

Kinetics and Interpenetration of Ionically Self-Assembled Dendrimer and PAZO Multilayers

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Multilayer films comprised of a generation 3.0 dendrimer and NLO-active polyanion PAZO were formed by ionic self-assembly. The films were studied by UV–visible spectroscopy, single-wavelength ellipsometry, and second-harmonic generation. We show that the multilayer formation mechanism involves an initial adsorption of the polymer that reaches saturation after 5 min, while conformational changes equilibrate after 10 min. The terminal layer is more loosely packed than the nonterminal layers that have interpenetrated zones containing both the dendrimer and PAZO. Most of the anisotropic order of the NLO-active chromophores is thought to exist at the interfacial regions between these layers. From SHG polarization studies, we determine the angle of these ordered PAZO chromophores to be $20.5^\circ \pm 5^\circ$ with respect to the surface normal.

Introduction

Dendrimers are a new class of functional materials containing highly branched regular structures. When appropriately functionalized, these macromolecules can serve a variety of purposes, including catalysis, coatings, drug-transport and light-emitting diodes.^{1–6} For example, structural modifications can result in dendrimers with hydroxyl and carboxylate surfaces (hydrophilic) or alkyl surfaces (hydrophobic).⁷ More interesting is the possibility of mixed hydrophilic and hydrophobic surfaces. Host–guest complexation within the confines of dendrimers is also an active research area.⁸ Assembly of chemically modified dendrimers within polyelectrolyte sandwiches lend themselves to potential applications in molecular recognition and chemical/biological sensors. Another recent discovery is the important role dendrimers play in energy and charge-transfer systems within polyelectrolyte superlattices.⁹

In this work, we take advantage of the ionic assembly effect to construct polyelectrolyte superlattices between polyanions. Polyelectrolyte self-assembly¹⁰ and spin-assembly¹¹ are maturing to the point where one can control polyelectrolyte deposition onto a charged substrate. This level of control, together with the availability of structurally diverse polyelectrolytes with interesting optical properties, such as luminescence and non-linear optical activity, makes polyelectrolyte self-assembly an excellent way of depositing dendrimeric layers between polyanionic interlayers.

This work examines the detailed structure of multilayered thin films fabricated from generation 3.0 dendrimer (poly(propyleneimine)) and PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt])

assembled on a glass substrate (Figure 1). In particular, we focus on structural and conformational changes within the multilayered polyelectrolyte film in the presence of the NLO-active PAZO interlayers. The PAZO polyanion contains a conjugated azobenzene group, which contains both an electron donor (OH) and an electron acceptor (SO₂) (Figure 1b). This highly polarizable NLO-active chromophore has a $\pi \rightarrow \pi^*$ transition near 355 nm, and therefore, the relative amount of PAZO in the film can be spectroscopically monitored. We use UV–visible spectroscopy to study the kinetics of adsorption of PAZO on the underlying dendrimer film. We investigate the equilibrium kinetics both with respect to saturation coverage and conformation relaxation. Other groups have also studied polyelectrolyte multilayer systems using second-harmonic generation.^{12–16} Ellipsometry is used to determine the relative thickness of each layer and investigate the differences between films containing PAZO as the outer layer and those containing terminal dendrimer. Along with complementary second-harmonic generation (SHG) measurements, we show that terminal PAZO layers are loosely packed but collapse upon the addition of dendrimer layers. The data also provides evidence that these compact layers are interpenetrated to some degree with neighboring layers. The SHG data also suggests that most of the orientational order of the chromophore units of PAZO arise at the interfaces between polyanionic and polycationic layers. A polarization study reveals that these chromophores orient at $20.5^\circ \pm 5^\circ$ with respect to the surface normal.

Experimental Procedure

Materials. A polycation, generation 3.0 dendrimer (poly(propyleneimine)) and a polyanion, PAZO (poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt]), were used as received from Aldrich. Ultrapure water (resistivity > 18 M Ω /cm) was used in all the polymer solutions and substrate preparations. Polymer solutions were prepared at various molarities based on the molecular weight of the repeat

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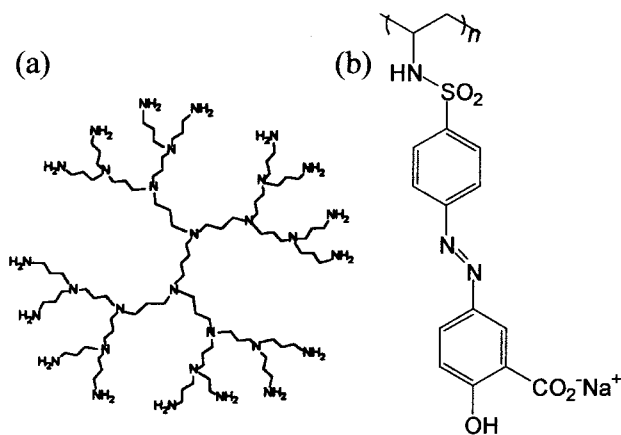


Figure 1. Chemical structure of (a) a generation 3.0 dendrimer and (b) PAZO.

unit. The pHs of the dendrimer and PAZO solutions were 12 and 6.8, respectively.

Film Assembly. The films were assembled on glass substrates that were pretreated with a 70:30 solution of sulfuric acid and hydrogen peroxide for 1 h at 80 °C (piranha etch treatment). The substrates were thoroughly rinsed with deionized water and sonicated in water for 15 min to remove all traces of the piranha solution. The clean glass substrates were then immersed in the dendrimer solution for 5 min at room temperature, rinsed with copious amounts of water and dried with a stream of nitrogen. The substrate was then immersed in the PAZO solution for a predetermined amount of time and rinsed and dried as before. When a slide was used to build 10 bilayers, the slide was immersed in the PAZO solution for 5 min. This was repeated 9 times. A layer is defined as a deposition of either dendrimer or PAZO. A bilayer consists of a deposition of dendrimer, followed by PAZO. For the kinetics measurements, a single layer of dendrimer was adsorbed onto the slide as described above. After rinsing and drying, the slide was immersed in PAZO for a predetermined amount of time. After the UV-visible spectrum was taken, the slide was then re-immersed in the PAZO solution for another predetermined amount of time. The slide was rinsed and dried after every deposition of PAZO. The immersion was repeated until the total amount of immersion time reached 20 min. The films remain clear, not opaque or cloudy, throughout all the experiments.

Optical Measurements. UV-visible spectra were recorded at a 1 nm resolution on a Perkin-Elmer Lambda 19 spectrometer between 250 and 700 nm. The SHG Maker fringe measurements were carried out in transmission geometry under nonresonant conditions using p-in and p-out beam polarizations.^{17–19} A Nd:YAG laser (New Wave MiniLase) provided 8 ns pulses at a repetition rate of 10 Hz for fundamental excitation at 1064 nm. The energy density at the sample was ~ 2 mJ/mm². The transmitted SHG signal at 532 nm was measured as a function of the incident angle from the normal (0°) to 69° as the sample was rotated in 1° steps under computer control.²⁰ The transmitted SHG signal was separated from the fundamental beam using a series of optical color glass filters and a 532 nm notch filter. The signal was passed through a polarization analyzer and detected using a photomultiplier tube and gated integrator. The SH data points were averaged over 40 laser pulses. The SHG signal from a Y-cut quartz crystal was used as a reference. For the SHG polarization experiments, the sample was fixed at an angle of 52°, the maximum location of a single fringe, while the input polarization was rotated from s-polarization to p-polarization and back to s-polarization.

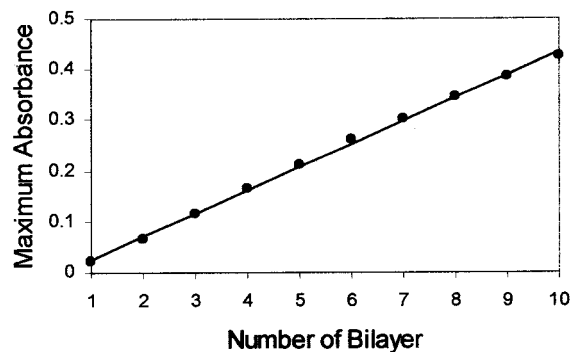


Figure 2. Plot of the peak UV-visible absorption of the system showing linearity from 1 to 10 bilayers with PAZO as the terminal layer.

Ellipsometry. Ellipsometric measurements were taken on a null ellipsometer (Rudolph Research Auto EL). The ellipsometer was operated at 632.8 nm with a spot size of ~ 2 mm and a 70° angle of incidence. The film thicknesses were calculated from the phase shift and amplitude ratio ellipsometric parameters using previously reported procedures.²¹ The overall error in the film thicknesses is approximately ± 2 Å. The thickness was measured at five points in a cross-shaped pattern, approximately 3 mm between each point. The reported thicknesses are an average of these five measurements.

Results

Deposition and Kinetics. UV-visible spectra of films assembled on a glass substrate were taken from 250 to 700 nm after each layer from 1 to 10 bilayers for a 1.0 mM dendrimer/1.0 mM PAZO system. Figure 2 illustrates that the peak UV-visible absorbance of the chromophore increases linearly from 1 to 10 bilayers with PAZO being the terminal layer.

To determine how long it takes for maximum adsorption of the PAZO solution onto a dendrimer layer to occur, the UV absorption of a glass slide containing dendrimer was measured after the slide was immersed in PAZO solution for times varying from 15 s to 20 min. Both 0.5 and 1.0 mM solutions of PAZO were studied. The concentration of the dendrimer was held at 1.0 mM. The absorbance maxima are plotted versus time in Figure 3a. For both concentrations, the maximum absorption is reached in approximately 5 min. As expected, the maximum absorption is greater for 1.0 mM than for 0.5 mM. Figure 3b shows the wavelength of the maximum absorption. For 1.0 mM PAZO, the peak absorption wavelength reaches an asymptotic value after 9 min, while for 0.5 mM PAZO, the peak absorption wavelength is still red-shifting after 10 min.

Ellipsometry. Ellipsometric thickness measurements were taken to determine the thickness of the film after the addition of each layer, either dendrimer or PAZO. Figure 4 shows the thickness of the film after each layer. For either dendrimer or PAZO as the outer layer, there is an overall growth in the thickness of the film. The first three layers show an approximately linear increase in film thickness. However, after 2 bilayers (thickness of ~ 43 Å), the addition of the dendrimer layer causes an overall decrease in the thickness of the film. The magnitude of this decreased thickness increases for each subsequent bilayer.

Second-Harmonic Generation. Second-harmonic generation was used to determine the nonlinear optical efficiency of the polymer film and the angle of the chromophore with respect to the surface normal. Figure 5 shows the Maker fringes generated from the 10 bilayer film as it was rotated from 0° to 69°. The

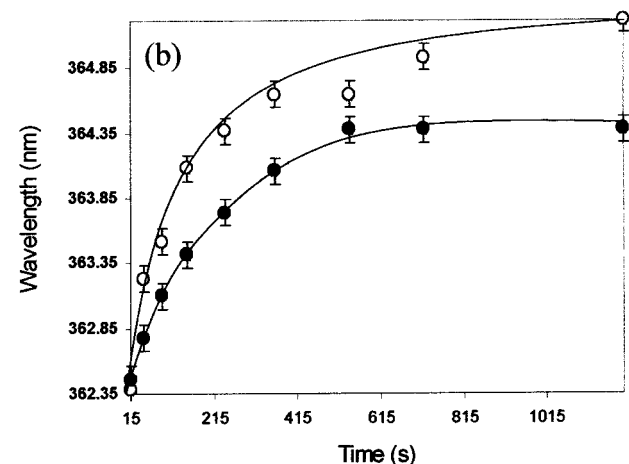
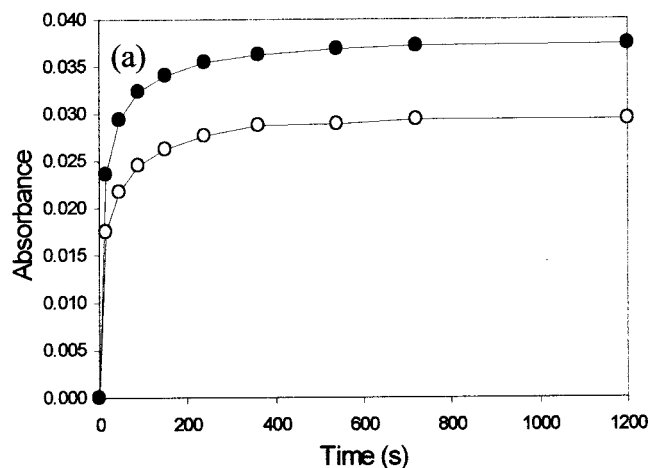


Figure 3. (a) Peak UV-visible absorption plotted vs time for a single bilayer of dendrimer/PAZO and (b) the wavelength of the peak UV absorption plotted vs time. The concentration of dendrimer is held fixed at 1.0 mM, and two concentrations of PAZO are used (0.5 mM, open circles; 1.0 mM, filled circles).

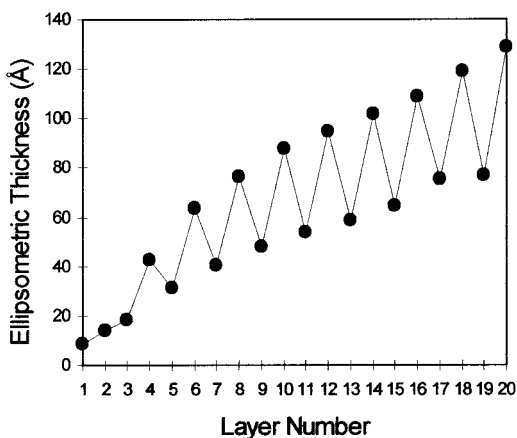


Figure 4. Ellipsometric thickness measurements for 1–20 layers (a total of 10 bilayers). The terminal layer is dendrimer for the odd layers and PAZO for the even layers.

Maker fringes were also recorded after every layer of either dendrimer or PAZO. The SHG signal at 52 degrees is plotted in Figure 6 with PAZO or dendrimer as the outer layer. The SHG signal reaches a plateau after three bilayers and is also significantly weaker when dendrimer is the outer layer.

The angle of the PAZO chromophore with respect to the surface normal was determined by measuring the p-polarized SHG signal as a function of the rotation of the input polarization.

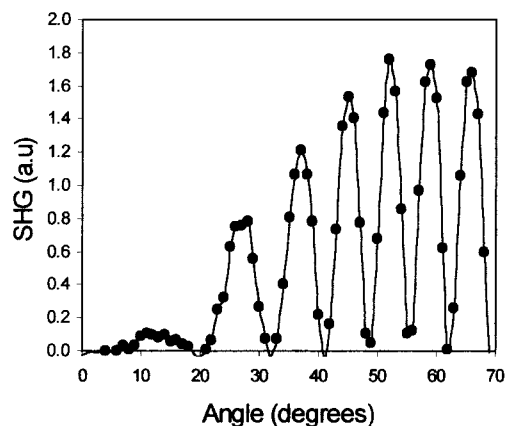


Figure 5. SHG Maker fringes generated from a 10 bilayer dendrimer/PAZO film as it is rotated from 0° to 70°.

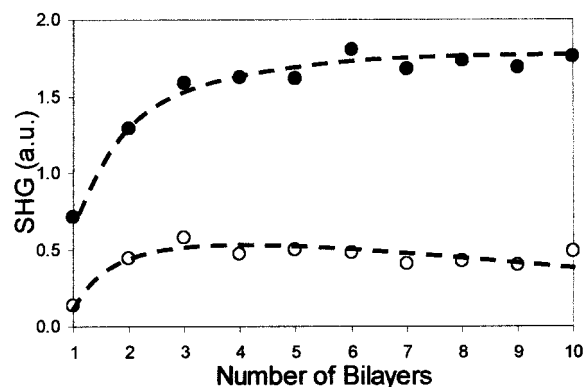


Figure 6. Comparison of the SHG signal generated when dendrimer (open circles) or PAZO (filled circles) is the outer layer. The maximum signal from the film at 52° to the incident laser beam is plotted for each bilayer.

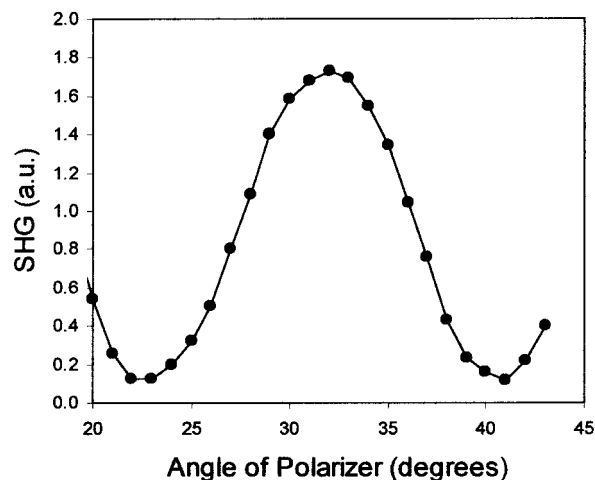


Figure 7. SHG signal as the input polarization is rotated from s-p-s for a 10 bilayer film of dendrimer/PAZO.

Figure 7 shows the SHG signal as the input polarization is rotated from s-p-s.

Discussion

Deposition. The linear increase in the peak UV absorbance indicates that equivalent amounts of PAZO are being adsorbed onto the dendrimer in each bilayer. An interesting observation is that the wavelength of the peak absorption shifts to the red as the number of bilayers increases (Figure 8). Possible explanations for this red shift include changes in the packing

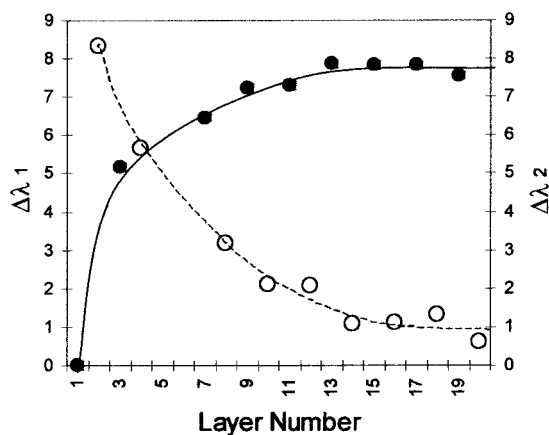


Figure 8. Plot of the shift, relative to the first bilayer, in the UV-visible absorption from 1 to 10 bilayers ($\Delta\lambda_1$, filled circles) and the shift due to the addition of dendrimer to the terminal PAZO layer ($\Delta\lambda_2$, open circles).

density, the self-organization of the chromophores or the conformation of the polymer. After four bilayers are deposited, the red shift relative to the first bilayer ($\Delta\lambda_1$) for each subsequent bilayer remains constant at approximately 7.5 nm. The red shift is smaller (from approximately 5 to 6 nm) for the first three bilayers. Since the substrates are negatively charged and we have previously shown²² that the substrate can have a significant effect on the deposition of polymer layers, we again are likely seeing an effect of the substrate on the film characteristics. In previous work, we found that the substrate effect persisted for a PEI (poly(ethylenimine))/PAZO system for four bilayers, a thickness of approximately 80 Å.¹¹ Four bilayers of the dendrimer/PAZO system (Figure 4) is also approximately 80 Å. The influence of the substrate appears to persist for a limited distance into the film. Figure 8 also shows the red shift in the location of the peak UV absorbance ($\Delta\lambda_2$) that occurs upon the adsorption of the dendrimer layer onto the outermost PAZO layer. This red shift decreases as more bilayers are added to the substrate and is nearly zero after 10 bilayers. The interactions between the dendrimer and the PAZO have a greater influence on the UV absorbance when the polymers are closer to the substrate.

Since the pH of the polymer solution can affect the charge density of the polyelectrolytes, the pH of the dendrimer was kept at 12, while the PAZO solution had a pH of 6.8.^{23,24} No buffering solution was used to help maintain the pH of the solutions. However, it was not observed that the pH of the solutions changed significantly during the assembly process. At low pHs, the dendrimer and PAZO molecules can be protonated, but since our solutions are basic or nearly neutral, this is not a concern. However, the charge density of the dendrimer or PAZO could change when it is dipped in the PAZO or dendrimer solution, respectively. The effect of the changing pH conditions on the packing density of the films will be explored in future studies.

Kinetics. A red shift is also observed, as the PAZO deposition time increases. Figure 3b shows the time dependence of the wavelength of the peak absorbance for both 0.5 and 1.0 mM solutions of PAZO. The observed red shift is small, fewer than 3 nm, but it is present for both concentrations of PAZO. Although the adsorption of PAZO reaches a maximum after approximately 5 min, Figure 3b shows that the polymer chains in the film are still undergoing conformational changes for a much longer time. For the 1.0 mM solution, the changes appear to stabilize after 9 min. However, even after 20 min, the UV-

visible spectrum of the molecules adsorbed from the 0.5 mM solution is still changing. This conformational relaxation leads to gradual changes in the packing density and self-organization of the chromophores in the films. This change in self-organization of the chromophores does not cause the films to be cloudy due to phase separation. These changes are occurring on the molecular level. At the lower concentration of PAZO, there are fewer molecules adsorbed onto the dendrimer, and therefore, there is more room for them to rearrange. Thus, it takes longer for the system to reach equilibrium, and the red shift is greater for the lower concentration system. Although the dendrimer/PAZO systems reach equilibrium in the amount of PAZO adsorbed in 5 min, it takes at least twice as long to reach conformational equilibrium. For overall equilibrium in the system, one must wait at least 10 min for the system to equilibrate. Similarly, Tsukruk et al. have seen in a PAA (poly(allylamine))/PSS (poly(styrenesulfonate)) system that it takes a deposition time of over 10 min to reach a conformational equilibrium of the polymer layers.²⁵ Their results are based on AFM images of the films during formation.

Ellipsometry. As shown in Figure 4, the overall thickness of the dendrimer/PAZO film increases with each bilayer. However, after two bilayers have been constructed, we infer that the adsorption of the dendrimer layer onto the PAZO layer collapses the underlying film and the overall thickness becomes considerably less than that of the two-bilayer film (Figure 9). The dendrimer molecules interpenetrate the PAZO layer and cause densification and thinning of the PAZO polymer chains. The decrease in thickness is not caused by a desorption of the PAZO upon addition of the dendrimer, because the UV spectra (not shown) show that there is <2% decrease in the absorbance when the dendrimer layer is assembled on the film. This small decrease cannot be the only cause for the $35 \pm 5\%$ drop in the ellipsometric thickness after the dendrimer layer is adsorbed. At pH 7, the PAZO molecules are still negatively charged and can repel one another and form a loosely packed layer on top of the dendrimer layer. Since dendrimer is positively charged, when it adsorbs onto the PAZO and interpenetrates the polymer, it shields the negative charges on the PAZO molecules and allows them to pack closer together. Also, since dendrimer contains outer primary amine groups, hydrogen bonding with PAZO may further encourage mixing between the two layers.

Second-Harmonic Generation. The minima of the Maker fringes generated by the film assembled on both sides of the substrate are almost zero, indicating that we have nearly identical films on both sides of the glass substrate (Figure 5). The drying of the films after the adsorption of each layer has no effect on the second-harmonic signal, which levels off after three bilayers (Figure 6). This asymptotic behavior has been previously observed in related systems and is attributed to reduction in charge density.^{22,26} We also observe that there is a decrease in the SH signal when dendrimer is the outer layer (Figure 6). Since we observe no reduction in the amount of PAZO adsorbed from the UV-visible spectra, the attenuation in the SHG signal must be caused by a change in the ordering of the PAZO chromophore dipole due to the subsequent addition of dendrimer (Figure 2). When PAZO is added to a dendrimer layer, the PAZO dipoles closest to dendrimer are aligned due to the electric field generated by the underlying positively charged molecules. This produces a net SHG signal. When dendrimer is the terminal layer, there will be on average a smaller net dipole due to dipole reversal at the outermost dendrimer/PAZO interface. We have previously observed this interfacial dipole reversal in other polyelectrolyte films.²² The interpenetration of the dendrimer

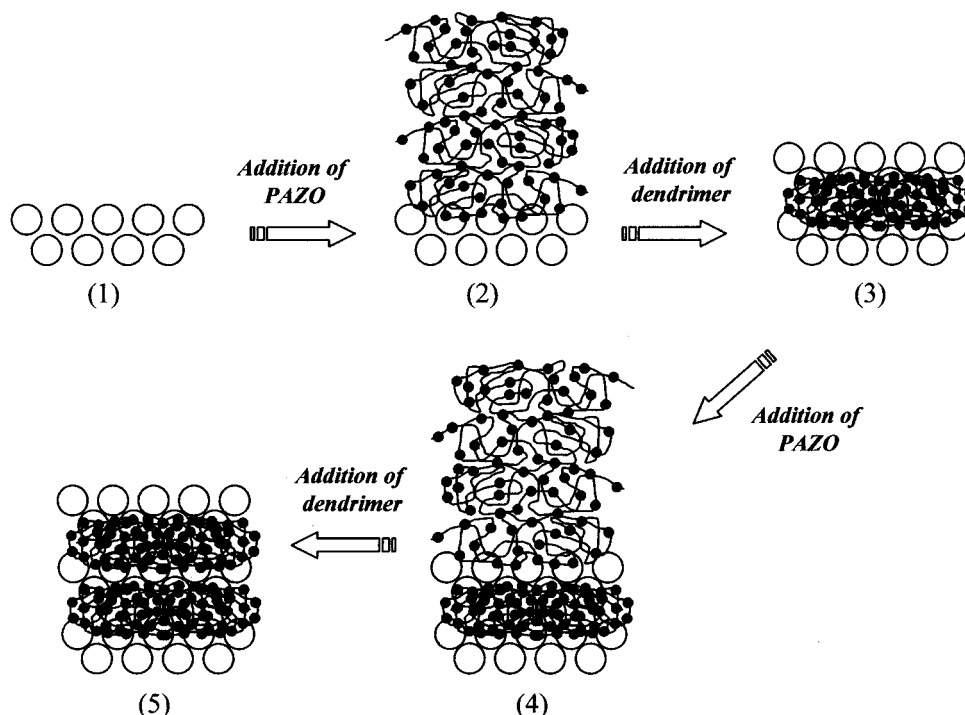


Figure 9. Schematic of the dendrimer/PAZO multilayer system showing the interpenetration of the dendrimer molecules into the PAZO polymer and the collapse of the film. (1) A terminal dendrimer layer. (2) A loosely packed layer of PAZO on a dendrimer layer. (3) A collapse of the PAZO layer when dendrimer is adsorbed onto it. (4) Another layer of loosely packed PAZO on top of the dendrimer and collapsed PAZO layers. (5) A second collapse of the underlying PAZO layer when dendrimer is adsorbed.

molecules into the PAZO layer is also consistent with this theory of interfacial dipole reversal. However, in this case, the PAZO dipoles order at the interfaces between pure PAZO and the mixed zone of dendrimer and PAZO.

By measuring the second-harmonic signal generated by the film as the input polarization is rotated from s to p to s, we can determine the net orientation of the PAZO chromophore.^{27,28} Assuming that the thin film has uniaxial symmetry along the direction of the surface normal, there are only two independent tensor elements in the nonlinear optical coefficient. They are χ_{zzz} and $\chi_{zxx} = \chi_{zyy} = \chi_{xzx} = \chi_{xxz} = \chi_{yzy} = \chi_{yyz}$. We also assume that there is a narrow distribution of molecular orientation angle and a single dominant element, $\beta_{\zeta\zeta\zeta}$, of the molecular hyperpolarizability tensors. The average molecular orientation of the chromophore is given by $\chi_{zzz}/\chi_{zxx} = 2\langle\cot^2\psi\rangle = 2\cot^2\langle\psi\rangle$, where ψ is the orientation angle between the surface normal and the principal molecular tensor component, $\beta_{\zeta\zeta\zeta}$. For the dendrimer/PAZO 10-bilayer-thin film, the net orientation of the PAZO chromophores was determined to be $20.5^\circ \pm 5^\circ$ (Figure 7).

Summary

We have identified two distinct equilibria during the formation of the PAZO/dendrimer multilayer film. It takes approximately 5 min for saturation adsorption of the polymer to be established and at least an additional 4 min for conformational equilibrium to be reached. PAZO adsorbs as a loosely packed film and upon adsorption of dendrimer, the film collapses to a more compact form. We describe these inner multilayers as interpenetrated with most of the orientational order of the PAZO chromophore at the interfacial region between the interpenetrated zones and the pure PAZO or dendrimer layers. The positively charged outermost dendrimer layer causes the negatively charged chromophores of the PAZO to orient in the opposite direction at the interface. This leads to partial cancellation of the observed

second-harmonic signal. Therefore, the PAZO terminated layers will always give larger SH signals than those capped with the dendrimer. The angle of these chromophores was determined to be $20.5^\circ \pm 5^\circ$ with respect to the surface normal.

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