Probing Polymer Adsorption Using an Emissive Semiconductor Substrate: Adsorption of Poly(acrylic acid) onto Cadmium Selenide

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ABSTRACT: Quenching of the photoluminescence (PL) intensity of single-crystal CdSe by adsorption of poly(acrylic acid) (PAA) from methanol solutions is introduced as a sensitive probe of polymer interactions with a semiconductor surface. Comparison with the influence on CdSe PL of methanol solutions of acrylic acid (AA), propionic acid (PrA), and methyl acrylate (MA), along with IR data, indicate that surface binding leading to PL quenching involves the carboxylic acid proton. Over the range of PAA molecular weights studied in methanol (2K−100K), the dependence of PL quenching on concentration is found to be insensitive to PAA chain length, indicating that the same fraction of CdSe surface sites are used. The PL profile of a surface COOH-derivatized dendrimer (PAMAM−COOH) differs markedly, suggesting that PAA chains uncoil upon adsorption. The time dependence of the PL decay for the PAA/methanol system indicates diffusion-controlled adsorption kinetics. Implications of the use of this methodology for characterizing semiconductor−polymer interfaces are discussed.

Introduction

The photoluminescence (PL) intensity of single crystal semiconductors, such as CdSe, can be highly sensitive to adsorbate interactions localized at the surface, providing a convenient tool for monitoring a wide variety of interfacial processes. In this way, we have characterized the adsorption behavior of a number of molecular systems, both in the gas phase and solution, including amines, ketones, transition metal complexes, and surfactants and their aggregates.[1−5] A particularly noteworthy trend, which we describe as a “photoluminescence litmus test”, has emerged: Lewis acids induce a quenching in semiconductor PL intensity relative to a reference ambient, while Lewis bases produce the opposite effect, an enhancement in PL intensity. These effects have been attributed to an adsorbate-induced shift in electron density within the semiconductor, leading to a change in surface electric field (depletion width), thereby affecting the radiative recombination of photogenerated electron−hole pairs. Additionally, the adsorbate may influence the PL intensity by affecting the surface recombination velocity of electron−hole pairs within the semiconductor.

A particularly attractive feature of this approach has been that valuable information about adsorption onto chemically etched CdSe surfaces can be obtained with minimal preparation of the surface: Chemical etchants such as bromine/alcohol solutions that are commonly used under ambient conditions generally leave physically and chemically heterogeneous surfaces that provide a wide variety of binding environments. Despite the highly heterogeneous nature of the CdSe surfaces employed, it has been possible to characterize adsorbate binding features by studying families of adsorbates whose steric and electronic properties could be systematically varied.

Over a certain concentration range, the magnitude of the PL response correlates with the ambient concentration of the adsorbate, allowing relative changes in surface coverage to be monitored. Results to date suggest that the sensitivity of semiconductor PL is limited to interactions occurring, at most, within a few monolayers of the surface;[6] the implication of this surface sensitivity for polymer adsorbates is especially attractive, with the potential for characterizing the initial adsorption layer.

The ability to characterize polymer adsorption is critical for a number of technologically important applications, such as coatings and adhesives, chromatography, colloid stabilization, and sensors. Experimental and theoretical studies have demonstrated that the presence of a surface can induce fractionation of a polymer sample, owing to a variety of competitive adsorption processes.[7−9] Such fractionation may be driven by various combinations of enthalpic, entropic, and kinetic effects. For example, enthalpic effects dominate when chains can be distinguished owing to the presence of “sticker” groups, such as terminating or repeat units, differing significantly in surface binding energy.[10−12] For a homopolymer sample, fractionation can be driven purely by entropic effects due to the presence of a distribution of chain lengths.[13,14] Additionally, the kinetics and chain dynamics of the adsorption and desorption events can lead to discrimination among subpopulations of chains, promoting binding of otherwise weakly adsorbing polymers.[15]

A number of techniques have previously been used to characterize polymer adsorption, including ellipsometry, optical reflectivity, FTIR−ATR, and, recently, total internal reflectance fluorescence (TIRF), a method that relies on the availability of polymer chains labeled with a nonintrusive fluorescent tag.[7,13,16] The first two methods provide a measure of *total* adsorbed material at the substrate surface, whereas the latter two methods are sensitive to interactions within the near-surface region, with the probe beam extending beyond the surface up to a distance on the order of micrometers into the overlying bulk solution.[7,10,17] The critical interactions with the surface may occur in a much narrower region, ultimately defined by the first adsorbed layer. Experimental characterization of this single layer is highly desirable for confirmation of theoretically predicted parameters, such as the fraction of bound sites in each chain, as defined by the loop-to-train ratio. Furthermore,

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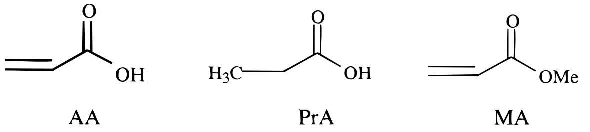
Scheme 1



most studies to date have been limited to silica surfaces. The ability to study adsorption at surfaces other than silica, particularly those of inorganic semiconductors, is desirable, as polymer adsorption at such surfaces is becoming increasingly important in a number of applications, especially in the electronics industry.

In this study, we report the performance of a photoluminescent semiconductor substrate as a probe of interactions at the polymer/semiconductor interface. Specifically, we show that adsorption of poly(acrylic acid) (PAA) from methanol solution onto single-crystal CdSe can be monitored through reversible quenching of substrate PL. Our results indicate that the flexible PAA chains adopt conformations that utilize a similar distribution of binding sites at the CdSe surface, irrespective of chain length. Through comparisons with model compounds, acrylic acid (AA), propionic acid (PrA), and methyl acrylate (MA), Scheme 1, we infer that the acid proton is critical for surface binding and that self-association among the carboxylic acid functionalities also influences the adsorption behavior. Additionally, we use the time dependence of the substrate PL response to extract information about the nature of the adsorption kinetics for the PAA/methanol system.

Experimental Section

Materials. Single-crystal *c*-plates of n-CdSe, having resistivities of ~2 Ω·cm, corresponding to a doping level of ~ 5×10^{15} cm^{-3}, were obtained from Cleveland Crystals, Inc. The crystals were cut to approximate dimensions of 5 × 5 × (1−3) mm. A fresh surface was prepared for each experiment by etching the crystals in Br_2/MeOH solution (~1:15 v/v) for about 30 s, or until the shiny Cd-rich (0001) face was revealed. Etching was immediately followed by MeOH rinsing and subsequent sonication in MeOH for ~20 min. The crystals were dried under a stream of dry nitrogen before mounting in the cell.

Acrylic acid (AA), methyl acrylate (MA), propionic acid (PrA), and acetophenone were obtained from Aldrich (99%) and were immediately used following fractional vacuum distillation. Acrylic acid was distilled with gentle heating over copper gauze (Alfa Aesar), which was also packed into the still-head, to prevent polymerization.[18] The purified monomers were handled under dry nitrogen at all times. Polyamidoamine dendrimer, surface-functionalized with carboxylic acid groups (PAMAM−COOH), was obtained from Aldrich (10% solution in methanol, generation 3.5). The solvents methanol (Fisher, 99.9%) and cyclohexane (Fisher, 99.7%) were dried under nitrogen by distillation over magnesium methoxide and calcium chloride, respectively. The method of solution preparation was found to be critical in obtaining reproducible PL behavior for experiments conducted in cyclohexane as solvent. These solutions were prepared via syringe transfer through septa into flasks that had been oven-dried and purged with dry nitrogen before use.

The poly(acrylic acid) (PAA) samples that were used are summarized in Table 1, with sample characteristics provided by the indicated supplier. The polymer samples (2K−100K) were purified from aqueous solution by cation-exchange along a column (AG 50W-X8 H-form, BioRad). The column packing was washed several times with 1 N HCl, followed by several rinses with deionized water prior to use. The 250K PAA sample was converted from the Na salt via ultrafiltration using repeated washes with 1 N HCl solution, followed by repeated rinses with deionized water. The purified PAA samples were dried to constant weight by rotovaporation with gentle heating (<80 °C), and stored in a desiccator under nitrogen.

Table 1. Poly(acrylic acid) (PAA) Samples Used for PL Experiments

M_w[a]	polydispersity	end group	supplier
2K	<2	bisulfite	Rohm & Haas
4.5K		bisulfite	
20K		sulfate	
50K		sulfate	
100K		sulfate	
250K[b]	1.5	vinyl; hydroxyl	American Polymer Standards

[a] Approximate weight-average molecular weight, as given by supplier. [b] Purchased as the sodium salt and converted to the acid, as described in the Experimental Section.

PL Studies. CdSe substrates, prepared as described above, were mounted onto a glass rod between Teflon spacers, and fitted into a glass cell having an approximate inner diameter of 20 mm. The cell was equipped with a sidearm inlet and a valve with a Teflon stopcock at the base to allow for exchange of solutions, as previously described.[19] With this setup, the adsorption experiment was effectively carried out under static conditions. The sample cell was purged with dry nitrogen throughout the experiment. The shiny Cd-rich face of the semiconductor sample was illuminated using ultraband gap 633 nm excitation from a Melles-Griot model 80 HeNe laser or the 514 nm line of a Coherent Innova 90 Ar$^+$ laser, at a power density of <10 mW/cm^2. Semiconductor PL was collected by a fiber optic interfaced to a 512-element Oriel Instaspec II diode array detector. At low spectral resolution (1 nm), the position of the PL maximum at 720 nm was insensitive to adsorbates, serving as a convenient marker for monitoring the PL intensity as a function of time and chemical ambient. The PAA solutions were generally introduced into the cell in order of increasing molecular weight in studies of molecular weight dependence, and in order of increasing concentration in studies of concentration dependence.

Temperature-controlled experiments in cyclohexane were performed using a similar sample cell that was equipped with an outer water jacket. The cell temperature was regulated to within ±0.1 °C using a Precision R20 circulator. It was necessary to use an Oriel Instaspec IV CCD detector for these experiments in order to obtain a reasonable signal-to-noise level.

Characteristic adsorption times were determined for the PAA solutions as a function of polymer molecular weight and concentration by single exponential fits to the initial part of the experimental PL decay curves. Linear and higher exponential functions yielded considerably poorer fits to the data and were often irreproducible from one run to the next. A minimum acquisition time of 6 s necessary for a reasonable signal-to-noise level ultimately limits the temporal resolution of these experiments. The region used for the exponential fit was defined by the first or second data point following the solution exchange (i.e., the maximum PL value following solution exchange) and the end point for the region, the position of which was varied until a satisfactory exponential fit to the initial decay was obtained. In defining the beginning of the region for the analysis, the first data point was used if a spike was present in the data to mark the solution exchange, and the second data point was used if no spike was apparent in order to allow for the time taken to switch solutions. The variability in the time-constant for the PL decay obtained in this way was ~±30%. For consistency, such comparisons across a series were only made for data obtained using the same CdSe surface. Prior to each such measurement, the surface was rinsed repeatedly with solvent until the original solvent PL baseline intensity was restored. Since decay times were found to be unaffected by stirring the solution during adsorption, the data presented were obtained under static conditions. By assuming a close-packed adsorbed monolayer,

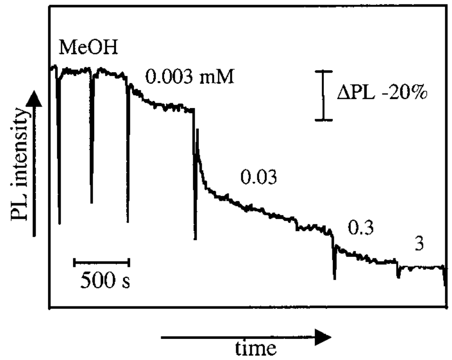


Figure 1. Relative changes in CdSe PL intensity induced by adsorption of PAA-250K from methanol solution. Concentrations on a functional group basis are indicated in the figure. PL intensity is monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm. Spikes are an experimental artifact, corresponding to draining and replacing the ambient solution.

we estimate a *maximum* change in bulk solution concentration, owing to the adsorption event, of less than 1% for the most dilute polymer solution (2 μg/mL) used for studying the adsorption kinetics.

IR Studies. Surface IR experiments of films of PAA on CdSe were conducted using the synchrotron source at the University of Wisconsin Synchrotron Radiation Center. The samples were prepared by dipping the freshly etched semiconductor crystal into methanol solutions of PAA of varying concentrations, followed by slow evaporation of the solvent in air by partially covering the sample. The samples were analyzed under dry nitrogen in external reflection mode using a NicPlan microscope, interfaced to a Nicolet Magna 550II IR spectrometer, equipped with a liquid nitrogen-cooled $^1/_4$ mm MCT detector. The spectra were collected using 100 scans and 4 cm^{-1} resolution at a magnification of 32×. The mirror velocity was set at 5 cm/s in order to avoid interference from a 60 Hz component in the synchrotron beam. Film thicknesses were highly nonuniform as viewed under the microscope. Patches where the film was thinnest, as indicated by minimal or no dispersion of white light when viewed under the microscope, provided the best spectra.

Solution IR spectra of acrylic acid in cyclohexane and methanol were obtained using a Nicolet 740 FT-IR spectrometer, equipped with a standard room-temperature DTGS detector. Spectra were collected at a resolution of 4 cm^{-1} using 16 scans. The signal-to-noise ratios of the spectra were optimized using a variable path length cell with Teflon spacers and by interactive subtraction of the solvent background. NaCl salt plates were used for the measurements in cyclohexane, while CaF_2 plates were necessary for studies in methanol in order to avoid effects from dissolved salts.

Results and Discussion

All PL experiments were conducted with CdSe single crystals etched in Br_2/MeOH. It is important to emphasize that because the crystals are handled in air, surface hydroxides and oxides are likely present, in addition to possible bromine-containing species resulting from the etching procedure.

A typical adsorption profile, as probed by monitoring the CdSe PL intensity ($\lambda_{max} \sim 720$ nm), is shown in Figure 1 for methanol solutions of poly(acrylic acid) having M_w of 250K (PAA-250K). The adsorption behavior shown is common to the PAA samples investigated in this study (Table 1). Specifically, adsorption of PAA onto CdSe induces a reversible quenching in PL intensity relative to the solvent baseline, consistent with previously established PL behavior for adsorption of an acid onto this surface.[19,20] Low laser intensities have been used to minimize photoeffects on adsorption; our intensities correspond to a regime where we have previously seen no dependence of fractional PL response on intensity for adsorption of a carboxylic acid onto CdSe.[19]

The onset of the PL response occurs at PAA concentrations in the range of (0.2−2) μg/mL, corresponding to repeat unit concentrations between 3 and 30 μM, with such variations typical from one surface to another. The magnitude of the PL response increases with polymer concentration and ultimately saturates at ~40−90% quenching for a PAA concentration of 0.02−0.2 mg/mL ([−COOH] = 0.3−3 mM), depending on the CdSe surface, with ~70−80% quenches most typical. Over the course of an experiment conducted on the same surface, the reproducibility of a PL response for a given analyte concentration is constant to within ±10%. Although not shown in Figure 1, PAA adsorption is reversible, as indicated by a gradual recovery of the PL intensity upon repeated solvent rinses; typically, ~ 1 h is required to reestablish the solvent baseline.

The PL behavior of PAA can be influenced by a number of factors, including the nature of the surface binding interactions with the polymer's functional groups, and the size and conformation of the adsorbing polymer chains. In sections I and II below, we present results that relate the PL signature to the surface binding properties and adsorption kinetics of PAA, respectively. In characterizing the nature of the surface binding interactions of PAA, we selected model compounds to investigate systematically the effects on PL of specific structural features. The parent monomer, acrylic acid (AA), and derivatives propionic acid (PrA) and methyl acrylate (MA) represent model compounds that were used to characterize the effects of functional groups on PL behavior. Polyamidoamine dendrimer, surface-functionalized with carboxylic acid groups, PAMAM−COOH, was used to mimic the adsorption of the chains as rigid coils as a means of examining conformational effects on PL behavior.

I. Surface Binding Properties

(a) PL Behavior of the Monomer and Derivatives: Effects of Ligating Functionality and Aggregates. As seen in Figure 2a, the onset of the PL response to adsorption of PrA from methanol solution occurs at a PrA concentration of 3 μM. Relative to the solvent baseline, the PL intensity is reversibly quenched with increasing concentration, up to a saturation value of typically between 30 and 50% quenching at a concentration of ~0.1 mM. The concentrations at which the onset and saturation of the PL response occur are similar to those found for the PAA samples. Repeating the experiment with AA produces similar behavior, as shown in Figure 2b in a comparison of the PL adsorption profiles, indicating that the vinyl group in AA is not critical for surface binding. Additionally, this comparison demonstrates that the PL behavior is not sensitive to the effects of electronic conjugation in AA, suggesting that the AA monomer and derivatives can be used to gain insight into electronic effects on the PL behavior of PAA. Interestingly, repeating the PL experiment with MA produces no PL response, even for the most concentrated solutions studied (up to 30 mM), suggesting that the acid proton is critical for surface binding that elicits a PL response. This observation is in agreement with a diminished PL response (30−50% quenches vs

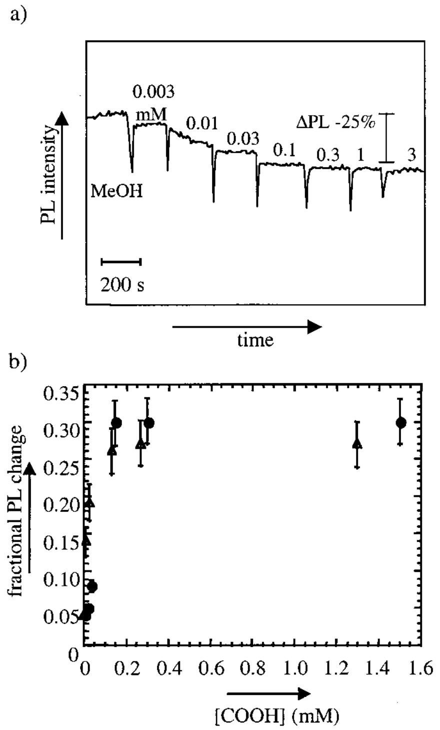


Figure 2. (a) Relative changes in CdSe PL intensity induced by adsorption of PrA from methanol solution at the indicated PrA concentration. The origin of the spikes is described in Figure 1. (b) Comparison of PL adsorption profiles, obtained on the same etched CdSe surface, for adsorption from methanol solution of PrA (△) and AA (●). The fractional PL change (quenching) is given relative to the PL intensity of pure solvent. For both parts a and b, the PL intensity is monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm.

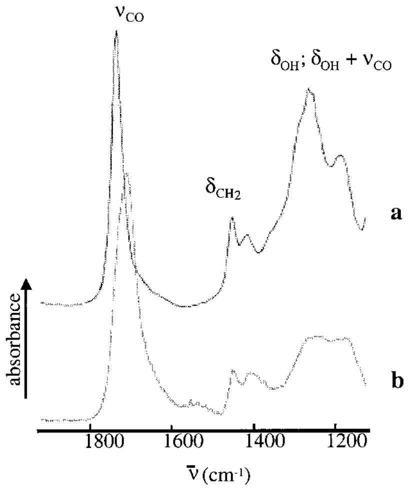
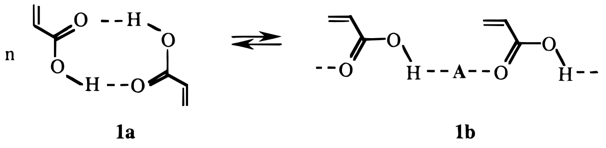


Figure 3. Surface FT-IR spectrum obtained in external reflection mode, a, of a PAA-2K film on a CdSe substrate. Shown for comparison is b, the transmission spectrum of bulk PAA on NaCl salt plates. Both spectra were collected at a resolution of 4 cm^{-1}. The indicated peak assignments are based on refs 21 and 27.

~70−80% for fresh solutions) found for PAA/methanol solutions that were more than a week old, for which partial esterification of PAA was evident by IR spectroscopy.

Presented in Figure 3 is the surface IR spectrum of a film of PAA on CdSe as an independent check of PAA binding sites. Compared to the transmission spectrum of the bulk film on salt plates, the carbonyl stretching frequency, ν_{CO}, is shifted considerably to higher energy, from ~1725 cm^{-1} in the bulk material to ~1740 cm^{-1} in the surface-bound film, with the latter being indicative of a free CO stretch.[21] Also, the much sharper ν_{CO} peak in the surface IR spectrum reflects a narrower distribution of carbonyl-based interactions. These observations indicate that PAA does not bind to the surface directly through the carbonyl oxygen, suggesting that ligation directly through the acid proton may be highly favored, as inferred above from our PL studies of the monomer. Unfortunately, this could not be confirmed directly via IR experiments, owing to the presence of overlapping broad peaks in the O−H stretching region (~3000 cm^{-1}), as well as overlapping combination bands in the O−H bending region of the spectrum (~1300 cm^{-1}).

Scheme 2



A is a monomer or a hydrogen-bonding solvent molecule

It is well-known that carboxylic acids form hydrogen-bonded aggregates such as **1a** and **1b**, as illustrated for AA in a simplified view in Scheme 2. The position of the equilibrium is sensitive to acid concentration, temperature, and solvent polarity.[22−26] Similar association behavior has been noted for PAA and related polymers and can potentially influence the PL adsorption profile.[27−29] In an attempt to explore the effects of solution aggregation on substrate PL, we undertook studies of AA and PrA in nonpolar solvents such as cyclohexane and toluene, in which closed dimers (**1a**) are the dominant species. Over the concentration range studied in our PL experiment, 0.03−30 mM, the magnitude of PL quenching increases with AA concentration in cyclohexane or toluene, reaching typical values of only ~20−45% quenching for 30 mM solutions. Similar results are found for PrA in cyclohexane.

In contrast, in a protic solvent like methanol, both **1a** and **1b** are present in comparable amounts. As noted earlier, saturation of the PL response for adsorption from methanol solution occurs at a much lower concentration of ~0.1 mM (see Figure 2b), a solution concentration several hundred times more dilute than that required for saturation of the PL response in cyclohexane. A shift in the association equilibrium to open aggregates at higher concentrations (~10 mM) has been noted in the literature for several carboxylic acids in nonpolar solvent systems such as cyclohexane.[22,25,26] Such a gradual shift in equilibrium may be mirrored by PL as a continual increase in response with concentration in cyclohexane, suggesting that the open aggregates, **1b**, might be the species responsible for the observed PL sensitivity in this solvent.[30]

Another way to check this hypothesis is to enhance dimer dissociation by some other mechanism, such as heating, which shifts the association equilibrium away from the closed dimers.[31] As summarized in Figure 4, the PL response is found to increase significantly when a cyclohexane solution at a given concentration of AA is heated from 25 to 75 °C, consistent with the notion that the open aggregates are largely responsible for the observed PL sensitivity.[32] As a control experiment, we

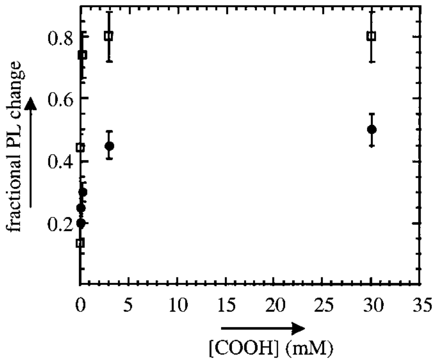


Figure 4. Comparison of the PL adsorption profiles for adsorption of AA from cyclohexane solutions at 25 (●) and 75 °C (□). The fractional PL change (quenching) for each solution is given relative to the PL intensity of pure solvent, at the corresponding temperature. The data at the two temperatures were collected using the same etched CdSe surface. The PL intensity was monitored at 720 nm, using excitation at 514 nm. The adsorption curve at 25 °C was reproduced upon returning to the lower temperature.

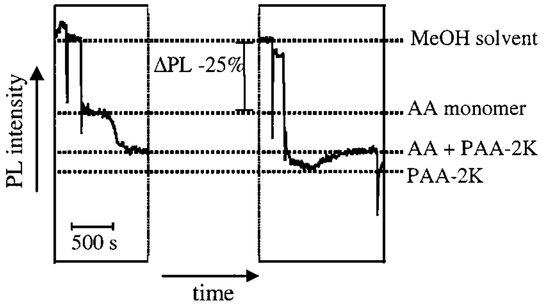


Figure 5. PL experiment carried out under competitive adsorption conditions for AA and PAA-2K at concentrations corresponding to saturated PL responses. Initially the monomer is introduced into the cell; an equal volume of the polymer solution of the same carboxylic acid concentration is then added. After the solvent baseline is reestablished following multiple methanol rinses, the experiment is performed in the reverse order. The PL signatures characteristic of the AA and PAA-2K solutions by themselves are indicated in the Figure. The PL intensity is monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm; $[-\mathrm{COOH}]_{\mathrm{monomer}} = [-\mathrm{COOH}]_{\mathrm{polymer}} = 0.3$ mM = 0.02 mg/mL.

conducted adsorption studies in cyclohexane solution over the same temperature range for acetophenone, an adsorbate which does not self-associate. The magnitude of the PL response to acetophenone, previously shown to induce PL quenching, was found to be independent of temperature, further supporting our hypothesis.[3]

(b) Competitive Adsorption of PAA and AA. Shown in Figure 5 is a comparison of the PL behavior of AA and PAA-2K in methanol solution, conducted under conditions of competitive adsorption. As seen in the figure, although the solution concentrations are equivalent on a monomer unit basis, i.e.,

$[-\mathrm{COOH}]_{\mathrm{monomer}} = [-\mathrm{COOH}]_{\mathrm{polymer}}$, the polymer solutions consistently produce a larger PL response. On the basis of our data, it is not possible to distinguish between differences in the nature of binding sites or in absolute surface coverage in accounting for this observation; however, this result was consistently reproduced by each of the polymer samples studied in Table 1.

We took advantage of the unique PL signatures of PAA and AA to compare directly their surface affinities. From Figure 5, the PL signature of the mixed solution is independent of the order in which the adsorbates are introduced into the sample cell, indicating the reversible nature of adsorption for both AA and PAA-2K. The PL intensity of the mixed solution lies closer to that of the polymer solution, which we believe reflects the presence of a mixed adsorbed layer comprising mainly PAA. The binding enthalpy per repeat unit is expected to be similar for both polymer and monomer, since it was inferred from PL experiments above that the acid proton is critical for surface binding for both adsorbates; additionally, the onset and saturation of the PL response in methanol occur at similar values of [−COOH], indicating a similarity in surface affinity. Preferential adsorption of polymer in such a case is typically entropically driven, as has been reported in the literature for numerous other systems: Adsorption of a polymer chain corresponds to the release of a large number of small molecules from the surface, increasing the total entropy of the system.[7,8]

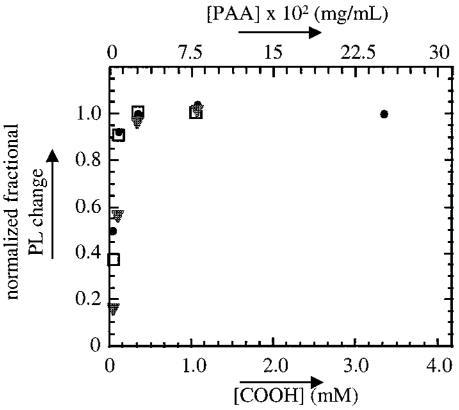


Figure 6. Plot of the normalized fractional PL response as a function of PAA concentration in methanol solutions for PAA-2K (●, □) and PAA-100K (▼). Two data sets are shown for the PAA-2K sample to illustrate the reproducibility of the experiment. The data have been normalized against the maximum PL response for each sample to correct for variations in CdSe surfaces. The estimated error in each value is ±0.1. The PL intensity was monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm.

(c) Effect of Polymer Molecular Weight and Architecture. Over the range of molecular weights studied (2K−100K, Table 1), the polymer chain conformation varies from extended to coiled as the chain length increases.[33] Surprisingly, the PL adsorption profile is found to be insensitive to chain length, and therefore chain conformation in solution, as demonstrated by Figure 6 in a comparison of the PAA-2K and PAA-100K samples. This implies that the magnitude of the response is governed only by the concentration of binding functionality, [−COOH], and that conformational differences in solution do not provide an impediment to surface site occupation. Presuming the PL sensitivity is limited to interactions occurring within a few monolayers of the surface, the fractional PL change effectively provides a relative count of the number of bound polymer segments across this chemically equivalent series, if we assume that the energetic distribution of occupied CdSe surface sites is similar across such a series of chains.[34] The results in Figure 6 suggest that, once at the surface, the chains adopt conformations that allow a similar fraction of surface CdSe binding sites to be occupied, regardless of chain length, reflecting the flexible nature of PAA chains.

These results prompted us to wonder what the PL adsorption profile would be like if the chains adsorbed

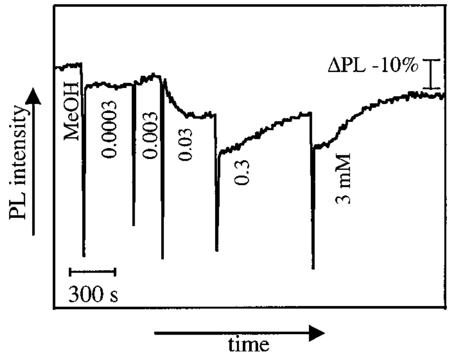


Figure 7. Relative changes in CdSe PL intensity resulting from exposure to methanol solutions of PAMAM dendrimer, surface-functionalized with COOH groups (PAMAM−COOH). The concentrations on a functional group basis are indicated in the Figure. The PL intensity was monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm.

as rigid coils. To address this question, we chose PAMAM−COOH to mimic a rigidly spherical PAA coil. Figure 7 displays a PL adsorption profile characteristic of the adsorption of the PAMAM dendrimer studied. Unlike the behavior of the linear chains, as the adsorbate concentration increases, the PL response to the dendrimer does not continually increase; instead, the dendrimer profile features a sudden reversal in signature, at [−COOH] = 0.3 mM. Such a significant difference in character between the PL profiles for the dendrimer and linear chains further suggests that the linear chains do not adsorb as coils but undergo spreading at the surface in order to maximize the number of contact sites per polymer chain.

II. Adsorption Kinetics

PAA adsorption from methanol solution produces PL responses featuring a kinetic profile dependent on polymer molecular weight and concentration. Since end groups can potentially have a strong influence on adsorption behavior, only the PAA-(2K−100K) series, sharing a similar end group functionality (Table 1), was used for these studies.[10,12] Figure 8a provides a comparison of adsorption and desorption kinetics for the PAA-2K and PAA-100K samples. Upon introduction of the lower molecular weight species, the PL intensity reaches a steady-state value within the temporal resolution of ∼6 s currently employed in our experiments. In contrast, the PAA-100K sample takes considerably longer to achieve the same steady-state value, typically on the order of hundreds of seconds. Figure 8b presents a semilog plot of the same adsorption data. Although the overall adsorption profile is nonexponential, the initial part of the curve was crudely estimated using a single-exponential decay, according to $e^{-t/\tau}$, to obtain a quantitative comparison. The time to decay to 1/e of the initial PL intensity, τ, was thus used to compare the relative adsorption kinetics as a function of PAA molecular weight and concentration.

Figure 9a is a double-logarithmic plot illustrating the effect of polymer molecular weight on $1/\tau$ across the series studied. According to polymer solution theory for diffusion-controlled adsorption, the polymer diffusion constant, $D \propto 1/\tau$, scales with molecular weight according to $D \propto MW^{-\gamma}$, where γ has a value of 0.5 for low molecular weight chains in a good solvent.[7,16a] As demonstrated in Figure 9a, the trend in the data are well described by a slope of −0.5, consistent with diffusion-controlled kinetics. A valid quantitative comparison of the desorption kinetics was impractical, as it was difficult to simultaneously control parameters affecting desorption over a reasonable experimental time scale. Qualitatively, it is obvious from Figure 8a that desorption of the longer chains is a much slower process, consistent with previous reports in the literature for other polymer systems.[16b]

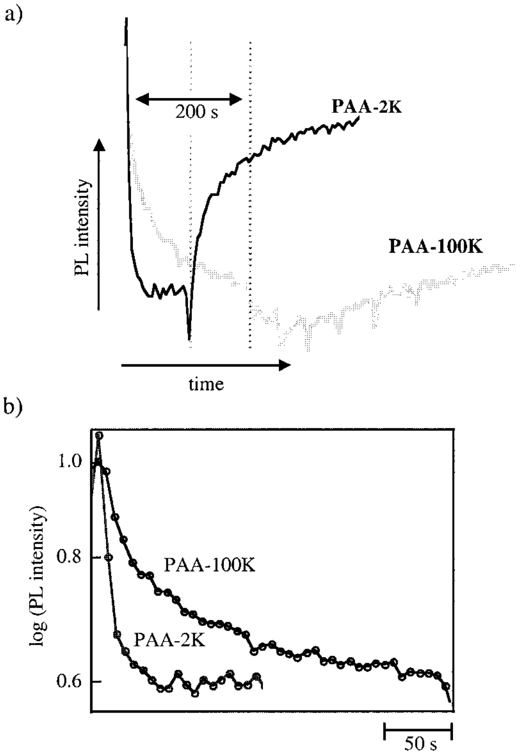


Figure 8. (a) Adsorption kinetics for PAA-2K and PAA-100K from methanol solutions, as monitored by CdSe PL. The vertical dashed lines represent the onset of solvent rinses, inducing desorption. (b) Same adsorption data shown as a semilog plot. The concentration of polymer for both experiments is 0.2 mg/mL. PL intensity was monitored at the CdSe emission maximum of 720 nm, using excitation at 633 nm.

Another test for diffusion-controlled kinetics is to vary polymer concentration for a sample of given molecular weight. The linear trend in the data for the PAA-2K and PAA-100K samples, shown in Figure 9b for PAA-100K, suggests that adsorption is diffusion-controlled.[16b] It should be noted, however, that true transport-limited behavior should exhibit a zero intercept, which is not found in Figure 9b despite the generous estimates in error bars. We speculate that this may be a result of a changing surface over the course of an experiment. As noted in the Experimental Section, the PAA solutions are introduced to the CdSe surface in order of increasing solution concentration; thus, it is possible that the most concentrated and most dilute solutions experience somewhat different surface conditions.

Following the initial adsorption event, the PL intensity falls off nonexponentially (see Figure 8b), reaching an apparent steady-state value that remains constant for at least an hour. Dynamics of adsorbed chains have long been suspected to occur over lengthy time scales on the order of hours, leading to long-lived nonequilibrium states.[15,35−37] Our PL experiment might be expected, in principle, to be sensitive to the formation of additional polymer contacts over time, and should lead to a gradual increase in PL response. However, at least

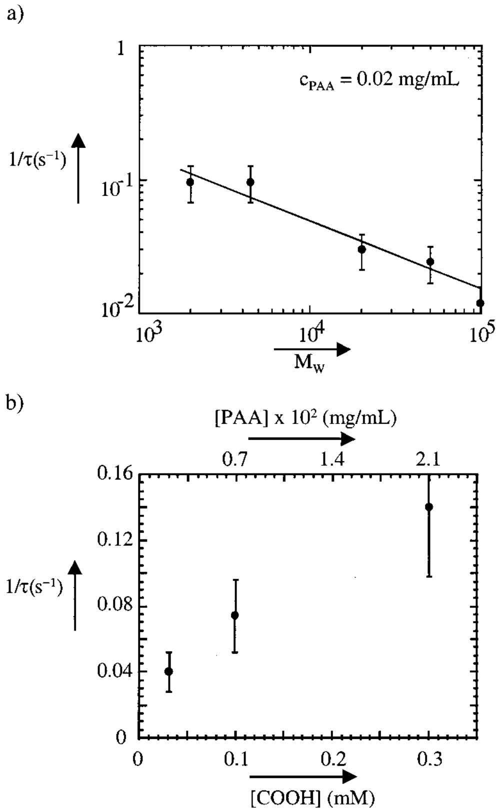


Figure 9. (a) Effect of PAA molecular weight on initial adsorption kinetics. The line represents the trend predicted by polymer solution theory for a diffusion-controlled process (see text). (b) Effect of PAA concentration on initial adsorption kinetics, shown for PAA-100K. The current temporal resolution for the experiment is ~6 s, placing a lower limit on $1/\tau$ for higher concentrations (not shown in plot). For both plots, a and b, the initial rate of adsorption is characterized by the characteristic PL decay, τ, obtained from single-exponential fits to the initial part of the PL decay curve. The error bars represent the maximum variability for a series of reasonable exponential fits to the corresponding PL data. The data shown in (a) and (b) are for adsorption of PAA from methanol solution, using 633 nm excitation and the 720 nm emission maximum of CdSe to monitor the PL. Whereas the data within each plot above were collected on a common CdSe surface, plots a and b are for two different CdSe surfaces.

over the time scale and experimental resolution studied, there appears to be no significant change in surface binding of the adsorbed PAA samples based on the constant PL signal that is established.

Conclusions

We have demonstrated that the photoluminescent semiconductor CdSe can be used both as the adsorbent and as a direct probe of polymer adsorption onto its surface. Since PL sensitivity is limited to interactions occurring within a few monolayers of the surface, for a chemically equivalent series of chains, the fractional PL change effectively provides a relative count of the number of polymer segments directly bound to the surface, assuming that the energetic distribution of occupied CdSe surface sites is similar across the series. Using this approach, characterization of the initial polymer contact layer is possible. Through comparisons with PL-based studies of selected model systems, including the monomer, derivatives thereof, and a dendrimer, we were able to identify key structural features affecting polymer adsorption. Formation of the initial adsorbed layer for the polymer system studied was found to be governed by diffusion-controlled kinetics.

We believe that the methods introduced in this work can be extended to many other polymer systems to provide insight into the processes governing formation of the initial adsorption layer. Ultimately, because the substrate PL response essentially provides a count of the number of binding segments, there exists the potential to determine experimentally an average loop-to-train ratio of the adsorbing polymer for comparison with theory.

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(30) We attempted to correlate the PL behavior in cyclohexane with direct evidence of a shift in the association equilibrium by studying the carbonyl region of the solutions of AA by IR spectroscopy. Strong absorptions due to cyclohexane ultimately limited the sensitivity of the IR experiment and the concentration range that could be studied to 0.03−3 mM. A shoulder, at 1725 cm^{-1}, on the main peak at 1705 cm^{-1}, first becomes evident for the 0.3 mM AA solution, and persists at 3 mM. It is well-established in the literature that the peak at 1705 cm^{-1} arises from the presence of closed dimers. The identification of the peak at 1725 cm^{-1} is less certain, and is thought to be due to open aggregates. For the limited concentration range examined in this study, deconvolution of the carbonyl peaks did not indicate a significant change in the absorbance ratio $A(1725\ \mathrm{cm}^{-1})/A(1705\ \mathrm{cm}^{-1})$. These results prevent us from attributing with certainty, the difference in PL behavior of the cyclohexane system to a shift in the association equilibrium of Scheme 2.

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(33) For the shortest chain (PAA-2K), there are approximately 27 repeat units; the apparent persistence length for PAA in a good solvent, like water, is reported to be less than ~20 Å, or about six monomer units. See, for example: (a) Muroga, Y.; Noda, I.; Nagasawa, M. *Macromolecules* **1985**, *18*, 1576. (b) Reed, C. E.; Reed, W. F. *J. Chem. Phys.* **1991**, *94*, 8479.

(34) This is a reasonable assumption considering the following: (a) the geometric constraints, on a segmental basis, are similar for a series of polymers differing in molecular weight only, and (b) the binding energy and energetic surface site requirements are similar for each polymer, since the same binding functionality is always present.

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