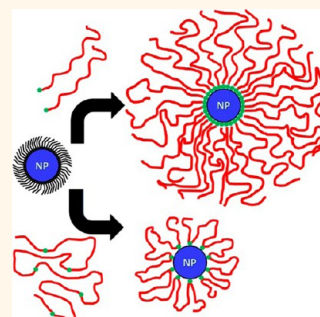


Polymer Ligand Exchange to Control Stabilization and Compatibilization of Nanocrystals

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ABSTRACT We demonstrate polymer ligand exchange to be an efficient method to control steric stabilization and compatibilization of nanocrystals. A rational design of polymer binding groups and ligand exchange conditions allows to attach polymer brushes with grafting densities $>1 \text{ nm}^{-2}$ to inorganic nanocrystals for nearly any nanocrystal/polymer combination using only a few types of binding groups. We demonstrate the potential of the method as an alternative to established grafting-from and grafting-to routes in considerably increasing the stabilization of inorganic nanocrystals in solution, to prepare completely miscible polymer nanocomposites with a controllable distance between nanoparticles, and to induce and control aggregation into percolation networks in polymeric matrices for a variety of different nanocrystal/polymer combinations. A dense attachment of very short polymer ligands is possible enabling to prepare ordered nanoparticle monolayers with a distance or pitch of only 7.2 nm, corresponding to a potential magnetic storage density of 12.4 Tb/in². Not only end-functionalized homopolymers, but also commercially available copolymers with functional comonomers can be used for stable ligand exchange, demonstrating the versatility and broad potential of the method.



KEYWORDS: nanocomposites · nanoparticles

Nanocrystals and polymer nanocomposites are of immense interest in fundamental research as well as in a large variety of industrial applications. As an example, semiconductor nanocrystals (quantum dots) are used in medical applications as fluorescent tags,^{1,2} as LEDs³ or tunable lasers^{4,5} in optical applications, or for energy conversion in photovoltaic cells.^{6–8} Magnetic nanocrystals find applications as contrast agents in magnetic resonance imaging,⁹ or metal nanoparticles in catalytic applications.¹⁰ The stability of nanocrystals in solution is crucial to prevent agglomeration with loss of functionality. The combination of nanocrystals and a polymer matrix leads to nanocomposites. These composites could have enhanced mechanical,¹¹ optical¹² or electrical¹³ properties, but uncontrolled agglomeration often prevents the enhancement and even deteriorates many useful properties. Therefore, it is of great importance to avoid or, even better, to control the agglomeration of nanocrystals.

The most common way to efficiently stabilize nanocrystals against agglomeration is to cover them with a polymeric brush. Such sterically stabilized particles are known to form stable colloidal solutions¹⁴ or, if the polymer brush is compatible with a polymer matrix, to form well dispersed nanocomposites.¹⁵ There are two established approaches to form a polymer brush on a surface. The first approach is the grafting-from method. By this method the polymer is grown from initiator groups which have been covalently linked to the nanocrystal surface¹⁶ to obtain a covalently bound polymer layer. The polymer density depends on the grafting density of the initiator groups. The grafting-from method allows a variety of different polymerization types such as radical, anionic and cationic polymerization. Because of the covalent bond of the polymer a grafting density of 0.4 nm^{-2} is sufficient to stabilize nanocrystals.¹⁷ A drawback of this method is the need to develop a new initiator coupling reaction scheme for each new

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nanocrystal-polymer combination. Further, there is no straightforward way to control nanocrystal agglomeration, if this would be desired.

The second approach is the grafting-to method. This method has the advantage that polymers could be presynthesized with established polymerization procedures for a state-of-the-art control of composition, architecture, and polydispersity. The preformed polymer will be covalently bound to the nanocrystals by a chemical reaction between a functional end group of the polymer and a functional group at the nanocrystal surface.¹⁸ Again, a drawback is the need to establish new functional group linking schemes for each new nanocrystal-polymer combination. In addition, a control of agglomeration cannot easily be achieved, and due to steric repulsion of the attached polymer chains, high grafting densities are hard to reach.

A concept to work around establishing new covalent linker chemistries is to coat nanocrystals with a shell of silica, for which covalent attachment schemes for initiators and covalent binding groups have been well established.^{19–21} However, this requires to develop and optimize new nanocrystal-silica core/shell-growth procedures, which is not a trivial task. Therefore, a versatile method that would allow stable, high-density polymer attachment for a large variety of nanocrystal-polymer combinations would be highly desirable.

A possible approach could be based on the exchange of nanocrystal surface ligands. State-of-the-art methods to prepare inorganic nanocrystals²² yield nanoparticles that are stabilized by alkyl phosphines, amines or carboxylic acids. These groups have proven to be most efficient in controlling nanocrystal growth during synthesis, and to provide stability of the final particles in solution. The exchange of these surface ligands with polymers could be an attractive route for a flexible and versatile polymer attachment. So far, the exchange of coordinating surfactants has been only reported for short organic molecules²³ and thiol-functionalized polymers.^{24,25} The exchange with short organic molecules is mostly used to attach new functional groups to the nanocrystal surface or to transfer the nanocrystals into another solvent.^{26–28} The exchange with thiol groups is specifically used for gold nanocrystals because of the high affinity of gold to thiols, providing bonding that is nearly as strong as a covalent bond.

Here, we outline a polymer ligand exchange method which is broadly applicable to stabilize a large variety of different nanocrystal-polymer combinations. It is based on coordinative surface binding, which is successfully used in nanocrystal synthesis. We demonstrate the versatility of this ligand exchange method for the preparation of a variety of different polymer brush stabilized nanocrystals and show the potential for solution stabilization, nanocomposite compatibility, nanoparticle distance control to sub-10 nm pitch

structures, and the controlled agglomeration to form percolation networks.

RESULTS AND DISCUSSION

Thermodynamic Considerations. The coordinative ligand exchange can be thermodynamically described by a reaction $\text{NP-L1} + \text{L2} \rightleftharpoons \text{NP-L2} + \text{L1}$, where NP-L1 are the nanocrystals (NP) coated with the original low-molecular weight ligand L1, and NP-L2 are the nanocrystals coated with the desired polymer ligand L2. From the law of mass action it follows that the concentration of the desired polymer-coated nanocrystal is given by

$$[\text{NP} \cdot \text{L2}] = K \frac{[\text{NP} \cdot \text{L1}][\text{L2}]}{[\text{L1}]} \quad (1)$$

where K is the equilibrium binding constant. In order to achieve a high yield of NP-L2, one has to choose ligands with a large binding constant K , work with a large excess of polymer ligand L2, and remove the originally bound low-molecular weight ligand L1.

Ligands with suitable binding constants for ligand exchange procedures can be identified in a rational way by using Pearson's hard/soft acid/base (HSAB) principle. Most of the metals or metal ions in nanocrystals can be characterized as soft acids (Cd^{2+} , Ag^0 , Au^0) or as borderline acids (Fe^{2+} , Pb^{2+} , Zn^{2+}). Oxidic nanoparticles (ZnO , Fe_2O_3) can be considered as hard bases. Accordingly, the metals would best be coordinated by soft bases such as thiols, phosphines or phosphonates, or borderline bases such as pyridine. Hard bases would be best stabilized by hard acids, such as carboxylic acids. For a given ligand, the binding strength could be further increased by using multi-dentate ligands.

Not surprisingly, the above choice of ligands corresponds to the set of ligands which are used in the currently most efficient synthetic procedures of nanocrystals, *e.g.*, by hot injection routes, where alkyl oleates (*e.g.*, oleic acid), phosphines (*e.g.*, trioctyl phosphine (TOP)), phosphonates (*e.g.*, trioctylphosphine oxide (TOPO)) are commonly used to stabilize nanoparticles during synthesis.²²

An important issue when using polymeric ligands is to *not* use the ligands having the highest binding strength, but somewhat more moderate binding. A certain reversibility of surface coordination and de-coordination is needed to obtain dense brush layers for sufficient steric stabilization of the nanocrystals in solution or compatibilization in polymer nanocomposites. This reversibility allows polymer chains to relocate on the nanoparticle surface to facilitate attachment of further polymer chains to increase the brush density. The importance of chain relocation on nanocrystal surfaces has been recently shown by HRTEM, and has a pronounced effect on the colloidal stability and aggregation.²⁹

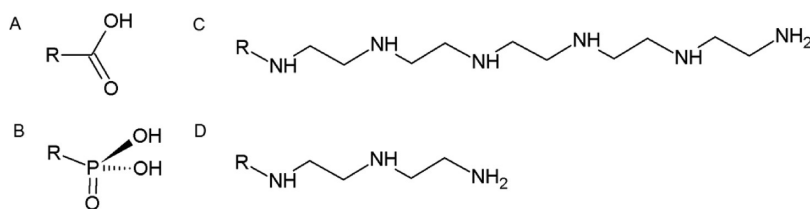


Figure 1. Suitable coordinating groups for polymer ligand exchange: (A) carboxylic acid (-COOH), (B) phosphonic acid (-PO(OH)₂), (C) pentaethylenhexamine (-PEHA), and (D) diethylenetriamine (-DETA). R represents the polymer chain, which in the present study comprises polystyrene (PS), poly(methyl methacrylate) (PMMA), and polyisoprene (PI).

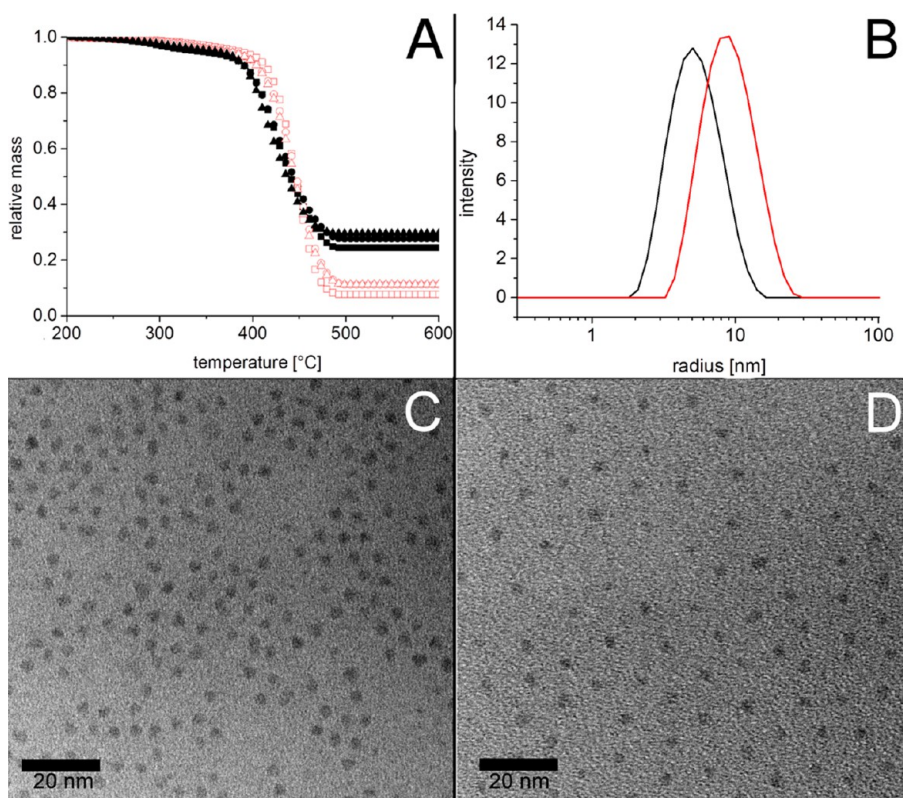


Figure 2. (A) TGA measurements of the ligand exchange steps (red = quantitative steps; black = selective steps; squares = step 1; circles = step 2; triangles = step 3). (B) Particle size distribution measured by DLS measurements in THF of 3 nm CdSe nanocrystals stabilized with oleic acid (black) and after ligand exchange with polystyrene-PEHA 2700 g/mol (red). TEM images of the CdSe nanocrystals with oleic acid (C) and with polystyrene-PEHA 2700 g/mol (D). The increased interparticle distance after coating with polystyrene is a clear indication of stable polymer brush binding.

In line with these considerations we observe that optimal for polymer ligand exchange procedures are (1) combinations of PbS-, Fe₃O₄-, ZnO- (borderline acids Pb²⁺, Fe²⁺, Zn²⁺) and CdSe-, Ag-nanoparticles (soft acids Cd²⁺, Ag⁰) with multidentate amines (hard bases) such as diethylenetriamine (DETA) or pentaethylenhexamine (PEHA), or (2) Fe₃O₄-, ZnO-nanoparticles (hard bases) with the hard acid RCOOH. PEHA can nearly be considered a general purpose ligand, since it also very well stabilizes oxidic, hard base nanocrystals such as ZnO and Fe₃O₄ where it coordinates to the metal centers. The structure of the respective polymer ligands are shown in Figure 1. Polymers used as examples in the present work include polystyrene (PS), polyisoprene (PI), and poly(methyl methacrylate) (PMMA) in combination with the coordinating

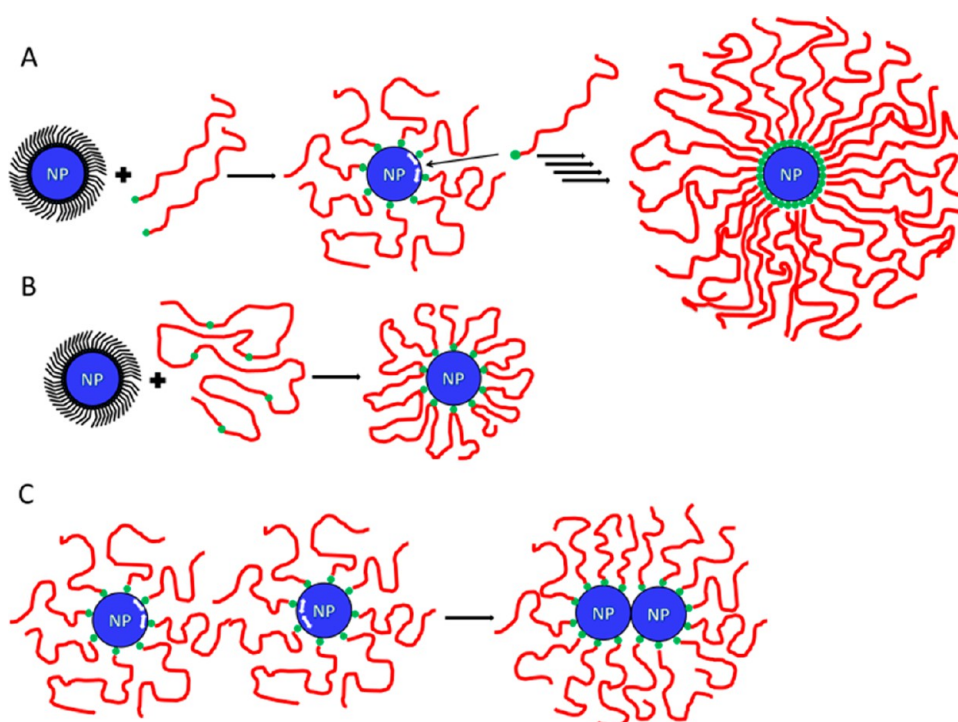
groups -COOH, -PEHA, or -DETA to act as polymeric ligands L2. Many other polymers such as polyethylene (PE), poly-3-hexylthiophene (P3HT), and poly(ethylene oxide) will work as well.³⁰ In principle, nearly every polymer which could be functionalized with one of the coordinating groups above should be suitable for the ligand exchange procedure. The same holds for the choice of nanocrystals, where in this work Ag-, Au-, CdSe-, PbS-, Fe₃O₄-, and ZnO-nanoparticles are investigated.

The nanocrystals used in the present study were originally coated with oleic acid, since they were synthesized by thermal decomposition of their oleate complexes, an established state-of-the art procedure to prepare highly crystalline monodisperse nanocrystals in large quantities.²² For the ligand exchange

procedures described below, the oleic acid L1-coated nanocrystals were dissolved in a common solvent (THF) together with a large excess of the polymeric ligand L2. Generally we find that just mixing the components in dilute solution is insufficient to achieve complete polymer ligand exchange. We attribute this to the good steric stabilization provided by oleic acid (L1), which was chosen to bind sufficiently strong to limit the growth and stabilize the nanocrystals during their synthesis. Thus, in the sense of eq 1 the concentrations [NP-L1] and [L2] must be considerably increased to achieve complete ligand exchange. We find that this can be accomplished by precipitating the nanoparticles and polymeric ligands *via* the addition of a common nonsolvent (ethanol) to bring nanoparticles (NP) and polymer ligands (L2) in direct contact thereby considerably increasing the local polymer segment density. This step is in the following termed *quantitative precipitation*. As oleic acid (L1) is soluble in ethanol, this will simultaneously deplete ligand L1 from the mixture which further promotes ligand exchange. In a second step, the precipitate, a mixture of NP-L2, free polymeric ligand L2, and remaining amounts of oleic acid (L1), is redissolved in THF. To subsequently remove excess free polymeric ligand and remaining oleic acid, the NP-L2 nanoparticles undergo a *selective precipitation* by the stepwise addition of small amounts of the nonsolvent ethanol. The selective precipitation of NP-L2 in the presence of free polymeric

ligand L2 is possible due to the low entropy of mixing of high molecular weight polymers. The entropy of mixing of polymers in solution is proportional to $1/N$, where N is the degree of polymerization. In our context, polymer-coated nanoparticles can be considered as very high molecular weight polymers with a much lower solubility compared to the free polymer chains. Thus, they precipitate at much less nonsolvent content compared to the free polymer. This principle is the basis of established procedures for polymer fractionation. Depending on the desired purity of the NP-L2, each of the quantitative and selective precipitation can be repeated. The progress in removing ligands L1 and excess L2 can be monitored by thermo gravimetric analysis (TGA). The stability against aggregation in solution can be assessed by dynamic light scattering (DLS), and in the dry state by transmission electron microscopy (TEM).

Ligand Exchange Monitoring. As a first example for the ligand exchange procedure we describe the preparation of polystyrene (PS) brush coated CdSe nanocrystals with PS-PEHA as a polymer ligand (L2) starting from oleic acid coated nanocrystals. Grafting-from or grafting-to procedures to coat CdSe-nanocrystals with polystyrene have been published, but are synthetically challenging^{26,31} The polymer ligand exchange can conveniently be followed by thermo gravimetric analysis. The TGA-curves in Figure 2 (A) show that already after the first quantitative precipitation the amount of



Scheme 1. (A) Nanocrystal coated with oleic acid (black), which is exchanged against a polymer (red) with a coordinating end-group (green). Because of the surface mobility of the end groups, bound polymer chains can relocalize on the surface to facilitate attachment of further polymer chains to yield very high brush densities. (B) The possibility to employ copolymers as polymer ligands to obtain dense polymer brushes. (C) Relocalization of surface-bound polymer to allow controlled agglomeration into nanoparticle dimers, and subsequently chains and networks

oleic acid in the mixture has reduced to below 3 wt % as deduced from the small decrease of the relative mass from 1.00 at 250 °C to 0.97 at 350 °C. The drop of the relative mass between 380 and 480 °C is due to the thermal degradation of the polystyrene chains. This is supported by reference measurements of pure oleic-acid coated nanocrystals and pure polystyrene in the Supporting Information (Figure S1). As seen in Figure 2 (A), the solid nanoparticle content is 8% after the first quantitative precipitation, increasing to 13 wt % after the second and to 14 wt % after the third quantitative precipitation due to the removal of free unbound polystyrene chains. The excess of free polymer chains is considerably further reduced by selective precipitation, where the solid content increases to 22 and 28 wt %, finally nearly saturating at 30 wt %, indicating an almost complete removal of free polymer ligand.

With the mean diameter and the bulk density of the nanocrystals, the molecular weight of the polymer, and the ratio of polymer to nanocrystals from the TGA measurement a grafting density of 1.2 nm^{-2} can be calculated for the CdSe-polystyrene particles shown in Figure 2. This grafting density is much higher than the grafting densities reported for the covalent grafting-to and grafting-from methods.¹⁷ These high grafting densities can be explained with the mobility of the polymer chains on the particle surface due to the reversible coordinating and decoordination of the ligands, as illustrated in Scheme 1.

The obtained polymer-brush coated nanoparticles are well stabilized in solution and in bulk. The measured particle size distributions of oleic acid- and polystyrene-coated CdSe-nanoparticles dispersed in solution (Figure 2 (B)) show the increase of the hydrodynamic radius expected for the attachment of a spherical polymer brush, and no signs of agglomeration. TEM-images (Figure 2 (C,D)) show the increase of the interparticle distance after attachment of the polymer chains.

Increased Solution Stability. Also metal nanocrystals can be polymer brush-coated *via* the ligand exchange procedure. We investigated silver nanocrystals which are relevant for many applications where their unique plasmonic properties or their antibacterial properties are exploited. A specific issue for small (5 nm) silver nanoparticles is the lack of long-term stability in solution³² as shown in Figure 3. After 2 weeks in THF solution the nanocrystals have become polydisperse due to aggregation and fusion into larger nanoparticles. We found that the ligand exchange with PS(16k)-DETA yielded silver nanocrystals coated with a dense polystyrene brush which considerably improved steric stabilization. Even after several months there was no noticeable change of the size distribution of the silver nanocrystals.

Nanoparticle Distance Control. For many applications it is important to control the distance between

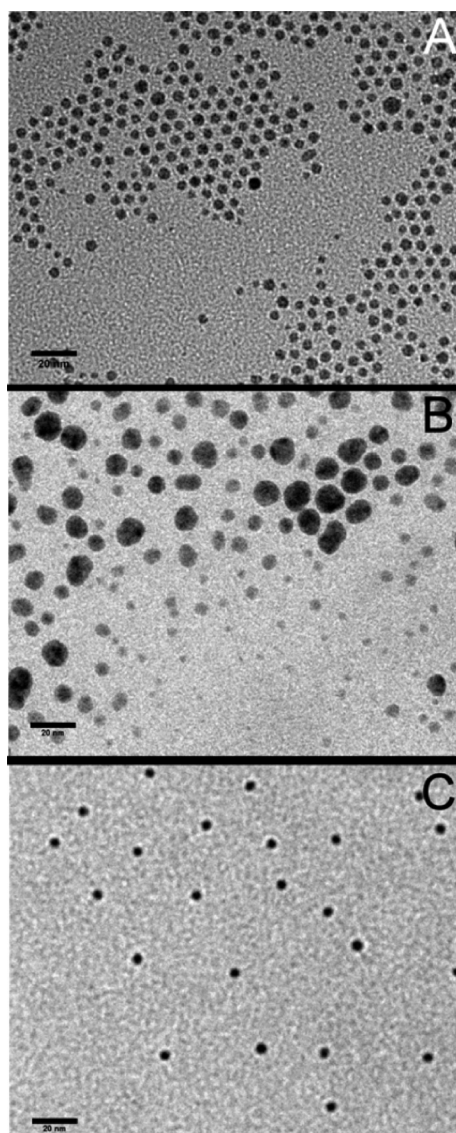


Figure 3. TEM images of silver nanocrystals (A) after synthesis with oleic acid as surfactant, (B) after 2 weeks in THF with oleic acid as surfactant and (C) after 2 weeks with a polystyrene (PS-DETA) brush in THF solution, prepared by the ligand exchange method (scale bars are 20 nm).

nanocrystals on surfaces or in bulk, *e.g.*, in magnetic storage layers to achieve high storage densities, or in the active matrix of hybrid solar cells to adjust the nanoparticle distance to the exciton diffusion length. Because of the high grafting density achievable by the ligand exchange method the polymer brushes are dense and homogeneous, resulting in a well-defined and controllable interparticle distance. The distance can be varied *via* the molecular weight of the polymer ligands. Figure 4 shows the example of iron oxide nanocrystals which were coated with PS-DETA and PS-PEHA with different molecular weights. For iron oxide nanoparticles also a covalent grafting-to/grafting-from method has been developed, which, however, is quite involved.³³ As shown in Figure 4, we demonstrate that by adjusting the PS molecular

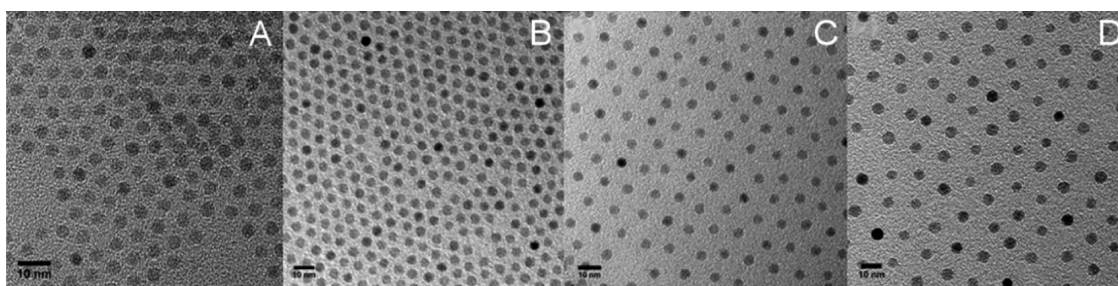


Figure 4. TEM images of 5 nm Fe_3O_4 nanocrystals coated with (A) oleic acid, and polystyrene ligands of different molecular weights, *i.e.*, (B) 1000, (C) 3450, and (D) 8450 g/mol (scale bars are 10 nm). We note the interparticle distance in (B) is smaller than that of oleic acid, with a distance below 10 nm (7.2 nm), which is relevant for magnetic storage layers.

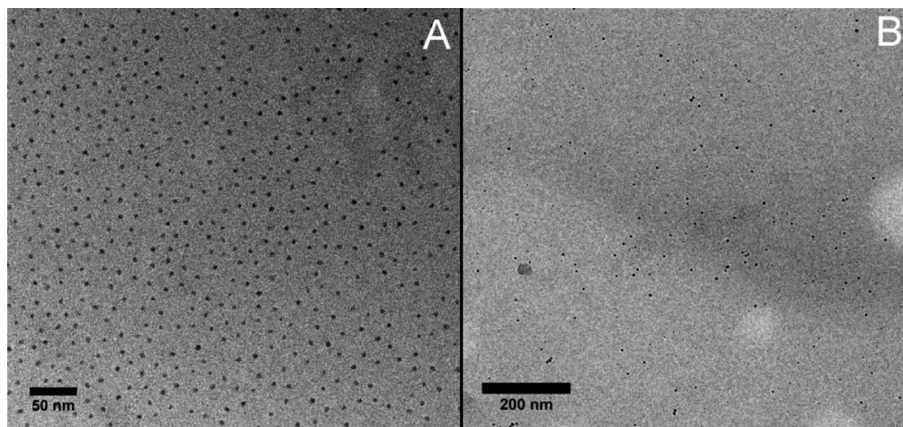


Figure 5. TEM images of 7 nm PbS nanocrystals coated with polyisoprene (PI-PEHA) 15 000 g/mol (A) and 15 nm Ag -nanocrystals coated with PMMA-*co*-polymethacrylic acid (Aldrich, M_w 34 000 g/mol, 1.6% methacrylic acid) in a PMMA matrix (2 wt %) (B).

weight, the center-to-center distances between the nanocrystals can not only be increased, but also *decreased* compared to the distance resulting from the original oleic acid layer. The smaller distance is remarkable, since it demonstrates the possibility to prepare polymer-stabilized nanocrystal assemblies with a distance or pitch smaller than 10 nm, in our case 7.2 nm, corresponding to a potential magnetic storage density of 12.4 Tb/inch², which is very high, and not possible with current state-of-the-art block copolymer templating procedures.³⁴ This control over the distance is a very useful tool for the generation of nanocrystal superlattices.³⁵

As an example for a further nanocrystal-polymer combination we show in Figure 5A polyisoprene-coated PbS -nanocrystals obtained by ligand exchange with PI-PEHA. Polyisoprene is a viscous liquid, but the PI-coated nanocrystals are solid, indicating strong reinforcement of the nanocomposite due to the nanocrystals.

Extension to Copolymer Ligands. So far we used end-functionalized homopolymers as polymeric ligands for the ligand exchange procedure. However, also copolymers can be used as ligands, which considerably broadens the variability of available polymeric ligands and provides a route for up-scaling, since many functional copolymers are commercially available.

Scheme 1 (B) shows how copolymers can similarly coordinate to the nanocrystal surface *via* functional comonomers to form flower-like, dense polymer brushes. Here the brush thickness depends on the molar fraction of binding groups. In Figure 5 (B) we show the example of Ag -nanocrystals coated with poly(methyl methacrylate) (PMMA) by ligand exchange with a commercially available PMMA-*co*-polymethacrylic acid copolymer (Aldrich, M_w 34 000 g/mol, 1.6% methacrylic acid), incorporated into a PMMA-homopolymer. Also in this case, high ligand densities for sufficient stabilization in solution and compatibilization with PMMA-matrices can be achieved. Using these copolymers we could prepare up to 20 g of PMMA-coated ZnO -nanoparticles for reinforcement and surface hardening for PMMA- ZnO -nanocomposites on the kg-scale.

Controlled Nanocrystal Aggregation. For nanocomposites it is often desired to *not* have singly dispersed nanocrystals, but to rather have aggregated nanocrystal assemblies to increase, *e.g.*, electrical or thermal conductivity. Examples are hybrid solar cells where the semiconductor nanocrystals should form a percolation network to provide sufficient electrical conductivity. Here, nanocrystals with coordinatively bound polymers, attached *via* ligand exchange, open a route for a controlled aggregation into percolation networks.

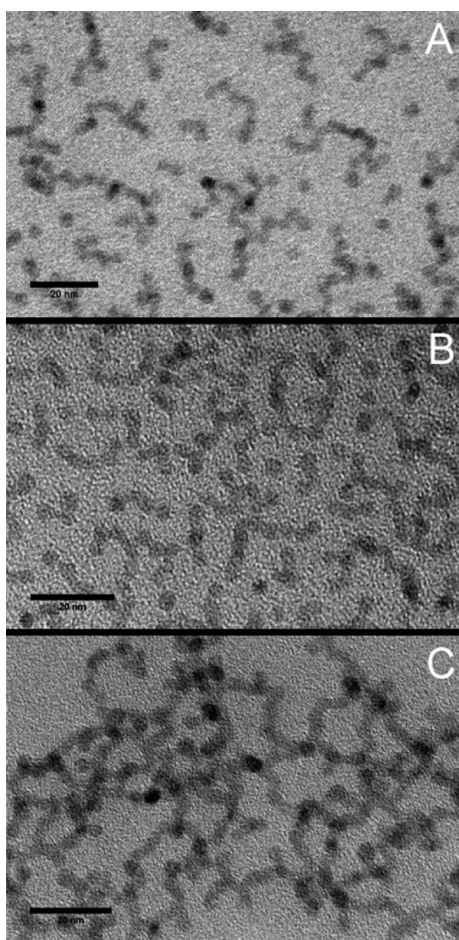


Figure 6. TEM images of 4 nm CdSe nanocrystals with a polystyrene brush forming (A) single crystals and short multiplet chains; (B) short chains and networks; (C) a percolating branched network (scale bars are 20 nm).

The stabilization of the nanocrystals depends on the binding strength of the ligand and the density of the polymer brush. By using a ligand with lower binding strength and/or reducing the excess of polymer ligand [L2] in the ligand exchange procedure, the stability of the polymer-coated nanocrystals against aggregation can be reduced in a controlled fashion. Upon

aggregation, polymer ligands can relocate on the nanoparticle surface (see Scheme 1 (C)) to stabilize extended string-like assemblies that form cross-links and thus efficiently percolate into a continuous network.^{29,36} Such a controlled aggregation would not be possible with covalently bound polymers. With the example of polystyrene-stabilized CdSe-nanocrystals we show that by variation of the ligand excess in the ligand exchange procedure it is possible to tune the stability and aggregation of the nanocrystals from a stable, singly dispersed, well-separated state (Figure 2) to slightly aggregated, string-like multiplet assemblies (Figure 6 (A,B)), and eventually to a continuous percolation network, as shown in Figure 6 (C). This can be favorably employed, *e.g.*, in active matrices of solar cells, where in a first step well-stabilized nanocrystals can be incorporated at high volume fractions with good homogeneous dispersion and no clustering, and then aggregated into a dense percolation network by, *e.g.*, thermal destabilization in the polymer matrix.

CONCLUSIONS

We show that polymer ligand exchange is a very versatile method to coat nanocrystals densely with a spherical polymer brush, shown for a variety of nanocrystal/polymer combinations including PS-PEHA@CdSe, PS-DETA@Ag, PS-PEHA@Fe₃O₄, PI-PEHA@PbS, and PMMA-*co*-PMAc@ZnO, for which otherwise suitable linker chemistries involving covalent attachment of initiators for grafting-from or functional groups for grafting-to would have to be developed. A rational design of the coordinating groups for polymer ligand exchange is possible and a set of a few different ligands is sufficient to apply this procedure to nearly every nanocrystal/polymer combination. We show the excellent solution stability of the polymer-coated nanocrystal, the possibility to adjust interparticle distances, the possibility to aggregate the particles in a controlled way into percolation networks, and the use of commercially available copolymers to broaden the scope of the method.

MATERIALS AND METHODS

Chemicals. Cyclohexane (Aldrich) and tetrahydrofuran (THF, Aldrich) were purified by distillation from a sodium–potassium alloy and from the benzophenone–potassium adduct. Isoprene (Aldrich) was purified successively by distillation from CaH₂ (Aldrich) and di-*n*-butyl magnesium (Aldrich). Ethylene oxide (AirLiquide) was purified by distillation from CaH₂ and *n*-butyl lithium (Aldrich). All other chemicals were used as received, which include sodium oleate (TCI Europe, >97.0%), *sec*-butyl lithium (1.4 M in cyclohexane; Aldrich), tetrahydrofuran (THF, Sigma-Aldrich, 99.9%), cadmium acetate dihydrate (Sigma-Aldrich, 98%), octadecene (Sigma-Aldrich, tech.), methanol (AppliChem, tech.), silver nitrate (Sigma-Aldrich, ≥99%), triethylamine (Sigma-Aldrich, ≥99%), acetone (AppliChem, tech.), iron chloride hexahydrate (Sigma-Aldrich, >98%), hexane (Sigma-Aldrich, 95%), oleic acid (Alfa Aesar, 90%), *sec*-butyl lithium

(Sigma-Aldrich, 1,4 M in cyclohexane), ethylene oxide (Sigma-Aldrich, 99.5%), 1,1'-carbonyldiimidazole (CDI, Sigma-Aldrich, reagent grade), chloroform (Aldrich, anhydrous, amylene stabilized), pentaethylenhexamine (PEHA, Sigma-Aldrich, tech.)

Nanocrystal Synthesis. Cadmium selenide nanocrystals were synthesized by the method of Cao³⁷ *via* the thermal decomposition of cadmium oleate. Silver nanocrystals were synthesized after Nakamoto³² *via* the reduction of silver oleate. Iron oxide nanocrystals were synthesized after Hyeon³⁸ *via* thermal decomposition of iron oleate. The lead sulfide nanocrystals were synthesized as reported by Hines.³⁹ Zinc oxide nanocrystals were synthesized by hydrolysis of zinc oleate in organic solvent as reported by our group.⁴⁰ Detailed procedures are described in the Supporting Information.

Polymer Ligand Synthesis. Polystyrene (PS) was synthesized by living anionic polymerization with *sec*-butyl lithium as initiator

at $-70\text{ }^{\circ}\text{C}$ in THF. The polymerization was terminated either with ethylene oxide to obtain a hydroxyl end group or with CO_2 to obtain a carboxylic acid end group. The hydroxyl end group was subsequently activated by CDI and reacted with PEHA or DETA to create a multivalent amine function.

Polyisoprene (PI) was synthesized by living anionic polymerization in cyclohexane. The polymerization was initiated with *sec*-butyl lithium at $30\text{ }^{\circ}\text{C}$ and terminated with ethylene oxide to obtain hydroxyl terminated PI. The hydroxyl end group was subsequently activated by CDI and reacted with PEHA or DETA to create a multivalent amine function. Detailed procedures are described in the Supporting Information.

Ligand Exchange. The ligand exchange consists of two phases. In the first phase the nanocrystals in solution were mixed with an excess of the polymer followed by three cycles of quantitative precipitation, centrifugation and dissolving. The excess of polymer was removed in the second phase composed of three cycles of selective precipitation, centrifugation and dissolving. In a typical exchange 100 mg of 3 nm CdSe nanocrystals were dissolved in 5 mL of THF. To the nanocrystal solution 1 g of polystyrene ligand (PS-X) in 10 mL of THF was added. After the two solutions were completely mixed 50 mL of ethanol was added for quantitative precipitation. The precipitate was separated by centrifugation at 3250 g. The supernatant was discarded and the precipitate was dissolved in 10 mL of THF. This procedure was repeated two times. Subsequently ethanol was added slowly until precipitation occurs. The precipitate was separated by centrifugation at 3250 g. After centrifugation the supernatant was checked for remaining nanocrystals by fluorescence or color. If there were remaining nanocrystals more ethanol was added and the precipitate was separated again. This was repeated until no nanocrystals remain in the supernatant. The supernatant was discarded and the precipitate was dissolved in 10 mL of THF. This procedure was repeated two times.

Characterization. The nanocrystals were characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS). The coated nanocrystals were characterized by TEM, DLS and thermo gravimetric analysis (TGA). TEM images were obtained on a Zeiss 922 Omega microscope. For the DLS measurements a Malvern Zetasizer Nano SZ were used. The TGA measurements were performed with a Mettler Toledo TGA1 with alumina pans, under nitrogen flow and a heating rate of 20 K/min.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Synthesis information, additional TEM images of ligand exchange examples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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