a number of surface-sensitive techniques including ellipsometry, atomic force microscopy (AFM), and UV−vis spectroscopy.[18] Initial studies were made on the photoalignment properties of the Direct Red 80 (DR80)−polycation pairs, which were found to have high anisotropies after irradiation with linearly polarized UV light.[19] The incorporation of a photochromic moiety using this technique is very attractive due to the possibility of creating new light-sensitive optical materials and devices from these films.[10,14]

Experimental Section

Materials. The anionic (sulfonated) azobenzene dyes used for these experiments include the following: Direct Red 80 (DR80) or Sirius Red, MW = 1373.09, λ_{max} = 528 nm; Direct Blue 71 (DB), MW = 1029.98, λ_{max} = 582 nm; Acid Blue 113 (AB), MW = 681.66, λ_{max} = 561 nm; Chicago Sky Blue (CSB) or Direct Blue 1, MW = 992.82, λ_{max}= 618 nm; Direct Yellow 50 (DY), MW = 956.83, λ_{max}= 394 nm. These azo dyes were all obtained from Aldrich Chemicals and handled using proper safety procedures.[20] Purification of the dyes involved recrystallization using solvent mixtures (typically with DMF and ethanol), followed by extensive cold solvent washing. Purity was followed by thin-layer chromatography. The chemical structures of the dyes are shown in Figure 1. A representative molecular dimension of the dyes is given for the dimension of DR 80 (using Chem 3D molecular modeling software), 3.4 nm × 0.8 nm, assuming an all-trans configuration. The cationic polymers used are as follows: poly(diallyldimethylammonium chloride) (PDADMAC; MW = 100000), poly(allylamine hydrochloride) (PAH; MW = 50000−65000), poly(sodium 4-styrenesulfonate) (PSS; MW = 70000). All were commercially available from Aldrich and used without further purification. Filtered aqueous solutions (Milli-Q water with 18.2 MΩ resistivity) of the dyes and polymers were prepared with a concentration of 0.001 or 0.001 M per repeat unit. The pH for the dipping solutions was maintained at pH 6.5, with the polyions (except for PAH) and the dyes expected to be strongly charged even at this pH. The pH for the PAH:dye complex solutions was adjusted with HCl and NaOH. For surface functionalization of the flat substrates, we used a self-assembled monolayer (SAM)[21] procedure with (3-aminopropyl)-triethoxysilane (Aldrich, 0.1% in acetone) for the silicon wafer and glass substrates. The quality of deposition for thicker films can be improved by the initial deposition of five pair layers of PAH and PSS polyelectrolytes.

Layer-by-Layer Deposition. The layer-by-layer adsorption of the polyanion and polycation species was done following the Decher approach.[3] The glass slides (25 mm × 40 mm × 0.5 mm) were used as substrates for UV−vis spectroscopy, while silicon wafers were used for ellipsometry. The substrates were cleaned using previously reported preliminary washing and Piranha solution treatment and were functionalized immediately by a SAM.[21] The automated polyion deposition was carried out using a HMS series programmable slide stainer apparatus (Carl Zeiss, Inc.). In general, the sequence involved alternating between oppositely charged solutions of the dye or polymer and the substrate surface. The immersion time in each solution was 15 min and was sufficient for charge overcompensation (or reversal),[16,18,22] followed by 2 min of immersion in deionized water and then 1 min in a bath with flowing deionized water. The rinsing solutions were changed after the deposition of every five pair layers. This cycle was repeated until the desired number of pair layers was obtained. Using this procedure, for example, up to 50 pair layers were deposited for the DR 80 dye with PDADMAC.

Measurements. UV−vis spectra were obtained using a Perkin-Elmer Lambda 20 spectrophotometer equipped with a polarized spectroscopy setup at the UV and visible regions. Null ellipsometric thickness measurement was performed using the Multiskop (Optrel, Germany) ellipsometer with a 632.8 nm He−Ne laser beam at 70° incidence as the light source. Both δ and ψ values and thickness data were measured and calculated with an assumed refractive index of 1.54.[23] Thickness values of 3 points on each sample were measured and averaged as the final result. Atomic force microscopy (AFM) of the sample surface morphology was obtained in air by using a PicoScan system (Molecular Imaging, Arizona)

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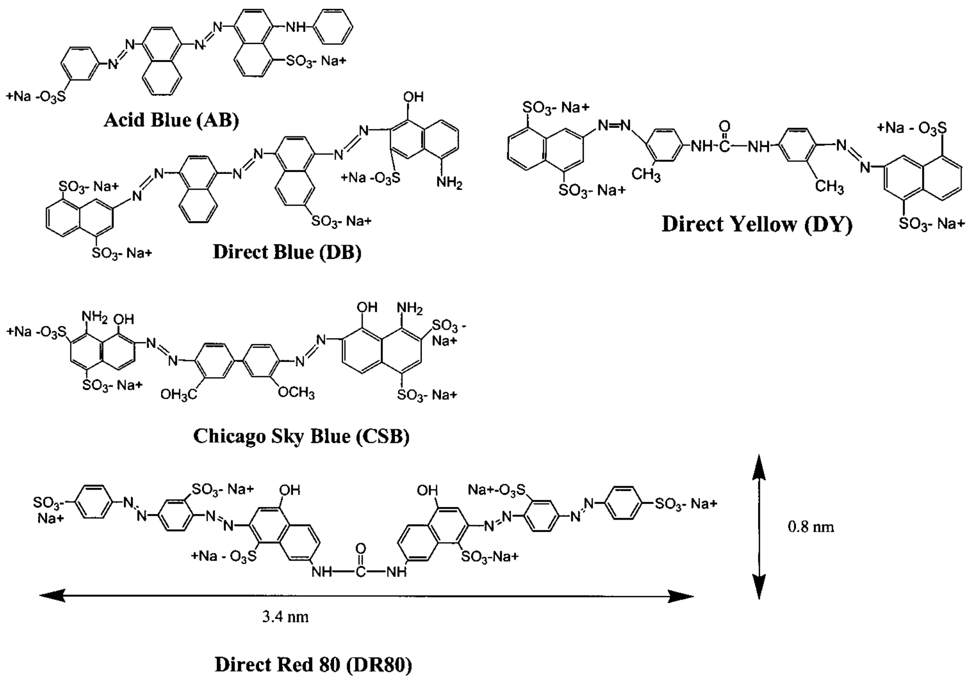

Dye	Length (nm)	Width (nm)
Direct Red 80 (DR80)	3.4	0.8
Direct Yellow (DY)	2.3	0.5
Acid Blue (AB)	1.8	0.8
Direct Blue (DB)	2.4	0.8
Chicago Sky Blue (CSB)	2.0	0.5

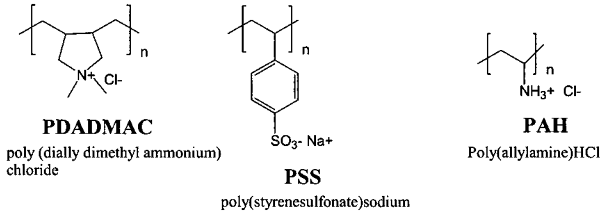

Figure 1. Chemical structures of the anionic azobenzene dyes and the cationic polymers. The dimensions were determined by Chem-3D software and assume an all-trans configuration.

equipped with an 8 × 8 μm scanner. The magnetic AC (MAC) mode was used for all the AFM images. A MAC lever, a silicon nitride based cantilever coated with a magnetic film, was used as the AFM tip. The force constant of the tip was 0.5 N/m, and the resonance frequency was around 100 kHz. All samples were measured inside a suspension chamber to minimize ambient disturbance.

For the photoalignment procedure, the film was irradiated for a period of 3600 s with a 150 W Hg lamp (Oriel Corp.) with a band-pass filter (350 nm) for UV light or a color filter (>430 nm) for visible light. The distance from the lamp was kept at 10 cm. The polarizer was placed between the sample substrate and the filter and set initially at the $\theta = 0°$ phase for the parallel orientation of the irradiated light. The dichroic ratio, DR, is defined as the absorbance ratio of the perpendicular, $A_{90°}$, and parallel, $A_{0°}$, absorbances, DR = $A_{90°}/A_{0°}$, by polarized UV–vis spectroscopy.

Results and Discussion

Layer-by-Layer Adsorption Followed by UV–Vis Spectroscopy. UV–vis spectroscopy was primarily used to investigate the assembly process of the dye layers and aggregation phenomena.[16,23] UV–vis spectra for the different dye–polymer PDADMAC pairs are shown in Figure 2. In all cases the absorbance increased linearly in proportion to the number of dye–polymer pair layers. This means that the charge overcompensation (reversal) during adsorption was sufficient to proceed with each subsequent deposition. The films were clear, transparent, and uniform with good optical quality as seen by the naked eye. The λ_{max} values attributed mostly to the π–π* transition for the dye–polycation pairs are given in Table 1. The highest absorption/layer number value was observed with the DR80 dye (Table 3). The molecular structure of the dye as shown in Figure 1 shows that DR80 has four azobenzene groups per molecule, DB has three, and CSB, AB, and DY have two. Thus, the number of absorbing azobenzene groups and conjugation length seemed to be consistent with the highest molar absorptivity, ϵ_{max}, being observed with DB followed by DR80, those of CSB and AB roughly being comparable, and that of DY being the least. Typical values for azobenzene in isooctane are $\epsilon_{max} = 22600$ and $\lambda_{max} = 318$ nm for a trans configuration.[24] The DR80 dye pair was also

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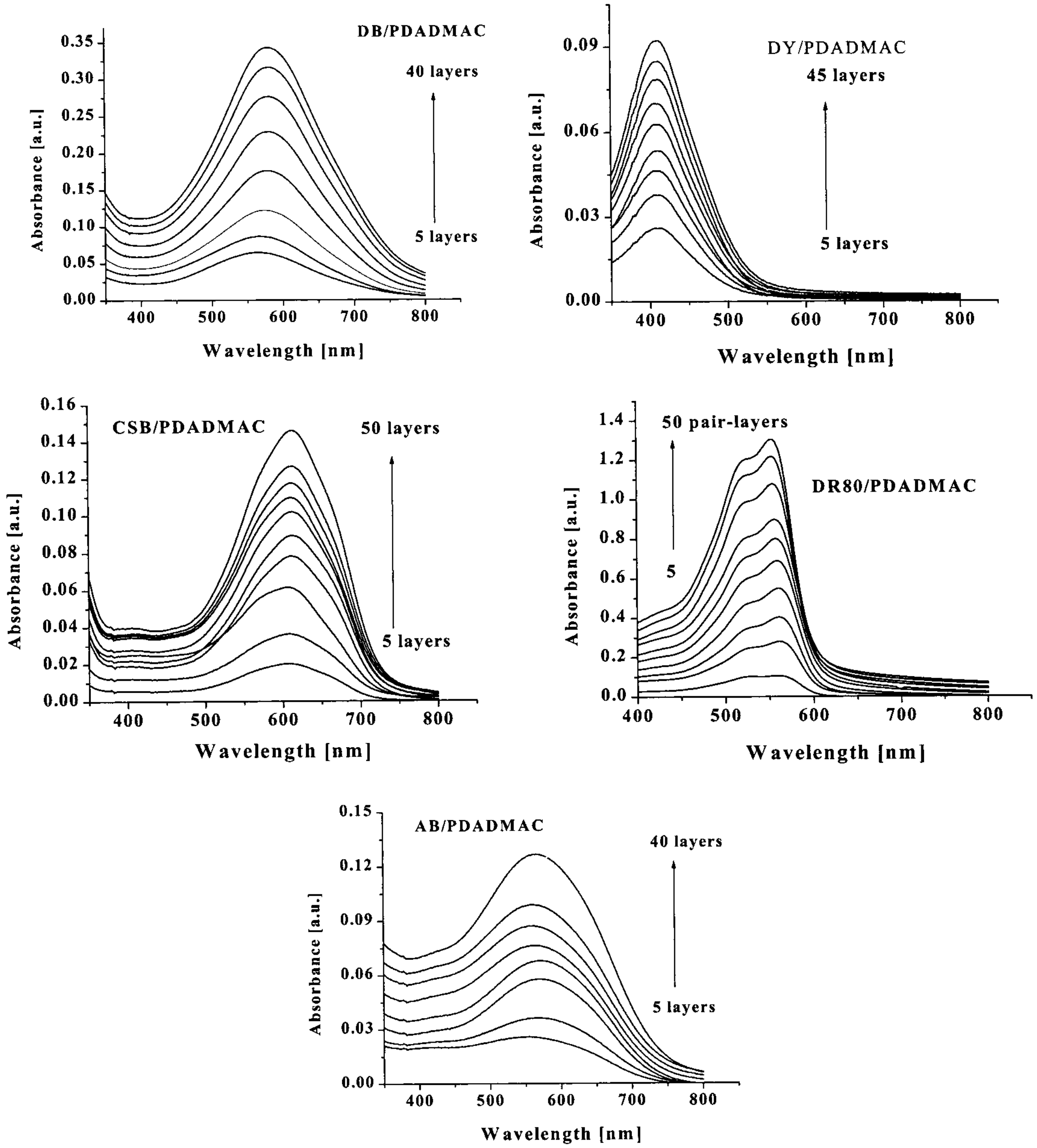

Figure 2. UV–vis spectra of the films as a function of layer number. The absorbance is observed to increase linearly with increasing layer number. Polarized spectroscopy did not show any dichroic behavior on the as-deposited films.

Table 1. Summary of Optical Properties of the Dye–Polycation Pairs

dye	aq soln (10^{-5} M), λ_{max} (nm)	calcd ϵ_{max} (M^{-1} cm^{-1})	$\Delta\lambda_{max}$[a] (nm)	film at 40 pair layers with PDADMAC, λ_{max} (nm)/A (au)
DR80	528	42000	34 (red)	562/1.3
DB	582	48000	2 (blue)	580/0.35
CSB	618	36000	8 (blue)	610/0.15
DY	398	28000	14 (red)	408/0.095
AB	561	40000	3 (red)	564/0.13

[a] $\Delta\lambda_{max}$ (nm) is the difference between the absorption λ_{max} of the solution and that of the thin films of the dye.

strongly red-shifted in absorbance compared to their solution spectra as shown in Table 1 to as much as 34 nm compared to the aqueous 1 × 10^{-5} M solution without PDADMAC and 38 nm with PDADMAC (Table 2). The aggregation of dye molecules in an ordered structure (with corresponding dipoles) results in a splitting of the excitation energy levels.[14b,16] As a consequence, shifts in the absorption spectra are observed, depending on the mutual orientation of the interacting dipole moments.[11b] When the dipole moments are parallel, a hypsochromic (blue) shift occurs (H band). If the transition dipoles are in-line, rather than parallel, the spectra exhibit a bathochromic (red) shift and the aggregates are termed J-aggregates (J-band). As molecular layers, the red-shift behavior for DR80 primarily suggests the formation of J-aggregates where the orientation of the dye aggregates can be described as tilted.[7] DY and AB are red-shifted and DB and CSB slightly blue-shifted. The red shift with DY is also significant, and further studies are needed for comparison with DR80. However, for AB, DB, and CSB, these values are within the deviation observed with different layer thicknesses and are not deemed significant in determining a particular aggregation trend.[16] Comparison of the λ_{max} values with an increasing number of layers reveals that the shift in value occurs intermittently as shown in Figure 3. This reveals that the degree of aggregation tends to shift with thickness, and is perhaps influenced by the packing order achieved

Table 2. Comparison of Values for the Different Dye−PAH Combinations as a Function of pH

dye	aq soln (10^{-5} M), $\lambda_{\max}$ (nm)	with 1:1 PDADMAC, $\lambda_{\max}$ (nm)	pH 2, $\lambda_{\max}$ (nm)	pH 4, $\lambda_{\max}$ (nm)	pH 6, $\lambda_{\max}$ (nm)	pH 8, $\lambda_{\max}$ (nm)	pH 10, $\lambda_{\max}$ (nm)	pH 12, $\lambda_{\max}$ (nm)
DR80	528	524	520	524	518	516	580	540
DB	582	585	562	550	550	546	551	580
CSB	618	612	611	610	612	612	585	593
DY	398	406	416	406	403	410	403	397
AB	561	553	547	543	533	530	553	560

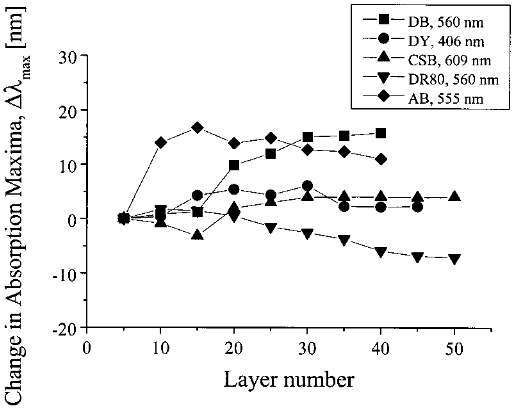

Figure 3. $\lambda_{\max}$ change vs layer number for each of the dye−polymer pairs with respect to the first five layers. The $\lambda_{\max}$ values of the first five layers are indicated for each dye. The absorbance of the films was generally red-shifted compared to that of solution.

Table 3. Summary of Ellipsometric Thickness Data

dye	av thickness/ pair layer (nm)	av absorbance /pair layer (au)	av absorbance /thickness (au/nm)
DR80	1.91	0.032	0.017
DB	1.17	0.008	0.007
CSB	0.92	0.004	0.006
DY	0.90	0.002	0.003
AB	0.86	0.003	0.004

after the addition of each layer. These trends were not reproducible and varied from film to film, but the degree of deviation was consistent. For example, this type of behavior was recently observed in layer-by-layer films of poly{1−4-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl sodium salt} or PAZO with polyethylene imine (PEI), where a weak red shift was observed in the first part of the deposition followed by a blue shift as the number of pair layers increased.[16] This is at best attributed to a shifting packing arrangement or reorganization with increasing layer thickness consistent with a self-healing capacity of these types of films.[1] Another trend worth noting is that the total absorbance per pair layer is much higher with DR80 compared to the other dye pairs (also Table 3). Nevertheless, the magnitude of the red shift with DR80 is significant in terms of its aggregation properties correlated with the measured thickness by ellipsometry. Previous studies with other azobenzene dyes, Congo Red (CR)[7] and PAZO,[16] with PDADMAC pair layers also revealed a red shift but not to the degree observed with DR80.

A previous investigation by Kunitake et al. showed that the shape of the spectra can be influenced by aggregation on the outermost layer, i.e., dye or polycation.[7] This was demonstrated on films where protonation on a tetraphenylphorphyrinesulfonic acid (TPPS) indicated aggregation and influenced peak ratios at 439 and 488 nm. In our case, no peak shift was observed even when the dyes were deposited as the last layer. The spectra observed are consistent with the behavior of previously investigated azobenzene−polymer pairs such as CR and Ponceau S, which are similar in structure.[7] The behavior of these charged azobenzene molecular dyes is in contrast though to the aggregation of charged bolaform azobenzene amphiphiles.[25] As previously studied by Hong et al., bolaform azobenzene dyes have a tendency to form strong H-aggregates in solution and adsorb as aggregates with little spectral change.[23]

Dye Aggregation Behavior in Polycation Solutions. To investigate further the aggregation phenomena of these dyes with polycations, comparisons of the UV−vis spectra of the films with the spectra of various polyelectrolyte complex solutions were made. These polyelectrolyte complexes (PECs) demonstrate the effect of electrostatic charge interaction between polymer and dye aggregation in solution.[26] The aqueous solution spectra of the dyes with PDADMAC showed little difference in shape compared to their individual dye solutions. Some were red- or blue-shifted up to 8 nm at the most (Table 2). Since PDADMAC has a uniform charge density from the ammonium group independent of pH, the character of the PEC behavior must be predominantly influenced by the conformation of the polymer.[26,31d] To investigate further the dye aggregation behavior with the charge density of the polycation, we measured the change in $\lambda_{\max}$ values with dilute 1:1 solutions (1×10^{-5} M) of the polymer−dye combinations with PAH at various pH values. PAH has amine groups that can be selectively protonated to increase or decrease the cationic charge with pH. The values are summarized for the PAH dye combinations in Table 2. No isosbestic points were observed on the overlay spectra of the dye−PAH pairs at different pH values. By comparing the large shift in $\lambda_{\max}$ values between Tables 1 and 2, it is clear that aggregation in solution is influenced primarily by charge pairing in solution during PEC formation.[27] For example, at a lower pH where more amine groups are protonated, AB, DB, and DR80 are strongly blue-shifted, indicating the formation of strong H-aggregates in solution. At higher pH (unprotonated), DR80 becomes red-shifted. No clear explanation can be given to this behavior at present. In general, complexation in solution is primarily driven by entropy, accompanied by liberation of undissociated low molar mass counterions (ion exchange).[27] The higher energy excitonic interaction of the chromophores indicates that the cationic complexation with the polymers

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forces the dyes to aggregate where greater π-stacking is achieved in the case of a blue shift.[11b,23] Only DY, which is similar in charge density and molecular dimension with the CSB dye, showed a slight red shift with polycation complexation. Previous investigations on azobenzene dye (with sulfonate groups) aggregation with cationic amphiphiles and polymers at low concentrations have shown the cooperative effect of complexation with oppositely charged molecules.[26b] It was proposed that a more favorable hydrophobic binding site is created during complexation, promoting further adsorption of more dye molecules, resulting in H-aggregation.[26b] The aggregation behavior at higher concentrations, ionic strengths, and temperature was not investigated, and the possibility of observing lyotropic liquid crystalline behavior cannot be precluded.[26b]

Salt Effect on Aggregation and Adsorption. Studying the effects of salt and aggregation determines the role of secondary valence charges on polyelectrolytes.[28] With bolaform amphiphiles, addition of salts usually results in increased H-aggregation behavior, which aids in adsorption to oppositely charged surfaces.[11,23] An increase in charge density on the adsorbing species would favor thinner adsorption layers, whereas increasing charge density at the surface would favor thicker adsorbed layers.[29] For the low molecular weight azobenzene dyes it is important to determine the effect of salt concentration with aggregation and in promoting adsorption to the oppositely charged surface. It is important to know whether there is a gain in entropy or enthalpy by aggregation prior to adsorption.[1,29]

The salt effects on the DR80 dye–polymer pair were investigated. The results showed that high salt concentrations tend to promote aggregation in solution, which in turn promotes adsorption of the aggregates to surfaces.[23,30] Thicker layers can be deposited from solutions having a higher salt concentration. This was demonstrated for the DR80–PDADMAC pair where the absorbance and thickness were measured with different salt concentrations as shown in Figure 4. The aggregation limit was easily reached even with 0.515 M salt concentration, showing higher absorption intensities and thickness compared to films without salt. Unlike the effect of polycation complexation, the addition of salt resulted in a red shift for DR80 in solution. This indicates that salts tend to cause aggregation for DR80 by charge screening in solution, leading to lower energy excitonic interaction between dye molecules. This behavior is very different from that of azobenzene bolaform amphiphiles.[23] Clearly, further investigations are needed to understand the salt effect on the other dyes and to categorize a particular behavior with these classes of azobenzene dyes as a whole.

Ellipsometry Thickness Measurements. The optical thickness data reveal a linear type of deposition trend with these dye–polymer combinations consistent with the UV–vis absorbance linear increase. A plot of thickness as a function of layer number is shown in Figure 5. The thickness/layer increase was highest for the DR80–PDADMAC pair and the least for the DY–PDADMAC pair. The individual PDADMAC layer was determined as 0.7 nm on the basis of previous measurements and average values for PSS–PDADMAC pair layers.[31c]

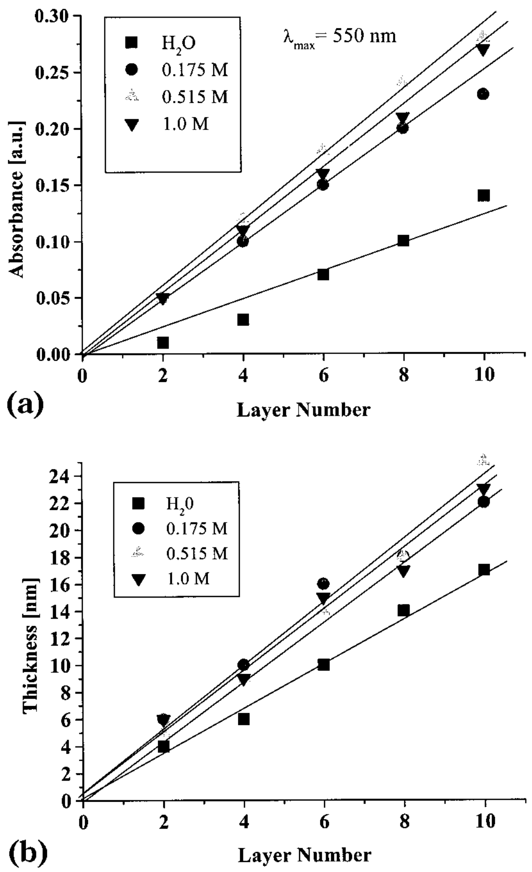

Figure 4. Salt concentration effect on DR80–PDADMAC pairs: (a) absorbance with layer number 2–10 pair layers; (b) thickness with increasing layer number. Linear correlation was done with the least-squares method.

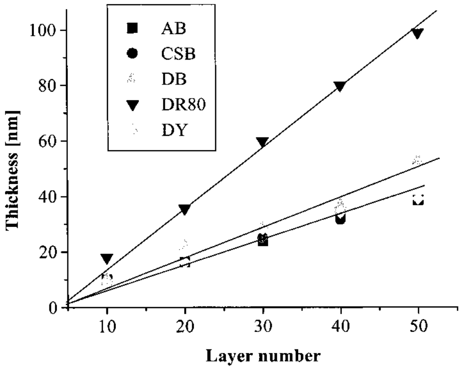

Figure 5. Thickness (nm) with increasing layer number for each of the azobenzene dye–polycation pairs. The ellipsometric thickness for each pair layer pair is consistent with linear growth. Linear correlation was done with the least-squares method.

The measured average thickness for the DR80 pair layer, 19.1 Å, is smaller than the long axis of the

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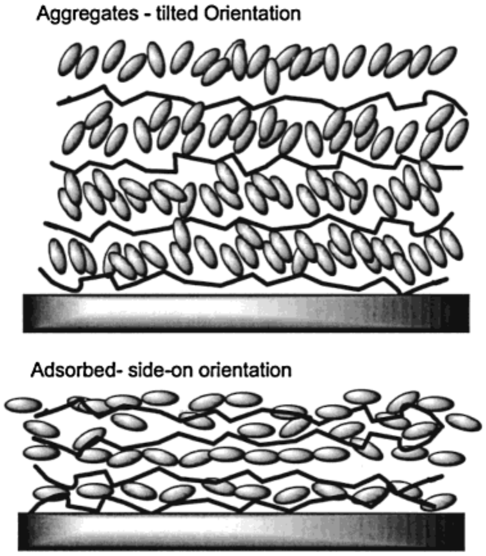


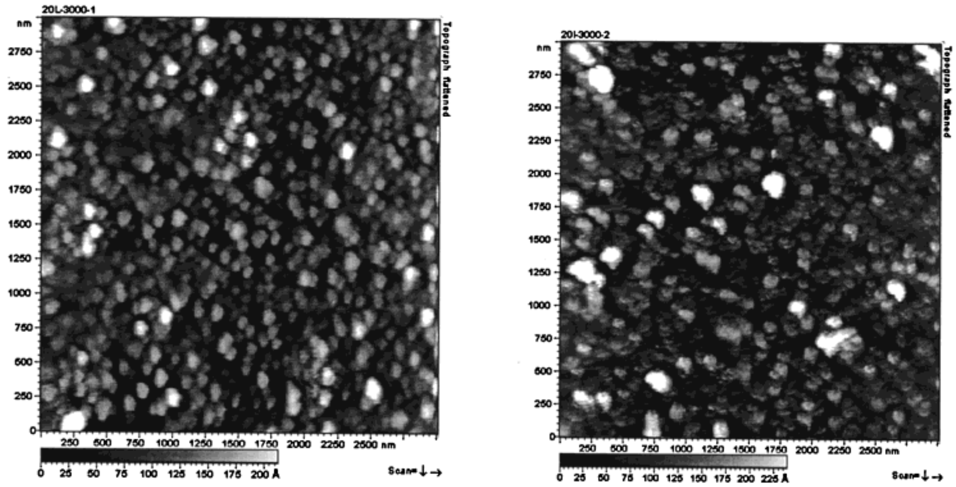
Figure 6. A schematic diagram showing the different orientations of dyes and their aggregates. A tilted J-aggregation behavior is expected for the DR80 domains, whereas the rest of the dyes are expected to have a side-on orientation leading to thinner pair layers.

extended molecule (34 Å) and the thickness of the PDADMAC layer (7 Å) combined,[7] but is larger than the short axis (8 Å) plus the thickness of the PDADMAC layer (7 Å), 15 Å, in a fully extended conformation, i.e., the trans isomer. The red shift in UV−vis spectra suggests that the DR80 molecules formed domains with significant J-aggregates (Figure 6). These thickness data if averaged over a flat surface are compatible with a tilted aggregation of the molecules in a regularly packed layer where molecules are closer to the plane of the substrate rather than the normal.[7] The combined thickness of the CSB−PDADMAC pair layer ($20 + 7 = 27$ Å) where CSB is normal to the surface is large compared to the measured average thickness of the pair layer. However, by assuming a side-on (parallel) orientation ($5 + 7 = 12$ Å), the measured average thickness is reasonable. The observed average thickness of 9 Å (see Figures 1 and 6) can also be a consequence of undulations in the polymer layers.[31] These dyes are essentially complexed together with the polymer layers in a side-on orientation without aggregation.[28] The fact that very low absorbance/ layer values were observed with CSB, DY, and AB compared to DR80 confirms the much thinner layer and smaller dye concentrations per layer. For the DB dye pair layer, the slightly higher optical density can be attributed to its higher molar absorptivity, but the measured thickness is more consistent with a side-on orientation, similar to the other dyes (Figure 6). In all these dyes, we assume that the maximal pairing of the sulfonate groups with the preceding cationic surface is favored, i.e., satisfies the mechanism of the alternate adsorption.[29,30] The dye molecules may not fully cover all the polymer surface during adsorption, but the fact that a linear growth was observed indicates that a favorable charge reversal occurs sufficient for the next oppositely charged polycation to adsorb.[29,30] It is necessary however to do ζ-potential or streaming potential measurements to determine exactly the extent of charge reversal.[29b] The intermittent change in absorbance shift with thickness (blue or red shift of the $\lambda_{\max}$) as shown in Figure 3 seems to verify that a reorganization or self-healing of the films occurs as the deposition progresses. Experiments using X-ray reflectivity and surface plasmon spectroscopy are important to confirm the observed pair layer thickness and layer roughness and will be reported in the future.[18] With ellipsometry it is possible to obtain an average pair layer thickness value although the surface may actually be rough.

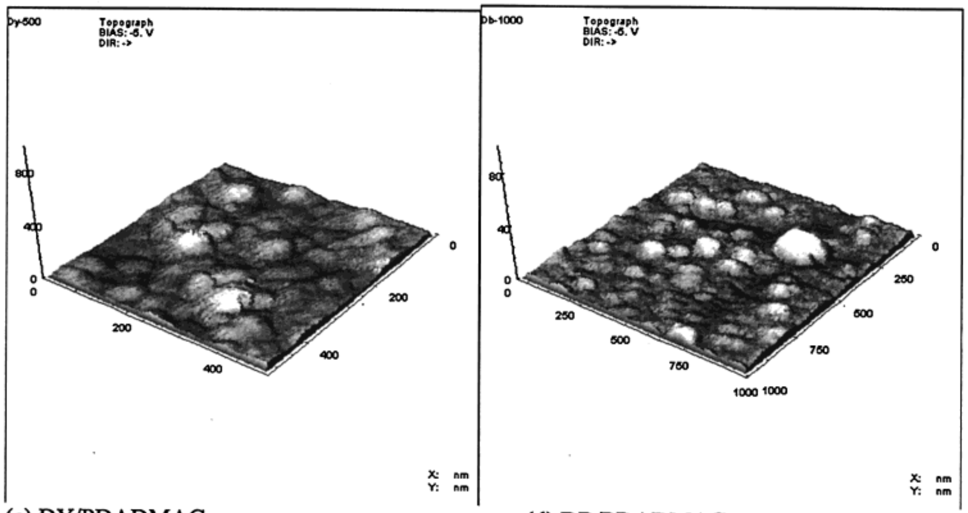
AFM Images of the Films. The morphology of the 40 pair layer dye−PDADMAC films was observed by AFM with the dyes deposited as the last layer (Figure 7). Further analysis was made on the different morphologies with different layer numbers and polymer pairs but was not included for brevity.[18] Clearly the surface topography shows a nonsmooth but homogeneous film with the round-shaped domains varying in size with thicker layers. The films are amorphous and suggest an isotropic growth showing no preferred orientation. No transition was observed from globular domains to lamellae (microcrystallinity) with increasing layer thickness. In general, the roughness increases with increasing number of layers. Roughness was determined from the histogram as rms 2−5 nm for thicker layers (40 pair layers) and 1−3 nm for thinner films (10 pair layers). The difference is largely due to the presence of larger and more irregular patches with thicker layers broadening the size histogram. The average thickness measured by ellipsometry does not distinguish this surface roughness but rather is an average value of the incident light and is therefore insensitive to roughness as observed by AFM.

The morphology of the dye−polycation films except for those with DR80 can be characterized as being dominated by the globular morphology of the polymer PDADMAC.[31d] The size of these globular domains varies between 150 and 250 nm in diameter. The films are generally homogeneous over large areas, e.g., several micrometers square, and are pinhole free. The DR80 morphology is very different from that of the rest of the dyes, exhibiting much larger domain sizes with clearly defined grain boundaries. This seems consistent with the observed aggregation phenomena of these films where the observed morphology is dominated by the dye aggregates.[25] The domain sizes are on the order of 500−800 nm in diameter and are uniformly distributed on the surface. It is unknown whether the aggregates within the domains exhibit anisotropic orientations. We believe though that the aggregation behavior within these domains is key to the interesting photoalignment behavior observed with DR80. In general, layer-by-layer films are isotropic and are not influenced by the deposition direction unlike LB films.[4]

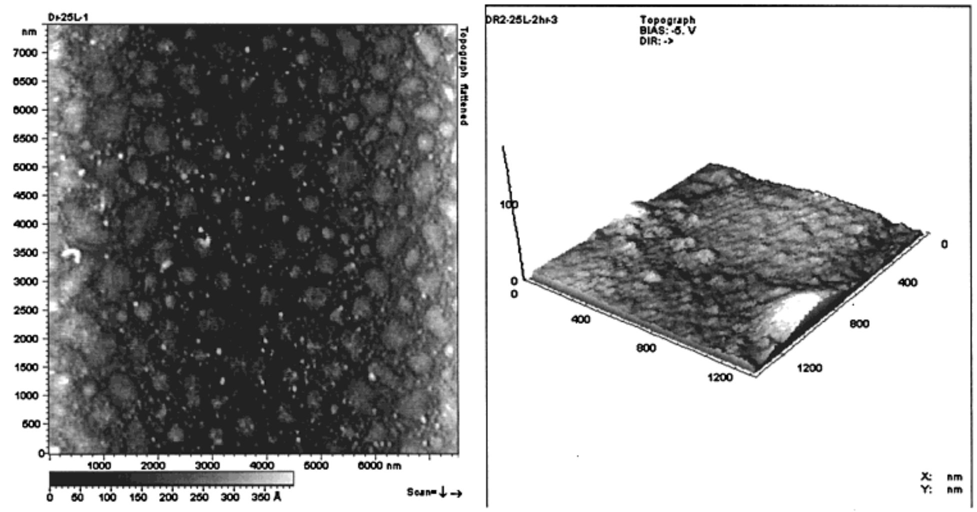
Photoisomerization Studies. Excitation by linearly polarized UV light causes azobenzene-doped films to undergo an anisotropic photoisomerization. The different dye−polymer pair layers were initially investigated for their photoalignment behavior. Only the DR80 showed enough photoalignment behavior to warrant initial studies in correlation with its unique aggregation behavior. Further studies are being done with the other dyes. We found that the azobenzene DR80 can be selectively excited with linearly polarized UV light to



(a) AB/PDADMAC (b) CSB/PDADMAC



(c) DY/PDADMAC (d) DB/PDADMAC



(e) DR80/PDADMAC (f) DR80/PDADMAC

Figure 7. Morphology of the dye−polycation layers: (a) AB−PDADMAC, 40 pair layers (b) CSB−PDADMAC, 50 pair layers, (c) DY−PDADMAC, 45 pair layers (d) DB−PDADMAC, 40 pair layers, (e) DR80−PDADMAC, 50 pair layers, (f) DR80−PDADMAC, 50 pair layers. The morphology of all the dye−PDADMAC pairs except for those with DR80 is predominantly globular and is attributed to PDADMAC. The roughness is rms 2−5 nm for thicker layers (40 pair layers) and 1−3 nm for thinner films (10 pair layers). DR80 has domains from 500 to 800 nm in diameter with clear grain boundaries. The dyes are isotropically distributed aggregates within these domains.

give high anisotropy in these films. Previous investigation by Tieke et al.[12] and Hong et al.[23] have shown the possibility of photoisomerization of bolaform amphiphilic azobenzene dyes prepared using the layer-by-layer

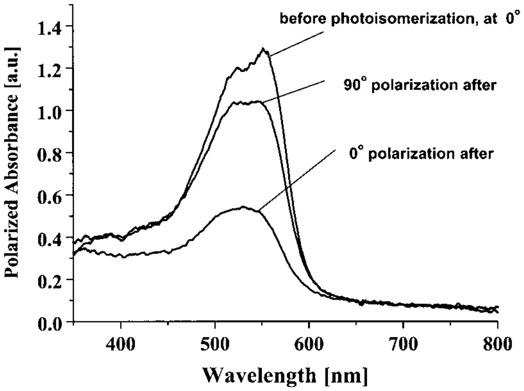


Figure 8. Polarized UV−vis spectra of the DR80−PDADMAC with 50 pair layers after selectively polarized photoisomerization with visible light >430 nm. The plot shows the spectra before photoalignment, and after photoalignment at $\phi = 0°$ (parallel) and $\phi = 90°$ (perpendicular) with respect to the polarizer. DR = $A_{90°}/A_{0°}$ was calculated as 2.

method.[32] This dichroism was demonstrated by Hong et al. on bolaform azobenzene amphiphiles deposited with different salt concentrations.[23] A *Z*-form-rich photostationary state can be expected for the $\pi-\pi^*$ transition, and the *E*-form is expected as a major component upon exposure to visible light for the $n-\pi^*$ transition.[32] This means that no decay of the photoalignment can be realized with the azobenzenes if subjected only to visible light irradiation for the $n-\pi^*$ transition. Using this principle, it is possible to selectively irradiate the films where the *E*-isomer photostationary states are enhanced.[33]

Initially, the DR80−PDADMAC ultrathin film was irradiated with visible polarized light (initial $\theta = 0°$ phase set arbitrarily) normal to the substrate plane. A high dichroism was observed with a DR = 2 (Figure 8) between the parallel, $\phi = 0°$, and perpendicular, $\phi = 90°$, polarizations by absorption spectroscopy. The intensity of the of the UV−vis spectra perpendicular, $\phi = 90°$, to the polarization of the irradiated light, $\theta = 0°$, was higher. This indicated that the dye long axis oriented predominantly perpendicular with respect to the polarization, θ, of incident actinic light. The change in anisotropy occurred after 45 min of irradiation time using the current setup. Thus, irradiation of the film with visible linearly polarized light >430 nm as a function of time resulted in an in-plane reorientation of the dye molecules to afford anisotropic alignment. The fact that DR80 formed J-aggregates within the domains is believed to be responsible to the high in-plane dichroism observed with linear photoisomerization. Our initial studies with UV light irradiation did not show significant trans−cis photoisomerization within the observable time frame.[16,19] Further investigations will be made on the photoisomerization process and the factors affecting the anisotropy of these films. The fact that a unique behavior exists for the DR80−PDADMAC pair layers compared to other dyes suggests that the aggregation and domain formation have an important role in the photoalignment process. We are also investigating possible applications for liquid crystal alignment, photopatterning, and formation of holographic surface relief gratings. Recent studies on in-plane orientational order of lyotropic chromonic liquid crystalline dyes prepared using the layer-by-layer self-assembly technique have been reported.[34]

Conclusion

In this study, we investigated the alternate deposition of multicharged azobenzene dye molecules with polycations. The low molecular weight chromophoric azobenzene dye derivatives have different aggregation behaviors depending on the type of polycation, effect of pH on charge density, and self-limiting aggregation behavior of each dye. The DR80 was unique in that it produced significant J-aggregation behavior. The other dyes essentially formed charge-paired complexes with a side-on orientation to the polymer. The optical density, thickness data, and morphology correlated with the orientation and complexation behavior of the dye molecules. Studies were made on the DR80−polycation pair, which was found to have significant photoalignment properties with linearly polarized UV light. The incorporation of a photochromic moiety using this technique is very attractive due to the possibility of creating new light-sensitive materials and optical devices. Further studies will also be made on the behavior of the other dyes.

Acknowledgment. Technical support from Molecular Imaging Inc. and Optrel, GmBH, and helpful discussions and collaboration with Futao Kaneko, Akira Baba, Kazunari Shinbo, and Keizo Kato are gratefully acknowledged. Partial support from the University of Alabama at Birmingham Faculty Development Program is acknowledged.

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