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# The hydrodynamic size of polymer stabilized nanocrystals

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**Abstract**
For many emerging applications, nanocrystals are surface functionalized with polymers to control self-assembly, prevent aggregation, and promote incorporation into polymer matrices and biological systems. The hydrodynamic diameter of these nanoparticle–polymer complexes is a critical factor for many applications, and predicting this size is complicated by the fact that the structure of the grafted polymer at a nanocrystalline interface is not generally established. In this work we evaluate using size-exclusion chromatography the overall hydrodynamic diameter of nanocrystals (Au, CdSe, $d < 5$ nm) surface coated with polystyrene of varying molecular weight. The polymer is tethered to the nanoparticles via a terminal thiol to provide strong attachment. Our data show that at full coverage the polymer assumes a brush conformation and is 44% longer than the unbound polymer in solution. The brush conformation is confirmed by comparison with models used to describe polymer brushes at flat interfaces. From this work, we suggest an empirical formula which predicts the hydrodynamic diameter of polymer coated nanoparticles based on the size of the nanoparticle core and the size of the randomly coiled unbound polymer in solution.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Nanocrystals are the subject of intensive study due to the striking size-dependence of their physical and chemical properties [1–9]. However, for many emerging applications—most notably those in medicine and self-assembly—these materials must be processed from and applied in liquid solutions. In such settings nanocrystals are often coated with terminally grafted linear polymers [10–13]. These serve to passivate their surfaces and prevent aggregation through steric stabilization. These organic components define the interface of the nanoparticle with the external world, and are thus enormously important in predicting and controlling nanocrystal properties such as solubility and hydrodynamic size [14–17]. These solution phase features can be very difficult to measure and predict. In particular the overall size of a polymer coated nanoparticle is a challenge to engineer *a priori* since polymers can exist either as randomly coiled or extended structures at an interface [18–20]. Models for polymer behaviour at flat interfaces describe these states and their dependence on factors such as polymer molecular weight and degree of coverage [21–23]. In this work, we examine polymer coated nanocrystals fully coated with polymers as they represent the most stable and common configuration. Using size-exclusion chromatography we measure their hydrodynamic size with angstrom resolution and derive a general relationship between the overall size of the polymer coated nanoparticle and the dimensions of its individual constituents.

Polymers as nanoparticle capping agents present an interesting structural question because of their ability to exist in multiple conformations [21–23]. Unbound polystyrene in a good solvent such as toluene has a randomly coiled conformation which maximizes the accessibility of all possible polymer conformations [14]. When terminally tethered to

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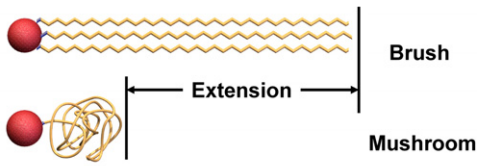


**Figure 1.** The above image shows thiol terminated linear polystyrene tethered to a nanocrystal surface. Polystyrene may adopt a mushroom (random coil) or brush (extended) structure depending on polymer coverage.

a *flat* surface at low polymer coverage, the polymer chain can extend slightly to contact the surface, but remains mostly coiled. This conformation is classified as a 'mushroom' structure (figure 1). When polymer coverage rises to the point where the interchain distance is less than the Flory radius, the polymer chain extends significantly because of steric crowding by neighbouring molecules [18–20, 24–26]. This extended conformation, known as a 'brush', is characterized by a large region of relatively high polymer concentration with a parabolic segment density profile. Figure 1 shows an extreme caricature of a brush conformation. Actual polymer brushes usually possess noticeable coiling of the polymer chain. In the brush regime the polymer length scales linearly with its molecular weight and with the cube root of the polymer coverage [19, 20, 25–31]. Qualitatively, these structural characteristics have been observed for nanoparticle–polymer interfaces when the core sizes are quite large. For example, polystyrene on silica nanoparticles ($d > 20$ nm) is shorter at low coverage than at high coverage, consistent with models of a transition from a mushroom to a brush structure [18, 32–34]. Polystyrene terminally bound to gold has also been observed to contribute more to the hydrodynamic diameter of the complex than would be suggested from its size as a random coil when unbound in solution, leading to the conjecture that at the high coverages studied the polymer takes on a brush conformation [35–37].

Because most applications employ fully coated nanoparticles, our work focuses on describing the effect of polymer molecular weight on the hydrodynamic diameter of nanoparticles at saturation or full coverage. For these experiments sample hydrodynamic size must be determined to better than several angstroms in order to develop an accurate model to predict the hydrodynamic diameter (HD) of polymer coated nanoparticles. The recent application of size-exclusion chromatography (SEC) to the quantitative measurement of nanocrystal hydrodynamic diameter suggests it is well suited for this application [38, 39]. SEC can distinguish between nanocrystalline samples that differ in hydrodynamic diameter by only 1 Å. When used in tandem with electron microscopy to determine nanocrystal core size, SEC analysis can be used to determine the size of surface bound polymers on a nanocrystal when the material is fully coated:

$$\mathrm{HD} = D_c + 2(T_{\mathrm{shell}}), \qquad (1)$$

where HD is the hydrodynamic diameter of the polymer coated nanoparticle, $D_c$ is the diameter of the nanocrystal core, and $T_{\mathrm{shell}}$ is the thickness of the polymer shell.

In this report, we use a thiol terminated polystyrene bound to both gold and cadmium selenide nanocrystals (core diameters from 2 to 3 nm) as model systems. Not only is the surface curvature very high for these small nanocrystals, but for most molecular weights studied the polymer is approximately the same size as the nanocrystal. Such a situation is increasingly common in nanoscience where the most striking size dependent changes often occur in materials with extremely small diameters. These data show that polystyrene on gold nanocrystals adopts a brush conformation with a length that, at saturation coverage, is $45 \pm 6\%$ longer than that of the unbound random polystyrene coil. The length of the bound polymer scales linearly with molecular weight following the predictions of scaling and mean-field theory for polymer brushes on flat surfaces. Polystyrene on CdSe nanocrystals is also evaluated and found to extend $42 \pm 11\%$ over the unbound random coil. This shows the generality of polymer brush formation on nanoparticles and permits the hydrodynamic diameter of polymer coated nanocrystals to be estimated from $\mathrm{HD} = D_c + 2(1.44 D_{\mathrm{RC}})$, where $D_{\mathrm{RC}}$ is the diameter of the unbound random polymer coil in solution and $D_c$ is the diameter of the core nanocrystal.

## 2. Experimental methods

### *2.1. Synthesis of Au nanoparticles*

Au nanoparticles ($d$ 2.1 nm) stabilized with oleylamine were synthesized according to the method by Leff *et al* [5]. Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O$; >99.9%), oleylamine ($C_{18}H_{35}NH_2$; tech 70%), and sodium borohydride ($NaBH_4$; 99%) were purchased from Aldrich. Tetraoctylammonium bromide ($N(C_8H_{17})_4Br$; >99%) was purchased from Fluka and Optima toluene ($C_7H_8$; 99.8%) was purchased from Fischer Chemicals. Ethanol (190 proof) was purchased from Aaper Alcohol. All chemicals were used as received. Deionized water (18.2 MΩ) was obtained from a Millipore Milli-Q UV Plus filtration system. A solution of 0.112 g $HAuCl_4{\cdot}3H_2O$ in 25 ml deionized water was prepared in a 250 ml Erlenmeyer flask. While stirring, a solution of 0.365 g tetraoctylammonium bromide in 25 ml toluene was added to the Au salt, resulting in a two-phase mixture. The mixture was stirred rapidly until all colour was transferred to the upper organic phase. Next, a solution of 0.829 g oleylamine in 25 ml toluene was added to the mixture, resulting in white cloudiness. A final solution of 0.165 g $NaBH_4$ in 25 ml deionized water was added to the stirring two-phase mixture. This removed the cloudiness and resulted in a dark brown/purple organic phase. The reaction mixture was stirred overnight and remained open to air.

After 12 h, the coloured organic phase was collected and rotary evaporated to 5 ml using a Büchi R-200. 250 ml of ethanol was added and the sample was left in the freezer for 24 h to ensure complete precipitation of the nanoparticle product. The nanoparticles were collected by vacuum filtration on filter paper and washed with an excess of cold ethanol. Once dried, the precipitate was redissolved in 50 ml toluene and stored in a refrigerator.

### *2.2. Synthesis of CdSe nanoparticles*

CdSe nanoparticles were synthesized following the procedure reported by Krueger *et al* [39]. Cadmium oxide (CdO; 99.99%), selenium powder (Se; 99.5%), oleic acid ($C_{18}H_{34}O_2$; tech 90%), 1-octadecene ($C_{18}H_{36}$; tech 90%; ODE), and trioctylphosphine ($(CH_3(CH_2)_7)_3P$; tech 90%; TOP) were purchased from Aldrich and used as received. 0.255 g CdO, 1.88 g oleic acid, and 80 ml ODE were loaded into a 250 ml three-neck flask and heated to 300 °C under $N_2$. When the mixture became clear and colourless, a solution of 0.08 g Se powder dissolved in 0.42 g TOP and 3 ml ODE was quickly injected. The reaction was quenched at varying times after injection (20–30 s) by adding 40 ml of room temperature ODE to obtain 3.0 and 3.6 nm diameter CdSe nanocrystals. After cooling, 15 ml of this solution was purified by adding 15 ml of acetone to precipitate impurities. After 20 min, the cloudy solution was centrifuged for 10 min at 4200 rpm to remove unreacted cadmium oleate, a reaction precursor. In a new centrifuge tube, an excess of acetone was added to the decantate and the mixture was centrifuged for 20 min at 4200 rpm to precipitate all nanocrystals. The solid precipitate was redissolved in 50 ml toluene and stored at room temperature.

### *2.3. Synthesis of polystyrene coated nanocrystals*

Polystyrene coated nanocrystals were prepared via a ligand-exchange approach using a terminal thiol to permanently attach polystyrene to the surface of Au and CdSe nanocrystals. Linear thiol terminated polystyrene of the following molecular weights was purchased from Polymer Source Incorporated: 1230, 1650, 2300, 2500, 5800, and 7700. Due to the small amounts of polymer routinely handled in this research ($\sim 1 \times 10^{-3}$ g), stock solutions of polymer dissolved in toluene were prepared and were delivered via micropipette. Typical stock solution concentrations were 0.025 g polymer/ml toluene. Polymer coated nanocrystals at saturation coverage were synthesized by the addition of a metered amount of polymer stock solution to a vortexing solution of as-prepared nanoparticles. This is represented as a weight-to-weight ratio of polystyrene to nanoparticles ($W_{PS}/W_{NP}$). After addition of the polymer to the nanoparticles, the mixtures were allowed to sit overnight to permit complete reaction.

A typical synthesis of polystyrene coated nanocrystals is as follows: 91.2 $\mu$l of 7700 $M_w$ polystyrene stock solution ($2.28 \times 10^{-3}$ g polymer) was added to 100 $\mu$l of as-prepared Au nanocrystals ($5.0 \times 10^{-4}$ g Au) while vortexing ($W_{PS}/W_{Au} = 4.56$). After the mixture sat overnight it was then transferred to a sample vial and taken for analysis.

Cadmium selenide nanocrystals coated with long chain alkane thiols (1-hexane thiol, 1-dodecane thiol, and 1-octadecane thiol, Aldrich) were synthesized in a similar manner. 20 $\mu$l of the desired thiol were added to 500 $\mu$l of the as-synthesized nanoparticles and stirred for 1 min. The mixture was allowed to sit overnight and was then taken for analysis.

### *2.4. Size-exclusion chromatography*

Polystyrene coated nanocrystals were analysed using a Waters Alliance 2690 chromatographic system with photodiode array (model 996) and differential refractive index (model 410) detectors. Typical injection volumes were 50 $\mu$l; chromatographic resolution was 1.0 s. Retention times were not dependent on injection volume. Injected samples of polystyrene coated Au and CdSe nanocrystals were monitored at 505 and 517 nm, respectively. Nanocrystals coated with polystyrene were analysed with a 10 000-Å pore size column (Polymer Labs PLgel 5 $\mu$m, model 1110-6540). Nanocrystals coated with only long chain alkane thiols were analysed with a 1000-Å pore size column (Polymer Labs PLgel 5 $\mu$m, model 1110-6530). Separations of Au nanocrystals used a toluene mobile phase while CdSe required a solution of 0.1 M TOP in toluene. A flow rate of 1 ml min$^{-1}$ and a column temperature of 30 °C were used for all separations. Polystyrene calibration standards (Polymer Labs EasiCal PS-2) were used to calibrate the SEC columns and provide the relationship between retention time and hydrodynamic diameter. The solution phase hydrodynamic diameter of these standards was determined using the following equation:

$$\mathrm{HD} = 2\left\{\frac{3M_w\eta}{10N_A\pi}\right\}^{1/3}, \qquad (2)$$

where $M_w$ is the weight average molecular weight, $\eta$ is the intrinsic viscosity, and $N_A$ is Avogadro's number [40]. The intrinsic viscosity was determined using the Mark–Houwink equation

$$\eta = K\{M_w\}^a. \qquad (3)$$

Constants $K$ and $a$ are dependent on polymer composition, solvent, and temperature [41]. Larger polymer standards elute at shorter times as expected for a size-exclusion mechanism (figure 2(a)). Standard models for SEC predict a natural

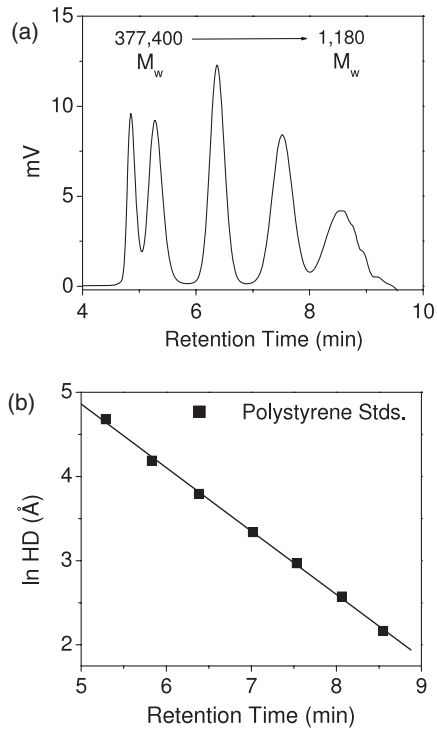


**Figure 2.** The SEC columns are calibrated using polystyrene standards. (a) Monodisperse standards of known size are analysed using the system set-up and a calibration plot (b) is made relating sample retention time to hydrodynamic diameter.

log relationship between retention time and hydrodynamic diameter, and thus define calibration curves of the type shown in figure 2(b). This range of retention times, 6–8 min, is typical for these PLgel columns. The good linearity indicates that over these elution times materials are in the optimal range for separation and detection.

In developing a formula to predict the HD of polymer coated nanoparticles, we often compare the measured HD of these samples to the HD of the unbound randomly coiled polymer. The HD of the polystyrene random coil could not be measured directly using SEC due to enthalpic interactions of the thiol terminus with the stationary phase. Therefore, the HD was calculated using the same equations (2) and (3) used to obtain the HD for our polystyrene calibration standards discussed above. The measured HD of polymer coated nanoparticles is also compared to the length of totally extended polystyrene. This was calculated assuming a rigid carbon backbone with a monomer length of 2.55 Å. The monomer length was calculated using a PM3 geometry optimization in Gaussian 03 [42]. This is a highly extended conformation that is not meant to reflect a physically possible brush conformation. It is shown to put our data in perspective.

### *2.5. Determination of saturation coverage*

An important aspect of this work is to confirm that the polymer coated nanoparticles studied are indeed at saturation coverage. Unless this condition is met we cannot use equation (1) to deduce the polymer contribution to the measured hydrodynamic diameter. Figure 3(a) displays chromatograms of gold nanocrystals treated with different amounts of 7700 $M_w$ polystyrene. As the polymer content ($W_{PS}/W_{Au}$) is increased, the sample retention time smoothly decreases, indicating growth of the nanoparticle HD. To ensure that the nanocrystals were saturated, the polymer content was increased until no further shift in sample retention time was evidenced, as shown by the dashed line. This was performed for each polymer/nanocrystal combination to ensure surface saturation. Figure 3(b) shows the sample HD as a function of polymer content for gold nanoparticles coated with selected polymer molecular weights. The HD is derived from the sample retention time and clearly shows how the sample size reaches a stable maximum upon addition of sufficient polymer. It was determined that 4.56 $W_{PS}/W_{Au}$ and 30 $W_{PS}/W_{CdSe}$ were sufficient to reach saturation for gold and cadmium selenide respectively.

It is important to note that this method does not ensure that every available surface binding site is full. It is likely that the binding of polystyrene to the nanoparticle surface reaches an equilibrium that is mediated by the polystyrene already attached to the nanoparticle. This attached polystyrene could sterically limit the accessibility of additional polymer molecules to unfilled surface sites yielding a surface that is well passivated although not completely bound up [23]. For our research, total binding of all surface sites is not critical. We are more interested in whether or not thiol terminated polystyrene has reacted with as many surface sites as is possible, be that all of them or some fraction. By increasing the polymer content to the point where the sample HD no longer changes, our method ensures that no additional polystyrene is binding to the nanoparticle surface. This indicates that the reaction is finished and that saturation has been reached.

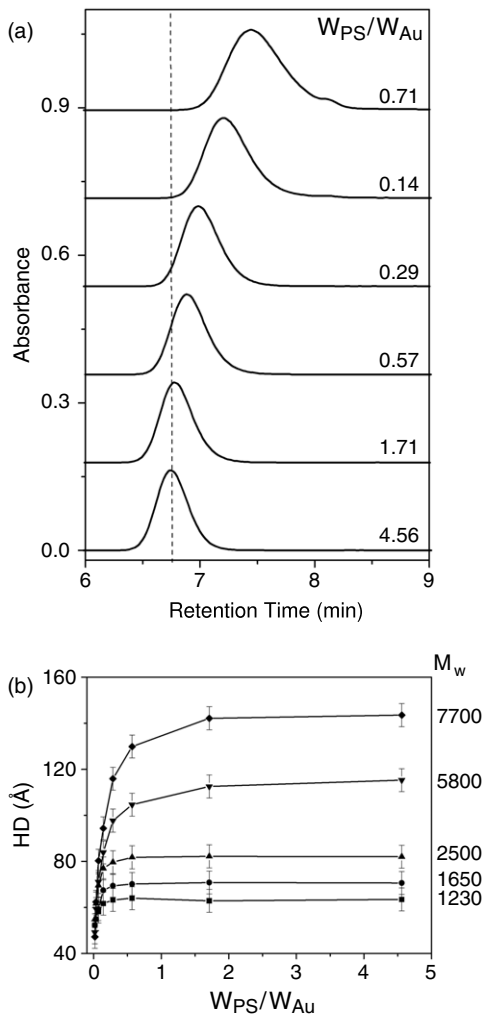


**Figure 3.** Saturation of the nanoparticle surface with polymer was verified using SEC. (a) Overlaid chromatograms of Au nanoparticles complexed with 7700 $M_w$ polystyrene. The sample retention time decreases to a stable minimum with increase in polymer content ($W_{PS}/W_{Au}$), indicating surface saturation. (b) The HD of the coated nanocrystals increases with polymer content until the nanoparticle surface is totally saturated.

### *2.6. Transmission electron microscopy (TEM)*

Figure 4 shows histograms and representative images for both Au and CdSe nanocrystals. All TEM images were gathered on a JEOL 2010 operating at 200 kV with a single tilt, multi-sample holder. Samples were drop cast from toluene onto 400-mesh formvar carbon coated copper grids (Ted Pella, 01822). These were observed at magnifications ranging from 50 000 to 100 000×. Over 1000 nanocrystals were sized for each sample using ImagePro analysis software. Origin 6.1 was used to generate histograms of particle size.

## 3. Results and discussion

Central to this work is the use of SEC as a quantitative method for measuring the size of ligands bound to the surface of nanoparticles with angstrom accuracy. Figure 5 illustrates the technique using CdSe nanocrystals coated with

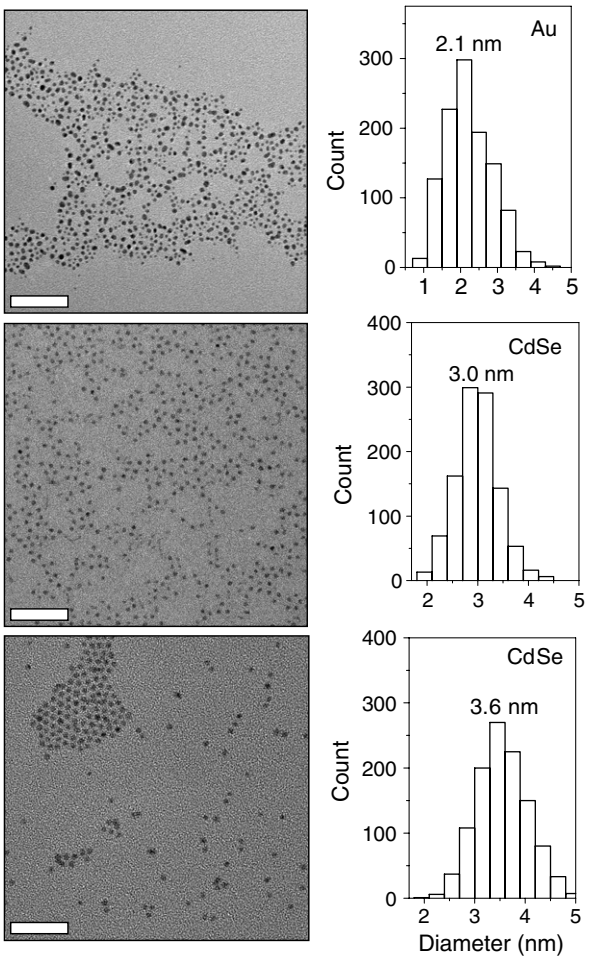


**Figure 4.** Sample core sizes were determined using TEM. Both gold (2.1 nm diameter, std. dev. = 0.65, $N = 1124$), CdSe (3.0 nm diameter, std. dev. = 0.42, $N = 1053$), and CdSe (3.6 nm diameter, std. dev. = 0.52, $N = 1123$) were analysed for size and polydispersity. The scale bar represents 40 nm.

conventional short chain alkane thiols as an example. Overlaid chromatograms of 3.6 nm CdSe nanoparticles coated with 1-hexane, 1-dodecane, and 1-octadecane thiol (figure 5(b)) show that SEC easily distinguishes between samples with capping agents of different length. Samples coated with longer thiols elute first, indicating their larger overall HD. A calibration curve for the column converts the retention time of each sample to HD. Using the equation in figure 5(a), $\mathrm{HD} = D_c + 2(T_{\mathrm{shell}})$, the capping agent thickness ($T_{\mathrm{shell}}$) is determined by simply subtracting the core diameter from the sample HD and dividing by two. Thus it is straightforward to determine the effective size of ligands bound to nanocrystals.

For short alkane thiols, the measured hydrodynamic diameter using SEC agrees well with a structural model which assumes the alkane thiols are fully extended. The illustration in figure 5(a) shows the composition of a typical nanoparticle; the overall HD is equal to the diameter of the nanoparticle core ($D_c$) plus two times the thickness of the coating ($T_{\mathrm{shell}}$). Figure 5(c) plots the HD of each sample as determined from SEC as well as the HD calculated based on the core diameter (3.6 nm) and the extended length of the thiols ($C_6$ 0.71; $C_{12}$ 1.33; $C_{18}$ 1.95 nm). This is the effective length of the thiols assuming a 63° contact angle with the nanocrystal surface and a 1.15 Å linear carbon–carbon distance [43]. The slope of the line is 1 and represents a perfect correlation between $\mathrm{HD_{SEC}}$ and $\mathrm{HD_{CALC}}$. This confirms that short capping agents, such as the alkane thiols shown here, assume a fully extended molecular conformation.

Qualitatively, polymer capping agents show similar behaviour to these molecular systems; coating nanocrystals with polymers of higher molecular weights result in larger nanocrystal sizes in solution. Figure 6 shows overlaid chromatograms of gold nanocrystals fully coated with thiol terminated polystyrene of varying $M_w$ (weight average molecular weight). There is a steady shift towards earlier retention time with higher $M_w$. This trend indicates that nanocrystals coated with higher $M_w$ polystyrene possess a larger HD than those coated with lower $M_w$. This behaviour is analogous to the case of alkane thiols presented earlier.

An important difference for polymers at nanocrystal surfaces, as opposed to alkane thiols, is the large structural change they experience upon binding to a nanocrystal. When compared to calculated values for the HD of the unbound random polystyrene coil, the length of polystyrene conjugated

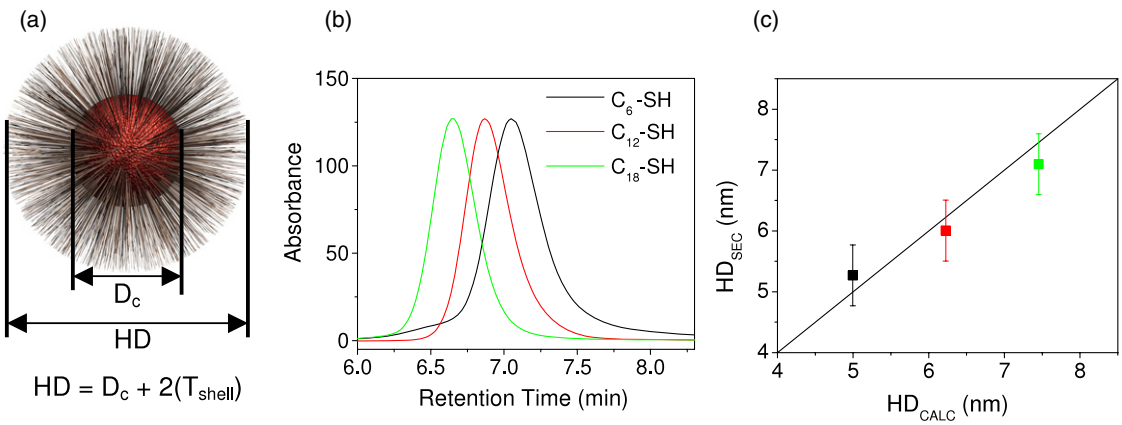


**Figure 5.** Nanoparticle coating thickness is determined using a geometric model. (a) The hydrodynamic diameter (HD) is calculated from core diameter ($D_c$) and surface-coating thickness ($T_{\mathrm{shell}}$) (see equation (1)). (b) SEC detects the difference in capping agent length between CdSe nanoparticles coated with 1-hexane, 1-dodecane, and 1-octadecane thiol. (c) The hydrodynamic diameter for these coated nanoparticles determined from SEC is compared to expected values for 3.6 nm CdSe core plus literature values for the shell thickness. The line slope is set to 1.

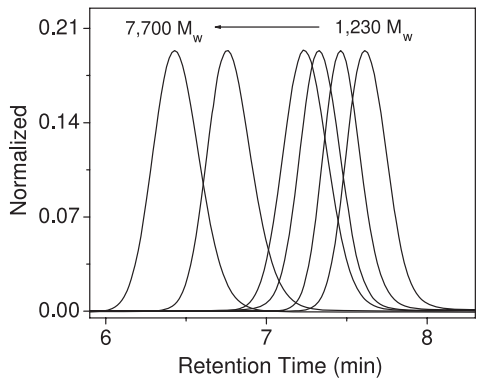


**Figure 6.** SEC easily detects nanoparticles coated with polystyrene of varying $M_w$. $M_w$ from left to right: 7700, 5800, 2500, 2300, 1650, 1230. The HD of the polymer coated nanocrystals increases with polymer $M_w$.

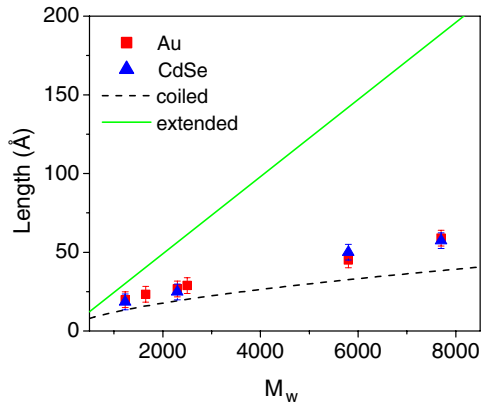


**Figure 7.** The length of unbound polystyrene (random coil and fully extended), and polystyrene attached to Au and CdSe nanocrystals is graphed as a function of $M_w$. Polystyrene bound to Au and CdSe nanocrystals is an average of $45 \pm 6\%$ and $42 \pm 11\%$ larger than the polystyrene random coil, respectively. The linearity of the plots for Au and CdSe confirm that polystyrene assumes a brush conformation.

to Au nanocrystals at saturation coverage is an average of $45 \pm 6\%$ larger. Figure 7 shows how polymer length depends on $M_w$ for unbound polystyrene (random coil and fully extended), polystyrene bound to Au nanocrystals and polystyrene bound to CdSe nanocrystals. Polystyrene bound to CdSe nanocrystals (3.0 nm) is an average of $42 \pm 11\%$ longer than the unbound random coil and compares closely with the results of Au. This suggests that the extension of polymers when bound to nanocrystals is a general trend, applicable to a wide range of polymer coated nanocrystal systems. It also shows the generality of SEC for determining the coating thickness on nanocrystals. The percent extension for each $M_w$ is as follows: Au [48 (1230), 47 (1650), 39 (2300), 43 (2500), 38 (5800), 54% (7700)]; CdSe [38 (1230), 29 (2300), 53 (5800), 50% (7700)].

This extension of polymers when bound to nanocrystals, even those much smaller than the polymer, can be easily explained using models of polymers at interfaces. When unbound polymers are in solution, the many repeating units present in polymer chains introduce a multitude of possible structural conformations. The propensity to maximize the accessibility of these new conformations becomes a driving force in determining the general shape of the polymer molecule. In the case of neutral linear polymers such as polystyrene, this results in a random coil conformation when unbound in solution [14]. When terminally bound to a flat surface, the need to access many conformations must compete with the steric crowding of neighbouring chains. Thus an equilibrium between a coiled and extended conformation is developed (figure 1) [25]. In the polymer literature these two conformations are referred to as a 'mushroom' or 'brush' state, respectively, and they are characterized by very different hydrodynamic diameters as compared to the random coil found in solution.

On nanocrystals, the polymers at the interface are found to be 30–50% longer than the unbound random coils found in solution, and these values are indicative of polymers in a brush conformation. Indeed the presence of any significant extension indicates a brush regime [23]. Scaling and mean-field theory predictions for polymer brushes on flat surfaces provide

$$L \propto N\sigma^{1/3}, \tag{4}$$

where $L$ is the polymer length, $N$ is the number of monomer units, and $\sigma$ is the polymer coverage. $N$ is related to molecular weight by the following relation:

$$N = \frac{M_w}{S_w}, \tag{5}$$

where $S_w$ is the molecular weight of the monomer [25]. Thus, for brushes, polymer length scales linearly with molecular weight. Shown in figure 7, the length of polystyrene bound to Au and CdSe also scales linearly with molecular weight with $R^2$ values of 0.99. This provides further evidence of a brush conformation on the surface of the nanocrystals when at saturation coverage. Interesting, figure 7 shows that polystyrene bound to Au and CdSe is actually closer in length to the unbound random coil than the fully extended conformation. This is because the fully extended conformation represents a highly exaggerated brush state only possible for solid polymer crystals. It is shown for comparison only.

Although useful for establishing the presence of a brush conformation, the linear growth of the polymer length with molecular weight is unexpected for nanocrystals. Due to the surface curvature of spherical nanocrystals, the influence of steric crowding should decrease with distance from the nanocrystal surface. At large distances from the surface, there is enough volume for the remaining tail of the polymer to coil randomly. This analysis suggests that at high $M_w$ the plot of polymer length versus $M_w$ should no longer be linear but should curve down slightly as does the plot for randomly coiled polystyrene. It is interesting to note that this linear behaviour is also observed for polystyrene bound to larger silica spheres [34]. It is possible that this effect may occur at higher molecular weights than those studied here. This remains an interesting question for further research.

The behaviour observed here for polystyrene should be a general property for most neutral linear polymers on nanocrystals. Based on the extension observed for polystyrene on Au and CdSe nanocrystals, equation (1) can be modified

as follows to calculate the hydrodynamic diameter of polymer coated nanocrystals.

$$\mathrm{HD} = D_c + 2(1.44 D_{\mathrm{RC}}). \quad (6)$$

The diameter of the unbound random coil, $D_{\mathrm{RC}}$, is calculated using equations (2) and (3). Terminally bound polymers will find an equilibrium between a conformation that minimizes interchain interactions and one that maximizes the accessibility of available polymer conformations. Based on this, models predict the dimensions of terminally bound polymers to scale linearly with molecular weight. This was observed for polystyrene bound to both Au and CdSe nanocrystals, suggesting that the behaviour may be general and applicable to a wider range of nanocrystal–polymer systems.

## 4. Conclusions

The conformation of thiol terminated polystyrene bound to gold nanocrystals was determined as a function of $M_w$ using size-exclusion chromatography. We show that polystyrene exists as a brush conformation on the nanocrystal surface at saturation coverage. This is qualified by a 45 ± 6% expansion over the unbound randomly coiled polymer when attached to gold nanocrystals and a 42 ± 11% expansion when attached to CdSe nanocrystals. From this it is possible to predict the length of polymer tethered to nanocrystals. Additionally, the polymer length increases linearly with $M_w$ in accordance with predictions for polymer brushes on flat surfaces. These observations suggest that the hydrodynamic size of nanoparticle–polymer complexes can be predicted from the dimensions of each component separately.

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## References

[1] Asokan S, Krueger K M, Alkhawaldeh A, Carreon A R, Mu Z Z, Colvin V L, Mantzaris N V and Wong M S 2005 *Nanotechnology* **16** 2000–11
[2] Brust M, Walker M, Bethell D, Schiffrin D J and Whyman R 1994 *J. Chem. Soc. Chem. Commun.* (7) 801–2
[3] Bunge S D, Krueger K M, Boyle T J, Rodriguez M A, Headley T J and Colvin V L 2003 *J. Mater. Chem.* **13** 1705–9
[4] Colvin V L, Goldstein A N and Alivisatos A P 1992 *J. Am. Chem. Soc.* **114** 5221–30
[5] Leff D V, Brandt L and Heath J R 1996 *Langmuir* **12** 4723–30
[6] Murray C B, Norris D J and Bawendi M G 1993 *J. Am. Chem. Soc.* **115** 8706–15
[7] Peng Z A and Peng X G 2001 *J. Am. Chem. Soc.* **123** 183–4
[8] Qu L H, Peng Z A and Peng X G 2001 *Nano Lett.* **1** 333–7
[9] Yu W W, Falkner J C, Shih B S and Colvin V L 2004 *Chem. Mater.* **16** 3318–22
[10] Hong R, Fischer N O, Emrick T and Rotello V M 2005 *Chem. Mater.* **17** 4617–21
[11] Ishii T, Suzuki Y, Akiyama Y, Otsuka H, Kataoka K and Nagasaki Y 2005 *Kobunshi Ronbunshu* **62** 81–6
[12] O'Neal D P, Hirsch L R, Halas N J, Payne J D and West J L 2004 *Cancer Lett.* **209** 171–6
[13] Takae S, Akiyama Y, Otsuka H, Nakamura T, Nagasaki Y and Kataoka K 2005 *Biomacromolecules* **6** 818–24
[14] Bridger K, Fairhurst D and Vincent B 1979 *J. Colloid Interface Sci.* **68** 190–5
[15] Bridger K and Vincent B 1980 *Eur. Polym. J.* **16** 1017–21
[16] Farmer S C and Patten T E 2001 *Chem. Mater.* **13** 3920–6
[17] Perruchot C, Khan M A, Kamitsi A, Armes S P, Watts J F, von Werne T and Patten T E 2004 *Eur. Polym. J.* **40** 2129–41
[18] Auroy P, Mir Y and Auvray L 1992 *Phys. Rev. Lett.* **69** 93–5
[19] Field J B, Toprakcioglu C, Ball R C, Stanley H B, Dai L, Barford W, Penfold J, Smith G and Hamilton W 1992 *Macromolecules* **25** 434–9
[20] Field J B, Toprakcioglu C, Dai L, Hadziioannou G, Smith G and Hamilton W 1992 *J. Physique* **2** 2221–35
[21] Degennes P G 1980 *Macromolecules* **13** 1069–75
[22] Degennes P G 1981 *Macromolecules* **14** 1637–44
[23] Degennes P G 1987 *Adv. Colloid Interface Sci.* **27** 189–209
[24] Habicht J, Schmidt M, Ruhe J and Johannsmann D 1999 *Langmuir* **15** 2460–5
[25] Ruhe J 2004 Polymer brushes: on the way to Tailor-made surfaces *Polymer Brushes* ed R Advincula, W Brittain, K Caster and J Rühe (Weinheim: Wiley–VCH) pp 1–31
[26] Ruths M, Johannsmann D, Ruhe J and Knoll W 2000 *Macromolecules* **33** 3860–70
[27] Alexander S 1977 *J. Physique* **38** 977–81
[28] Fytas G, Anastasiadis S H, Seghrouchni R, Vlassopoulos D, Li J B, Factor B J, Theobald W and Toprakcioglu C 1996 *Science* **274** 2041–4
[29] Karim A, Satija S K, Douglas J F, Ankner J F and Fetters L J 1994 *Phys. Rev. Lett.* **73** 3407–10
[30] Mansfield T L, Iyengar D R, Beaucage G, McCarthy T J, Stein R S and Composto R J 1995 *Macromolecules* **28** 492–9
[31] Milner S T, Witten T A and Cates M E 1988 *Macromolecules* **21** 2610–9
[32] Almusallam A S and Sholl D S 2005 *Nanotechnology* **16** S409–15
[33] Bartholome C, Beyou E, Bourgeat-Lami E, Cassagnau P, Chaumont P, David L and Zydowicz N 2005 *Polymer* **46** 9965–73
[34] Savin D A, Pyun J, Patterson G D, Kowalewski T and Matyjaszewski K 2002 *J. Polym. Sci.* B **40** 2667–76
[35] Corbierre M K, Cameron N S and Lennox R B 2004 *Langmuir* **20** 2867–73
[36] Corbierre M K, Cameron N S, Sutton M, Laaziri K and Lennox R B 2005 *Langmuir* **21** 6063–72
[37] Corbierre M K, Cameron N S, Sutton M, Mochrie S G J, Lurio L B, Ruhm A and Lennox R B 2001 *J. Am. Chem. Soc.* **123** 10411–2
[38] Al-Somali A M, Krueger K M, Falkner J C and Colvin V L 2004 *Anal. Chem.* **76** 5903–10
[39] Krueger K M, Al-Somali A M, Falkner J C and Colvin V L 2005 *Anal. Chem.* **77** 3511–5
[40] Mori S and Barth H G 1999 *Size Exclusion Chromatography* 1st edn (Berlin: Springer Laboratory) p 234
[41] Brandrup J, Immergut E H and Grulke E 1999 *Polymer Handbook* 4th edn (New York: Wiley)
[42] Frisch M J *et al* 2004 *Gaussian 03, Revision C.02* (Wallingford, CT: Gaussian Inc.)
[43] Porter M D, Bright T B, Allara D L and Chidsey C E D 1987 *J. Am. Chem. Soc.* **109** 3559–68